EVALUATING THE EFFECTS OF WASTEWATER TREATMENT ON MARINE SEDIMENT CHEMISTRY IN HALIFAX HARBOUR, NOVA SCOTIA

by

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ABSTRACT

This study presents results on the spatial and temporal variability of metals and organic contaminants in sediments from Halifax Harbour, Nova Scotia. Decreases in sediment contaminant concentrations due to the initiation of advanced primary wastewater treatment (2009-2010) were not observed. Results from this work provide pre-industrial background and present-day contaminant concentrations as they were at the commencement of wastewater treatment in 2009 – 2010, which are essential for measuring the success of the Harbour Solutions Project and future wastewater treatment efforts. Results indicate that future upgrading to secondary treatment levels will likely affect concentrations of dissolved contaminants to a greater extent than particle-bound contaminants. Concentrations of polycyclic aromatic hydrocarbons (PAHs), lead, zinc, and copper have not changed substantially in the last 20 years. Decreases in mercury concentrations are likely the result of increased source control. Increases in concentrations of alkylated PAHs relative to parental PAHs suggest increased input from petrogenic sources.

LIST OF ABBREVIATIONS AND SYMBOLS USED

Σ – total

\# – number of aromatic rings

°C – degrees centigrade

ΔG° – change in standard Gibbs free energy

% – percent

‰ – per mille

μL – microlitre

μm – micrometre

AAS – atomic absorption spectroscopy

Ac – acenaphthene

AN – anthracene

AVS – acid volatile sulphides

Ay – acenaphthylene

BA – benz(a)anthracene

BaP – benzo(a)pyrene

BDL – below detection limit

BF – benzo(b&j)fluoranthene

BP – benzo(g,h,i)perylene

Bq – becquerel

CCME – Canadian Council of Ministers of the Environment

CH – chrysene

cm – centimetre

Cop. – coprostanol

CSMMWE – Canada-wide Strategy for Managing Municipal Wastewater Effluent

da - day

DBA - dibenz(a,h)anthracene

DBT – dibenzothiophene

dec. deg. – decimal degrees

dpm – disintegrations per minute

E_H° – reduction potential

F – Faraday constant

Fl – fluorene

FL – fluoranthene

g – gram

G – Gibbs free energy

GC-MS – gas chromatography-mass spectrometry

HCl – hydrocholoric acid

HDPE – high-density polyethylene

HF – hydrofluoric acid

HMW – high molecular weight

HNO_3 – nitric acid

HRM – Halifax Regional Municipality

HSP – Harbour Solutions Project

ID – identification number

IP – indeno(1,2,3-cd)pyrene

ISQG – interim sediment quality guideline

ka – kiloannum

kJ – kilojoule

km – kilometre

L – litre

LMW – low molecular weight

m – metre

max. – maximum
mg – milligram
min. – minimum
mL – millilitre
mm – millimetre
mM – millimolar
mo – month
mol – mole
MW – molecular weight
MWRA – Massachusetts Water Resources Authority
n – charge number
N – normal
NA – not analyzed
ng – nanogram
No. – number
NOAA – National Oceanic and Atmospheric Administration
OC – organic carbon
PA – phenanthrene
PAC – polycyclic aromatic compound
PAH – polycyclic aromatic hydrocarbon
PAHp –parental polycyclic aromatic hydrocarbon
PAHa – alkylated polycyclic aromatic hydrocarbon
% PAHa – percent alkylated polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
Per – perylene
PEL – probable effect level
ppb – parts per billion
ppm – parts per million
PY – pyrene
R – critical value of correlation coefficient
Ret – retene
s – second
S.D. – standard deviation
sed. - sediment
SEM – simultaneously extracted metals
SF – soft
SO – soupy
SQV – sediment quality values
ST – stiff
TDS – total dissolved solids
u – atomic mass unit
UV – ultraviolet
wt. % – weight percent
WWTF – wastewater treatment facility
yr – year

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CHAPTER 1: INTRODUCTION

1.1 SCOPE OF PROJECT

Wastewater treatment is vital to ensuring a healthy marine ecosystem in Halifax Harbour, Nova Scotia. For more than 250 years effluents have been released into the harbour through approximately 105 untreated municipal and private wastewater outfalls (Figure 1.1) (Metro Engineering Inc. 1993). These effluents, which include residential raw wastewater and wastes from industry and hospitals, contain numerous contaminants (e.g. mercury, cadmium, lead, polycyclic aromatic hydrocarbons (PAHs)) toxic to humans and other organisms. Many of these contaminants have been identified by Environment Canada as priority substances (Environment Canada and Health Canada 1989, 1995). A contaminant is a substance present in sufficient concentrations to be above background levels, while a pollutant is a contaminant which has the potential to or does cause harm to an ecosystem (flora or fauna). As stated by Chapman (2007), "All pollutants are contaminants, but not all contaminants are pollutants." Although a secondary wastewater treatment facility (WWTF) and a primary WWTF have been in operation along the shores of Halifax Harbour for more than 35 years, they treat only 35% of the wastewater discharged into the harbour. Halifax Regional Municipality (HRM) has recently constructed three advanced primary WWTFs as part of the Harbour Solutions Project (HSP) in an effort to improve the quality of the marine environment.

As a condition of approval for the HSP under the Canadian Environmental Assessment Act, HRM is required to monitor water quality, but not sediment quality, to assess whether the defined water quality objectives for the harbour are met with wastewater treatment in place (HRM 2010a). However, many contaminants are preferentially concentrated in sediments and as a result, marine sediments have been the main repository of contaminants in Halifax Harbour for more than 250 years (Buckley and Winters 1992). Benthic and epibenthic organisms living at or near the sediment-water interface can be adversely affected by these contaminants. Sediment redox conditions are

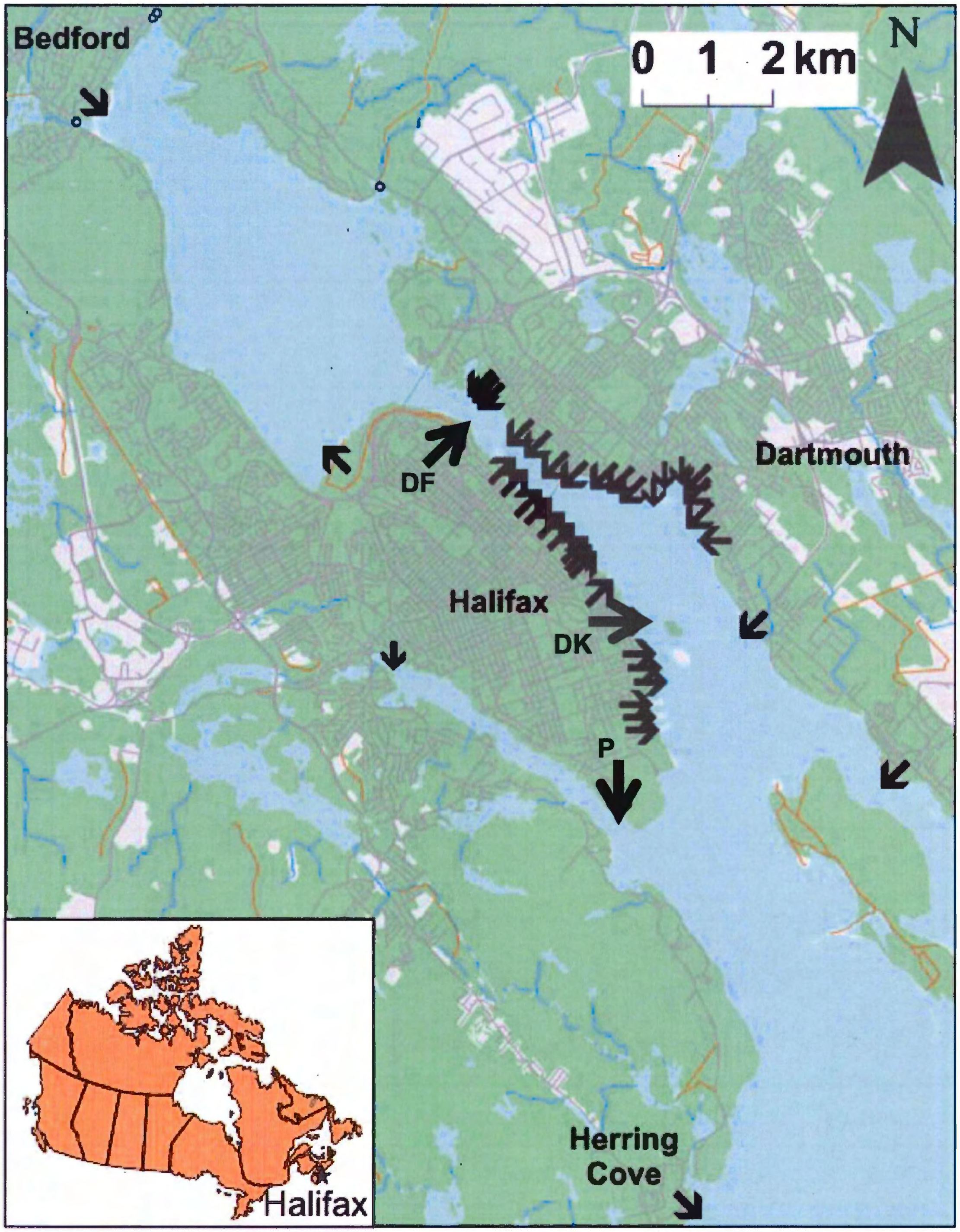


Figure 1.1 Map showing the locations of the major wastewater outfalls which released untreated wastewater into Halifax Harbour as of 1992 (from Buckley and Winters 1992). The locations of the major consolidated outfalls at Duffus Street (DF), Duke Street (DK), and in Point Pleasant Park (P) are denoted by the large arrows.

likely to change following increased wastewater treatment due to decreased organic loading (Salomons et al. 1987, Chapman et al. 1998, Luoma and Rainbow 2008), which may affect the bioavailability of these legacy contaminants. As such, both water and sediment quality conditions must be determined prior to the initiation of wastewater treatment in order to provide a baseline against which the effectiveness of the treatment program can be evaluated.

Through the examination of temporal and spatial changes in sediment chemistry, this study determined whether contaminant concentrations have changed in the last 10 to 20 years since the last major studies examining sediment chemistry in Halifax Harbour were conducted. In addition, the effects of the recent initiation of advanced primary wastewater treatment on sediment chemistry were assessed. Wastewater from the community of Bedford (part of HRM) has been treated through secondary treatment at the Mill Cove WWTF for more than 40 years. To predict the effects that advanced primary and future upgrading to secondary treatment (as recommended by the CCME) may have on sediment chemistry in the harbour, the effects of wastewater treatment on the receiving waters of the Mill Cove WWTF (Bedford Bay) were evaluated. Results from this research allow a pre-treatment set of baseline concentrations (metals, PAHs, and coprostanol) to be established against which the future success of the HSP can be measured. Pre-industrial baseline contaminant concentrations were also ascertained using sediment cores in order to provide a proper context for understanding the effect industrialization has had on sediment contamination levels. The results from this study help to highlight the importance of incorporating monitoring of marine sediment chemistry into harbour quality screening programs. Conclusions from this research will be incorporated into an ongoing multidisciplinary study evaluating the success of the HSP by examining water circulation, sediment chemistry, water chemistry, and marine organisms in Halifax Harbour. This multidisciplinary approach is a cost effective, practical approach to evaluating source reduction programs like the HSP.

1.1.1 San Francisco as an Example

San Francisco is an excellent example of a city which utilized environmental data (organic and metal contaminants in sediments, water, and tissue) to inform management practices in San Francisco Bay. The Bay is the largest estuarine system in western North America and more than 150 years of urban development (including mining of mercury, gold, and copper), the release of municipal and industrial waste, and decreased flushing of the Bay due to freshwater diversions have adversely impacted the Bay's marine ecosystem (Flegal et al. 2007a). For example, silver concentrations in sediments and biota collected from San Francisco Bay in the 1980s were some of the highest ever measured in an estuarine system (Flegal et al. 2007b). Bioaccumulation of mercury in fish in the Bay has rendered them unfit for human consumption (Conaway et al. 2007). Flegal et al. (2005) identified more than 200 publicly owned treatment works and industrial plants discharging effluent into San Francisco Bay. Although San Francisco has greatly decreased effluent discharge, several legacy contaminants such as silver, mercury, and organochlorines remain a concern (Conaway et al. 2007, Connor et al. 2007, Davis et al. 2007, Flegal et al. 2007b). Emerging contaminants (e.g. flame retardant compounds, perfluorochemicals) are also of concern (Hoenicke et al. 2007).

Based on data collected through the Bay Protection and Toxic Cleanup Program and its successor, the San Francisco Estuary Regional Monitoring Program, a set of sedimentary guidelines specific to the San Francisco Bay has been developed (Gandesbery and Hetzel 1998, Gandesbery et al. 1999). Similar guidelines based on biological effects are in the process of being developed by the California Environmental Protection Agency. Water and sediment quality in the San Francisco Bay are monitored on an annual basis, while bivalve accumulation is monitored on a biennial basis (San Francisco Estuary Institute 2008). In particular, sediment quality monitoring has been used to inform management decisions regarding "the identification of sediment 'toxic hot spots' and reference areas; the clean-up of numerous sites in the region that require information about background contaminant levels; and the continued dredging ... that requires testing and comparisons to a reference, or background concentration" (San Francisco Estuary Institute 2008). San

Francisco is in the process of developing a new Sewer System Master Plan, which will address problems associated with the current sewer system and treatment plants over the next thirty years.

1.1.2 Boston as an Example

Three hundred years of waste discharge from the Boston metropolitan area has severely impacted Massachusetts Bay and Boston Harbour. As a result of political and legal action throughout the 1980s, the Massachusetts Water Resources Authority (MWRA) developed and implemented a clean-up program to improve Boston's sewage system and as a result water and sediment quality (Bothner and Butman 2007). Several key goals of the program included reducing point source contaminants, repairing and improving the sewage collection and combined sewer overflow systems, upgrading sewage treatment from primary to secondary levels, discontinuing discharge of sewage effluent directly to the harbour, and constructing an ocean outfall in Massachusetts Bay (Bothner and Butman 2007). In addition, the MWRA established a monitoring program in partnership with the United States Geological Survey to assess the effectiveness of the clean-up program, which included collecting pre-outfall baseline sediment concentrations. In September 2000 sewage discharged from the Boston metropolitan area was diverted from Boston Harbour outfalls to a new outfall in Massachusetts Bay. Metal concentrations in surface sediments have, on average, decreased by 50% in the last twenty five years (Bothner and Butman 2007). The MWRA's clean-up program has resulted in a 90% decrease in carbon loadings and benthic habitats in Boston Harbour have shifted to a more aerobic state (Diaz et al. 2008).

1.2 MARINE SEDIMENT CHEMISTRY

While sediments are often described as a sink for contaminants, they can also act as a source as contaminants can become remobilized long after the source of contamination has been shut off (Salomons et al. 1987, Farmer 1991, Chapman et al. 1998). For example, changes in water temperature or organic matter input can result in the remobilization of contaminants. As well, sediments are not necessarily stationary once deposited. Dredging, storms, tidal currents, anchor dragging, and bioturbation allow buried sediments to become resuspended and to interact with the overlying water column (DeLaune and Smith 1985, Salomons et al. 1987, Zhuang et al. 1994, Peterson et al. 1996). As concentrations of metals and non-ionic lipophilic organic contaminants (coprostanol and some PAHs) are orders of magnitude higher in sediments than in water, small changes in the exchange between the two may have a significant impact on the concentration of contaminants in solution (Luoma 1989). Because marine sediments act as both a source and a sink for contaminants and provide habitats for both benthic and epibenthic organisms, vital members of marine ecosystems, screening marine sediments should be an integral component of marine monitoring programs.

1.2.1 Metals

The following sections describe the key geochemical and sedimentological characteristics of metals in marine sediments that are essential for understanding the distribution and fate of metals in marine environments. The first section will discuss the effects redox conditions have on the speciation of metals, while the second section will discuss the role organic carbon (OC) plays in controlling these redox conditions through bacterially mediated reactions. The final section will examine how grain size affects the distribution of metal contaminants in sediments and how these effects can be mitigated when examining concentrations of metals in sediments.

1.2.1.1 Redox Conditions

Reduction potential (E_H) is a measure of the tendency of a chemical species to accept electrons and therefore become reduced relative to the standard hydrogen electrode (Stumm and Morgan 1996). Redox potential is related to Gibbs free energy (G) through the following equation:

$$E_H^\circ = -\Delta G^\circ / nF$$

where E°_H is the standard redox potential of the reaction, ΔG° is the standard Gibbs free energy change in the reaction, n is the charge number, and F is the Faraday constant. Redox potential is used to examine the distribution of redox-sensitive chemical species (e.g. ferrous and ferric iron) and to justify the sequence in which oxidizing agents are hypothesized to be consumed in the environment. Increases in reduction potential can cause metal sulphides to oxidize releasing sediment-bound metals to the pore water (Salomons et al. 1987), which in turn increases metal bioavailability (Zhuang et al. 1994, Peterson et al. 1996). As summarized by Chapman et al. (1998), reduction potential can change as a result of bioturbation, bioirrigation, sediment resuspension and changes in rates of particle deposition. Some trace metals can be remobilized by the oxidation of anaerobic sediments (Chapman et al. 1998). In summary, reducing the influx of wastewater and therefore organic matter to a water body could have a profound effect on its chemistry and biota.

Marine sediments and the overlying water column can generally be divided into three parts: the oxic layer, the oxic-anoxic interface, and the anoxic layer. In sediments, the oxic layer is characterized by high concentrations of organic matter and high bacteria counts (Salomons et al. 1987). Oxidation reactions are dominant in this layer and precipitation of iron and manganese oxyhydroxide minerals, which strongly bind metals, is favoured. The majority of benthic organisms live in oxic sediments, (Rhoads 1974, Aller and Aller 1986). Infaunal organisms may live in reducing sediments, but they create connections to overlying oxic sediments to receive their required oxygen (Luoma and

Rainbow 2008). This results in the creation of microzones of oxic sediments (mm to cm scale) within reducing sediments (Charbonneau and Hare 1998).

The position of the oxic-anoxic interface is defined as the zero oxygen interface (Luoma and Rainbow 2008), where the rate of incoming diffusing oxygen is equal to the rate of oxygen consumption. Its position is controlled by the deposition of organic material, bacterial consumption of this material, and the penetration of oxygen as a result of physical processes (e.g. resuspension) and biological processes (e.g. bioturbation) (Aller 1978, Sundby 1990). The oxic-anoxic interface has a strong influence on the stability of chemical species. In well-mixed waters (e.g. Halifax Harbour) the location of this interface is in the sediments, while in some strongly stratified lakes and basins (e.g. Black Sea) it is found within the water column (Salomons et al. 1987).

Iron/manganese hydroxides, carbonates, organic matter, and clay minerals act as carriers of trace metals through the water column (Salomons et al. 1987). The four predominant factors which affect the mobility and bioavailability of sediment-bound metals are pH, redox conditions (speciation), salinity, and organic complexation (Förstner et al. 1986). Redox conditions in pore waters have a strong control on the solubility of contaminants. For example, diagenetic cycling of iron and manganese results in enrichment of iron and manganese in near-surface oxic sediments (Farmer and Lovell 1984). As iron and manganese oxyhydroxides are buried, they become reduced, releasing the divalent cations of iron and manganese (as well as any co-precipitated trace elements) which migrate upwards and precipitate in near surface oxic sediments. This enrichment process can also apply to some trace metals (e.g. arsenic) (Johnson and Farmer 1987). Resuspension of these enriched sediments can result in the release of trace metals (Farmer 1991). In sediments, the speciation of trace metals is controlled by bacterially mediated reactions resulting in the oxidation of organic matter and reduction of sulphate, iron, and manganese.

1.2.1.2 Decomposition of Organic Matter

The decomposition of organic matter plays a central role in controlling the speciation of contaminants in both marine and freshwater environments and can result in the release of trace metals from bottom sediments to the water column (Farmer 1991). A widely accepted simple model for the decay of organic matter involves the consumption of different oxidizing agents (oxygen, nitrate, ferric iron, sulphate) through a series of bacterially mediated reactions (e.g. Froelich et al. 1979, Burdige 2006). Although these reactions are generally presented as occurring in sequence (Figures 1.2 and 1.3), some reactions may overlap others or not occur depending on conditions within the environment (e.g. availability of chemical species, bacteria present, etc.) (Canfield and Des Marais 1991, Canfield 1993).

In general, as long as free oxygen is available it acts as the initial terminal electron acceptor during the oxidation of organic matter (Figure 1.2 reaction 1). Reaction 1 will proceed until sufficient oxygen has been consumed such that the reduction potential drops low enough to allow the next most efficient oxidant (nitrate) to be consumed. Once oxygen has been consumed, nitrate reduction begins (Figure 1.2 reaction 2). Nitrate reduction is important because it has a strong influence on the availability of nitrate (an essential nutrient), but can also affect pH if bacteria reduce the nitrate to ammonium (Figure 1.2 reaction 2b) (Drever 1997). Following nitrate reduction, manganese oxide, ferric hydrous oxides, and sulphate are reduced according to reactions 3, 4 and 5 (Figure 1.2), respectively. The products of sulphate reduction (H_2S and HS^-) are highly toxic to most aquatic species. In addition, reduction of ferric iron and sulphate can result in the formation of insoluble metal (lead, copper, mercury) sulphides, which can play an important role in limiting the bioavailability of these potentially toxic elements (Chapman et al. 1998). When oxidizing agents are no longer available, the decomposition of organic matter continues through methanogenesis and fermentation reactions (Figure 1.2 reaction 6).

Oxic respiration

$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$ $\Delta G^\circ = -475$ (1)

Denitrification and nitrate reduction

$5\{CH_2O\} + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$ $\Delta G^\circ = -448$ (2a)

$2\{CH_2O\} + NO_3^- + 2H^+ \rightarrow 2CO_2 + NH_4^+ + H_2O$ (2b)

Mn-oxide reduction

$\{CH_2O\} + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$ $\Delta G^\circ = -349$ (3)

Fe-oxide reduction

$\{CH_2O\} + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$ $\Delta G^\circ = -114$ (4)

Sulphate reduction

$2\{CH_2O\} + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$ $\Delta G^\circ = -77$ (5)

Methane production

$2\{CH_2O\} \rightarrow CO_2 + CH_4$ $\Delta G^\circ = -58$ (6)

Figure 1.2 Organic matter oxidation reactions and their associated changes in Gibbs free energy (ΔG°) in kJ/mol of CH_2O. From Canfield (1993), modified from Berner (1980). $\{CH_2O\}$ refers to the formula of an average organic substance.

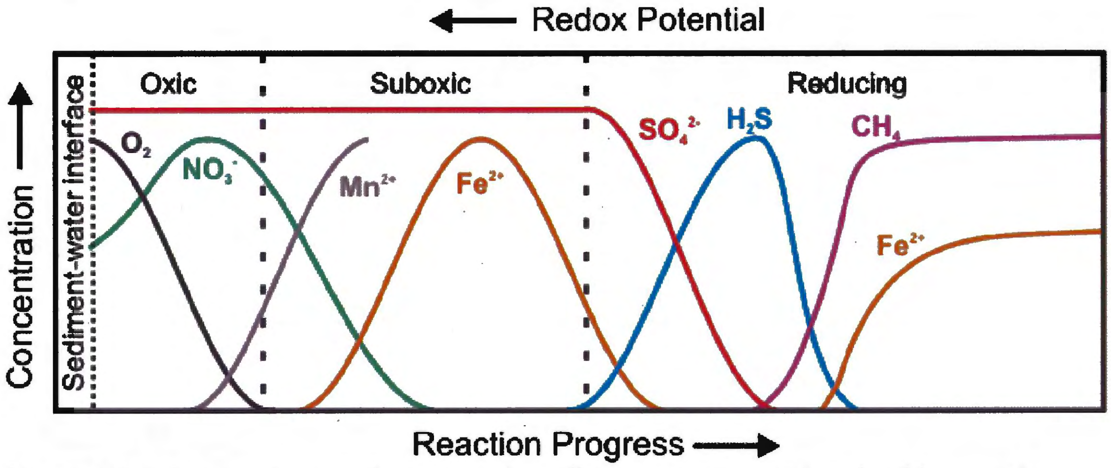


Figure 1.3 Select products and reactants in sediment pore waters involved in organic matter oxidation reactions. From Schulz and Zabel (2006).

1.2.1.2.1 Estimating Present-day Sediment Accumulation Rates

Cranston (1999) developed a method for using changes in ammonium and sulphate concentrations in pore waters to estimate present-day sediment accumulation rates. The steps used in this method are as follows. The concentration of sulphate decreases with sediment depth as organic matter is decomposed, while the concentration of ammonium increases with sediment depth (Figure 1.3) according to reactions 5 and 2b (Figure 1.2). Changes in the flux of OC are reflected by changes in the concentration gradient of sulphate and ammonium with depth through those reactions. These relationships can be used to determine present-day sedimentation rates as described by Cranston (1999). To begin, sulphate and ammonium concentrations are determined in sediment pore waters down core. Concentration gradients for sulphate and ammonium are then calculated by applying linear regression analysis to concentration/depth curves (Figure 1.4). Present-day sediment accumulation rates can then be calculated according to the following equations (where OC refers to the average OC content of the sediment from which the pore waters were collected):

$$\text{Present-day sedimentation rate (cm/ka)} = 10 \times (\text{-sulphate gradient (mM/m)/OC (\%)})$$

$$\text{Present-day sedimentation rate (cm/ka)} = 100 \times (\text{ammonium gradient (mM/m)/OC (\%)})$$

Gradients can be used to estimate present-day sedimentation rates when the correlation coefficient between sulphate/depth and ammonium/depth is statistically significant (i.e. p-value < 0.05).

1.2.1.3 Grain Size Effects

Grain size can have a profound effect on the distribution of contaminants in sediments. In general, clays provide a greater surface area per unit mass to which contaminants can bind, have net negatively charged surfaces and high cation exchange capacities relative to

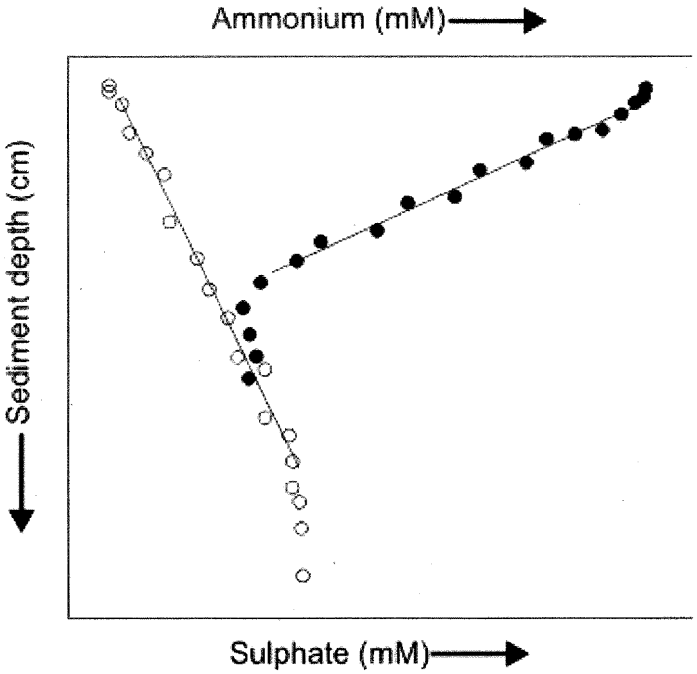


Figure 1.4 Sample pore water core profile. Concentrations of ammonium (○) and sulphate (●) in pore water. The lines are representative of the gradients used to calculate the present-day sediment accumulation rate.

coarser-grained materials (e.g. sands). Therefore it is important to account for variations in sediment grain size when interpreting sediment geochemistry, particularly when comparing samples with different proportions of clay, silt, and sand. Strategies that have been developed to eliminate grain size effects include physical separation of grain sizes, normalization, and regression.

1.2.1.3.1 Granulometric Methods

Granulometric methods often involve separation of grain sizes followed by chemical analysis of each grain size separate. However, this method is time consuming, labour intensive, and expensive and is therefore not recommended for large sample suites (Loring 1991). In addition, sieving and other granulometric techniques can alter the chemical characteristics of sediments and result in the release of relatively soluble phases during sample processing. Organic contaminants are often analyzed following sieving and further processing to achieve samples below a certain size fraction in order to reduce the variability between analytical results. If sampling environments contain relatively homogenously sized grains, grain size effects will be minimal.

1.2.1.3.2 Normalization

Normalization is another commonly used technique for eliminating grain size effects and involves normalizing concentrations of a chemical species of interest by another chemical species (e.g. iron, OC, aluminum, lithium) or sediment characteristic (e.g. percent of a particular grain size). One has to be careful when choosing the normalizing species or characteristic as the wrong choice can bias the results. As well, the resulting normalization is a ratio rather than an absolute concentration making results more difficult to interpret. Normalization can be used to establish whether changes in the concentration of a contaminant are due to changing grain size or to other factors (e.g. anthropogenic influences).

Geochemical approaches compensate for both mineralogical and grain size variation (Loring 1991). For example, iron is used as a normalizing factor as it commonly coats particles and is a constituent of many clay minerals, therefore variations in grain size (surface area) will be reflected by changing concentrations in iron. However, areas where redox conditions are not stable render iron inappropriate for normalization as iron is strongly affected by redox processes (Luoma and Rainbow 2008). Organic carbon is also commonly used to normalize results. However, OC can itself be a contaminant and can be tied directly to anthropogenic influences and therefore is often not an appropriate normalizing factor, particularly in areas impacted by sewage (Daskalakis and O'Connor 1995). Unlike OC, anthropogenic sources do not generally make a large contribution to aluminum levels in sediments. Because clays are commonly composed of aluminosilicates, concentrations of aluminum are commonly proportional to grain size. However, using aluminum to normalize results from sandy sediments can distort results as the normalization results in very small numbers (Feng et al. 1999). As well, aluminum concentrations do not vary with grain size in glacially derived sediments due to the abundance of aluminum in feldspars rendering it unsuitable as a normalizing factor in data sets from such environments and further eliminating aluminum as a candidate for a universal normalizing factor (Loring 1991). Unlike aluminum, lithium can be used to normalize data sets from glacially derived sediments as it is not usually present in feldspars. In addition, lithium is found in the latticework of clays, is not tied to anthropogenic inputs, is generally found in sufficient concentrations to be easily measured, and can be tied to grain size variations (Loring 1991).

1.2.1.3.3 Regression

Another method used to remove grain size effects is regression. In this method, the data is normalized using a chemical species like lithium and then a baseline regression is determined using data that is unaffected by anthropogenic contamination. The baseline regression is then subtracted from the rest of the data yielding data without grain size bias. However, this method requires a fairly large data set and the establishment of a sediment geochemistry baseline unaffected by anthropogenic contamination (e.g. Parsons and Cranston 2006).

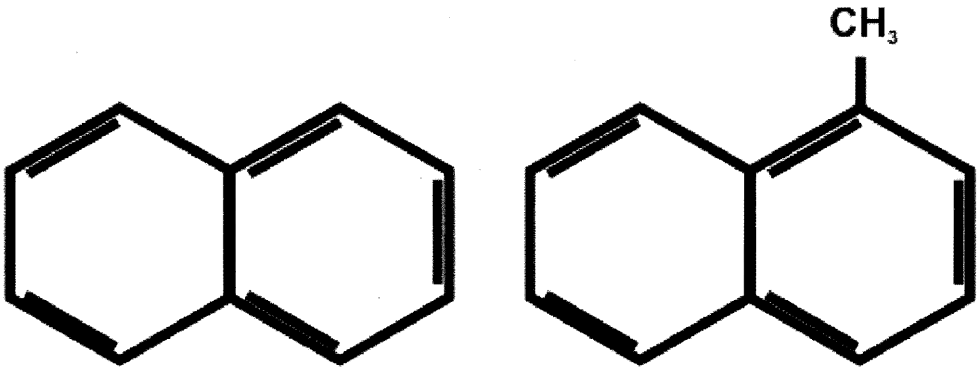
1.2.2 Organic Contaminants

Organic contaminants represent another class of contaminants which can have detrimental effects on organisms in marine environments. However, unlike metals which change speciation, organic contaminants degrade with time as a result of physiochemical and biological processes. Persistent organic pollutants (e.g. polychlorinated biphenyls (PCBs), PAHs) are a group of organic contaminants which are of interest due to their resistance to degradation, continued input, and impact on human health and the environment.

Polycyclic aromatic hydrocarbons were selected as analytes for this project based on previous research in many harbours, including Halifax Harbour (e.g. Hellou et al. 2002a). Both PAHs and polychlorinated biphenyls (PCBs) have been identified in harbour sediments at concentrations exceeding the probable effect level (defined as the level above which adverse biological effects occur frequently) of the Canadian Council of Ministers of the Environment (CCME) (1999) (Hellou et al. 2002a, 2002c). However, the import, manufacture, and sale of PCBs were banned in 1977 and their release into the environment was made illegal in 1985 (Environment Canada 2010a). Today trace levels of PCBs are found in the environment primarily as legacy contaminants and in remote environments as a result of long-range transport by global air currents (Health Canada 2006) and as such concentrations of PCBs, unlike PAHs, are not likely to be affected by increased wastewater treatment. Coprostanol (a hydrophobic sewage marker) and its isomer were selected as analytes as they have been found to bioaccumulate in mussel tissue (Yeats et al. 2008, Hellou et al. 2003), have been previously identified in harbour sediments (Hellou et al. 2008), and are persistent hydrophobic sewage markers. In the following sections the general chemical characteristics of both PAHs and select steroids, including coprostanol, are described.

1.2.2.1 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are a class of organic compounds which are composed of fused aromatic rings. They are often divided into two classes of compounds, parental and alkylated. Parental polycyclic aromatic hydrocarbons refer to those which do not have an alkyl group attached to the aromatic ring, while alkylated polycyclic aromatic hydrocarbons refer to those which have one or more alkyl group attached to the aromatic ring (Figure 1.5). For example, C2 naphthalene could refer to a naphthalene molecule with either two methyl groups or a single ethyl group. Because several PAHs have been identified as having mutagenic, carcinogenic, and teratogenic effects on organisms, PAHs are considered priority substances under the Canadian Environmental Protection Act (Environment Canada and Health Canada 1989). In particular, five PAHs (benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene) are considered toxic and a danger to human life or health and another nine PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene and naphthalene) have been classified as toxic and having a harmful effect on the environment under the Act. The two main



napthalene 1-methylnapthalene

Figure 1.5 Diagram of a parental and alkylated PAH. Napthalene is an example of a parental PAH and 1-methylnapthalene is an example of a corresponding alkylated PAH. Note the addition of a methyl group to the aromatic ring of 1-methylnapthalene.

sources of PAHs are spilling of fossil fuels and the incomplete combustion of materials (forest fires, garbage, volcanic eruptions) including fuels (e.g. wood, coal, diesel, fat), along with creosote, tires, asphalt and cigarette smoke. They are emitted from both natural sources (e.g. forest fires) and anthropogenic sources (e.g. coal combustion). Diagnostic ratios of PAHs (e.g. phenanthrene/anthracene) are often used to constrain their source. Tables 1.1 and 1.2 list some commonly used diagnostic ratios and their corresponding sources. Wood-burning and vehicle exhaust tend to contain higher concentrations of parental PAHs with 3, 4, and 5 rings, as these larger molecules are more likely to be incorporated into particles of soot (Richter and Howard 2000). Low concentrations of alkylated PAHs relative to parental PAHs are indicative of combustion sources, as alkylated PAHs are derived in greater abundance from fossil fuels (Wang et al. 1999 and references therein). PAHs are lipophilic and their distribution in sediments is strongly controlled by grain size and the concentration of OC (Baumard et al. 1999, Kim et al. 1999, Yang 2000).

The degradation of PAHs in the environment is thought to be predominantly through biological mechanisms (Park et al. 1990), although LMW (low molecular weight) PAHs do degrade through physical-chemical mechanisms (Cerniglia 1992, 1993). In particular, bacteria, fungi and algae are capable of metabolizing and breaking down PAHs (Cerniglia and Heitkamp 1989). High molecular weight (HMW) PAHs are less water

Table 1.1 PAH ratios as indicators of pyrogenic and petrogenic sources

Ratio	Source		
	Pyrogenic	Petrogenic	Mixture
AN / (AN + PA)	>1[a]	<0.1[a]	<1, >0.1[a]
FL / (FL + PY)	>0.5[a]	>0.4[a]	
BA / (BA + CH)	>0.35[a]	<0.2[a]	
IP / (IP + BP)	>0.5[a]	<0.2[a]	
(PA + AN + PY + FL) / (CH + CA + BF + BaP + IP + DBA + BP)	<1[b]	>1[b]	

anthracene (AN), phenanthrene (PA), fluoranthene (FL), pyrene (PY), benz(a)anthracene (BA), chrysene (CH), indeno(1,2,3-cd)pyrene (IP), benzo(g,h,i)perylene (BP), benzo(b&j&k)fluoranthene (BF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DBA)

[a] Yunker et al. 2002

[b] Soclo et al. 2000

Table 1.2 PAH ratios as indicators of hydrocarbon sources (from Hellou et al. 2002a)

Source	*PA/AN*	*FL/PY*
Halifax Harbour[a]	2.65 – 4.08	1.08 – 1.30
Fire soot[b]	3.2 – 4.2	0.7 – 1.5
Car soot[b]	1 – 5	0.9 – 1.3
Crankcase oil[b]	6 – 11	0.5 – 0.9
Fuel oil[c]	50	0.9
Sewage[c]	NA[d]	1.02 – 1.39
Street dust[c]	7.8	0.72 – 1.39
Highway run-off[c]	NA	2.88
Wood burning emissions[c]	2.14 – 11.17	0.76 – 1.37
Coke ovens emissions[c]	1.27 – 3.57	0.76 – 1.31
Municipal incinerators emissions[e]	NA	0.37
Sediment affected by coal burning[e]	3.40	1.10 – 1.79
Coke ovens[e]	0.50	0.62
Wood burning[e]	5.8	1.3
Highway dust[e]	4.7	1.4
Nova Scotia soils[f]	NA	0.5 – 1.9

[a] Hellou et al. 2002a

[b] O'Malley 1994

[c] Maher and Aislabie 1992

[d] Not available

[e] Christensen et al. 1999

[f] Windsor and Hites 1979, two sites close to Halifax

soluble and degrade less rapidly (Cerniglia 1992, 1993) than LMW PAHs. To a first approximation, PAH degradation rates are inversely proportional to the number of fused rings and are further reduced by ring substitution (e.g. alkylation) (Cerniglia and Heitkamp 1989). The rate at which PAHs degrade in the environment is dependent not only on the chemical structure of the PAH, but also on the physical-chemical conditions of the sediment and water and the numbers and types of microbes present. Talley et al. (2002) suggest that PAHs adsorbed onto coal-derived particles are less easily degraded and less mobile than those adsorbed onto clay/silt particles. The biodegradation of PAHs proceeds more rapidly in oxidized sediments than reducing sediments, as molecular oxygen facilitates the metabolism of PAHs by microbes (Cerniglia and Heitkamp 1989, Lima et al. 2005). However, Coates et al. (1996, 1997) demonstrated that LMW PAHs are capable of degrading under anoxic sulphate-reducing conditions in sediments heavily contaminated with petroleum-derived PAHs (33 ppm). However, in less contaminated sediments (4 ppm) LMW PAHs did not degrade. HMW PAHs were not found to degrade under anoxic sulphate-reducing conditions regardless of concentration. The rate of biodegradation is also affected by temperature. In the summer, degradation of PAHs proceeds more rapidly than in the winter, which may be due to the increased numbers of microbes and the increased metabolic activity of microbes in the summer (Lee and Ryan 1983). According to (Bauer and Capone 1988), degradation rates are higher for microbes that have been previously exposed to PAHs. Degradation rates of PAHs are nonlinear and generally decrease with time (Shuttleworth and Cerniglia 1995).

1.2.2.2 Coprostanol

The steroid coprostanol (5β-cholestan-3β-ol) is a hydrophobic sewage marker formed from the breakdown of cholesterol in the small intestine of several organisms including humans, cattle, sheep, and birds. It can also be produced *in situ* in sediments (Gaskell and Eglinton 1976). The concentration of coprostanol decreases away from its source and therefore can be used to determine the extent of the area affected by sewage influx (LeBlanc et al. 1992). Coprostanol degrades through the action of microbes more rapidly in aerobic sediments than in anaerobic sediments (Nishimura and Koyama 1977).

Nishimura and Koyama (1977) demonstrated that up to 90% of the coprostanol in anaerobic lake sediments at 15°C remained following a 450 day degradation experiment. Because coprostanol is relatively long lived in anaerobic environments, it has been used as a sewage marker to examine historical pollution in sediment cores. Venkatesan and Kaplan (1990) examined a core collected in Santa Monica Basin and found concentrations of coprostanol rapidly increased at depths corresponding to 1935 when effluent was first released in that area. Müller et al. (1979) examined coprostanol concentrations in a $^{210}Pb/^{137}Cs$ dated sediment core from Lake Constance, Germany and found that coprostanol persisted for more than 150 years. In contrast, Kelly (1995) developed a simple box model using successive inputs of sewage sludge over a 14 year period to predict coprostanol concentrations down core and found that subsequent sampling revealed that approximately 50% of the coprostanol had degraded over the 5 – 20 cm depth interval.

The concentration of coprostanol in human feces is significantly greater than the concentrations found in the feces of other species (Leeming et al. 1996), making it an appropriate sewage marker in urban environments (Takada and Eganhouse 1998). The ratio of coprostanol (5β-cholestan-3β-ol) to cholestanol (5α-cholestan-3β-ol) can be used to determine if the source of the coprostanol is anthropogenic (Grimalt et al. 1990). Coprostanol has a fecal origin, while cholestanol does not and is produced naturally in the environment through bacterial action. If the ratio (coprostanol/(coprostanol + cholestanol) is between 0.7 and 1, a human fecal origin is assumed. If the ratio is less than 0.3, the sediment can be described as uncontaminated. Samples with ratios that fall in between 0.3 and 0.7 cannot be described on the basis of this ratio alone. However, other diagnostic ratios describing the relationship between coprostanol and fecal origins are available. Grimalt and Albaiges (1990) examined ratios of coprostanol to cholesterol in water and sediment samples from several coastal areas with various sewage loads and suggest that a ratio greater than 0.2 is indicative of fecal contamination. Epi-coprostanol is formed during sewage treatment and can be indicative of the extent of sewage treatment and fecal material age. The ratio of epi-coprostanol to coprostanol can be used to measure age or extent of sewage treatment (McCalley et al. 1981). Using a ratio to examine coprostanol allows the effects of grain size and OC content to be minimized (Writer et al. 1995), as the distribution of coprostanol in sediments is strongly affected by grain size and OC content (Hatcher and McGillivary 1979, Takada and Eganhouse 1998).

1.2.3 Bioavailability

Bioaccumulation refers to the net absorption of a chemical of interest (e.g. trace metal) into an organism, while bioavailability is a measure of the concentration of a chemical absorbed by an organism relative to the concentration in the surrounding environment (Luoma and Rainbow 2008). Many factors (internal and external) affect the bioavailability of chemicals to biota. Both concentration and speciation are important as they affect the rate and degree to which a given organism will absorb a metal contaminant. Some ligands enhance bioavailability, while others decrease it (Chapman et al. 1998). As discussed by Hill (1997), toxicity is strongly linked to the chemical form (inorganic or organometallic) of the metal. In some cases the organometallic forms of trace metals are most toxic, while the inorganic forms are effectively non-toxic (e.g. tin). However, inorganic forms of arsenic and selenium are more toxic than their organic counterparts which are considered non-toxic. Both inorganic and organic forms of lead and mercury are toxic, although certain forms are more toxic. For example, elemental mercury is less bioavailable and hence less toxic than methyl mercury. Methyl mercury is produced through a biologically mediated reaction in anaerobic sediments, making estuaries a potential environment for mercury methylation (Choi and Bartha 1994).

The toxicity of PAHs is strongly affected by their molecular weight and structure (e.g. substitution). In addition, the presence of other chemicals (e.g. other PAHs) can affect their toxicity (Swartz et al. 1995). The uptake path for the more hydrophobic PAHs (HMW PAHs) is generally believed to be through ingestion of particles (Vives et al. 2005) or direct exposure to sediments (Kocan et al. 1996, Meador et al. 1995), while the uptake path for the more water soluble PAHs is thought to be respiration (Logan 2007). The lipophilic nature of PAHs makes them easily absorbed from the gastrointestinal tract of organisms (Cerniglia 1984). Although PAHs can degrade with time, the products of

PAH degradation are often more toxic than the parent compound (Shuttleworth and Cerniglia 1995).

In addition to characteristics of the chemical of interest itself, the surrounding environment (salinity, pH, temperature, presence of other contaminants) and exposure pathway also play a strong role in the bioavailability of chemical species (Förstner et al. 1986). Internal (biological) factors which affect bioaccumulation include the particular species being observed, body size, feeding rate, reproductive stage, and extent of previous exposure (Luoma 1989 and references therein). Contaminants can bioaccumulate via ingestion or uptake from solution. The contaminant's bioavailability in these different forms (sediment bound versus in solution) is dependent on the contaminant's chemical form (Luoma 1989). In addition, plants and animals can change the form of a metal (e.g. via digestion or extracellular secretions) thereby changing its bioavailability and hence its ability to bioaccumulate (Davies 1976, McKnight and Morel 1980, Luoma 1989). Bioturbation and bioirrigation can increase the exchange of contaminants between sediment and water and therefore affect bioavailability (Matisoff 1995, Peterson et al. 1996).

Bioavailability and bioaccumulation are the driving forces behind environmental assessments. Knowing the concentration of a contaminant in sediment is of little interest if there is no understanding of how that contaminant will affect the local biota (plant and animal). At what dose and exposure time varying organisms become affected by contaminants is of central interest to conducting environmental assessments (Chapman et al. 2003). Some chemical species are beneficial at low concentrations and detrimental at high concentrations (e.g. zinc) (Luoma and Rainbow 2008). In particular, when examining contaminants in sediments one should have an understanding of the bioavailability of that contaminant to benthic and epibenthic fauna. Contaminants can become biomagnified upwards through the food web as flora and fauna which have bioaccumulated contaminants are consumed by other fauna (Luoma and Rainbow 2008). The relationship between metal concentrations in sediments and in benthic species has been described as weak at best (Luoma 1989). However, metal concentrations in sediments can be used as a guide to look at areas where increased attention should be focussed (Chapman et al. 1999).

1.2.3.1 Acid Volatile Sulphides

Chemical extraction methods are commonly used to approximate the bioavailability of contaminants in sediments. One of the most common methods used for anoxic sediments is the measurement of acid volatile sulphides (AVS) and simultaneously extracted metals (SEM) (Di Toro et al. 1990, 1992, 1996, Allen et al. 1993). Acid volatile sulphides are authigenic sedimentary sulphides that can be digested in the laboratory following the addition of dilute hydrochloric acid. These AVS represent a pool of sulphides that can bind divalent cations in anoxic sediments, thereby decreasing the bioavailability of some metals. The molar ratio of the AVS to SEM is widely used in environmental and marine studies as a proxy for bioavailability. When the molar concentration of AVS exceed that of the SEM (SEM/AVS < 1), the metals are assumed to be in the form of sulphides and not biologically available. However, when the SEM are in excess of the AVS (SEM/AVS > 1) the metals are assumed to be bioavailable and therefore potentially toxic.

Although widely used, this method is generally not recommended for estuarine environments. It assumes a quasi-equilibrium state between contaminants in sediments and in water, which is unlikely to be achieved in an estuarine environment as the variable salinity in estuarine environments provides a strong control on bioavailability (Chapman and Wang 2001). The ratio of AVS to SEM is assumed to be representative of the portion of the trace metal of interest bound to the sediment surface which is made bioavailable by interstitial water. However, many deposit feeders ingest sediment particles, potentially increasing the bioavailability of trace metals in a way not accounted for by the AVS/SEM method (Lee et al. 2000). More complicated models created to predict the bioavailability of sediment-bound metals are available (e.g. Carbonaro et al. 2005). However these models are not sufficiently advanced to be applied in all situations (Carbonaro et al. 2005).

1.2.4 Sediment Quality Values

Many governments have developed environmental guidelines outlining acceptable concentrations of contaminants in sediments in an effort to protect benthic and epibenthic organisms and their habitats. The limitations of using these sediment quality values (SQVs) have been well documented (e.g. Chapman et al. 1999, Chapman and Wang 2001, Babut et al. 2005). Both Environment Canada and the National Oceanic and Atmospheric Administration (NOAA, USA) have developed similar sets of sediment quality guidelines using the effects level/ranges approach. Environment Canada uses two values in their assessments, the interim sediment quality guideline (ISQG) and the probable effect level (PEL). The lower value (ISQG) is defined as the level below which adverse biological effects rarely occur. As discussed in Section 1.2.3, the higher value (PEL) is defined as the level above which adverse biological effects occur frequently (CCME 2002). These values are based on adverse biological effects on organisms observed under field and laboratory conditions. Care must be taken when applying SQVs as they are generic recommendations and are not meant to consider site specific or management factors. While SQVs can be appropriate for screening areas requiring further investigation, they must be used in conjunction with other environmental risk management methods to identify and prioritize contaminated sites. Sediment quality values for select metals and PAHs are listed in Table 1.3.

Sediment quality values are based on total dry sediment weight and do not account for differences in bioavailability as a result of changes in chemical speciation, but do allow changes in grain size to be taken into account. They need to be evaluated in the context of the background concentration of the contaminant in the area of interest, rather than using a blanket value for all environments. This is particularly true for metals, which can exhibit wide ranges in background concentrations as a result of natural geological variability between different watersheds. For example, Painter et al. (1994) found that background concentrations of cadmium in 20% of lake and stream sediments (18,804 of 97,133 samples) collected throughout Canada exceeded the SQV used to screen ocean dumping. In addition, SQVs have been developed for fresh and marine waters (CCME

Table 1.3 Sediment quality values (dry weight) of select metals and PAHs (CCME 2002)

Substance	ISQG	PEL
Cadmium	**0.7 ppm**	**4.2 ppm**
Chromium	**52.3 ppm**	**160 ppm**
Copper	**18.7 ppm**	**108 ppm**
Lead	**30.2 ppm**	**112 ppm**
Mercury	**130 ppb**	**700 ppb**
Zinc	**124 ppm**	**271 ppm**
Acenaphthene	**0.00671 ppm**	**0.0889 ppm**
Acenaphthylene	**0.00587 ppm**	**0.128 ppm**
Fluorene	**0.0212 ppm**	**0.144 ppm**
Phenanthrene	**0.0867 ppm**	**0.544 ppm**
Anthracene	**0.0469 ppm**	**0.245 ppm**
Fluoranthene	**0.113 ppm**	**1.494 ppm**
Pyrene	**0.153 ppm**	**1.398 ppm**
Benz(a)anthracene	**0.0748 ppm**	**0.693 ppm**
Chrysene	**0.108 ppm**	**0.846 ppm**
Benzo(a)pyrene	**0.0888 ppm**	**0.763 ppm**
Dibenz(a,h)anthracene	**0.00622 ppm**	**0.135 ppm**

2002), but at this time the CCME does not have guidelines governing acceptable levels of contaminants in estuaries even though estuaries represent a unique environment. The development of SQVs has been based on available data which has generally been limited to applications in temperate climates. However, the climate of Canada varies widely from temperate through to arctic climates and as such SQVs need to be implemented with care when examining areas with more extreme climate. Finally, SQVs can act as a guide for evaluating areas where concentrations of a chemical species are too high, but they do not provide any indication as to what may be considered too low for particular essential trace metals (e.g. zinc).

CHAPTER 2: BACKGROUND

2.1 GEOLOGICAL HISTORY OF HALIFAX HARBOUR

Over the last several decades, there have been numerous studies of marine geology and oceanographic conditions within Halifax Harbour (e.g. Miller et al. 1982, Hargrave and Lawrence 1988, Petrie and Yeats 1990, Fader and Petrie 1991, Fader and Buckley 1997). The results of these studies are well summarized in a recent publication by Fader and Miller (2008). Understanding the marine geology of Halifax Harbour is essential for assessing the transport pathways of contaminants and for determining why sediments are deposited more readily in some areas than others.

2.1.1 Formation of Halifax Harbour

Halifax Harbour is a 25 km long north-west oriented inlet in Nova Scotia, Canada. Figures 2.1 and 2.2 show the locations of geographic features and places of importance in the harbour. The evolution of the shape of the harbour has been strongly influenced by both bedrock type and erosional processes. The five main stages in the geological history of Halifax Harbour are: (1) the formation of a fluvial drainage system (ancient Sackville River) which began to develop during the Cretaceous, (2) the advance and retreat of Quaternary glaciers resulting in over-deepening of the ancient Sackville River channel, (3) the formation of the over-deepened Bedford Basin, a fresh to brackish lake between 6000 and 8000 years ago (Miller et al. 1982), (4) the development of a series of post-glacial lakes and connecting rivers, and (5) the flooding of those lakes by seawater approximately 6600 years ago (Miller et al. 1982, Shaw et al. 2009).

Halifax Harbour is mainly underlain by Halifax Group slates and Goldenville Group quartzites of the Meguma Supergroup, which are truncated by granitoids of the South Mountain Batholith along the southwest margin of the harbour. Glacial over-deepening was mainly limited to areas within the Goldenville Group, particularly those rocks which

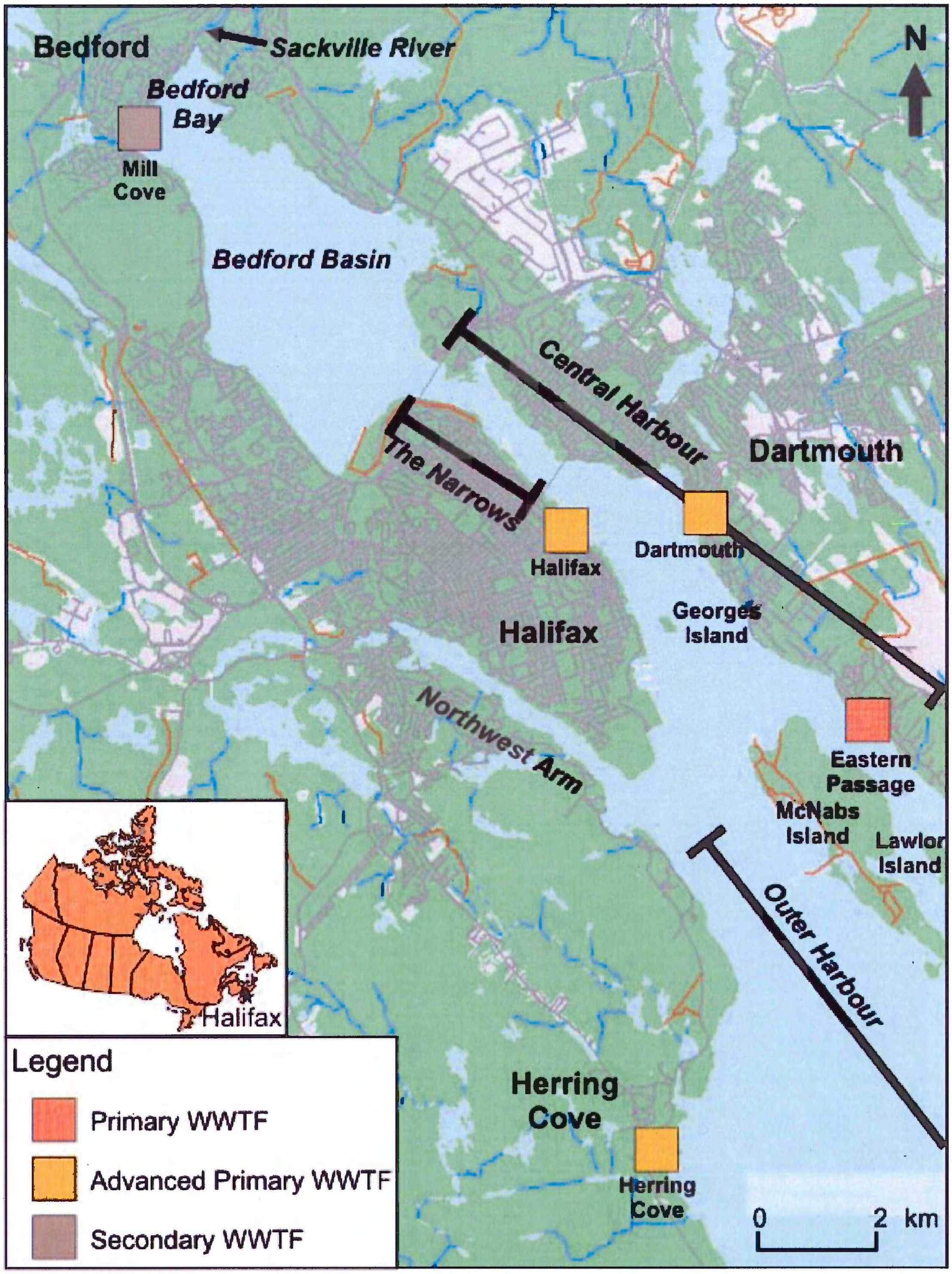


Figure 2.1 Map showing the locations of geographic features and WWTFs in Halifax Harbour.

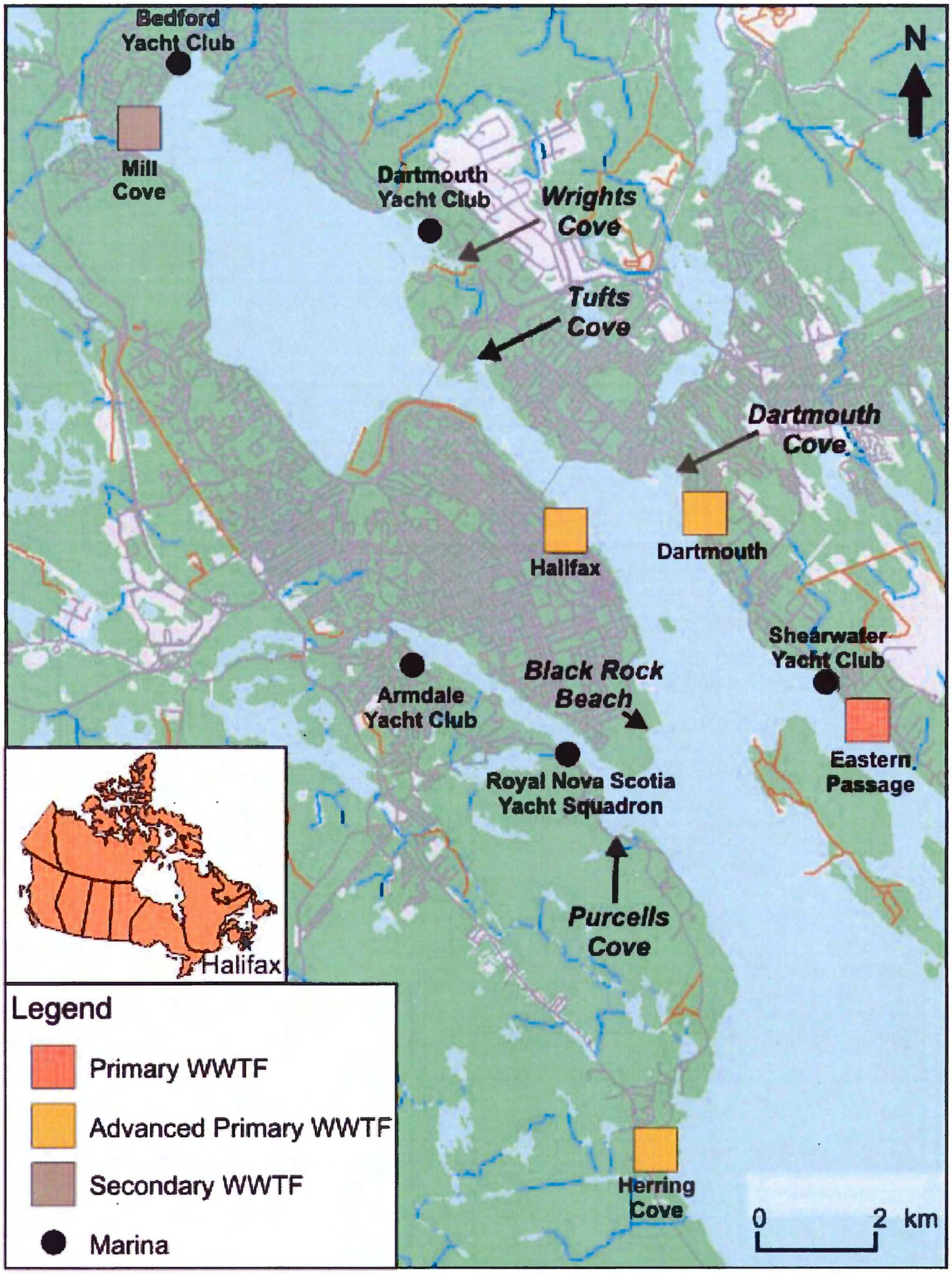


Figure 2.2 Map showing the locations of places of importance in Halifax Harbour.

were weakened during the formation of anticlines. This has led to the formation of wider areas in the harbour (e.g. the southern portion of Central Harbour) and deep basins (e.g. Bedford Basin), which act as sediment traps preventing contaminated sediments from being removed. The Narrows, which is underlain by the more resistant Halifax Group, was less affected by glacial erosion and overdeepening, and as a result is an area of high current energy where sediments are generally not deposited (Fader and Miller 2008).

2.1.2 Surficial Geology

Bedrock outcrops on the seafloor of Halifax Harbour in only a few areas. The majority of the harbour is covered by Wisconsinan glacial till, which is commonly overlain by sand, gravel, and clay. The bottom of the Narrows is characterized by a thin covering of sand and gravel overlying bedrock (Buckley and Winters 1992). Sediment in Bedford Basin is generally characterized by sandy clayey silt and clayey sandy silt averaging 3 – 5 m in thickness (Fader et al. 1991). Drumlins have been identified on the western side of Bedford Basin and to the north of Georges Island. Both McNabs Island and Lawlor Island were formed as a result of overlapping drumlins, while Georges Island is an isolated drumlin. As described by Buckley and Winters (1992), the bottom of Outer Harbour consists of sand and gravel but mainly bedrock, while Central Harbour and Northwest Arm are characterized mainly by clay.

2.1.3 Harbour Circulation

Petrie and Yeats (1990) developed a simple two-layer circulation model of Halifax Harbour based on two years of salinity data collected during monthly surveys. According to their model, lighter freshwater moves out of the harbour along the surface and denser saltier water moves inwards along the harbour bottom. According to this model, as fine-grained material from historical wastewater outfalls and drainage systems entered the surface waters, it flocculated and became heavier as it moved seawards. Eventually the particles became so heavy that they sank into the incoming bottom waters and were brought northward back into the harbour. Contaminated sediments entering the harbour are often contained in the harbour as a result of this circulation process.

The major source of freshwater into the harbour is the Sackville River, which has an average inflow rate of 5.3 m^3/s (Petrie and Yeats 1990). Additional sources of freshwater include numerous streams, wastewater outfalls, and rainfall, which together contribute twice the annual discharge of the Sackville River to the harbour (Petrie and Yeats 1990). According to Petrie and Yeats (1990), the strongest horizontal currents in the harbour occur in the Narrows and near McNabs Island, while the strongest vertical currents occur in the Narrows, around McNabs Island, and in the northern portion of Central Harbour (depending on run-off conditions). The weakest currents are found in Bedford Basin.

2.1.4 Sediment Input

According to Petrie and Yeats (1990), the major sources of sediment input in the harbour as of 1990 were wastewater (0.44 kg/s), primary productivity (2.7 kg/s), and the Sackville River (0.05 kg/s). MacNeil and Hurlbut (2000) used Petrie and Yeats' estimations of sediment input to predict the effects wastewater treatment would have on the suspended solids budget of the harbour. However, they reduced the wastewater input to 0.12 kg/s based on a sewage monitoring study conducted by SNC Lavalin in 1999. The new estimate of wastewater input is apparently more representative of average dry weather flow rather than Petrie and Yeats' estimate which represents an annual average including storm events. These results suggest that wastewater accounts for between 4 – 14% of the suspended solids present in the harbour depending whether one uses Petrie and Yeats' estimate or MacNeil and Hurlbut's. Advanced primary wastewater treatment in HRM is expected to remove between 75 – 90 % of suspended solids (see Table 2.2). Even if wastewater accounts for 14% of the suspended sediment input to the harbour and 90% of it is removed during advanced primary treatment, the expected effect on sedimentation rates in the harbour is likely to be small (<13% reduction in suspended sediment input) and will have a minimal effect on the average sedimentation rate in the harbour. Table 2.1 shows the levels of total suspended solids in Halifax Harbour observed when no advanced primary WWTFs were operating, when limited advanced primary WWTFs were operating, and when all advanced primary WWTFs were operating. These results indicate that there is little to no difference in the levels of total suspended solids measured in the water column of Halifax Harbour with the initiation of advanced primary wastewater treatment, further suggesting that wastewater treatment has minimal impact on sediment inputs in the harbour. While wastewater treatment is likely to have a substantial effect on sediment input in the harbour as a whole, a significant decrease in sediment input immediately adjacent to former wastewater outfalls would be expected.

Table 2.1 Total suspended solids in Halifax Harbour. WWTFs refers to the advanced primary WWTFs operating during the dates listed.

Date (month/year)	WWTFs	Minimum (mg/L)	Maximum (mg/L)	Mean (mg/L)
09/06 – 12/06[a]	none	<1.0	8	2.0
05/07 – 06/07[b]	none	0.9	10.0	3.8
09/08 – 12/08[c]	Halifax and Dartmouth	1.0	6.8	2.6
03/09 – 06/09[d]	Dartmouth, Herring Cove	<0.5	11.0	3.4
05/10[e]	Halifax (no UV treatment), Dartmouth, Herring Cove	<0.5	13.0	3.2

[a] AMEC Earth and Environmental 2010a
[b] AMEC Earth and Environmental 2010b
[c] AMEC Earth and Environmental 2010c
[d] AMEC Earth and Environmental 2010d
[e] AMEC Earth and Environmental 2010e

2.2 HUMAN HISTORY OF HALIFAX

Numerous books providing detailed chronicles of HRM have been published (e.g. Blakeley 1973, Bruce 1997, Raddall 2007). Halifax was founded as a military outpost for the British Government in 1749 by Governor Edward Cornwallis. The settling of Halifax by the British required vast tracks of land to be cleared, crops to be grown, and shoreline to be infilled. From 1749 onwards, Halifax Harbour was used as a repository for both domestic and industrial waste. The effects of the founding of Halifax on the harbour seabed have been considerable. Although there is substantial evidence of seasonal Mi'kmaq habitation and burial sites prior to the settling of Halifax by the British, the resulting anthropogenic effects were likely minimal (Fader and Miller 2008).

Halifax has a long tradition of marine industry. In 1758, the first naval dockyards in North America were opened in Halifax. Her Majesty's Canadian Dockyard was then expanded to include Stadacona (now Canadian Forces Base Halifax) in 1906. In 1837, the first yacht club in Halifax opened. Its name, the Royal Halifax Yacht Club, was later changed to the Royal Nova Scotia Yacht Squadron, which is still operating today (Figure 2.2). In 1872, the Intercolonial Railway opened, connecting Halifax to the rest of North America. Eight years later, Intercolonial opened the Deep Water Terminus, which allowed up to twelve steamers to dock simultaneously. In 1889, the Halifax Graving Dock Company opened the largest drydock facility on the Atlantic seaboard. During World War I, the harbour became a major shipping and naval port. In World War II, the harbour was Canada's principle staging area for transatlantic ship convoys. The prevalent use of Pb in marine paints and the high numbers of ships in the harbour during this period had a substantial influence on Pb levels in harbour sediments.

Dredging in the harbour continues to be used as a way to ensure that waters are sufficiently deep to allow ships to easily pass through. The dredged material is also used as a source of fill for construction. Several areas of Halifax Harbour have also been infilled to allow for shipping, industrial construction and residential construction along the shoreline: this practice continues today (e.g. in Bedford Bay).

As summarized by Fader and Miller (2008), the impacts of shipping and other anthropogenic activities on the seafloor have been characterized through acoustic and video surveys. Anchor furrows, more common in Central Harbour and Bedford Basin, have disturbed sediment up to a meter in depth. Dredge spoils, excavation pits, shipwrecks, and debris including waste containers, spilled cargo, pipes, cables, cars and timber have also been identified on the bottom of Halifax Harbour.

Today the harbour is used for shipping, recreation, fishing, public transportation and tourism. It is a major shipping port, which handles 1500 vessels a year (Halifax Port Authority 2010). It is used by civilians (e.g. Armdale Yacht Club, Bedford Yacht Club), industry (e.g. Imperial Oil Wharves serving the Dartmouth refinery, Ultramar Wharves serving the petroleum storage facility, Autoport), the government (e.g. Bedford Institute of Oceanography, Canadian Coast Guard) and the military (e.g. Canadian Forces Base Halifax, Canadian Forces Base Shearwater) (Fader and Miller 2008).

2.2.1 Human History of Bedford

Edwards (2007) provides a detailed chronicle of the history of Bedford. In 1749, a small fort was built near the Sackville River in what is now Bedford. The population grew slowly, but by the turn of the 19th century several sawmills had begun operating in the area due to Bedford's proximity to the Sackville River. In addition, a tannery, a dam, and a paper mill were built in the early 1800s in the area near Mill Cove. By the mid-19th century Bedford had a railway stop and a thriving ship-building industry. As the ship-building industry faded at the turn of the 20th century, other industries (e.g. fish hatchery, telephone service, woollen mill, and hydroelectric generation) were developed to meet the needs of and employ the growing population. Today, Bedford has a population of over 15,000 people (HRM 2008b).

2.3 SOURCES OF CONTAMINATION

Potential sources of contamination (metals and organic compounds) in the watershed of Halifax Harbour include domestic sewage, commercial and small industrial facilities (e.g. dry cleaners, photographers, car dealerships), institutions (e.g. universities, hospitals, military bases), large industrial facilities (e.g. oil refineries, Nova Scotia Power Corporation, Halifax Autoport), a former city dump along the southern shore of Bedford Basin, resuspended sediments, run-off, atmospheric inputs, and shipping discharges (e.g. spills) (Fournier 1990). In particular, likely sources of lead in the harbour include lead-based paints, leaded gasoline, coal fragments and coal combustion residues. Until the 1960s, lead was a common additive in marine paints. Similarly, the addition of lead to gasoline began to decline in the 1970s in Canada and was eventually prohibited in 1990 under the Canadian Environmental Protection Act. Buckley and Winters (1992) described a strong relationship between the high levels of lead and the locations of industrial shipyards in the harbour. Sources of copper and zinc are likely related to the use of marine paints. Copper is used as an antifouling agent in marine paints, while zinc is used as a rust inhibitor. Sources of mercury in the harbour include the use of coal fuels, industrial shipyards, and wastewater discharges.

The presence of PCBs in Halifax Harbour can generally be attributed to commercial sources, including dyes and used coal, as well as sewage input (Hellou et al. 2002c). Hellou et al. (2002b) suggest that the major sources of alkanes in the harbour are light oil (diesel) and terrestrially derived waxes, while the major source of terpanes is the widespread occurrence of used oil in the harbour. The fingerprint of PAHs in harbour sediments suggests a predominantly combustion source (crankcase oil and car soot) for these organic contaminants rather than a petroleum source (Hellou et al. 2002a).

Emerging contaminants are a broad classification of contaminants that are known or suspected to cause adverse ecological or human responses, but are not commonly monitored in the environment (United States Geological Survey 2009). They include personal care products, household products, pharmaceutical products, and flame retardants and have become of increasing concern over the last decade. Domestic garbage and wastewater are the most common sources of many emerging contaminants (e.g. Sanderson et al. 2004).

Although emerging contaminants are outside the scope of this research, they are known to contribute to the contamination of Halifax Harbour sediments (Robinson et al. 2009). Robinson et al. (2009) examined water and surface sediment samples from seven sites in Halifax Harbour for the presence of three potentially toxic estrogenic compounds. They found evidence of all three compounds in sediments, suggesting that degradation rates are too low to prevent these compounds from accumulating in the sediment. In addition, they determined that concentrations of all three compounds were highest in a sample of untreated wastewater from Mill Cove WWTF, indicating that wastewater is the source of these compounds. Comeau et al. (2008) examined final effluents from Mill Cove WWTF and water samples from four locations in Halifax Harbour for ten acidic drugs (including nonsteroidal anti-inflammatory drugs) and caffeine. They found evidence of small amounts of all ten acidic drugs and caffeine in the wastewater effluent and found evidence of some acidic drugs at all water sampling locations. In addition, they determined that the discharge of untreated wastewater into the harbour was the principal source of pharmaceuticals in their study area. Brun et al. (2006) also found evidence of pharmaceuticals in the final effluent from Mill Cove WWTF. They identified residues from eight of the twelve drugs they tested in Mill Cove effluents. However, only two drugs were detected in the receiving water for Mill Cove effluents, Bedford Bay.

2.4 WASTEWATER TREATMENT

There are two types of wastewater collection systems: combined wastewater and separate sewage collection systems. Combined wastewater collection systems mix run-off and sewage waste, while separate sewage collection systems only collect sewage waste. Heavy rainfall can overwhelm combined wastewater collection systems resulting in the release of untreated wastewater. It is very important to make a distinction between sanitary sewage and wastewater. Sewage is a subset of wastewater. According to Environment Canada (2010b) wastewater is defined as liquid wastes from sanitary sewage and stormwater. Sanitary sewage includes waste produced from residential, commercial and industrial sources. Stormwater is generated from precipitation (rainfall and melting snow) drained from urban surfaces including roadways, rooftops, and lawns.

The progression of wastewater treatment in and around Halifax Harbour is chronicled by HRM (2009). The first wastewater pipes were installed in Halifax in the 1850s and the first WWTF (Mill Cove) opened on the shores of Bedford Basin in 1970. This plant, a secondary WWTF, was subsequently expanded in 1981 and again in 1997. During the most recent expansion, a surge/flow equalization tank was built to allow wastewater to be stored during storm events. As a result, wastewater no longer bypasses Mill Cove WWTF, preventing untreated wastewater from being released into the harbour at this location. The Eastern Passage WWTF opened in 1974 and was downgraded from secondary to primary wastewater treatment in 1988. It is expected to be upgraded back to secondary wastewater treatment levels in the next five years (T. Blouin, Halifax Water, personal communication 2010). Three new advanced primary WWTFs have been commissioned under the auspices of the HSP.

The four commonly used levels of wastewater treatment are primary, advanced primary, secondary, and tertiary. The three levels of wastewater treatment used in HRM treatment facilities releasing effluent into Halifax Harbour are discussed below in Section 2.4.1 (primary, advanced primary), Section 2.4.2 (secondary) and are illustrated in Figure 2.3. The locations of those WWTFs are displayed in Figure 2.1.

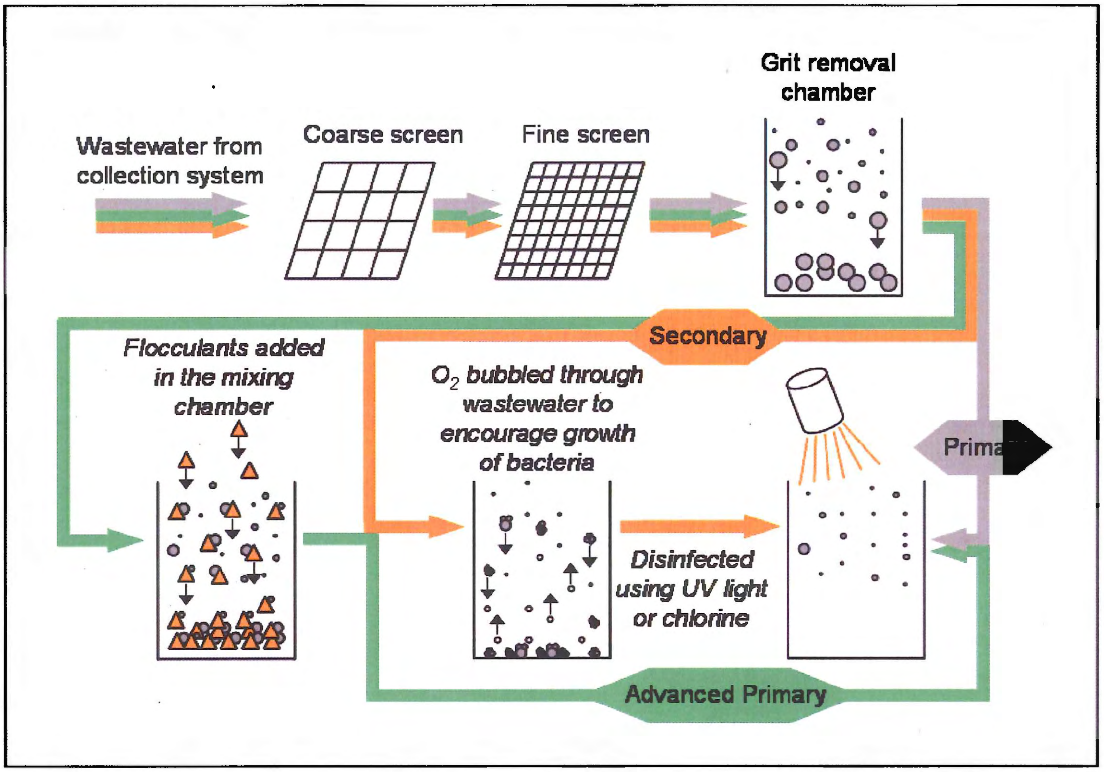


Figure 2.3: Processes in primary (grey stream), advanced primary (green stream), and secondary (orange stream) WWTFs.

2.4.1 Primary and Advanced Primary Wastewater Treatment

The specific steps in HRM's primary (Eastern Passage) and advanced primary WWTFs (Halifax, Dartmouth, and Herring Cove) are well summarized by HRM (2005a, 2008b). The first step in all wastewater treatment is to remove the coarse and then finer suspended material using a series of screens with different sized meshes. Additional grit is then removed in the grit removal chamber where the flow rate of the wastewater is carefully controlled allowing sand and gravel to settle. It is the addition of flocculants to the wastewater which separates advanced primary treatment (also known as chemically enhanced primary treatment or chemically assisted primary sedimentation process) from conventional primary treatment practices. In advanced primary systems, flocculants (e.g. alum, salts, lime, ionic polymers, non-ionic polymers) are added to the wastewater in the mixing chamber (Ahmed et al. 2005). HRM currently uses an anionic polymer as a flocculant and aluminum sulphate as a coagulant at its three advanced primary WWTFs (T. Blouin, Halifax Water, personal communication 2010). The flocculants bind to smaller particles making them larger and more likely to settle out. In addition they provide reactive surface area which assists in the removal of metals and organic contaminants through adsorption and co-precipitation. The treated wastewater is then disinfected using chlorine or high-intensity ultraviolet (UV) lights before discharge to the receiving water, Halifax Harbour.

Removal efficiencies for chemical oxygen demand (chemical procedure used to determine the amount of oxygen consumed when all the organic matter is oxidized to CO_2 and H_2O), biochemical oxygen demand (a subset of chemical oxygen demand which refers to the amount of oxygen potentially consumed if all the biodegradable organic matter is degraded), suspended solids, metals and PAHs that can be achieved through primary and advanced primary treatment are listed in Table 2.2. Removal efficiencies are quite variable for metals and PAHs. For example, Hunt et al. (1995) found that advanced primary treatment resulted in high removal efficiencies (72 – 86%) for silver, mercury, and lead and intermediate removal efficiencies (37 – 50%) for cadmium, copper, and zinc. They suggest that primary treatment does not result in substantial removal of nickel and zinc (removal efficiencies of 3 – 50%). Removal efficiencies for PAHs using primary treatment are strongly dependent on molecular weight. Bedding et al. (1995a) found that the removal efficiency of PAHs increased with molecular weight. Removal efficiencies are dependent are influenced by the initial concentration of the chemical on interest, its speciation, the operating parameters of the WWTF, the presence and concentrations of other contaminants, as well as other physical, chemical, and biological factors (Chipasa 2003).

Table 2.2 Removal efficiencies achieved through primary, advanced primary, and secondary wastewater treatment techniques

	Primary	Advanced Primary	Secondary
Biochemical oxygen demand	30%[a] 25 – 40%[b] 35%[c]	55 – 78%[a] 40 – 80%[b] 50%[c]	92%[a] 90%[d]
Chemical oxygen demand	30 – 35%[e]	60%[e] 30 – 70%[b] 45%[f]	90%[g]
Suspended solids	50 – 70%[b] 55%[a] 65%[c] 40 – 60%[h]	71 – 92%[a] 60 – 90%[b] 75%[c] <90%[h]	90%[d]
Metals	8 – 91%[i] 25%[c] 15%[h]	7 – 87%[f] 20 – 86%[i] <90%[h]	70 – 90%[j] 57 – 96%[k] 7 – 98%[i]
PAHs	21 – 63%[m] 35 – 86%[l] 32 – 79%[i]	71%[i]	99%[n] >85%[i]
Coprostanol	0%[o]		>94%[o]

[a] National Research Council 1993
[b] De Feo et al. 2008
[c] Jacques Whitford Environment Limited 2001
[d] HRM 2005c
[e] Huang and Li 2000
[f] Jiménez and Landa 1998
[g] Cao et al. 2008
[h] Halifax Harbour Cleanup Inc. 1993
[i] Hunt et al. 1995
[j] Chipasa 2003
[k] Shafer et al. 1998
[l] Bedding et al. 1995b
[m] Bedding et al. 1995a
[n] Reichert et al. 1971
[o] Takada and Eganhouse 1998 and references therein

2.4.2 Secondary Wastewater Treatment

The specific steps in HRM's secondary treatment facility (Mill Cove) are described by HRM (2005b). The initial stages of secondary treatment are similar to primary treatment and include the removal of suspended material using a series of screens and flow control. In secondary treatment, however, the wastewater is then treated using aerobic biological processes to further remove biological material. Oxygen is bubbled through the wastewater in the aeration chamber to encourage the growth of bacteria, which digest soluble organic contaminants and bind other contaminants to create a biological floc. The resulting particles are allowed to settle out before the treated wastewater is disinfected using chlorine or high-intensity ultraviolet lights. Table 2.2 lists the removal efficiencies for biochemical oxygen demand, chemical oxygen demand, suspended solids, metals and PAHs achievable through secondary treatment. Average removal efficiencies of select metals from Mill Cove WWTF from 2003 to 2008 are summarized in Table 2.3.

Table 2.3 Average influent concentrations, effluent concentrations, and removal efficiencies of select metals from the Mill Cove WWTF between 2003 and 2008 (S. Taylor, Halifax Water, personal communication 2009)

	Influent (μg/L)	Effluent (μg/L)	Removal Efficiency
Cadmium	<0.3	<0.3	-
Chromium	<0.2	<0.2	-
Cobalt	1	1	0%
Copper	36	14	61%
Iron	920	190	79%
Lead	1.7	0.6	65%
Manganese	400	200	50%
Mercury	0.19	<0.05	>74%
Nickel	4	4	0%
Zinc	77	35	55%

2.4.3 Harbour Solutions Project

The HSP involved building three advanced primary WWTFs (Halifax, Dartmouth and Herring Cove). The Halifax WWTF began operating in Fall 2007, but went offline in January 2009 and subsequently reopened in June of 2010. The Dartmouth facility began operating in Summer 2008, while the Herring Cove WWTF began operating in Fall 2009. A major component of the HSP was to combine the numerous outfalls releasing raw wastewater into the harbour into a single wastewater collection system (Jacques Whitford Environment Limited 2001). This new system of pipes diverts wastewater from the old outfalls to the WWTFs. It is capable of capturing up to four times the predicted average dry weather flow of wastewater for the year 2041 and conveying it to the WWTFs (Jacques Whitford Environment Limited 2001). However, when the flow limit is exceeded (e.g. during storm events), the overflow will be released directly into the harbour through individual combined sewage overflows. These combined sewage overflows are equipped with screens or baffles to remove floatables prior to releasing the wastewater into the harbour. These overflow events are expected to occur between 20 and 70 times per year. "The Halifax Harbour Task Force recommended a containment philosophy for the discharge of effluent from WWTFs and this has been supported by subsequent advisory groups" (Fader and Miller 2008), including the Harbour Solution Project. The locations of both the WWTFs and the outfalls were chosen to minimize their impact on the community and the marine environment. The outfalls allow the treated effluent to be discharged into the harbour avoiding sensitive areas and promoting dispersion with an initial dilution of at least 20:1 (Jacques Whitford Environment Limited 2001). In addition to building WWTFs and combining wastewater outfalls, the HSP requires the HRM to monitor harbour water quality on a biweekly basis. However, Buckley and Winters (1992) determined that many of the legacy metal contaminants in the harbour are sequestered in the sediments. As such, determining sediment quality as well as water quality is important in evaluating the success of the HSP.

2.4.4 Pollution Prevention Program

In conjunction with the HSP, the HRM has implemented a point source control program called the Pollution Prevention Program. The program was initially implemented in 1996 as the Source Control Strategy and has since been expanded through the 2000 Pesticide By-Law and the 2001 Wastewater Discharge By-Law (HRM 2010b). It is aimed at controlling the influx of toxic substances to wastewater, restricting their arrival in the harbour. As a complement to the HSP, it is key to ensuring a return to a healthy marine ecosystem for Halifax Harbour.

2.4.5 CCME Guidelines

The negative impacts of contaminants in untreated wastewater on aquatic ecosystems and to human populations have been well documented (Chambers et al. 1997). However, Canada has only recently developed a nation-wide approach to wastewater management, which was previously subject to shared jurisdiction. In 2009, the CCME developed the Canada-wide Strategy for Managing Municipal Wastewater Effluent (CSMMWE), which provides a set of guidelines outlining the standards municipalities must follow in managing wastewater effluent (CCME 2009). The CSMMWE identifies continued research into municipal wastewater effluent issues as a priority for future research endeavours.

The proposed Wastewater Systems Effluent Regulations, under the auspices of the Fisheries Act, are meant to meet the requirements established under the CSMMWE (Environment Canada 2010d). These regulations are intended "to reduce the risks to ecosystem health, fisheries resources and human health by decreasing the level of harmful substances deposited to Canadian surface water from wastewater effluent" (Environment Canada 2010d). They are designed to partially fulfill Canada's National Programme of Action, which it developed following the adoption of the Global Programme of Action for the Protection of the Marine Environment from Land-based Activities in 1995. These new regulations were published in Part I of the Canada Gazette on March 20, 2010, where interested groups and individuals were invited to comment on them for 60 days. Following registration, they will be phased in over a three year period.

As part of the regulations, environmental effects monitoring would be required for up to 13 years following the initiation of wastewater treatment. Environmental effects monitoring would be limited to water quality monitoring studies and biological monitoring studies. Although sediment samples will be collected during benthic invertebrate monitoring studies, only OC content and particle size distribution will be determined.

These regulations include discharge limits of common substances that are equivalent to what can be achieved using secondary wastewater treatment practices. In fact, secondary wastewater treatment is the level of treatment which all municipalities will eventually be required to attain (Environment Canada 2010d). Depending on the level of protection required by the effluent's receiving environment, municipalities will have ten, twenty or thirty years to meet this requirement. HRM will be required to meet these regulations as well, and will have to upgrade their newly built advanced primary WWTFs in the near future.

2.5 PREVIOUS RESEARCH

A number of studies have examined the toxicological, chemical and physical characteristics of Halifax Harbour. Concentrations of organic and metal contaminants in Halifax Harbour have been examined both spatially and temporally in several different mediums (e.g. sediment, water, mussel tissue).

2.5.1 Sediment Chemistry

Intensive research into the environmental impacts of wastewater and other anthropological activities on Halifax Harbour began in the early to mid 1970s (Hargrave and Lawrence 1988) and continues today. Prouse and Hargrave (1987) determined the sediment porosity, oxidation-reduction potential, organic matter content, OC content and nitrogen content in surface sediment samples from 102 stations throughout Halifax Harbour. They identified areas with strongly reducing sediments near oil refineries in Central Harbour on the Dartmouth side, near Mill Cove, in Northwest Arm and in Herring Cove. They found that strongly reduced sediments were also associated with high OC and nitrogen contents.

Gearing et al. (1991) examined hydrocarbon and metal contaminant levels in a single dated core from Northwest Arm. They found that contaminant levels have increased 100-fold since 1900. While concentrations of aliphatic hydrocarbons and metals (lead, zinc, copper, and mercury) have increased steadily, aromatic hydrocarbon levels peaked around 1950 and have been declining since that time. This study is the only published research looking at PAH levels in cores from Halifax Harbour.

Buckley and Winters (1992) examined the concentrations of metal contaminants in 274 surface sediment samples collected throughout the harbour. They used factor analysis techniques to explore relationships between contaminants (e.g. lead), dominant geochemical properties (e.g. OC), and predominant sediment type (e.g. clayey-silt). Their study suggests that settling of particle-bound metals is the most important method of deposition for the majority of metal contaminants in the harbour and that most of the contaminants are derived from wastewater effluents (untreated sewage and industrial waste) and waste deposits. The geochemical data used in their study was summarized by Winters et al. (1991) and discussed in detail by Buckley and Hargrave (1989).

Buckley et al. (1995) tested 27 dated sediment cores collected throughout the harbour for metals and OC. Results of their study identified wastewater outfalls and industrial centres in Central Harbour as the areas with the highest flux of total mercury, copper, zinc, and lead, particularly during the mid 20th century. While their results examined trends in contaminants through time, the cores were generally not long enough to characterize pre-industrial sediment conditions for all contaminants of interest. Longer cores (>1.5 m) would allow a pre-industrial baseline for specific contaminants to be established, even in areas most heavily impacted by wastewater.

Hellou et al. (2002a) looked at concentrations of PAHs in surficial sediments and inter-tidal mussels at 21 and 18 sites in the harbour, respectively. Determining the concentrations of contaminants in both sediments and mussels can provide an understanding of contamination levels in both benthic and pelagic habitats and clarify the relationships between contaminant concentrations in the water column (pelagic habitat) and surficial sediments (benthic habitat). Hellou et al. (2002a) determined that the relative concentrations of PAHs in sediments and mussels differ between locations which is unsurprising given the different solubilities of different PAHs. They found that concentrations of 13 parental PAHs in sediments exceeded the CCME's SQVs in most areas of the harbour. The predominant source of PAHs in both sediments and mussels was combustion processes based on diagnostic PAH ratios (see Table 1.1). Concentrations of PAHs in sediments were found to be highest in Northwest Arm and near a wastewater outfall in Central Harbour. Relatively low concentrations were observed in Outer Harbour and near the Mill Cove and Eastern Passage WWTFs.

Hellou et al. (2002b) determined the concentrations of alkanes, terpanes, and aromatic hydrocarbons in the same surficial sediments as those analyzed by Hellou et al. (2002a). The results from this study correspond well to Hellou et al. (2002a) in that concentrations of contaminants in the immediate vicinity of the Mill Cove and Eastern Passage WWTFs were low relative to adjacent sample areas.

Few studies in Halifax Harbour have included coprostanol as a contaminant of interest. Hellou et al. (2008) examined coprostanol levels in sediments, while Yeats et al. (2008) and Hellou et al. (2003) evaluated coprostanol levels in mussel tissue and Pocklington et al. (1987) studied coprostanol levels in the waters of Bedford Basin. However, none of these studies examined coprostanol levels in sediments cores.

2.5.2 Sedimentation Rates and Redox Conditions

Buckley et al. (1995) determined redox conditions in the harbour using sulphate and ammonium concentrations, alkalinity, and redox potentials of pore water from sediment cores. Their results confirm the reducing nature of harbour sediments and suggest that reducing conditions exist within 1 cm of the sediment-water interface near Dartmouth Cove, northeast of McNabs Island, near the Halifax WWTF and in Northwest Arm. In addition, they determined sedimentation rates in Halifax Harbour using ^{210}Pb-dated segments of cores. According to their results, sedimentation rates in the harbour range from 0.04 to 1.2 cm/year and are greatest in Central Harbour, intermediate in Northwest Arm, and lowest in Bedford Basin.

Cranston (1994) also examined sedimentation rates in Halifax Harbour. However, he used geochemical pore water gradients and OC concentrations to establish present-day sedimentation rates, which were generally lower than Buckley et al.'s (1995) results determined using conventional dating methods on the same cores. Cranston's method gave present-day sedimentation rates of 0.04 to 0.30 cm/year in the harbour.

2.5.3 Bioaccumulation of Contaminants

Several contaminants in the harbour have been found to have biological effects on aquatic organisms. Tay et al. (1992) used sediment toxicity, bioaccumulation, and chronic effects tests to examine the effect of metals and organic contaminants in Halifax Harbour on six aquatic species. The results of their sediment toxicity tests suggest that PAH levels in the harbour are sufficiently high to produce adverse biological impacts on two of the six species studied. They also found lesions in the livers of winter flounder, which they suggest are a result of chronic exposure to contaminated sediments. However, they did not find a relationship between biological effects on the organisms and concentrations of metals in the sediments, which they attribute to the sequestration of metals by the sediments in insoluble forms of sulphide.

Prouse and Ellis (1997) examined imposex (masculinisation) in dogwhelks (sea snails) from several areas along the Atlantic seaboard in Eastern Canada. All sites surveyed in Halifax Harbour showed either the absence of dogwhelks or significantly imposexed dogwhelks. Imposex in dogwhelks has been linked to contamination by tributyltin and is commonly used as a bioindicator of tributyltin (Matthiessen and Gibbs 1998).

Hellou et al. (2003) examined the bioaccumulation of PAHs, PCBs, coprostanol, and metals in mussels collected at three sites in Halifax Harbour and compared those results to indicators of mussel health. They found that concentrations of contaminants were highest in areas adjacent to wastewater outfalls in Central Harbour and that a higher proportion of males than females were present in those areas. Mussels collected in less contaminated areas of Central Harbour showed evidence of feminizing effects.

Hellou and Law (2003) studied the stress-on-stress responses of two types of mussels collected from the same areas of the harbour as those examined by Hellou et al. (2003). They found that mussels from the less contaminated area (lowest concentrations of PAHs) were less stressed, while those from the most contaminated area (highest concentrations of PAHs) were most stressed as indicated by the LT_{50} tolerance test.

Hellou et al. (2005a) examined concentrations of PAHs in water, particulate matter, and inter-tidal mussels from the three sites in Halifax Harbour previously studied by Hellou et al. (2003). They found a greater proportion of bioaccumulated alkylated PAHs in mussels in the spring than in the fall when bioaccumulated parental PAHs were dominant. The relative concentrations of PAHs in water, particulate matter and mussels were found to differ between locations. In addition, they determined that increased contaminant levels in sediments and water were not necessarily reflected by bioaccumulation in aquatic species. However, they do suggest that sediment disturbance can make PAHs more bioavailable to mussels, which is likely to be important as redox conditions change following increased wastewater treatment. They hypothesize that advanced primary wastewater treatment will reduce the amount of larger more hydrophobic parental PAHs deposited in the harbour, but is unlikely to affect the amount of smaller PAHs like alkylated naphthalenes and fluorenes.

Hellou et al. (2005b) studied the behavioural response of *Corophium volutator* (an amphipod) to contaminated reference sediments, including sediments from Halifax Harbour. The amphipods displayed avoidance response behaviour to five sediment samples collected from the harbour in which the concentrations of PAHs were above the PEL recommended by the CCME.

Scott et al. (2005) examined benthic foraminiferal assemblages in cores from Halifax Harbour and New Bedford Harbour (Massachusetts) to determine how faunal changes relate to geochemical parameters. They determined that the presence and abundance of foraminifera change in response to elevated lead, copper, and zinc levels, high organic loading, and increased suspended particulate matter. In particular, they found that inputs of OC into Halifax Harbour have increased from the 1960s which is reflected by the increase in agglutinated foraminifera tests. In contrast, they found that the relatively more contaminated New Bedford Harbour (PCBs in particular) hosts more calcareous foraminifera tests.

In summary, the HSP is expected to result in a significant decrease in the influx of raw wastewater and contaminated surface run-off into Halifax Harbour and, as a result, a decrease in contaminant levels in the sediments. The majority of studies discussed above were completed more than a decade ago and do not document changes in the levels of contaminants in sediments since that time. In order to gauge the success of the HSP, the concentrations of contaminants immediately prior to and during wastewater treatment must be examined.

CHAPTER 3: METHODS

3.1 SAMPLE COLLECTION

Four different sampling devices were used during the course of this investigation, allowing Halifax Harbour sediments to be studied from pre-industrial times to the present-day. Vibracoring is capable of recovering cores of significant length (up to 6 m) that cannot reasonably be collected using other methods and, as such, was used to collect deep sediments suitable for establishing pre-industrial baseline concentrations (Figure 3.1). However, vibracoring causes sediment to become resuspended near the sediment-water interface; therefore, slow cores and gravity cores were also collected to adequately resolve recent changes in sediment chemistry near the sediment-water interface (Figures 3.2 and 3.3). Gravity and slow cores were collected at a high spatial density adjacent to the Mill Cove WWTF to provide information about changes in sediment chemistry resulting from secondary wastewater treatment. Finally, gravity and slow cores provided greater sampling density than vibracores alone. In all cases, cores were stored upright and below 4 °C immediately following collection. Grab samples were collected in an effort to establish present-day conditions and to determine if any changes in sediment chemistry had occurred following the initiation of wastewater treatment (Figure 3.4). Table A.1 provides a detailed sampling summary (including locations and water depths) of both sediment cores and sediment grab samples. Figures 3.5 and 3.6 show the locations in Halifax Harbour from which sediment cores and sediment grab samples were collected, respectively. The author was involved in vibracore collection, as well as cataloguing and sampling of vibracores, slow and gravity cores. In addition, the author participated in collecting grab samples during the April 2009 sampling event.

3.1.1 Vibracoring

Three vibracores (3 – 6 m in length) were collected in Halifax Harbour in 1993 and an additional seven vibracores (1 – 4 m in length) were collected in 2008 using a Rossfelder

Figure 3.1 Photograph of a vibracore being collected in Halifax Harbour. Note the significant length of the core barrel, which allows cores as long as 6 m to be collected.

Figure 3.2 Photograph of a slow core being collected in Halifax Harbour.

Figure 3.3 Photograph of a slow core collected from Halifax Harbour. Note the fine layer of reddish brown sediment at the top of the core, representative of the oxidized layer at the sediment-water interface which has been preserved through slow coring.

Figure 3.4 Photograph of a sediment grab sample being collected in Halifax Harbour using a Shipek grab sampler.

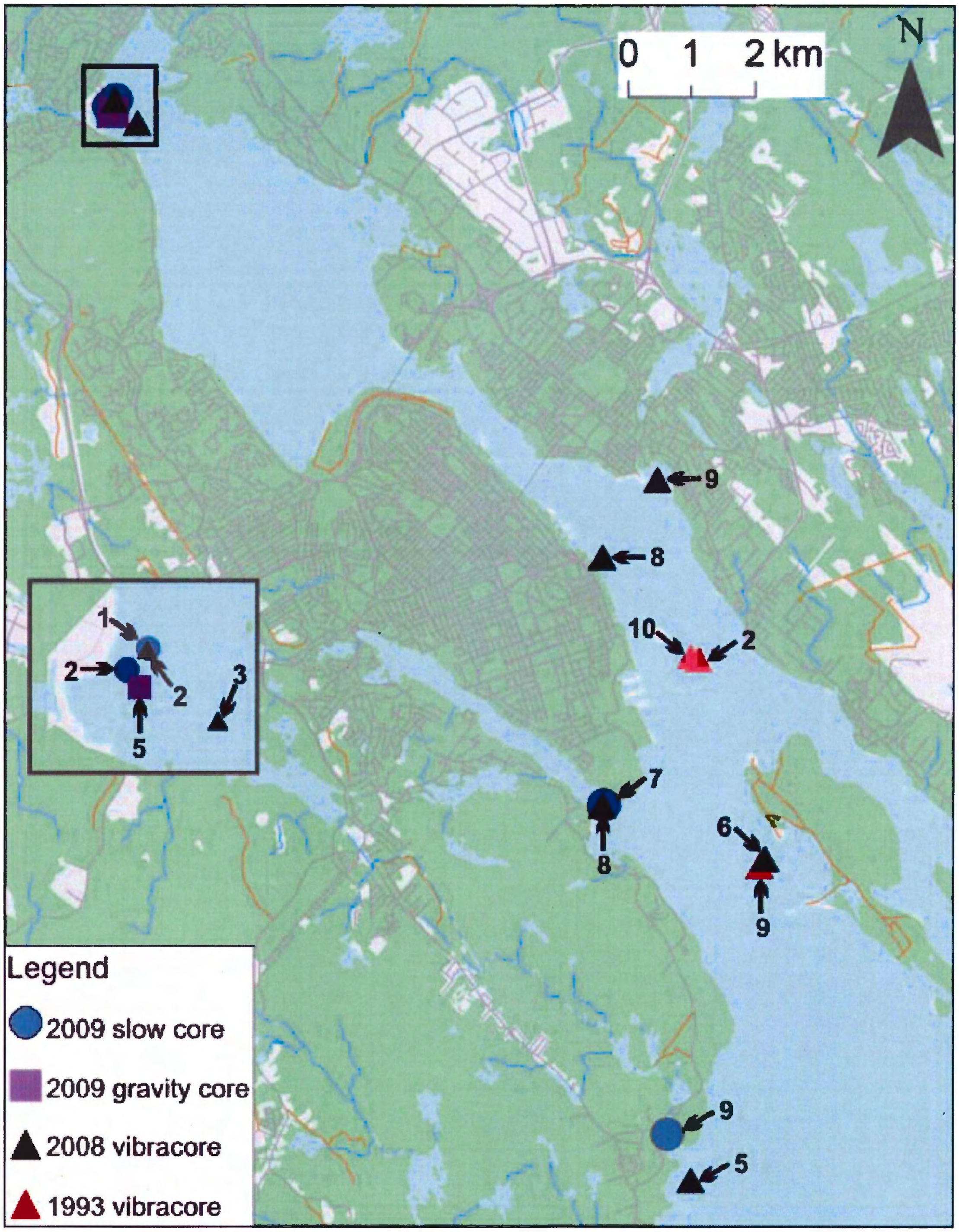


Figure 3.5 Locations of sediment cores collected from the study area. The cores were collected in 1993, 2008 and 2009.

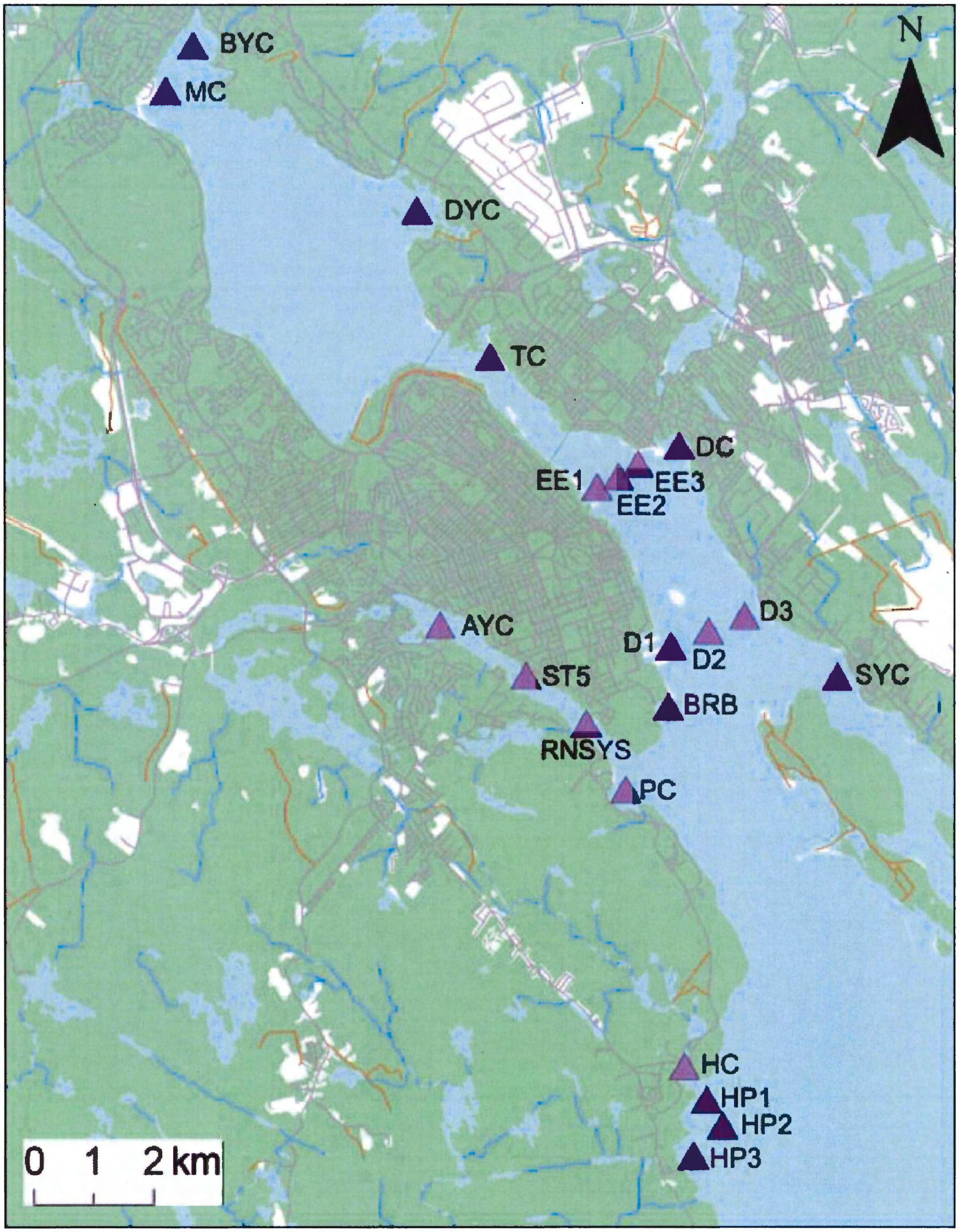


Figure 3.6 Locations of marine sediment grab samples collected from the study area. The samples were collected in 2008 and 2009.

vibracoring system. They were stored in a refrigerated storage facility at 4 °C immediately following collection. Cores were split using a wire splitting tool, logged, photographed and sub-sampled for both chemical and foraminiferal analysis. The remaining half of the core not sampled was returned to storage. Core descriptions and photographs can be found in Appendix H. Sub-samples for metals, OC, and radiometric analyses were collected using high-density polyethylene (HDPE) vials and freeze dried in preparation for analysis. Sub-samples for metals and OC analyses were collected at 1 – 5 cm intervals for the first 50 cm and at 5 – 10 cm intervals below 50 cm depth. Three of the vibracores collected in 2008 were sub-sampled for PAHs and coprostanol analyses at 4 – 6 cm intervals for the first 50 cm and at 50 cm intervals below 50 cm depth. Sub-samples for organic contaminant analysis were collected in borosilicate glass vials and were stored at 20 °C until analysis.

3.1.2 Slow Coring and Gravity Coring

Four hydraulically-damped slow cores and one gravity core were collected in April 2009 at sites adjacent to WWTFs and associated outfalls. They were stored in a refrigerated storage facility at 4 °C immediately following collection. These cores were vertically extruded at 1 cm intervals. Sediment sub-samples for chemical and foraminiferal analysis were collected from the centre of the extruded portion of the core, so as to avoid smeared sediment along the edges of the core liner. Excess material was sliced off before the core was extruded further for continued sub-sampling. Sub-samples for metals, OC, and radiometric analysis were collected at 1 cm intervals using HDPE vials and freeze dried in preparation for analysis. Pore water sub-samples were collected at 2 cm intervals in plastic centrifuge tubes for pore water analysis and immediately refrigerated. At intervals where sediment and pore water samples overlapped, pore water samples were collected and centrifuged to separate the pore water and the sediment for chemical analysis. Sub-samples for PAH and coprostanol analyses were collected in borosilicate glass vials at 10 cm intervals through the length of the core starting at the top of the core. They were stored at -20 °C until analyzed.

3.1.3 Grab Sampling

Grab samples from the top 1 – 2 cm of surface sediments were collected in polypropylene sample vials using a Shipek grab sampler at twenty-one sites around the harbour in March 2008, July 2008, October 2008 and April 2009. Nineteen of the twenty-one sampling sites correspond to HRM's water quality sampling sites. An additional two sites were chosen based on their proximity to the Mill Cove WWTF and Tufts Cove. The Shipek grab sampler is suitable for collecting sediments with variable grain sizes (soft mud to shelly, coarse samples), is stable in waters with strong currents, and can collect samples along slopes. Sub-samples collected from grab samples were stored in HDPE vials and freeze dried in preparation for inorganic chemistry. Sub-samples were also collected from grab samples for organic contaminant analyses and were frozen immediately following collection.

3.2 INORGANIC CHEMISTRY ANALYTICAL PROTOCOLS

3.2.1 Flame Atomic Absorption Spectroscopy

Samples were analyzed for chromium, cobalt, copper, iron, lithium, manganese, and zinc using flame atomic absorption spectroscopy (Varian SpectrAA 220FS). Lead was also analyzed using this technique in samples where the concentration of lead was >20 ppm. Approximately 500 mg of sample was loaded into polypropylene vials using a top-loading balance (Mettler AE263). The sample was dissolved using a modified *aqua regia* digestion of 2 mL of concentrated HCl and 2 mL of concentrated HNO_3 in a digestion block at 95 °C for six hours. Following digestion the sample was diluted up to 50 mL with Milli-Q water. Quality assurance/quality control procedures included analyzing sample duplicates, blanks, prepared standards and certified reference materials. All flame AAS analyses were completed at the Geological Survey of Canada (Atlantic)'s inorganic chemistry lab facilities. The author was involved in sample preparation for all samples analyzed using flame atomic absorption spectroscopy. Results were corrected using standard sample bracketing. Detection limits for various analytes are listed in Table 3.1.

3.2.2 Graphite Furnace Atomic Absorption Spectroscopy

Samples were analyzed for cadmium using graphite furnace AAS (Varian GTA 110). Samples with concentrations of lead below 20 ppm were also analyzed using this technique. Graphite furnace AAS is generally more time consuming than flame AAS, but is approximately a thousand times more sensitive. Sample preparation for graphite furnace AAS is the same as flame AAS (modified *aqua regia* digestion). Quality assurance/quality control procedures included analyzing sample duplicates, blanks, prepared standards and certified reference materials. All graphite AAS analyses were completed at the Geological Survey of Canada (Atlantic)'s inorganic chemistry lab facilities. The author was involved in sample preparation for all samples analyzed using graphite furnace atomic absorption spectroscopy. Results were corrected using standard sample bracketing.

Table 3.1 List of analytical detection limits in marine sediments

Component	Detection limit
Organic carbon (wt. %)	<0.01
Cd (ppm)	0.01
Co (ppm)	3
Cr (ppm)	10
Cu (ppm)	2
Fe (wt. %)	0.01
Hg (ppb)	5
Li (ppm)	2
Mn (ppm)	15
Ni (ppm)	3
Pb (ppm)	0.2 (12)[a]
Zn (ppm)	2

[a] detection limit using graphite furnace AA and (flame AA)

3.2.3 Solid State Atomic Absorption Spectroscopy

The concentration of mercury in sediments was determined using a direct combustion mercury analyzer (Leco AMA254). Between 25 and 350 mg of dried sample was weighed into a nickel boat on a top-loading balance (Sartorius LA120S). Sample weights were varied in an effort to ensure that sufficient mercury was available for analysis and that excessive mercury was not present which could damage the instrument. The expected concentration of mercury was estimated based on the OC content of the sample, and the depth and location from which the sample was collected. Concentrations of mercury in Outer Harbour, at depths greater than 1 m, and in low OC sediments were expected to be low and therefore larger sample sizes were required (e.g. 350 mg). Concentrations of mercury in Central Harbour, near the sediment-water interface and in high OC sediments were expected to be high and therefore smaller sample sizes were utilized (e.g. 25 mg).

The nickel boats were placed in the auto-loader sample carousel and the sample weight, sample identification, and boat location were entered into the Quicksilver computer program. In addition to samples, blanks, certified reference materials and duplicate samples were analyzed. Three blanks were analyzed at the beginning and end of each day's analyses (approximately 30 samples) and following samples with high mercury contents (>1000 ppb Hg). Certified reference materials and duplicate samples were analyzed every ten samples. This novel method allowed the concentration of mercury in sediments to be determined without chemical pre-treatment, which can lead to loss through volatization, precipitation, incomplete decomposition, and reagent contamination (Hall and Pelchat 1997). All solid state AAS analyses were completed at the Geological Survey of Canada (Atlantic)'s inorganic chemistry lab facilities. The author prepared and analyzed all samples for mercury.

3.3 ORGANIC CHEMISTRY ANALYTICAL PROTOCOLS

3.3.1 Organic Carbon

Organic carbon is an important analyte as it is widely distributed and has the ability to form complexes with metal ions and hydrous oxides, react with clay minerals and bind particles together. Analysis for OC was completed at the Geological Survey of Canada (Atlantic)'s chemistry lab facilities. The author prepared and analyzed all samples for organic carbon. A sub-sample of the freeze dried sediment used for inorganic chemistry analysis was utilized for OC analysis. Sediment was mixed using a spatula prior to weighing in an effort to increase sample homogenization. A 100 mg sub-sample of freeze dried sediment was weighed out into a porous ceramic crucible using a top-loading balance (Mettler P162N).

Because the carbon analyzer is unable to differentiate between organic and inorganic carbon, samples were acidified using 6 mL of 10% HCl in a fume hood to remove the inorganic carbon present in the sample. This procedure is based on the assumption that all the inorganic carbon is present as carbonates or bicarbonates and that all the inorganic carbon is removed using this method. In addition, it is assumed that no OC is lost through acidification, although HCl can cause limited volatilization of the OC and some polymerization of organics in the sample (e.g. Froelich 1980).

The sample was left in the fume hood to dry via evaporation. To remove residual acid, the sample was washed with 6 mL of deionized water three to four times and allowed to dry by evaporation between each addition. To each sample approximately 1 mL of iron chip accelerator and 1 mL of copper metal accelerator was added to help facilitate the combustion of the sediment samples.

Prior to sample analysis, the LECO WR 112 carbon determinator was calibrated using a carbon and sulphur steel standard (on the order of 0.050 ± 0.003 % carbon). Quality control/quality assurance protocols included sample duplicates, certified reference materials, and calibration standards. Detection limits for this method are <0.01 % OC (Table 3.1), which is more than sufficient for the purposes of this project. Results were corrected using standard sample bracketing with reference materials.

3.3.2 Polycyclic Aromatic Hydrocarbons and Coprostanol

Samples were analyzed for PAHs, coprostanol, epi-coprostanol, cholesterol, and cholestanol at ALS Environmental in Edmonton, Alberta. The parental and alkylated PAHs included in these analyses are shown in Tables 3.2 and 3.3, respectively. Samples were freeze-dried, ground, and sieved (<1 mm) before sonication in dichloromethane for soxhlet extraction. Following solvent reduction and exchange, column chromatography cleanup was completed. Activated copper was used to remove sulphur from the samples as required. Sulphur interferes with PAH analysis and quantification by gas chromatography-mass spectrometry (GC-MS) and must therefore be removed prior to analysis. A non-polar solvent was used to elute the PAHs, while coprostanol was eluted from a more polar fraction. Coprostanol and PAHs were concentrated and exchanged into isooctane prior to analysis and their concentrations were determined by GC-MS. Because harbour samples are complex mixtures with a wide variety of organic chemicals, GC-MS must be used rather than high performance liquid chromatography to adequately resolve the 33 PAHs targeted for analysis. Quality control/quality assurance procedures included duplicate analyses, blanks, spiked sodium sulphate matrix and National Institute of Standards and Technology reference materials. Results were corrected using surrogates if recoveries were between 50 – 80%. Correction was not required if surrogate recovery fell between 80 and 120%. Where surrogate recoveries exceeded 120% or were lower than 50% the entire set of results for the sample was discarded.

Table 3.2 Analyzed parental PAHs, their abbreviations in brackets, their corresponding molecular weights (u) (MWs), and number of aromatic rings (#)

PAH	MW	#	PAH	MW	#
Acenaphthene (Ac)	154	3	Dibenzothiophene (DBT)	184	3
Acenaphthylene (Ay)	152	3	Fluoranthene (FL)	202	4
Anthracene (AN)	178	3	Fluorene (Fl)	166	3
Benz[a]anthracene (BA)	228	4	Indeno[1,2,3-cd]pyrene (IP)	276	6
Benzo[a]pyrene (BaP)	252	5	Phenanthrene (PA)	178	3
Benzo[b&j&k]fluoranthene (BF)	252	5	Perylene (Per)	252	5
Benzo[g,h,i]perylene (BP)	276	6	Pyrene (PY)	202	4
Chrysene (CH)	228	4	Retene (Ret)	234	3
Dibenz[a,h]anthracene (DBA)	278	5			

Table 3.3 Analyzed alkylated PAHs arranged according to degree of alkylation

C1 PAHs	C2 PAHs	C3 PAHs
C1Acenaphthene		
C1 Benz(a)Anthracene/Chrysene		
C1 Dibenzothiophene	C2 Dibenzothiophene	C3 Dibenzothiophene
C1 Fluoranthene/Pyrene		
C1 Fluorene	C2 Fluorene	C3 Fluorene
1-Methylnaphthalene	C2 Naphthalenes	C3 Naphthalene
2-Methylnaphthalene		
C1 Phenanthrene/Anthracene	C2 Phenanthrene/Anthracene	C3 Phenanthrene/Anthracene

3.4 DATING TECHNIQUES

The four slow-cores were dated using ^{210}Pb and ^{137}Cs at the Atlantic Environmental Radioactivity Laboratory at the Bedford Institute of Oceanography. Dated segments of sediment cores were used to establish the timing of changes in sediment chemistry and to link these changes with historic industrial practices.

3.4.1 ^{210}Pb Dating

^{210}Pb has a half life of 22 years and can be used to date materials up to ~100 years old. However, ^{210}Pb is not easily detected as it is a weak beta emitter. Instead the activity of its granddaughter element ^{210}Po is measured. As these two elements are in secular equilibrium with each other, the activity of ^{210}Po can be used as a proxy for the activity of ^{210}Pb (e.g. Noller 2000).

Approximately 500 mg of sample was loaded into a Teflon bomb using a top-loading balance (Mettler Toledo AB204). The sample was digested using 4 mL of concentrated HNO_3 and 4 mL of concentrated HF. Prior to the addition of the acids, five drops of octan-1-ol were added to prevent the OC in the sample from immediately reacting with the acids. In addition, 100 μL of 209-Po Work Standard (NIST SRM 4326, 50.2 DPM/G, 2003-11-05) tracer was added to allow recovery to be evaluated. Samples were microwaved on high for 90 seconds prior to being transferred to beakers for dry down. In order to ensure that all the sample was transferred, the bomb was rinsed with ~ 40 mL of 0.5 N HCl and ~ 20 mL of concentrated HCl. Following near dry down (approximately 3 mL left in the beaker), 20 mL of concentrated HCl was added to the beaker and dried down again to near 3 mL. The addition of 20 mL of concentrated HCl followed by near dry down was repeated twice more. This solution was transferred to a centrifuge tube using 0.5 N HCl. Following 20 minutes in a centrifuge, 0.2 g of hydroxylamine hydrochloride and 0.2 g of ascorbic acid were added to the solution. Finally, the sample was electrodeposited onto a nickel disc which was analyzed using alpha counting spectrometry.

By examining a plot of ln(unsupported lead activity) versus sediment depth one can determine the depth at which unsupported lead is no longer present, which should correspond to approximately 100 years. This allows one to calculate an average sedimentation rate over the last 100 years and can also provide information regarding sediment disturbance or mixing (e.g. bioturbation). Sediment geochronologies were established by applying the constant flux, constant sedimentation rate model (Robbins 1978).

3.4.2 ^{137}Cs Dating

^{137}Cs was used to validate the ^{210}Pb results. Levels of ^{137}Cs above background are believed to be the result of nuclear testing in mid-1950s. A spike in ^{137}Cs previous to 1952 as determined using ^{210}Pb would suggest that the sediment in the core is disturbed and therefore care must be used when interpreting the sediment record (e.g. Noller 2000). Between 5 and 10 g of dried sediment sample was analyzed for ^{137}Cs using a hyperpure Ge gamma ray detector with a 1-cm-diameter well.

3.5 PORE WATER CHEMISTRY ANALYTICAL PROTOCOLS

Pore water chemistry samples were analyzed following methods outlined by Cranston (1999), which have a relative precision and accuracy of ± 5%. This method not only allows one to determine the redox conditions of the sediment, but also provides a method for establishing present-day sediment accumulation rates. Analysis of pore waters was completed at the Geological Survey of Canada (Atlantic)'s chemistry lab facilities. The author prepared and analyzed all pore water samples. Pore waters were filtered through 1 μm pore-diameter Nylon membrane filters and analyzed for ammonia, sulphate, and salinity. The residual sediments were freeze dried and analyzed for OC and inorganic chemistry.

3.5.1 Ammonium

The concentration of ammonium in the pore water was determined using a colourimetric method developed by Solorzano (1969). Samples were prepared by adding 5 mL of Milli-Q water and 100 μL of pore water or standard of a known concentration to 25 mL test tubes. Five hundred μL of phenol-ethanol solution and 500 μL of sodium nitroprusside solution were added to each test tube. Finally, 1 mL of oxidizing solution was added to each test tube, which following shaking were left standing for 2 hours to allow the colour to develop. The phenol-ethanol solution was prepared by dissolving 0.8 g of phenol in 100 mL of ethanol, while the sodium nitroprusside solution was prepared by dissolving 0.075 g of sodium nitroprusside in 50 mL of Milli-Q water. The oxidizing solution was prepared by adding 1 mL of sodium hypochlorite, 0.75 g of trisodium citrate and 0.04 g of sodium hydroxide to 50 mL of Milli-Q water. Following the two hour time period during which the blue colour indicative of ammonium developed, the colour absorbance was measured at 640 nm using a Brinkmann PC950 probe colourimeter.

The concentration of ammonium in the pore water was calculated using the calibration curve generated from a set of prepared standards at concentrations of 0 mM/L, 0.1 mM/L, 0.2 mM/L, 0.5 mM/L, 1.0 mM/L, 2.0 mM/L, 3.0 mM/L, and 4.0 mM/L. The relationship between absorbance and ammonium concentration is close to linear ($R^2 = 0.98$) and therefore the ammonium concentration in each pore water sample was easily calculated using simple bracketing of the calibration standards.

3.5.2 Sulphate

To determine the sulphate concentration of the pore water, 62.5 µL of a 1:10 HCl solution was added to a 2.5 mL aliquot of pore water sample. Subsequently 2.5 µL of a 10% $BaCl_2$ stabilized solution was added allowing a $BaSO_4$ precipitate to form over a period of five minutes. Following agitation the resulting turbidity was measured using a Hach DR/2400 spectrophotometer at 450 nm wavelength.

The concentration of sulphate in the pore water was calculated using the calibration curve generated from a set of prepared standards at concentrations of 0 mg/L, 6.25 mg/L, 12.5 mg/L, 25 mg/L and 50 mg/L. The relationship between absorbance and sulphate concentration is close to linear ($R^2 = 0.99$) and therefore the sulphate concentration in each pore water sample was easily calculated using simple bracketing of the calibration standards.

3.5.3 Salinity

Salinity was determined using diluted pore water samples. A 76 µL aliquot of sample was diluted with 10 mL of Milli-Q water and the conductivity of the resulting solution measured using a conductivity/TDS meter (Corning Checkmate 90). The conductivity of calibration standards at 0‰ and 35‰ (IAPSO Standard Seawater, Batch P149, October 5 2007) was also determined allowing the salinity of the sample to be calculated using simple standard bracketing of the calibration standards.

CHAPTER 4: RESULTS

Chapter 4 begins by summarizing the results of inorganic contaminant analyses (Section 4.1) and organic contaminant analyses (Section 4.2) from sediment grab samples and sediment cores. Due to monetary constraints only select cores and grab samples were analyzed for organic contaminants. As a result of time constraints only select cores were analyzed for all inorganic contaminants. Cores were selected from areas which would likely be most impacted by changes in wastewater treatment in the future. Although outside the scope of this thesis, all cores are expected to be analyzed for the remaining inorganic contaminants in the future. In Sections 4.3 and 4.4 the results of radiometric dating (^{210}Pb and ^{137}Cs) and pore water analyses are discussed, respectively. Substantial quantities of data were generated during the course of this research. The author chose to include only the figures and tables which illustrate the most central and important conclusions resulting from this study in the text of Chapters 4, 5, and 6. For the sake of readability and organization, the remaining figures and tables can be found in the appendices.

4.1 INORGANIC CHEMISTRY OF MARINE SEDIMENTS

Select inorganic geochemical data from sediment grab samples are summarized in Table 4.1 and shown in Figure 4.1, while all inorganic geochemical results from sediment grab samples can be found in Table B.1 and are shown graphically and pictorially in Appendix C. Sediment grab sample locations are shown in Figure 3.6. Sediment grab samples indicate that concentrations of cadmium, chromium, copper, lead, and zinc are highest near the Dartmouth Yacht Club (*DYC*), Tufts Cove (*TC*), and in Dartmouth Cove (*DC*) (Figures 4.2 and 4.3). Peaks in cadmium, chromium and zinc were also observed near Mill Cove (*MC*). Mercury concentrations were greatest in Dartmouth Cove (*DC*) and near Tufts Cove (*TC*) (Figure 4.4). Concentrations of copper, lead and mercury were also high in the northern portion of Central Harbour (near *EE1*, *EE2*, and *EE3*). High concentrations of lead were also found in Northwest Arm, near the Royal Nova Scotia Yacht Squadron (*RNSYS*). In general, concentrations of cadmium, chromium, copper, lead, zinc, mercury, and nickel were lowest near Herring Cove (*HP1*, *HP2*, *HP3*). With the exception of samples collected near Tufts Cove (*TC* – 39 ± 12 ppm), concentrations of nickel in Central Harbour, Bedford Bay, and Northwest Arm were relatively consistent, ranging from 18 – 33 ppm. Concentrations of cobalt were also found to be similar throughout the harbour, ranging from 5 – 17 ppm with the lowest concentrations observed in and around Herring Cove and the highest concentrations observed in Bedford Bay.

Inorganic geochemical results from sediment core samples can be found in Table B.2 and sediment core profiles of inorganic geochemistry can be found in Appendix E. Sediment core locations are shown in Figure 3.5. In general concentrations of zinc, copper, and lead in sediment cores reach a maximum at a depth of 5 to 30 cm with lower concentrations near the top of the core (<5 cm). Notable exceptions include cores collected from Bedford Bay (slow core 1 and gravity core 5), and Herring Cove (slow core 9), which had

Table 4.1 Summarized grab sample geochemical data (collected during all four sampling events)

		Outer Harbour				Northwest Arm			Bedford Basin		
		HP3	HP2	HP1	HC	RNSYS	ST5	AYC	DYC	MC	BYC
Organic carbon (wt. %)	min.	0.08	0.42	0.52	2.70	5.24	5.34	5.75	6.03	3.04	3.35
	max.	0.82	0.84	0.63	5.12	5.81	5.34	6.46	7.17	13.87	5.08
	median	0.29	0.66	0.58	4.05	5.63	5.34	6.22	6.55	5.98	3.59
	mean	0.40	0.64	0.58	3.98	5.56	5.34	6.16	6.57	7.22	4.01
	S.D.	0.38	0.21	0.08	1.12	0.29	-	0.31	0.47	4.65	0.94
Cd (ppm)	min.	<0.01	0.04	0.028	0.9	0.55	0.86	0.59	1.04	1.09	0.90
	max.	0.036	0.14	0.028	1.4	0.70	0.99	0.59	1.37	1.37	0.90
	median	0.022	0.09	0.028	1.1	0.62	0.93	0.59	1.21	1.23	0.90
	mean	0.022	0.09	0.028	1.1	0.62	0.93	0.59	1.21	1.23	0.90
	S.D.	0.020	0.07	-	0.4	0.11	0.09	-	0.23	0.20	-
Cr (ppm)	min.	<10	11	<10	12	35	38	25	40	33	30
	max.	9	12	7	29	62	38	83	52	51	36
	median	8	11	7	18	36	38	42	47	41	32
	mean	8	11	7	19	44	38	48	46	41	33
	S.D.	1	1	0	8	15	-	25	5	7	3
Cu (ppm)	min.	2	8	9	45	78	82	92	100	86	59
	max.	11	13	11	87	85	82	111	156	299	67
	median	8	11	10	66	80	82	104	127	110	59
	mean	7	11	10	66	81	82	103	127	151	62
	S.D.	4	3	1	18	4	-	9	24	99	4
Hg (ppb)	min.	<5	13	30	203	947	892	1009	650	565	207
	max.	24	35	49	535	1628	892	1216	1349	2654	330
	median	22	24	40	254	1023	892	1081	789	794	234
	mean	17	24	40	311	1199	892	1097	894	1201	257
	S.D.	10	11	13	155	373	-	98	330	974	64
Li (ppm)	min.	29	13	15	22	35	43	36	33	34	37
	max.	54	17	25	30	42	43	46	44	51	50
	median	38	15	20	25	42	43	40	37	40	41
	mean	41	15	20	26	40	43	40	38	41	43
	S.D.	13	2	7	4	4	-	5	5	7	7
Ni (ppm)	min.	6	9	7	12	21	28	23	23	18	27
	max.	8	14	10	15	26	28	31	30	33	32
	median	7	11	9	13	25	28	27	27	29	28
	mean	7	11	9	14	24	28	27	27	27	29
	S.D.	1	2	2	1	3	-	3	3	7	3
Pb (ppm)	min.	8	8	13	49	91	135	84	45	71	55
	max.	30	16	16	164	231	135	214	213	138	74
	median	20	15	14	110	192	135	163	187	81	73
	mean	20	13	14	108	171	135	156	158	93	68
	S.D.	11	4	2	51	72	-	56	78	31	11

Table 4.1 Summarized grab sample geochemical data (collected during all four sampling events)

		Outer Harbour				Northwest Arm			Bedford Basin		
		HP3	HP2	HP1	HC	RNSYS	ST5	AYC	DYC	MC	BYC
Zn (ppm)	min.	43	30	36	147	183	176	193	258	285	231
	max.	45	50	43	257	205	176	227	482	600	260
	median	44	43	40	197	196	176	217	361	325	236
	mean	44	41	40	199	195	176	214	366	384	242
	S.D.	1	10	5	51	11	-	15	92	148	15

Table 4.1 Summarized grab sample geochemical data (collected during all four sampling events) (cont'd)

		Central Harbour										
		PC	SYC	BRB	D1	D2	D3	EE1	EE2	EE3	DC	TC
Organic carbon (wt. %)	min.	5.25	2.80	2.12	3.17	3.73	2.83	2.22	4.54	4.09	4.76	7.28
	max.	5.77	3.31	4.56	4.06	3.89	3.36	4.30	5.05	6.76	5.87	11.10
	median	5.49	3.19	4.35	3.89	3.81	3.24	3.08	4.98	5.15	5.48	8.21
	mean	5.50	3.10	3.84	3.70	3.81	3.16	3.20	4.89	5.29	5.37	8.86
	S.D.	0.27	0.27	1.16	0.47	0.11	0.23	1.04	0.24	1.17	0.56	1.99
Cd (ppm)	min.	0.91	0.34	0.55	0.87	0.34	0.26	0.47	0.45	0.32	1.77	2.75
	max.	0.92	0.34	0.57	0.87	0.34	0.31	0.58	0.50	0.65	1.77	2.75
	median	0.91	0.34	0.56	0.87	0.34	0.29	0.53	0.48	0.49	1.77	2.75
	mean	0.91	0.34	0.56	0.87	0.34	0.29	0.53	0.48	0.49	1.77	2.75
	S.D.	0.01	-	0.01	-	-	0.04	0.08	0.03	0.23	-	-
Cr (ppm)	min.	23	29	20	26	27	24	19	28	33	42	39
	max.	88	32	33	28	30	32	39	41	38	48	88
	median	34	31	31	27	28	29	33	36	35	45	46
	mean	45	31	29	27	28	28	30	35	35	45	58
	S.D.	29	1	6	2	2	3	10	6	2	3	27
Cu (ppm)	min.	65	51	36	66	45	30	75	75	91	181	156
	max.	232	61	66	85	65	55	106	121	141	246	380
	median	75	53	65	75	55	47	100	119	129	192	321
	mean	112	55	58	75	55	45	94	108	122	206	285
	S.D.	81	5	14	13	14	11	16	22	23	35	116
Hg (ppb)	min.	603	341	205	518	410	386	437	1019	996	1820	1078
	max.	759	516	557	673	426	543	1884	1495	2770	2741	1810
	median	697	344	492	595	418	470	1111	1240	2514	2699	1282
	mean	689	401	436	595	418	467	1144	1248	2199	2420	1390
	S.D.	74	100	158	110	12	65	724	261	813	520	378
Li (ppm)	min.	35	30	28	29	29	30	30	30	29	29	24
	max.	40	34	41	31	32	33	43	38	40	33	36
	median	37	34	37	30	30	32	31	34	36	33	28
	mean	37	33	36	30	30	32	35	34	35	32	29
	S.D.	3	2	5	1	2	2	7	4	5	2	6

Table 4.1 Summarized grab sample geochemical data (collected during all four sampling events) (cont'd)

		Central Harbour										
		PC	SYC	BRB	D1	D2	D3	EE1	EE2	EE3	DC	TC
Ni (ppm)	min.	22	21	18	23	22	20	25	23	22	24	28
	max.	26	27	28	27	26	31	33	32	30	28	52
	median	24	21	25	25	24	22	27	30	25	25	36
	mean	24	23	24	25	24	24	28	29	25	26	39
	S.D.	1	3	4	3	3	5	4	4	3	2	12
Pb (ppm)	min.	76	57	48	95	64	73	72	87	100	426	161
	max.	166	61	91	175	73	102	426	171	187	1517	241
	median	103	59	80	100	68	82	324	136	148	945	180
	mean	112	59	75	123	68	85	274	133	146	962	194
	S.D.	39	2	20	45	6	12	183	34	36	546	42
Zn (ppm)	min.	148	127	118	158	102	78	137	200	163	315	748
	max.	207	148	172	233	148	143	271	214	230	547	4019
	median	157	131	155	195	125	118	155	202	214	430	816
	mean	167	136	150	195	125	114	188	204	205	431	1861
	S.D.	27	11	25	53	33	29	73	6	30	116	1869

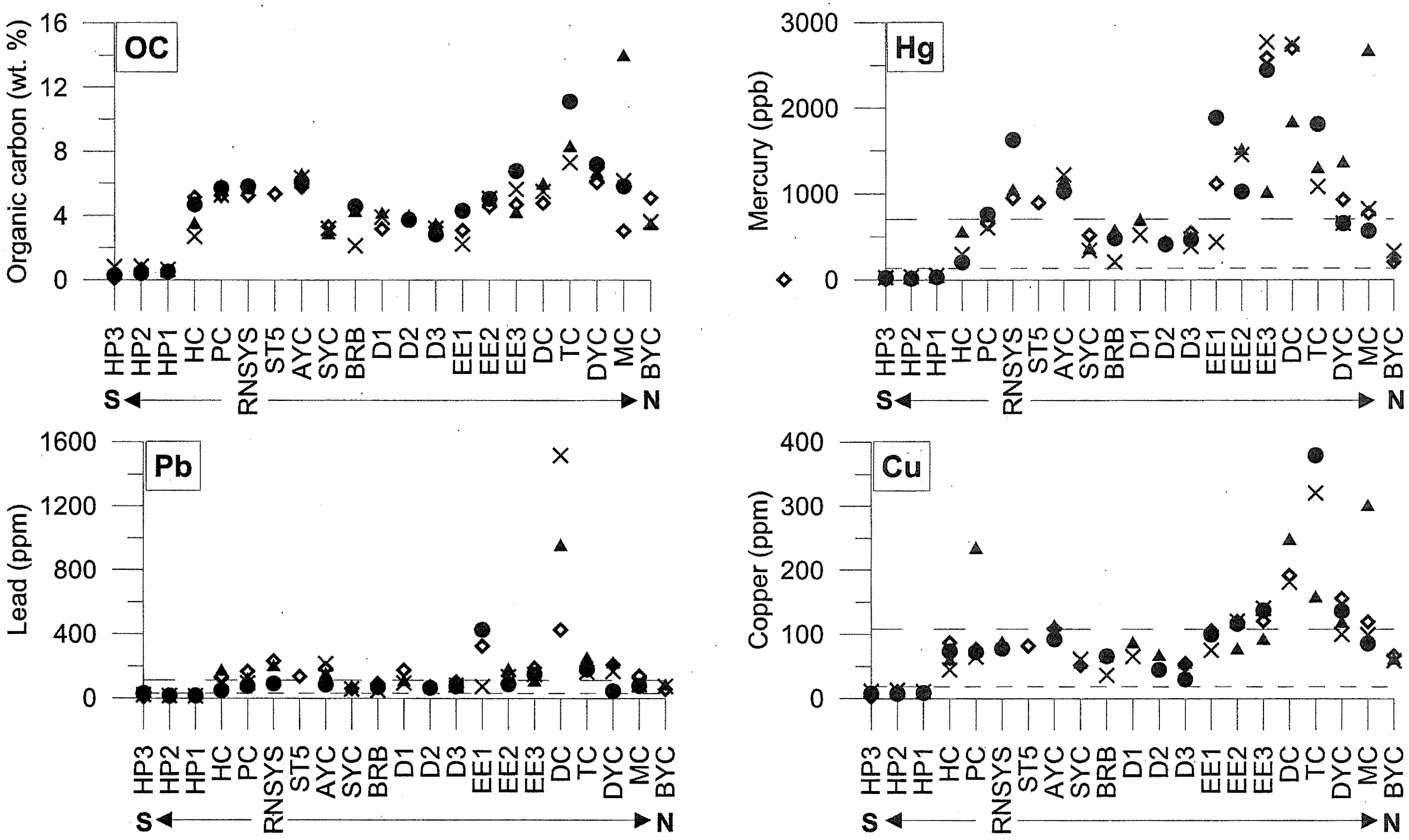


Figure 4.1 Plots of grab samples collected at four different times over a 15 month period (● March 2008, ◇ July 2008, ▲ October 2008, × April 2009) arranged from south to north (Figure 3.6). The short dashed line represents the ISQG (CCME 2002), while the longer dashed line represents the PEL (CCME 2002).

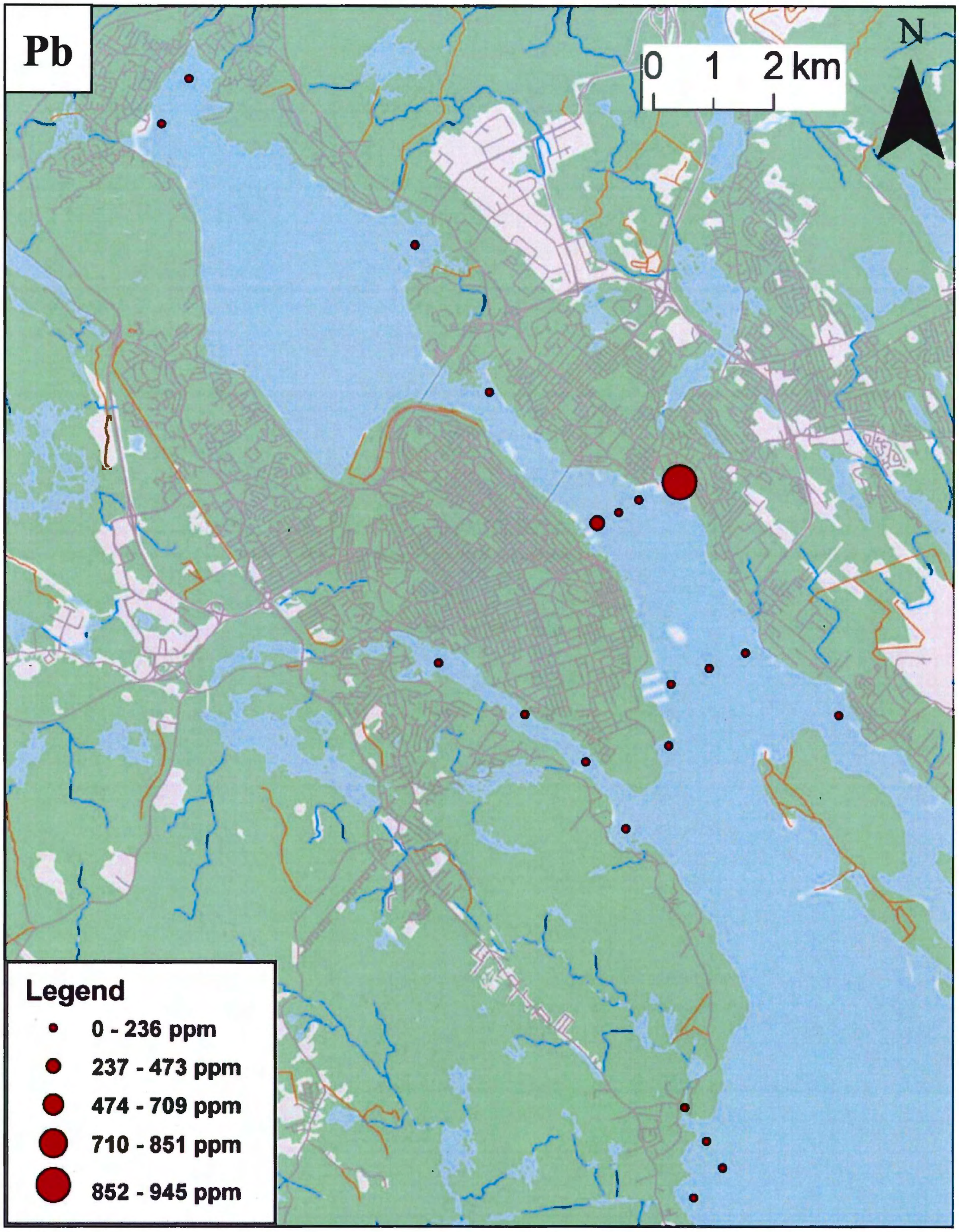


Figure 4.2 Proportional dot size map of median lead concentrations (ppm) in sediment grab samples collected during all four sampling events.

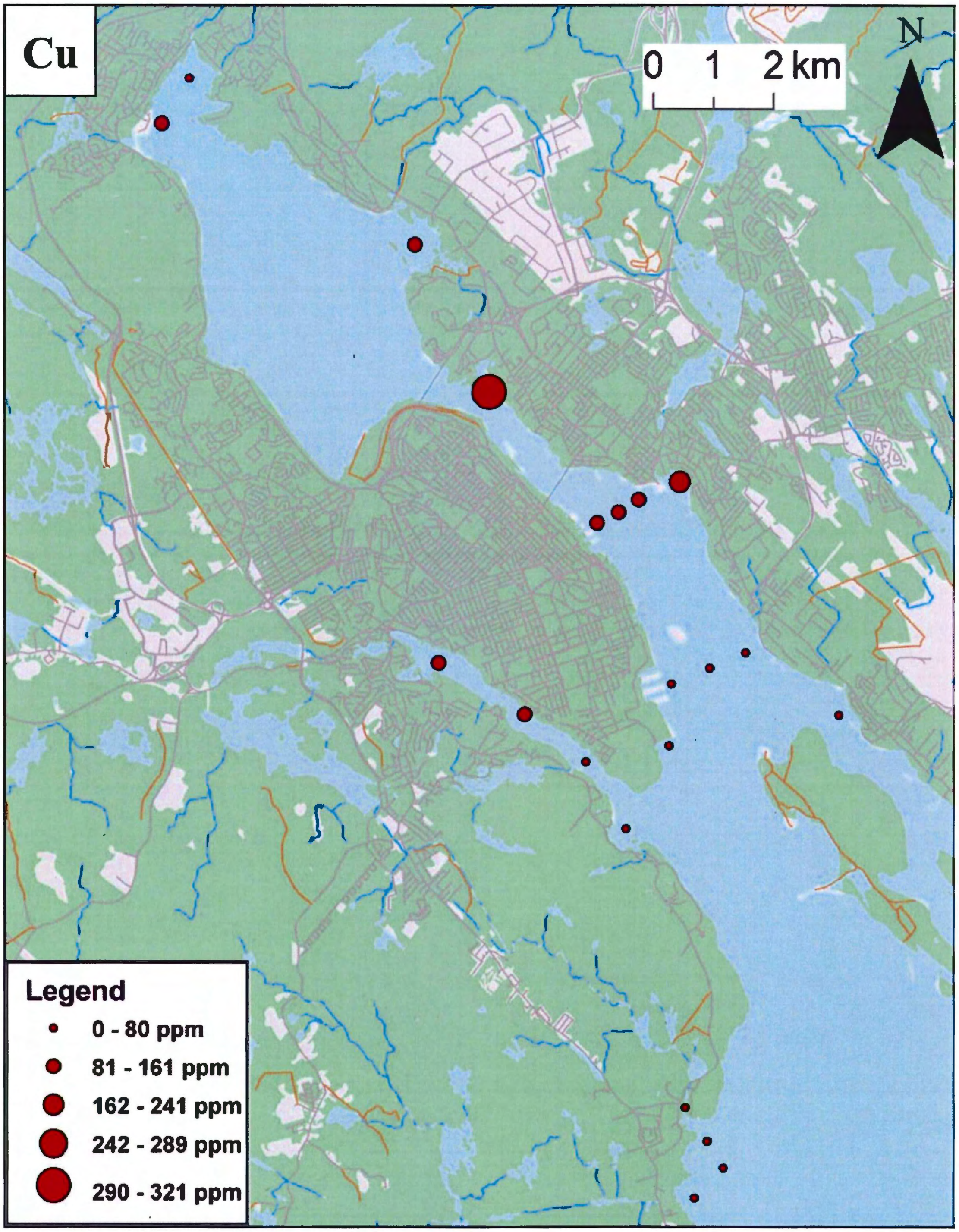


Figure 4.3 Proportional dot size map of median copper concentrations (ppm) in sediment grab samples collected during all four sampling events.

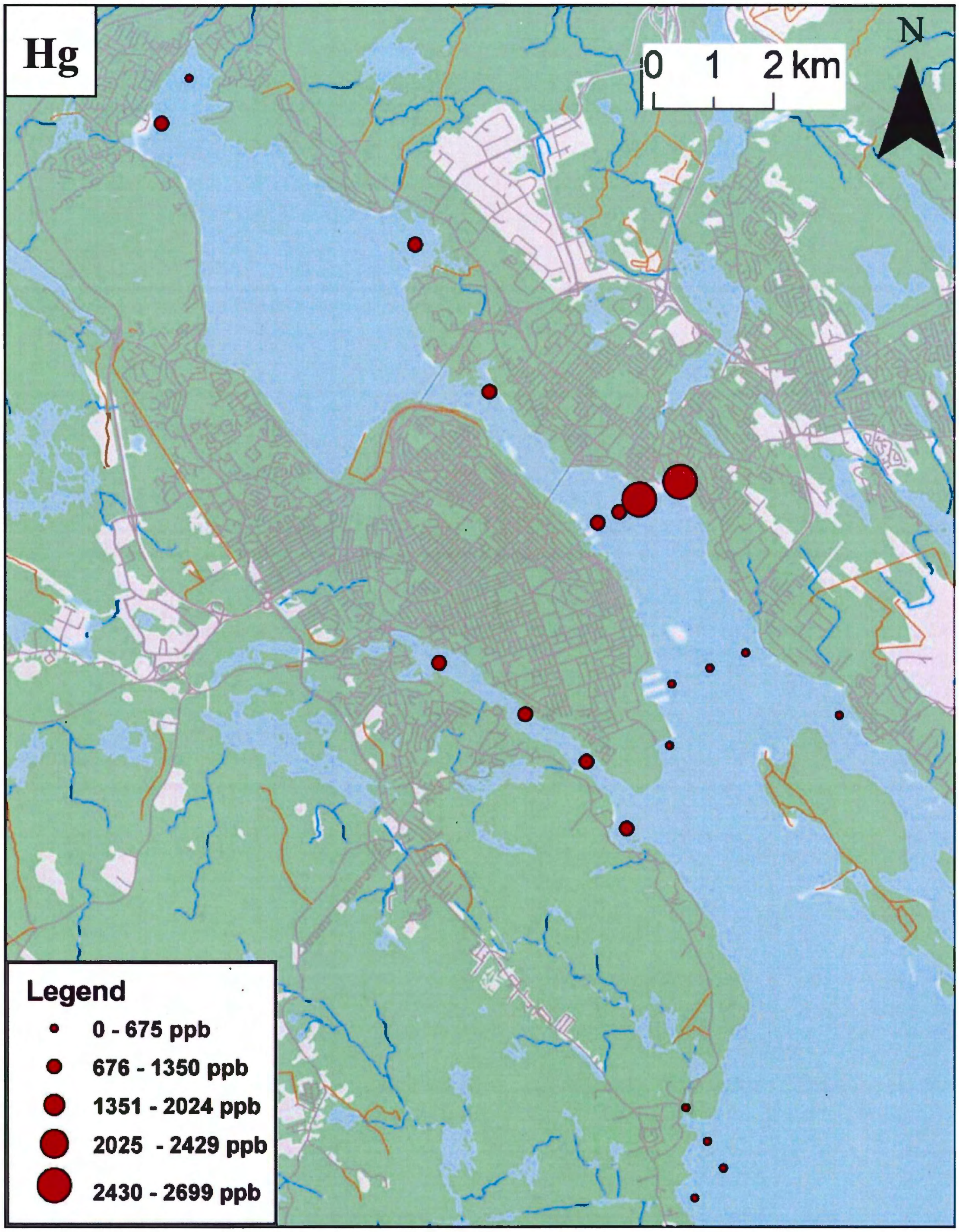


Figure 4.4 Proportional dot size map of median mercury concentrations (ppb) in sediment grab samples collected during all four sampling events.

peaks in lead concentration within the top 5 cm. Concentrations of zinc and copper in the near surface were highest in Bedford Bay (slow core 1, slow core 2, and gravity core 5). Near surface zinc concentrations were also high in the northern portion of Central Harbour (2008 vibracore 8). Concentrations of zinc, copper, and lead in gravity core 5 and slow core 8 in the near surface were variable and may still be increasing. A substantial peak in copper was observed in slow core 8 at approximately 20 cm depth, which is also matched by a peak in mercury at that depth. Concentrations of zinc and lead in 2008 vibracore 8 begin increasing at approximately 70 cm depth and 95 cm depth, respectively. Concentrations of both metals begin to decrease at approximately 10 cm depth. Vibracore 2 (1993) also contains high concentrations of lead beginning at 30 cm depth and reaching a maximum at 17 cm depth. Concentrations of zinc and copper in slow core 9 were also high, beginning to increase at 17 cm and reaching maximum concentrations near 10 – 12 cm depth.

Sediment cores collected in Bedford Bay (slow core 2), the northern portion of Central Harbour (2008 vibracore 8, 2008 vibracore 9), and the mouth of Northwest Arm (slow core 8) had the highest concentrations of mercury in the near surface. A marked increased in 1993 vibracore 2 in the top 5 cm was also observed. Slow core 2 displayed higher concentrations of mercury than either slow core 1 or gravity core 5. Maximum concentrations of mercury were generally observed in the top 20 cm of cores with the exception of 2008 vibracore 8, where mercury reached maximum concentrations between 10 and 60 cm depth.

The highest concentrations of nickel were observed in Herring Cove (slow core 9), Bedford Bay (slow cores 1 and 2) and in the southern portion of Central Harbour (1993 vibracore 2). Maximums were generally observed between 5 and 15 cm depth. Concentrations of chromium in sediment cores were relatively consistent down core in all sediment cores analyzed for chromium. In general, concentrations of chromium in sediment cores were below 35 ppm with the exception of 2008 vibracore 8, slow core 2, and slow core 1, which had concentrations as a high as 53 ppm. Concentrations of chromium in these cores begin to increase at approximately 20 – 25 cm depth.

Only the three 1993 vibracores were analyzed for cadmium. In general, concentrations of cadmium were greatest in 1993 vibracore 2 and lowest in 1993 vibracore 10, although a peak in 1993 vibracore 10 was observed at approximately 35 cm depth. Concentration profiles of most contaminants are substantially different in 1993 vibracore 2 and 1993 vibracore 10, which is surprising given their proximity to each other (<120 m). Similarly, concentration profiles of most metal contaminants are also substantially different between gravity core 5 and slow cores 1 and 2, which given their proximity (all within 200 m of each other) is unexpected.

4.2 ORGANIC CHEMISTRY OF MARINE SEDIMENTS

4.2.1 Organic Carbon

Select OC data from sediment grab samples is summarized in Table 4.1, while all OC results from sediment grab samples and sediment core samples can be found in Tables B.1 and B.2, respectively. Concentrations of OC were highest near Mill Cove (*MC*), the Dartmouth Yacht Club (*DYC*), Tufts Cove (*TC*), and the Armdale Yacht Club (*AYC*) (Figures 4.1 and 4.5). Organic carbon concentrations were lowest near Herring Cove (*HP1*, *HP2*, and *HP3*).

Sediment core profiles of OC can be found in Appendix E. In general, concentrations of OC varied from 3 to 8% down core. The profiles of slow cores 1 and 2 show a marked drop in OC concentration between approximately 10 and 20 cm depth, although the subsequent increase in OC just above 10 cm is greater in slow core 2 than slow core 1. A similar pattern was not observed in either gravity core 5 or 2008 vibracore 2, despite their proximity to slow cores 1 and 2. Concentrations of OC down core were lowest in 2008 vibracore 5, in which OC concentrations were less than 1% down the entire length of the core.

4.2.2 Polycyclic Aromatic Hydrocarbons

Concentrations of total PAHs (ΣPAH), total parental PAHs (ΣPAHp), alkylated PAHs (ΣPAHa), and % alkylated PAHs (% PAHa) in sediment grab samples and core samples are summarized in Tables 4.2 and 4.3, respectively. Organic contaminant core profiles can be found in Appendix E. Concentrations of individual PAHs in sediment grab and core samples are summarized in Appendix D. Retene, perylene and dibenzothiophenes are not included in calculations of total PAHs, parental PAHs, or alkylated PAHs.

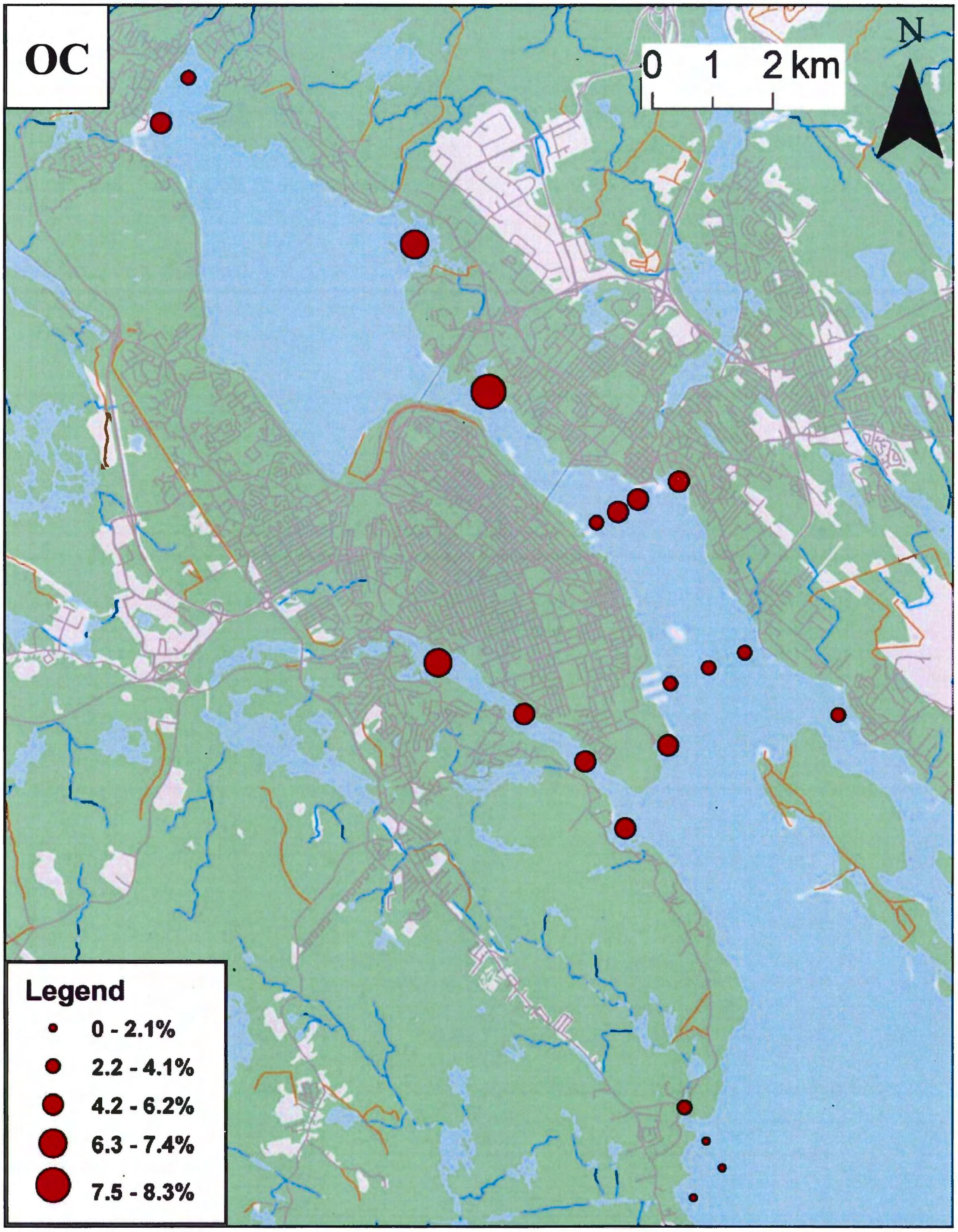


Figure 4.5 Proportional dot size map of median OC concentrations (wt. %) in sediment grab samples collected during all four sampling events.

Table 4.2 Grab sample PAH summary data

Cruise	Station	Lab ID	ΣPAH (ppm)	ΣPAHp (ppm)	ΣPAHa (ppm)	% PAHa
Apr. 09	BRB	20090200	10.749	6.204	4.545	42
Apr. 09	EE3	20090202	20.710	13.396	7.315	35
Apr. 09	HP3	20090203	0.667	0.358	0.309	46
Apr. 09	HP2	20090207	1.774	1.004	0.770	43
Apr. 09	HC	20090209	47.107	37.994	9.113	19
Apr. 09	AYC	20090210	35.090	24.513	10.577	30
Apr. 09	EE1	20090211	6.914	4.640	2.274	33
Apr. 09	HP1	20090213	0.952	0.645	0.307	32
Apr. 09	TC	20090215	12.093	7.934	4.158	34
Apr. 09	DC	20090216	19.064	12.926	6.138	32
Apr. 09	SYC	20090217	5.249	2.876	2.374	45

Concentrations of total PAHs, parental PAHs, and alkylated PAHs were highest in Herring Cove (*HC*), near the Armdale Yacht Club (*AYC*) in Northwest Arm, in Central Harbour (*EE3*) and in Dartmouth Cove (*DC*) (Figure 4.6). The highest concentrations of parental and alkylated DBT were also found at the same sites as the highest concentrations of total PAHs. Highs in PAHs in both sediment grab samples and sediment cores were observed in similar locations. Concentrations of total PAHs in cores were greatest in 2008 vibracore 8 from Central Harbour and slow core 9 from Herring Cove. The lowest concentrations were observed in 2008 vibracore 5 collected near Herring Cove. However, only two samples from this core were successfully analyzed and it is therefore difficult to make conclusive statements about this core.

Maximum concentrations of total PAHs were generally observed at approximately 20 cm depth in slow cores 1, 2, 8, and 9. Highs in total PAHs in 2008 vibracore 2 and gravity core 5 were observed in the top 1 cm of sediment, while highs in total PAHs in 2008 vibracore 8 were noted at a depth of 35 cm. Highs in total PAHs were reflected by highs in both parental and alkylated PAHs. The ratio of LMW parental PAHs to HMW parental PAHs is relatively consistent down core to a depth of 20 cm in all cores. All cores (with the exception of vibracore 5) have relatively consistent degrees of alkylation over the first 20 to 30 cm. It is only below these depths that an increase in % alkylation is seen in the vibracores.

Table 4.3 Sediment core PAH summary data

Cruise	Station No.	Lab ID	Sed. depth (cm)	ΣPAH (ppm)	ΣPAHp (ppm)	ΣPAHa (ppm)	% PAHa
2008-053	2	20080300	23	2.606	1.423	1.183	45
2008-053	2	20080302	27	2.048	1.161	0.887	43
2008-053	2	20080312	47	0.233	0.134	0.099	43
2008-053	2	20080317	57	0.225	0.122	0.103	46
2008-053	2	20080320	63	0.237	0.098	0.139	59
2008-053	2	20080322	67	0.415	0.178	0.237	57
2008-053	2	20080324	71	0.790	0.401	0.389	49
2008-053	2	20080334	122	0.285	0.088	0.197	69
2008-053	2	20080339	172	1.565	0.189	1.376	88
2008-053	2	20080344	222	BDL	BDL	BDL	-
2008-053	2	20080349	272	0.055	0.017	0.038	69
2008-053	5	20080403	1	0.043	0.043	BDL	0
2008-053	5	20080405	5				
2008-053	5	20080418	31	0.361	0.148	0.214	59
2008-053	5	20080420	35				
2008-053	8	20080583	1	33.590	22.540	11.050	33
2008-053	8	20080585	5	23.290	15.170	8.120	35
2008-053	8	20080588	11	57.070	39.470	17.600	31
2008-053	8	20080590	15	38.226	24.696	13.530	36
2008-053	8	20080593	21	43.186	30.516	12.670	31
2008-053	8	20080595	25	46.116	30.048	16.068	37
2008-053	8	20080598	31	51.734	33.871	17.863	36
2008-053	8	20080600	35	188.747	141.023	47.724	26
2008-053	8	20080607	49	44.678	29.456	15.222	35
2008-053	8	20080617	100	2.416	0.602	1.814	76
2008-053	8	20080632	250	0.133	0.037	0.096	72
2008-053	8	20080637	300	0.071	0.000	0.071	100
2008-053	8	20080642	350	0.072	0.006	0.065	91
2009-060	1	20090061	0.5	4.366	2.458	1.907	44
2009-060	1	20090072	11.5	6.803	4.193	2.610	39
2009-060	1	20090081	20.5	11.652	7.240	4.413	39
2009-060	1	20090084	23.5	6.756	4.358	2.397	35
2009-060	2	20090087	0.5	7.593	4.468	3.125	45
2009-060	2	20090097	10.5	7.337	4.200	3.138	45
2009-060	2	20090107	20.5	15.342	8.616	6.726	45
2009-060	2	20090109	22.5	7.128	4.384	2.745	38
2009-060	5	20090147	0.5	12.765	7.197	5.568	45
2009-060	5	20090157	10.5	8.926	5.419	3.507	40
2009-060	5	20090167	20.5	BDL	BDL	BDL	-
2009-060	5	20090177	30.5	3.516	2.008	1.508	43

Table 4.3 Sediment core PAH summary data (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	ΣPAH	ΣPAHp	ΣPAHa	% PAH
2009-060	8	20090111	0.5	14.740	9.852	4.889	34
2009-060	8	20090121	10.5	17.612	11.799	5.813	34
2009-060	8	20090131	20.5	30.706	20.281	10.426	35
2009-060	8	20090141	30.5	4.171	2.717	1.455	35
2009-060	9	20090031	0.5	23.594	17.178	6.417	28
2009-060	9	20090041	10.5	23.600	17.349	6.251	27
2009-060	9	20090051	20.5	26.783	19.166	7.617	29
2009-060	9	20090060	29.5	21.596	14.227	7.369	35

4.2.3 Coprostanol

Concentrations of steroids in sediment grab samples and core samples are summarized in Tables D.3 and D.6, respectively. Concentrations of coprostanol in sediment grab samples were highest in Dartmouth Cove (*DC*), near Tufts Cove (*TC*) and in Central Harbour in grab samples *EE1* and *EE3* (Figure 4.6). Coprostanol concentrations were lowest in samples collected near Herring Cove (*HP1*, *HP2*, *HP3*, and *HC*).

Highs in coprostanol concentrations in sediment grab samples and sediment cores were observed in similar locations in Halifax Harbour. Sediment core profiles showing coprostanol concentrations can be found in Appendix E. Concentrations were highest in the tops of slow core 2 (Bedford Bay), 2008 vibracore 8 (Central Harbour), and slow core 8 (Northwest Arm). In general, concentrations of coprostanol decreased down core, reaching background concentrations within the top 20 cm. Concentrations of coprostanol in 2008 vibracore 2 and 2008 vibracore 5 were below 0.5 ppm down the entire length of the core.

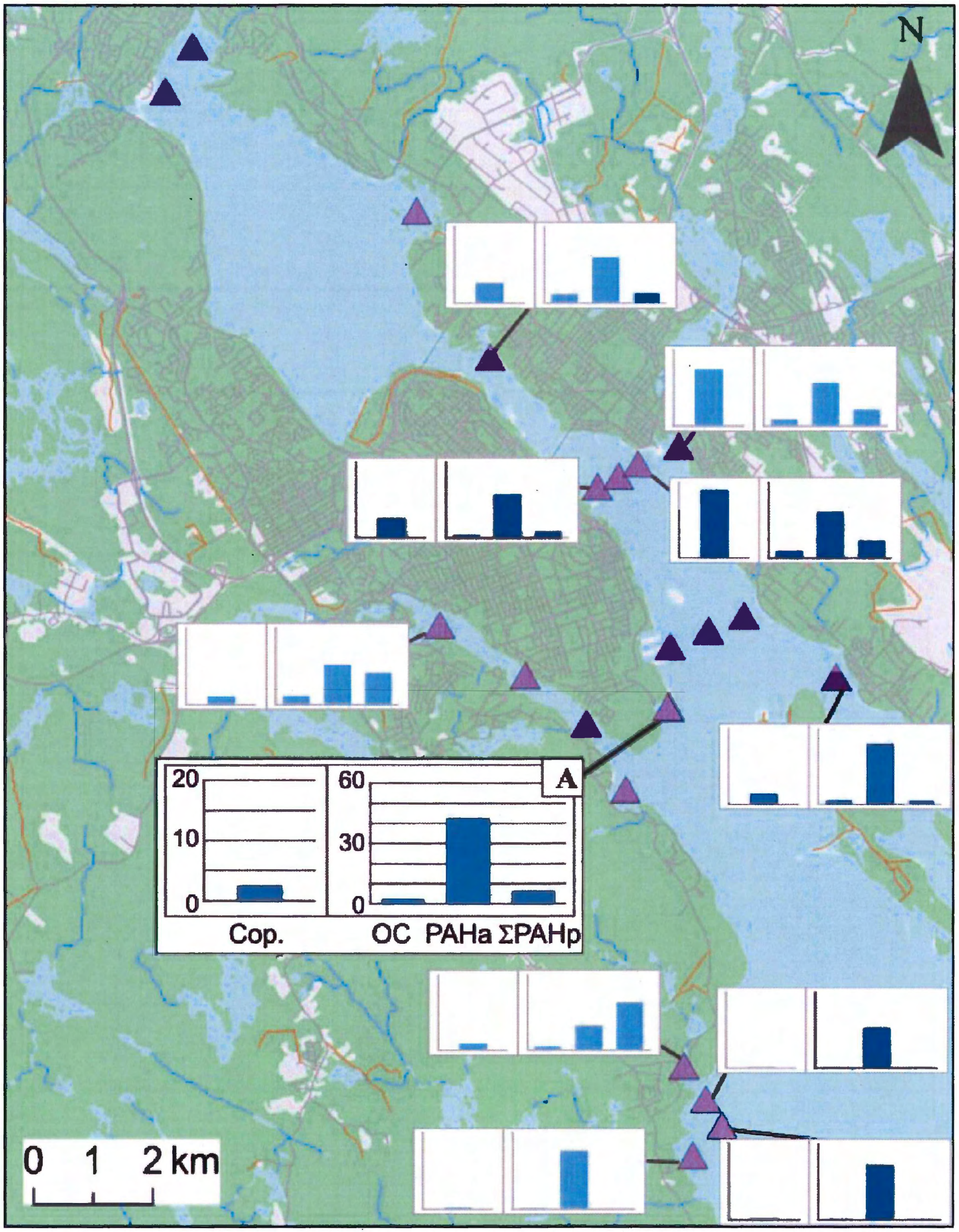


Figure 4.6: Variations in organic contaminant compositions of surficial sediments. Levels of coprostanol (Cop. in ppm), OC in %, % alkylated PAHs (PAHa in %), and sum of parental PAHs (ΣPAHp in ppm) in dry weight in grab samples. The scale used in Graph A is the same for all sites.

4.3 ^{210}Pb AND ^{137}Cs DATING OF MARINE SEDIMENTS

The four slow cores were selected for ^{210}Pb and ^{137}Cs dating as they provided the best opportunity for accurate dating since slow coring minimizes disturbance to the sediment-water interface relative to the other coring devices used in this study. In addition, two of the four cores are from near Mill Cove, which is an area of significant focus in this thesis. Results from dating analyses are summarized in Table G.1. Supported ^{210}Pb in Halifax Harbour was estimated to be 1.5 dpm/g (J. Smith, Fisheries and Oceans Canada, personal communication 2010).

4.4 PORE WATER CHEMISTRY OF MARINE SEDIMENTS

Results from pore water analyses are summarized in Table F.1, while pore water core profiles are shown in Appendix E. Salinity concentrations in slow cores 1, 2, and 8 and gravity core 5 are relatively consistent down core, ranging from 30.0 to 31.3‰. In slow core 9, salinity concentrations decrease down core from 31.2 to 26.0‰. Slow core 1, slow core 2, and gravity core 5 show similar profiles of sulphate and ammonium with depth, although concentrations of ammonium are higher in gravity core 5. Slow core 8 and slow core 9, however, show distinctive relationships between sulphate, ammonium, and depth. Both slow cores 8 and 9 display shallower slopes of sulphate and ammonium profiles with depth than slow core 1, slow core 2 and gravity core 5. Additionally, slow core 9 displays an increase in sulphate concentration and a decrease in ammonium concentration down to 5 cm, below which sulphate concentrations begin to decrease and ammonium concentrations increase.

CHAPTER 5: SPATIAL AND TEMPORAL CHANGES IN MARINE SEDIMENT CHEMISTRY

One of the key objectives of this research is to examine temporal and spatial changes in sediment chemistry resulting from increased industrialization and urbanization, and the initiation of wastewater treatment. Chapter 5 begins with an examination of the relationships between the different inorganic and organic analytes in both sediment cores and grab samples (Section 5.1). In Section 5.2 redox conditions in harbour sediments are considered. Average and present-day sediment accumulation rates are compared in Section 5.3. In Section 5.4 changes in the concentrations of both inorganic and organic contaminants in harbour sediments are discussed by examining sediment cores. Finally, in Section 5.5 the present-day concentrations of organic and inorganic contaminants in sediment grab samples are compared to results from previous studies. Temporal variations in inorganic and organic contaminants in sediments near the Mill Cove WWTF are presented and discussed in detail in Chapter 6.

5.1 CORRELATIONS BETWEEN ANALYTES

As discussed in Section 1.2.1.3, contaminant concentrations can be controlled by both natural (e.g. grain size, mineralogy) and anthropogenic processes (e.g. sewage input). Loring (1991) examined sediments from the St. Lawrence estuary, Gulf of St. Lawrence, Gulf of Paria (near Venezuela), and Florida and found that chromium, copper, and zinc generally co-vary strongly (R >0.75) with lithium. Table B.3 shows correlation coefficient relationships between OC and inorganic contaminants in pre-industrial marine sediments in core bottoms (marine sediments with concentrations below background levels as discussed in Section 5.4.1) from Halifax Harbour. With the exception of cobalt, chromium, copper, and zinc which show moderate correlations (R >0.50) with lithium, most contaminants do not co-vary appreciably with changes in lithium. These results suggest that changes in sediment grain size and/or mineralogy exert some control on the concentrations of cobalt, chromium, copper, and zinc, but are not a significant factor in controlling concentrations of other metals in the harbour. As such, the concentrations of inorganic contaminants were not normalized using lithium (or any other proxy for sediment grain size) before examining spatial and temporal variations throughout the harbour.

Previous studies have also indicated a significant correlation ($p = 0.01$) between metals and OC (Buckley and Hargrave 1989) and total PAHs and OC in surficial sediments ($p = 0.0001 - 0.0007$) (Hellou et al. 2002a) from Halifax Harbour. Table D.7 shows correlation coefficient relationships between PAHs, coprostanol and OC in sediment grab samples and the tops of sediment cores. Coprostanol shows moderate correlations with alkylated PAHs and OC. This is unsurprising as the source of PAHs in the wastewater is likely related to road runoff and industrial inputs, while the source of coprostanol would generally be domestic sewage. The primary source might be the same, but the secondary sources are likely different. It is also possible that wastewater in general is not a significant source of PAHs. Table B.4 shows correlation coefficient relationships between OC and inorganic contaminants in the top 10 cm of cores and in grab samples. Reasonably strong correlations (R >0.73) were observed between OC, cadmium, and copper, suggesting that these contaminants share a similar source.

5.2 REDOX CONDITIONS IN HARBOUR SEDIMENTS

As shown in Appendix E, pore water results from slow cores 1 and 2 (near Mill Cove), slow core 8 (mouth of Northwest Arm), and gravity core 5 (near Mill Cove) show concentrations of sulphate decreasing and concentrations of ammonium increasing down core. In slow core 9 (Herring Cove; Figure E.20B), sulphate concentrations begin to decrease and ammonium concentrations increase below a depth of 5 cm. Increases in sulphate and decreases in ammonium in pore waters in all the slow and gravity cores can be attributed to the decomposition of organic matter as discussed in Section 1.2.1.2. The production of ammonium and consumption of sulphate are suggestive of suboxic to reducing conditions at the sediment-water interface in Bedford Bay and the mouth of Northwest Arm, and in the near surface of sediments in Herring Cove. Buckley et al. (1995) also observed reducing conditions in sediments at or very near the sediment-water interface in Northwest Arm and the northern portion of Central Harbour near 2008 vibracore 8 (Figure 3.5). These results suggest suboxic to reducing conditions are predominant in Bedford Bay, Northwest Arm, and the northern portion of Central Harbour. As seen in sediments collected near Mill Cove (slow core 1, slow core 2, gravity core 5), reducing conditions persist despite wastewater treatment. However, the natural redox state of harbour sediments is likely dependent on the natural influx of organic matter deposition and mixing through water movement. Decreases in the input of organic matter into Central Harbour and the mouth of Northwest Arm due to increased wastewater treatment may result in a change from suboxic-reducing conditions to more oxic conditions in harbour sediments, particularly near the mouth of Northwest Arm as wastewater effluent will no longer be discharged into that area. Changing redox conditions may affect the mobility and bioavailability of sediment-bound metals (e.g. Förstner et al. 1986), which is likely to have significant implications for harbour fauna. Additionally, a change towards more oxic conditions is likely to result in an increase in the degradation rates of PAHs in the harbour. However, as previously discussed in

Section 1.2.2.1, degradation products of PAHs are often more toxic than the parent compound.

In slow cores 1, 2, and 8, and gravity core 5 salinity remains relatively constant down core. In slow core 9, however, salinity decreases from 31.2‰ at the top of the core to 26‰ at the bottom (Figure E.20B). This decrease may reflect a change in salinity with time. If salinity was lower in the past, salt may be diffusing downwards to this lower salinity pore water. This decreasing salinity profile could also reflect a source of freshwater at depth or the precipitation of salts from the pore water. To confirm that the precipitation of salts is causing the decrease in salinity, analysis of major ions in the pore water is required.

5.3 AVERAGE AND PRESENT-DAY SEDIMENT ACCUMULATION RATES

^{210}Pb and ^{137}Cs profiles for slow cores 8 and 9 are shown in Figure G.2, while pore water profiles showing present-day sediment accumulation rates can be found in Figure F.1. Sediment accumulation rates determined through ^{210}Pb and ^{137}Cs dating provide an estimate of the average sediment accumulation rate over approximately the last 100 years, while pore water analyses can lead to estimates of present-day sediment accumulation rates. Cranston (1999) demonstrated agreement between these two methods within an order of magnitude over a large range of sediment accumulation rates. Mixing through bioturbation and sediment reworking can substantially alter the sediment record. This effect on sediments is permanent, while pore water gradients are capable of re-establishing themselves and as such can be used to determine present-day sediment accumulation rates despite sediment mixing. The time required for the pore water gradients to re-establish themselves is dependent on the diffusion rate of the analyte in question and can be modelled with the following equation:

$$t = x^2 / (2 \text{ x } D_s)$$

where t is the time in years, x is the depth over which mixing has occurred in cm, and D_s is the diffusion coefficient of the analyte in sediment pore water in cm^2/s (Froelich et al. 1979). For example, using D_s for ammonium as $5.7 \text{ x } 10^{-6}$ cm^2/s (Schulz et al. 1994) and mixing over a depth of 20 cm, it would take one year for the ammonium gradient to re-establish itself following a perturbation over 20 cm. Similarly, using D_s for sulphate as $2.8 \text{ x } 10^{-6}$ cm^2/s (Schulz et al. 1994) and mixing over a depth of 20 cm, it would take two years for the sulphate gradient to re-establish itself following a perturbation over 20 cm.

Because sediments in Halifax Harbour receive unsupported ^{210}Pb inputs from atmospheric deposition, coastal waters and freshwater sources, one would expect unsupported ^{210}Pb inventories in sediments to be greater than the atmospheric inventory (Gearing et al. 1991). If unsupported ^{210}Pb inventories in harbour sediments are less than the atmospheric inventory it would suggest scouring and mixing of the sediment. The atmospheric flux of ^{210}Pb at the latitude of New York City is 0.90 – 1.00 dpm cm^{-2} year^{-1} (Turekian et al. 1977), which leads to a ^{210}Pb inventory of 28 – 32 dpm/cm^2. By comparing the atmospheric ^{210}Pb inventory and the inventories calculated for slow core 1 (62 dpm/cm^2), slow core 2 (66 dpm/cm^2), slow core 8 (24 dpm/cm^2) and slow core 9 (42 dpm/cm^2) one can make inferences regarding the history of sediment in the areas from which the cores were collected. Inventories in cores collected in Bedford Bay are suggestive of a net-depositional environment, while inventories in slow core 8 are suggestive of scouring and mixing in sediments near the mouth of Northwest Arm.

^{210}Pb and ^{137}Cs profiles of slow core 8 are suggestive of a low average sedimentation rate (<0.2 cm/year) and significant mixing as confirmed by the calculation of ^{210}Pb inventories in this core. Considerable mixing in this area may be the result of Hurricane Juan, which struck Halifax in 2003. The obvious impact on Point Pleasant (70% of trees were destroyed) which occupies the southernmost tip of peninsular Halifax suggests that this area likely experienced substantial winds and wave action, which may have lead to sediment erosion and mixing in this area. Mixing was also observed in slow core 9 (Herring Cove), in which sediments are mixed in the top few cm as indicated by the ^{210}Pb and ^{137}Cs profiles. A low average sedimentation rate (<0.2 cm/year) is indicated by the steeply sloped core profile. Sulphate and ammonium gradients in pore waters were used to calculate present-day sedimentation rates of 0.10 cm/year and 0.15 cm/year in slow cores 8 and 9, respectively (Figure F.1). Previous studies did not date sediment cores in these areas, so a direct comparison cannot be made. However, Buckley et al. (1995) and Cranston (1994) analyzed a core midway up Northwest Arm and determined an average sedimentation rate of 0.21 cm/year using conventional dating methods (Buckley et al. 1995) and a present-day sedimentation rate of 0.10 cm/year using pore water analyses (Cranston 1994). These results suggest that the present-day sedimentation rate in this area has not changed in the last 15 years.

5.4 TEMPORAL VARIATIONS IN MARINE SEDIMENT CHEMISTRY

5.4.1 Background Concentrations in Pre-industrial Sediments

Background concentrations based on previous research and the present study are listed in Table 5.1. Background concentrations in the current study were determined by examining sections of sediment vibracores in which concentration profiles for selected contaminants did not vary substantially at depth. Care was taken to ensure that only sections of cores that were marine sediments were examined by assessing the sedimentological and geochemical characteristics of the cores in question. Background concentrations are listed as a range of values rather than a single value, as different environments (bay versus inlet), varying water depths, and varying concentrations of OC and other major elements (due to naturally occurring variations in organic matter input, sediment type and input) can lead to varying background concentrations in a given area.

Background concentrations of chromium, mercury, and zinc determined in previous studies and the current study are substantially different. This difference is likely the result of insufficient lengths of cores from previous studies and differences in analytical techniques. Previous studies in Halifax Harbour have based background concentrations on sediments deposited prior to 1890 (Buckley et al. 1995). However, these cores were not sufficiently long to reach background concentrations of mercury or zinc. Results from the current study suggest that background concentrations of mercury were not reached until 120 cm depth in 2008 vibracore 8 (near downtown Halifax). To facilitate a rough comparison between Buckley et al.'s (1995) cores and the present study's core, it was assumed that Buckley et al.'s average sedimentation rates determined in cores collected near 2008 vibracore 8 (0.74 – 0.90 cm/year) are similar to the average sedimentation rate in 2008 vibracore 8. A depth of 120 cm in 2008 vibracore 8 would correspond to 1860 based on this assumption. In addition, mercury concentrations in the present study were

Table 5.1 Background concentrations of select contaminants

	Concentration (previous research)	Concentration (current research)	Concentration (combined)
Cadmium	**0.01 – 0.24 ppm[a]** **0.3 – 0.55 ppm[b]**	**0.1 – 0.8 ppm**	**0.01 – 0.8 ppm**
Copper	**12 – 38 ppm[c]**	**5 – 30 ppm**	**5 – 38 ppm**
Chromium	**11 – 69 ppm[a]** **65 – 106 ppm[b]**	**15 – 35 ppm**	
Mercury	**30 – 900 ppb[c]**	**<25 ppb**	
Nickel	**20 – 38 ppm[a]** **22 – 32 ppm[b]**	**1 – 30 ppm**	**1 – 38 ppm**
Lead	**0 – 44 ppm[c]**	**10 – 30 ppm**	**0 – 44 ppm**
Zinc	**75 – 133 ppm[c]**	**40 – 80 ppm**	
Phenanthrene	**0.043 ppm[d]**	**<0.07 ppm**	**<0.07 ppm**
Fluoranthene	**0.012 ppm[d]**	**<0.015 ppm**	
Coprostanol	**0.012 – 4.1 ppm[e]**		

_a_ Buckley et al. 1991
_b_ Le Blanc et al. 1991
_c_ Buckley et al. 1995
d Laflamme and Hites 1979, based on a single sample collected from a relatively uncontaminated area of the Gulf of Maine
_e_ Takada and Eganhouse 1998 and references therein, based on concentrations of coprostanol in sediments from around the world receiving no known sewage inputs

determined using a solid state mercury analyzer, while Buckley et al. (1995) used traditional cold-vapour AAS. Detection limits for traditional cold-vapour AAS are greater than 10 ppb, while solid state AAS has a working detection limit of 5 ppb.

Previous studies examining concentrations of metal contaminants in Halifax Harbour have used total dissolution procedures involving hydrofluoric acid (HF) (Buckley et al. 1991, Gearing et al. 1991, Winters et al. 1991, Buckley and Winters 1992, Tay et al. 1992, and Buckley et al. 1995), while the current study used a strong attack involving a modified *aqua regia* digestion (Section 3.2). The choice of a modified *aqua regia* dissolution was made for two reasons: (1) HF is very corrosive and must be handled with extreme care and (2) *aqua regia* dissolutions are satisfactory for evaluating contaminant levels in environmental monitoring as metals bound in relatively insoluble silicates are generally not a concern from an environmental standpoint (Hoenig 2001). In general the relatively low concentrations of chromium in harbour sediments are suggestive of a weak anthropogenic signal, which is unlikely to substantially overprint the natural variation in chromium concentrations. As such, the higher background concentrations observed in previous studies are likely a result of differences in dissolution procedure.

Background concentrations of PAHs were estimated by determining the concentrations of PAHs at depths corresponding to background concentrations of inorganic contaminants and by examining uncontaminated areas of the harbour (near Herring Cove). Given that PAHs degrade over time, these background concentrations should provide a conservative estimate of background levels of PAHs in Halifax Harbour. The affinity of PAHs for sediments with high OC content and the low concentrations of OC observed in the sediment grab samples collected near Herring Cove may mean that background concentrations of PAHs in the harbour are actually higher. However, sediment samples were sieved prior to analysis in an attempt to remove grain size effects and as a result grain size effects on PAH concentrations should be reduced. Background concentrations of phenanthrene and fluoranthene determined in this study (Table 5.1) compare reasonably well to those determined by Laflamme and Hites (1978).

Previous studies examining coprostanol in sediments which receive no known sewage inputs give a wide range of background concentrations (0.012 – 4.1 ppm) (Takada and Eganhouse 1998 and references therein). In the present study, no estimate of coprostanol in sediments was made as there is no area in the harbour not affected by fecal contamination (see Section 5.5.2).

5.4.2 Temporal Variations in Inorganic Contaminants

Buckley et al. (1995) determined that maximum concentrations of mercury, copper, lead, and zinc in Central Harbour were observed between 1920 and 1980, which is similar to the results observed in this study. Temporal changes in geochemistry in 2008 vibracore 8 are shown in Figure 5.1. Dates were calculated using sedimentation rates of 0.74 – 0.90 cm/year as determined from two nearby cores from Buckley et al. (1995). Results suggest that concentrations of mercury and lead in Central Harbour began to increase as early as 1870. Mercury concentrations peak between 1940 and 1990, while concentrations of lead peak between 1950 and 1980. Zinc concentrations begin to increase near 1910 and peak between 1970 and 1980. Concentrations of chromium begin to increase in 1980 and may still be rising, whereas concentrations of cobalt have increased steadily since 1910.

However, a concomitant increase in iron is also observable over that time period suggesting that increases in cobalt may be related to changes in mineralogy/grain size rather than anthropogenic influences. Background concentrations of most metals in 2008 vibracore 8 are reached in sediment depths corresponding to between 1870 and 1920. Gearing et al. (1991) examined a single core from Northwest Arm and determined that concentrations of copper, zinc, lead, and mercury increased from 1890 to 1970 and then began to decrease. They attributed the decrease in copper and zinc to a decrease in their use in marine paints and the decrease in lead to the discontinued use of leaded gasoline and the decreased use of lead in marine paints. Changes in the concentrations of mercury likely reflect the discontinued use of mercury in water-based paints (Gearing et al. 1991), stricter controls on mercury emissions (dental offices and hospitals), and the decreased use of coal (Environment Canada 2010c). The earlier increase in metals observed in Central Harbour relative to Northwest Arm likely reflects the earlier settling of peninsular Halifax. Decreases in metal concentrations observed in the Gearing et al. (1991) core in the top 5 cm were not observed in slow core 8 (Figure E.17). Instead, concentrations of mercury and zinc were relatively constant over the top 10 cm, likely as a result of mixing and scouring as indicated by the ^{210}Pb and ^{137}Cs results.

Despite their close proximity (<120 m), 1993 vibracores 2 and 10 have distinctly different profiles (Figures E.1 – E.4). Peaks in lead, mercury, copper, zinc, and cadmium observed in 1993 vibracore 2 are not observed in 1993 vibracore 10. It is possible that part of 1993 vibracore 10 was lost during collection. However, the profiles of 1993 vibracore 10 do not appear to be simply shifted down relative to the profiles of 1993 vibracore 2. For example, mercury concentrations in 1993 vibracore 10 do not reach background concentrations until 35 cm. Similarly, mercury concentrations in 1993 vibracore 2 reach background concentrations between 29.5 cm and 41.5 cm. Assuming there was not a difference in the flux of contaminants into sediments between 1993 vibracores 2 and 10, it appears that sediments in 1993 vibracore 10 have been mixed over as much as 30 cm. This may have occurred during collection. If sediment in 1993 vibracore 10 was quite soupy near the top, this would have resulted in more sediment mixing than expected. Alternatively, this may be the result of in situ mixing.

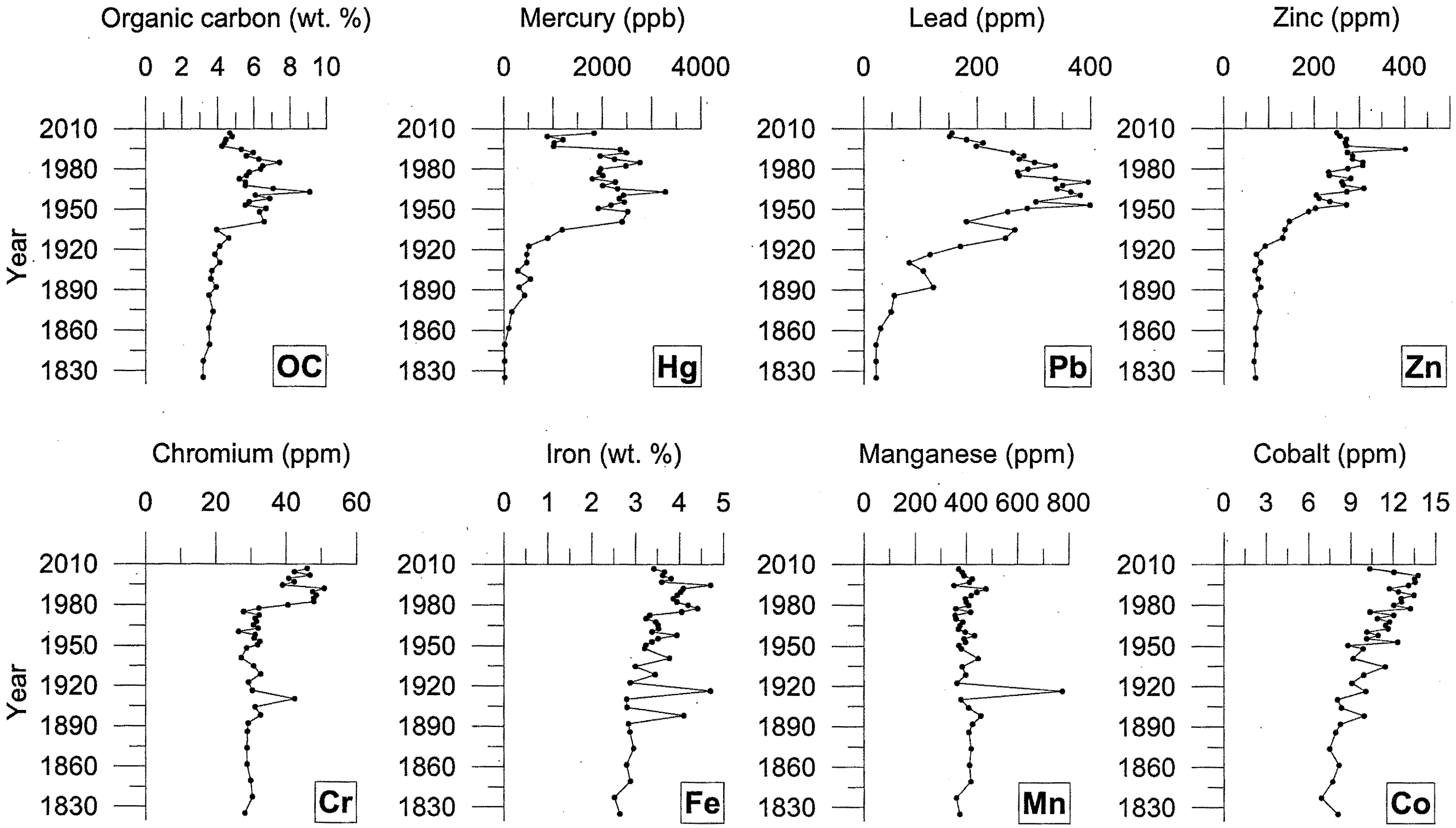


Figure 5.1 Temporal changes in the geochemistry of sediments in 2008 vibracore 8 (north of Georges Island, Figure 3.5). Dates were calculated using sedimentation rates from Buckley et al. (1995).

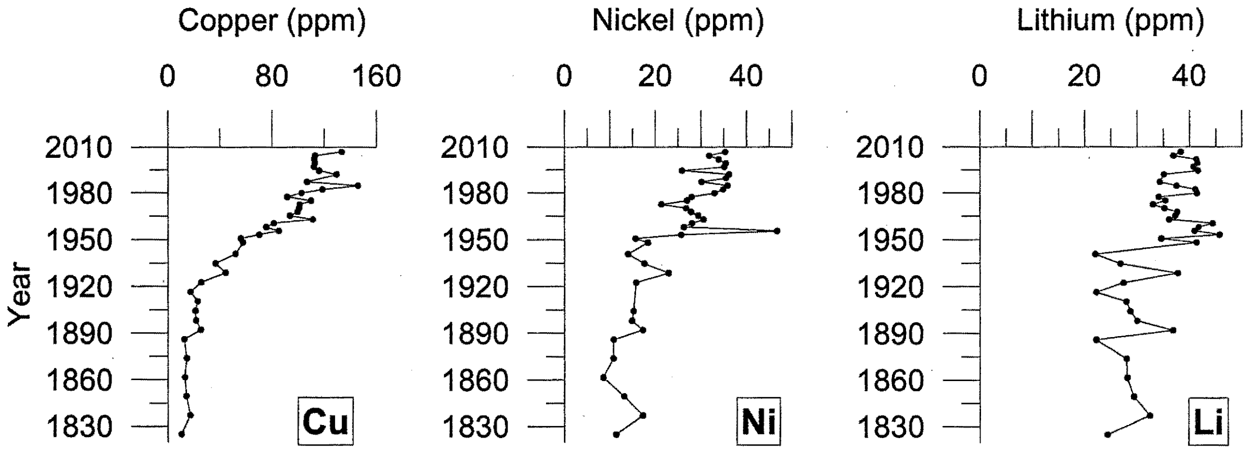


Figure 5.1 (cont'd) Temporal changes in the geochemistry of sediments in 2008 vibracore 8 (north of Georges Island, Figure 3.5). Dates were calculated using sedimentation rates from Buckley et al. (1995).

In general, concentrations of mercury, lead, zinc, and copper are decreasing in sediments from most areas of the harbour. In Herring Cove (slow core 9) zinc and chromium concentrations are relatively consistent throughout, as are lead and mercury concentrations in Outer Harbour and copper concentrations in the southern portion of Central Harbour. Concentrations of lead, copper, and zinc exceed the ISQG and concentrations of mercury exceed the PEL to depths of 10 to 15 cm in sediments from the mouth of Northwest Arm. Concentrations of metals in Outer Harbour are below the PEL for all elements considered. Mercury, lead, and copper concentrations exceed the ISQG in near surface sediments in 1993 vibracore 9. In Herring Cove concentrations of mercury, lead, copper, and zinc exceed the ISQG in the near surface and at depth (below 5 cm) the PEL for lead is exceeded. In the southern portion of Central Harbour (1993 vibracore 2) concentrations of mercury, lead, copper, and zinc exceed the ISQG in the near surface. In the northern portion of Central Harbour (2008 vibracore 8 and 2008 vibracore 9), concentrations of mercury exceed the PEL in the near surface, while concentrations of lead and zinc exceed the PEL in 2008 vibracore 8, highlighting the higher levels of contamination in the northern portion of Central Harbour.

5.4.3 Temporal Variations in Organic Contaminants

With the exception of slow core 9 (Herring Cove), sulphate-reducing conditions were observed at the sediment-water interface in all slow cores and the gravity core suggesting that sediments in the mouth of Northwest Arm and Bedford Bay are anoxic (Section 5.2). Similar results were observed by Buckley et al. (1995) in Northwest Arm and northern Central Harbour. Relatively low concentrations of LMW parental PAHs were observed in Halifax Harbour sediments (<12 ppm, with the exception of a single sample from 2008 vibracore 8 at 35 cm depth) relative to the sediments heavily contaminated by petroleum-derived PAHs (33 ppm) observed by Coates et al. (1996, 1997). The degree of alkylation in the top 20 cm of 2008 vibracore 2, slow cores 1, 2, 8, and 9 is relatively consistent suggesting that parental PAHs may not have degraded significantly relative to alkylated PAHs over that depth interval (Appendix D). In 2008 vibracore 8, the degree of alkylation is relatively consistent to a depth of 50 cm, likely reflecting the higher average sedimentation rate near downtown Halifax. Given the relatively low concentrations of LMW parental PAHs, the anoxic sulphate-reducing conditions in the majority of harbour sediments, and the consistency in degree of alkylation down to depths of 20 cm in cores (50 cm in 2008 vibracore 8), the results of this study suggest that degradation of both parental and alkylated PAHs is negligible down to these depths.

The highest concentrations of total PAHs were observed in Central Harbour (2008 vibracore 8) and Herring Cove (slow core 9). The parental PAHs which displayed the highest concentrations in sediment cores were benzo[b&j&k]fluoranthene, fluoranthene, and pyrene. Gearing et al. (1991) reached similar conclusions. They found that concentrations of benzofluoranthenes, fluoranthene, and pyrene in a single core from Northwest Arm were the most abundant PAHs down to a depth of 17.5 cm (corresponding to 1905).

Gearing et al. (1991) observed a subsurface maximum in combustion related parental PAHs (which they defined as phenanthrene, fluoranthene, benz[a]anthracene, chrysene, benzo[b&j&k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene) at 5 – 10 cm (corresponding to 1940 – 1960), which was attributed to the decline in wood and coal burning over the last 50 years. The subsurface maximums in combustion parental PAHs in the present study's cores match the subsurface maximum in total parental PAHs. The subsurface maximums observed in 2008 vibracore 8 are similar to those previously observed by Gearing et al. (1991). Based on the average sedimentation rates determined by Buckley et al. (1995) for a similar area of Central Harbour (0.74 – 0.90 cm/year), this would place the maximum concentration of combustion parental PAHs in 2008 vibracore 8 at a depth corresponding to 1965. Temporal changes in concentrations of inorganic contaminants in 2008 vibracore 8 are shown in Figure 5.2. Peak concentrations in both alkylated and parental PAHs are found in sediments corresponding to 1965. Peaks in alkylated and parental PAHs in undated cores (slow core 8 and slow core 9) were observed at 20.5 cm depth (Figure E.26).

As discussed in Section 1.2.2.1, low concentrations of alkylated PAHs relative to parental PAHs are indicative of combustion sources. The degree of alkylation (0 – 45%) in the top 20 cm of sediment cores (50 cm in 2008 vibracore 8) suggests greater input from pyrogenic sources of PAHs relative to petrogenic sources. As shown in Tables 1.1 and 1.2, diagnostic ratios of PAHs can be used to establish sources of PAHs. Diagnostic ratios of parental PAHs from this study are also generally suggestive of greater input from pyrogenic sources relative to petrogenic sources (Table 5.2). However, some diagnostic ratios (AN/AN+PA and FL/FL+PY) suggest a mix of both pyrogenic and petrogenic sources. Ratios of PA/AN and FL/PY in the top 20 cm of cores (50 cm in 2008 vibracore 8) are characteristic of sources of PAHs which include car soot, wood burning emissions, and naturally occurring Nova Scotia soils.

Dibenzothiophene is a sulphur heterocycle, commonly found in coal tar (McCarry et al. 1996). Alkylated dibenzothiophenes are derived from a variety of sources including mature crude oils, coals, and diesel fuels (Fedorak and Westlake 1983, Hellou et al. 2002a). The highest concentrations of dibenzothiophene in slow core 8, slow core 9 and 2008 vibracore 8 were found at the same depths as the highest concentrations of combustion parental PAHs, strengthening the supposition that these peaks are the result of a decline in wood and coal burning in the last 50 years.

Concentrations of PAHs in 2008 vibracore 8 and slow core 9 exceed the PEL for most PAHs down to a depth of 50 and 30 cm, respectively. The ISQG for most PAHs is exceeded down the entire core length of slow core 8. These results confirm that the most contaminated areas of the harbour with respect to PAHs are Central Harbour and Herring Cove, but that sediments in the mouth of Northwest Arm are also contaminated down to depths of 30 cm. Although the ISQGs and PELs are exceeded in many areas of the harbour, this does not mean these sediments would necessarily be toxic, but that these areas warrant further investigation to determine their toxicity. This is particularly true of Herring Cove, in which there is a scarcity of published data examining sediment chemistry.

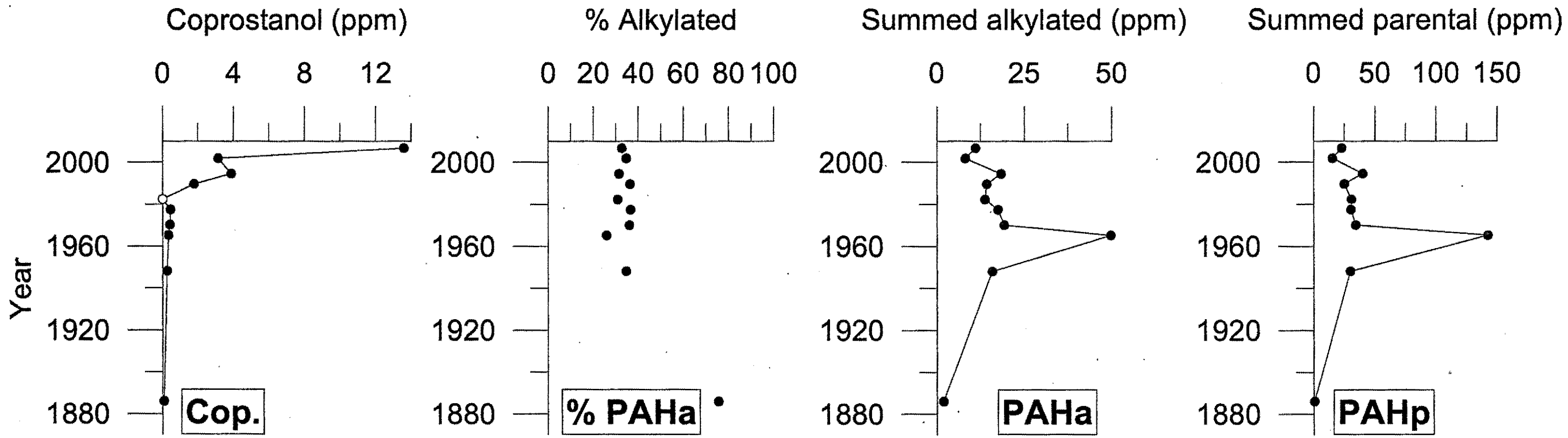


Figure 5.2 Temporal changes in the organic geochemistry of sediments in 2008 vibracore 8 (north of Georges Island, Figure 3.5). Dates were calculated using sedimentation rates from Buckley et al. (1995). Open symbols denote samples with concentrations below the detection limit of the analyte.

Table 5.2 Sediment core diagnostic PAH ratios

Cruise	Stn. No.	Lab ID	Sed. depth (cm)	AN/ AN+PA	FL/ FL+PY	BA/ BA+CH	IP/ IP+BP	PA+AN+PY+FL/ CH+BA+BF+BaP+IP+DBA+BP	PA/AN	FL/PY
2008-053	2	20080300	23	0.21	0.49	0.43	0.49	0.80	3.68	0.95
2008-053	2	20080302	27	0.20	0.49	0.43	0.50	0.85	4.04	0.98
2008-053	2	20080312	47	-	0.51	0.41	0.50	1.40	-	1.06
2008-053	2	20080317	57	-	0.49	0.47	0.50	1.00	-	0.95
2008-053	2	20080320	63	-	0.49	0.41	0.54	1.09	-	0.94
2008-053	2	20080322	67	0.27	0.49	0.39	0.35	0.91	2.75	0.96
2008-053	2	20080324	71	0.26	0.49	0.44	0.50	0.88	2.82	0.96
2008-053	2	20080334	122	-	0.44	-	-	-	-	0.79
2008-053	2	20080339	172	-	0.45	-	-	-	-	0.83
2008-053	2	20080344	222	-	-	-	-	-	-	-
2008-053	2	20080349	272	-	0.43	-	-	-	-	0.75
2008-053	5	20080403	1	-	0.50	0.29	-	0.33	-	1.00
2008-053	5	20080405	5							
2008-053	5	20080418	31	-	0.40	0.22	-	0.08	-	0.67
2008-053	5	20080420	35							
2008-053	8	20080583	1	0.26	0.52	0.43	0.52	0.92	2.79	1.09
2008-053	8	20080585	5	0.27	0.49	0.41	0.53	0.85	2.73	0.97
2008-053	8	20080588	11	0.25	0.52	0.43	0.54	1.27	3.01	1.08
2008-053	8	20080590	15	0.28	0.49	0.42	0.54	0.90	2.56	0.96
2008-053	8	20080593	21	0.26	0.52	0.42	0.52	0.84	2.83	1.06
2008-053	8	20080595	25	0.28	0.47	0.38	0.54	0.79	2.61	0.90
2008-053	8	20080598	31	0.27	0.47	0.41	0.54	0.87	2.66	0.90
2008-053	8	20080600	35	0.30	0.53	0.45	0.55	1.01	2.32	1.13
2008-053	8	20080607	49	0.26	0.47	0.45	0.53	0.82	2.83	0.88
2008-053	8	20080617	100	0.33	0.48	0.47	0.49	0.74	1.99	0.92
2008-053	8	20080632	250	0.26	0.45	-	-	7.76	2.88	0.83

Table 5.2 Sediment core diagnostic PAH ratios (cont'd)

Cruise	Stn. No.	Lab ID	Sed. depth (cm)	AN/ AN+PA	FL/ FL+PY	BA/ BA+CH	IP/ IP+BP	PA+AN+PY+FL/ CH+BA+BF+BaP+IP+DBA+BP	PA/AN	FL/PY
2008-053	8	20080637	300	-	-	-	-	-	-	-
2008-053	8	20080642	350	-	0.50	-	-	-	-	1.00
2009-060	1	20090061	0.5	0.40	0.53	0.49	0.51	0.84	1.51	1.14
2009-060	1	20090072	11.5	0.33	0.49	0.50	0.53	0.78	2.03	0.96
2009-060	1	20090081	20.5	0.33	0.48	0.50	0.53	0.77	2.07	0.92
2009-060	1	20090084	23.5	0.35	0.49	0.52	0.53	0.84	1.84	0.98
2009-060	2	20090087	0.5	0.37	0.53	0.51	0.53	0.74	1.70	1.13
2009-060	2	20090097	10.5	0.37	0.53	0.50	0.53	0.73	1.73	1.11
2009-060	2	20090107	20.5	0.31	0.49	0.49	0.52	0.77	2.21	0.95
2009-060	2	20090109	22.5	0.30	0.49	0.51	0.55	0.80	2.35	0.98
2009-060	5	20090147	0.5	0.35	0.49	0.49	0.55	0.82	1.85	0.97
2009-060	5	20090157	10.5	0.32	0.49	0.52	0.53	0.76	2.14	0.98
2009-060	5	20090167	20.5	-	-	-	-	-	-	-
2009-060	5	20090177	30.5	0.30	0.49	0.52	0.49	0.81	2.36	0.97
2009-060	8	20090111	0.5	0.31	0.54	0.52	0.54	1.05	2.20	1.16
2009-060	8	20090121	10.5	0.35	0.54	0.53	0.54	1.01	1.82	1.16
2009-060	8	20090131	20.5	0.31	0.51	0.51	0.56	1.01	2.18	1.04
2009-060	8	20090141	30.5	0.31	0.51	0.53	0.53	0.90	2.27	1.03
2009-060	9	20090031	0.5	0.49	0.55	0.44	0.52	0.78	1.05	1.21
2009-060	9	20090041	10.5	0.50	0.38	0.52	0.52	0.66	1.00	0.61
2009-060	9	20090051	20.5	0.35	0.49	0.55	0.54	0.86	1.87	0.97
2009-060	9	20090060	29.5	0.47	0.46	0.58	0.53	0.83	1.14	0.84

Highs in PAHs in slow core 9 are somewhat surprising as Herring Cove is largely a residential community. The relative contribution of alkylated PAHs (27 – 35% alkylation) in slow core 9 is indicative of combustion dominated sources for PAHs in Herring Cove, as are diagnostic PAH ratios. Contributions of alkylated PAHs are lower in slow core 9 than what is observed in the other cores collected in Halifax Harbour, suggesting greater input from combustion sources in this area. Ratios of PA/AN in slow core 9 are suggestive of car soot, while ratios of FL/PY are suggestive of several sources including Nova Scotia soils, car soot, crankcase oil, and sewage.

Diagnostic ratios of fecal contamination in Halifax Harbour sediment cores are summarized in Table 5.3. Diagnostic steroid ratios indicate fecal contamination of sediments in the top 0 – 5 cm of a core collected from Herring Cove (slow core 9) and in the top 0 – 10 cm of a core collected from the mouth of Northwest Arm (slow core 8). The vibracore collected from just outside Herring Cove (2008 vibracore 5) shows no evidence of fecal contamination down the entire length of the core.

Both steroid diagnostic ratios indicate that Central Harbour (2008 vibracore 8) has been subjected to contamination by sewage effluents. The lack of evidence for fecal contamination and the low concentrations of coprostanol below 15 cm depth (<0.5 ppm) could be due to degradation of steroids or could indicate uncontaminated sediments. However, given the known history of Halifax Harbour and Central Harbour in particular as receiving waters for sewage effluent for more than 250 years and the previously determined average sedimentation rate of 0.74 – 0.90 cm/year in Central Harbour (Buckley et al. 1995), it is unlikely that sediments would be uncontaminated even at 100 cm depth. It is far more likely that the ratios are indicative of steroid degradation. This would suggest a time scale of approximately 15 to 20 years for steroid degradation in Central Harbour.

Table 5.3 Sediment core diagnostic steroid ratios

Cruise	Station No.	Lab ID	Sed. depth (cm)	coprostanol/ coprostanol + cholestanol	coprostanol/ cholesterol
2008-053	2	20080300	23	0.32	0.32
2008-053	2	20080302	27	0.30	0.25
2008-053	2	20080312	47	-	-
2008-053	2	20080317	57	0.22	0.09
2008-053	2	20080320	63	-	-
2008-053	2	20080322	67	0.28	0.18
2008-053	2	20080324	71	0.34	0.16
2008-053	2	20080334	122	-	-
2008-053	2	20080339	172	-	-
2008-053	2	20080344	222	-	-
2008-053	2	20080349	272	-	-
2008-053	5	20080403	1	0.48	0.15
2008-053	5	20080405	5		
2008-053	5	20080418	31	-	-
2008-053	5	20080420	35		
2008-053	8	20080583	1	0.84	2.44
2008-053	8	20080585	5	0.75	2.57
2008-053	8	20080588	11	0.77	2.85
2008-053	8	20080590	15	0.73	2.61
2008-053	8	20080593	21	-	-
2008-053	8	20080595	25	0.47	0.43
2008-053	8	20080598	31	0.49	0.45
2008-053	8	20080600	35	0.49	0.63
2008-053	8	20080607	49	0.39	0.67
2008-053	8	20080617	100	0.35	0.11
2008-053	8	20080632	250	-	-
2008-053	8	20080637	300	-	-
2008-053	8	20080642	350	-	-
2009-060	1	20090061	0.5	0.49	0.28
2009-060	1	20090072	11.5	0.39	0.45
2009-060	1	20090081	20.5	0.15	0.18
2009-060	1	20090084	23.5	0.16	0.13
2009-060	2	20090087	0.5	0.65	0.95
2009-060	2	20090097	10.5	0.54	1.69
2009-060	2	20090107	20.5	-	-
2009-060	2	20090109	22.5	0.12	0.07
2009-060	5	20090147	0.5	0.34	0.33
2009-060	5	20090157	10.5	0.38	0.35
2009-060	5	20090167	20.5	-	-
2009-060	5	20090177	30.5	-	-

Table 5.3 Sediment core diagnostic steroid ratios (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	coprostanol/ coprostanol + cholestanol	coprostanol/ cholesterol
2009-060	8	20090111	0.5	0.74	0.68
2009-060	8	20090121	10.5	0.50	0.96
2009-060	8	20090131	20.5	0.45	0.59
2009-060	8	20090141	30.5	0.22	0.16
2009-060	9	20090031	0.5	0.71	0.27
2009-060	9	20090041	10.5	-	-
2009-060	9	20090051	20.5	-	-
2009-060	9	20090060	29.5	-	-

5. 5 SPATIAL VARIATIONS IN MARINE SEDIMENT CHEMISTRY

5.5.1 Spatial Variations in Inorganic Contaminants

There appears to be no pattern of change in the concentrations of contaminants with time in surficial (grab) samples when the concentrations of contaminants from each of the nine sites that were sampled during all four sampling events are examined (Figure 5.3). However, sediment grab samples collected in October 2008 and April 2009 may not be representative of the top 0 – 2 cm of surface sediment, as problems with sampling equipment were encountered during these two sampling events. Instead grab samples from these sampling dates may contain mixed sediment from the top 0 – 10 cm and therefore cannot be used to establish a timeline of changing contaminant concentrations over the 15 month period that sediment grab samples were collected.

Variations in concentrations at the same sites between sampling events are likely related to the heterogeneous nature of harbour sediments. Given the nature of the sampling apparatus and changes in ship movements it is impossible to sample at the exact same location from sampling event to sampling event. Concentrations of contaminants can vary substantially over a small scale particularly in dynamic areas with little net deposition, which can result in differences in concentrations of contaminants from samples collected in the same area. For example, Morrisey et al. (1994) examined the spatial distribution of copper, lead, and zinc in estuarine sediments in Botany Bay, Australia and determined that concentrations varied at a scale of 2 – 10 m.

Concentrations of lead, mercury, and copper in sediment grab samples exceeded the ISQG at all sampling sites in the harbour during all four sampling events with the exception of sediment grab samples collected near Herring Cove (*HP1*, *HP2*, and *HP3*) (Figures 3.6 and 4.1), which contain abundant shell hash. A single grab sample collected

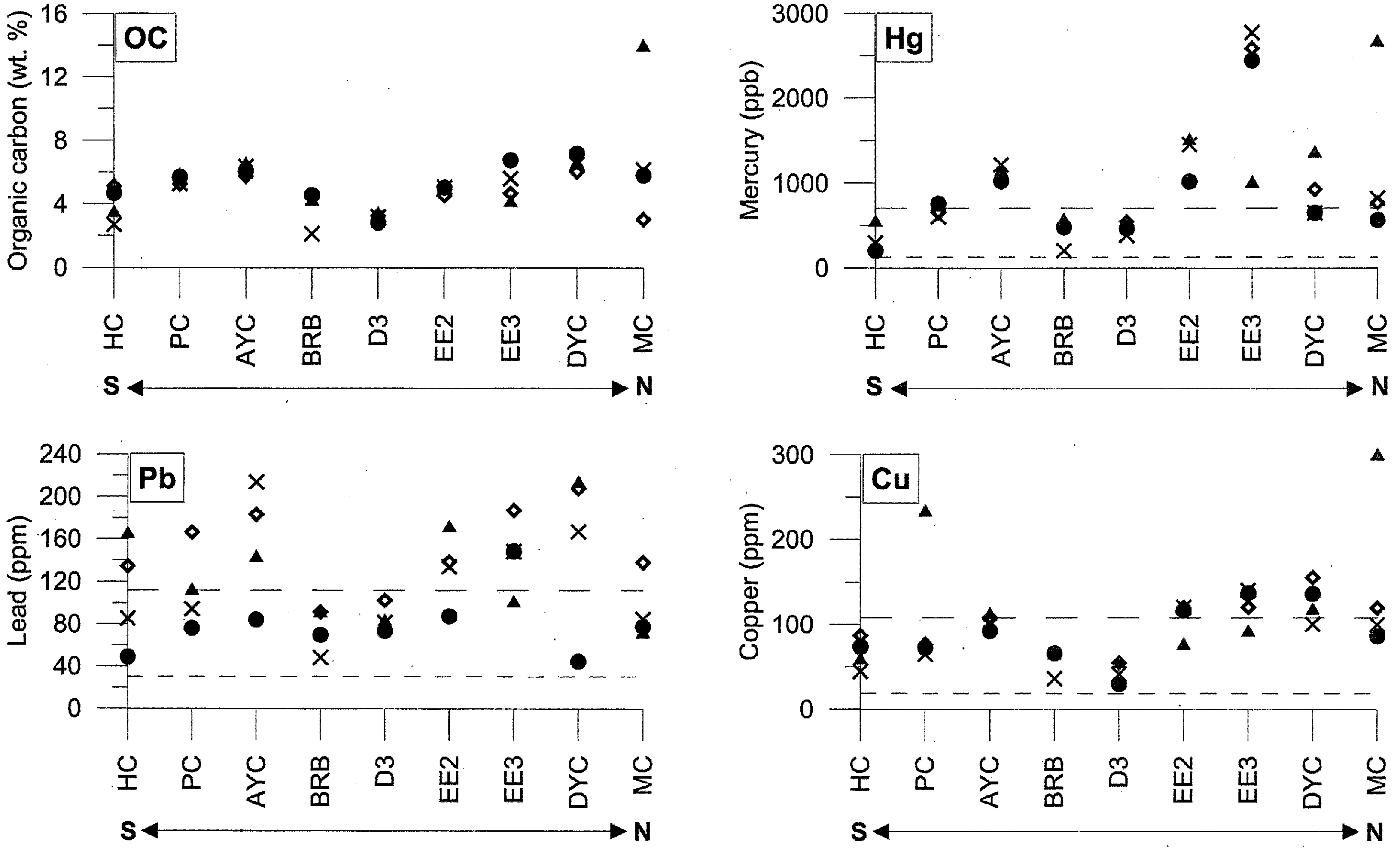


Figure 5.3 Plots of grab samples collected during all four different events arranged from south to north (● March 2008, ◇ July 2008, ▲ October 2008, × April 2009) (Figure 3.6). Only those grab samples that were collected during all four sampling occasions are shown. The short dashed line represents the ISQG (CCME 2002), while the longer dashed line represents the PEL (CCME 2002).

at *HP3* during the March 2008 sampling event exceeded the ISQG for lead. Grab samples that exceeded the PEL for lead, mercury, and copper during at least one sampling event were collected at 13, 11 and 8 sites, respectively. At three sites (*TC*, *DC*, *ST5*) grab samples were collected with concentrations greater than the PEL for lead and mercury during all events that these sites were sampled. At an additional four sites (*EE2*, *EE3*, *RNSYS*, *AYC*) the PEL for mercury was exceeded during all events that these sites were sampled. The PEL for copper was exceeded in grab samples collected from Dartmouth Cove (*DC*) and near Tufts Cove (*TC*) during all events that these sites were sampled. Concentrations of chromium exceeding the ISQG were only detected in four sediment grab samples (*TC*, *PC*, *RNSYS*, and *AYC*), which were collected in March 2008 (Figure C.1).

Canadian sediment quality guidelines are not available for nickel or cobalt. To evaluate nickel and cobalt contamination in Halifax Harbour, SQVs developed by the NOAA were used. The NOAA's threshold effects level (equivalent to the CCME's ISQG) for nickel is 15.9 ppm and the PEL for nickel is 42.8 ppm (NOAA 2008). Threshold effect levels and PELs are not available for cobalt. However, the background concentrations and apparent effects threshold (the highest concentration associated with a non-toxic sample) in marine sediments is 10 ppm and the lowest effect level (concentration that can be tolerated by most benthic fauna) in freshwater sediments is 50 ppm (NOAA 2008). Concentrations of nickel in sediment grab samples exceeded the threshold effects level in all areas of the harbour with the exception of samples collected from in and around Herring Cove (*HP1*, *HP2*, *HP3* and *HC*) (Figure C.1). However, the background concentration of nickel (1 – 30 ppm) in Halifax Harbour sediments exceeds the threshold effects level. The PEL was exceeded in a single sample collected near Tufts Cove (*TC*). With the exception of samples collected from in and around Herring Cove (*HP1*, *HP2*, *HP3* and *HC*), all areas of the harbour exceeded the apparent effects threshold on at least one sampling occasion. No samples collected contained levels of cobalt which exceeded the lowest effect level in freshwater sediments (Figure C.2).

Concentrations of zinc in sediment grab samples exceeded the ISQG at sampling sites in Northwest Arm, Bedford Basin, Bedford Bay and in the northern portion of Central Harbour (*EE1*, *EE2*, *EE3*, *DC*, and *TC*) during all sampling events (Figure C.1). Zinc concentrations exceeded the PEL during all sampling events in samples collected near Mill Cove (*MC*) and Tufts Cove (*TC*) and during multiple events in samples collected in Dartmouth Cove (*DC*) and near the Dartmouth Yacht Club (*DYC*). Concentrations of zinc were greater than background concentrations in all grab samples collected with the exception of those collected near Herring Cove (*HP1*, *HP2*, and *HP3*) and in the southern portion of Central Harbour (*D2* and *D3*). Buckley and Hargrave (1989) suggest that high concentrations of mercury and copper are indicative of municipal or domestic sewage, while high concentrations of zinc and lead are indicative of solid and industrial waste. The ISQG for Cd was exceeded in Herring Cove (*HC*), Northwest Arm (*PC*, *RNSYS*, *AYC*), Central Harbour (*D1*, *DC*, *TC*, *DYC*), and Bedford Bay (*MC*, *BYC*) on at least one sampling occasion (Figure C.1).

Concentrations of lead, mercury, and copper were greater than background concentrations (Table 5.1) at all sampling sites during all events with the exception of grab samples collected near Herring Cove (*HP1*, *HP2*, and *HP3*). Although the ISQG and PEL were exceeded at several sites in the harbour for a range of contaminants, this does not necessarily imply that these sediments are indeed toxic. Instead these results highlight areas of the harbour which warrant further investigation for toxic effects on biota living in and around these sites. As previously discussed, changes in redox conditions (increasingly oxic conditions) resulting from increased wastewater treatment may result in these metal contaminants becoming more bioavailable. As well, an increase in oxic conditions will increase degradation rates of PAHs. However, as previously stated the products of PAH degradation are often more toxic than the parent compound. As such, long-term screening programs should incorporate sediment chemistry monitoring.

Summary statistics for concentrations of metals in sediment grab samples from all four present-day sampling events (2008 – 2009) and from previous sampling efforts (1986 – 1988) are shown in Table 5.4. Sampling sites were grouped according to general

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (sampling locations are shown in Figure 5.4).

		Outer Harbour		Northwest Arm		Southern Central Harbour		Northern Central Harbour	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Organic carbon (wt. %)	minimum	0.08	0.09	5.24	5.46	2.12	0.13	2.22	2.53
	maximum	0.84	0.70	6.46	10.06	5.77	11.96	6.76	8.71
	median	0.58	0.54	5.78	5.92	3.81	3.61	4.84	4.74
	mean	0.53	0.45	5.83	6.18	3.90	3.56	4.74	4.87
	S.D.	0.26	0.27	0.44	1.09	1.01	1.83	1.13	1.43
	n	8	6	8	18	20	48	14	12
Cd (ppm)	minimum	<0.01	BDL	0.59	0.49	0.26	0	0.32	0.79
	maximum	0.14	0.19	0.99	2.08	0.87	4.14	1.77	5.26
	median	0.04	-	0.91	1.16	0.55	0.51	0.50	1.11
	mean	0.05	0.03	0.85	1.33	0.50	0.63	0.68	1.60
	S.D.	0.05	0.08	0.15	0.42	0.20	0.62	0.49	1.33
	n	5	6	5	17	9	48	7	12
Cr (ppm)	minimum	<10	-	25	89	20	36	19	87
	maximum	12	-	83	124	88	108	48	99
	median	9	-	39	92	31	85	37	92
	mean	9	-	45	97	32	83	36	93
	S.D.	2	-	18	11	14	21	7	5
	n	8	0	8	9	19	9	14	4
Cu (ppm)	minimum	2	2	78	68	30	4	75	93
	maximum	13	13	111	220	232	271	246	324
	median	10	6	89	102	63	61	121	116
	mean	9	6	92	104	68	63	130	138
	S.D.	3	4	13	33	42	39	48	64
	n	8	6	8	18	19	49	14	12

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (cont'd)

		Outer Harbour		Northwest Arm		Southern Central Harbour		Northern Central Harbour	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Hg (ppb)	minimum	<5	30	892	860	205	60	437	1040
	maximum	49	580	1628	3100	759	10580	2770	3180
	median	24	125	1024	1510	502	560	1657	1280
	mean	25	185	1110	1670	505	930	1749	1676
	S.D.	13	205	233	690	141	1670	786	734
	n	8	6	8	9	19	40	14	8
Li (ppm)	minimum	13	34	35	21	28	19	29	45
	maximum	54	64	46	102	41	93	43	79
	median	21	53	42	73	33	52	33	58
	mean	26	51	40	68	34	50	34	61
	S.D.	14	13	4	17	4	14	4	11
	n	8	6	8	18	19	49	14	12
Pb (ppm)	minimum	8	16	84	120	48	0	72	129
	maximum	30	16	231	304	175	751	1517	486
	median	15	16	163	215	82	68	159	191
	mean	16	16	159	217	88	111	344	230
	S.D.	7	0	55	58	33	148	408	123
	n	8	6	8	18	20	49	14	12
Zn (ppm)	minimum	30	27	176	174	78	44	137	214
	maximum	50	45	227	389	233	590	547	555
	median	43	36	201	230	148	155	208	264
	mean	42	36	202	241	146	171	250	305
	S.D.	6	8	18	44	35	101	113	116
	n	8	6	8	18	19	49	14	12

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (cont'd)

		Outer Harbour		Northwest Arm		Southern Central Harbour		Northern Central Harbour	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Ni (ppm)	minimum	6	155	21	15	18	0	22	14
	maximum	14	1738	31	739	31	1993	33	44
	median	9	1356	26	34	24	62	26	26
	mean	9	1185	26	181	24	266	27	27
	S.D.	3	562	3	261	3	505	3	9
	n	8	6	8	18	19	49	14	12
Fe (wt. %)	minimum	0.87	0.46	2.89	2.45	2.55	1.26	2.86	2.98
	maximum	1.67	1.46	4.20	5.23	3.62	14.15	4.78	5.11
	median	1.32	0.71	3.48	4.45	3.12	4.05	3.28	4.24
	mean	1.28	0.86	3.52	4.33	3.13	4.14	3.36	4.22
	S.D.	0.25	0.45	0.44	0.71	0.31	1.81	0.47	0.54
	n	8	6	8	18	19	49	14	12
Mn (ppm)	minimum	159	135	333	430	348	503	290	382
	maximum	351	697	402	766	506	820	440	724
	median	271	298	367	603	393	685	379	641
	mean	272	372	369	596	406	672	375	611
	S.D.	55	259	23	81	45	72	39	97
	n	8	6	8	18	19	49	14	12

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (cont'd)

		The Narrows		Wrights Cove		Bedford Bay	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Organic carbon (wt. %)	minimum	7.28	2.80	6.03	3.61	3.04	2.12
	maximum	11.10	11.80	7.17	6.41	13.87	7.33
	median	8.21	5.52	6.55	6.40	5.08	4.43
	mean	8.86	5.81	6.57	5.71	5.84	4.43
	S.D.	1.99	2.42	0.47	1.40	3.75	1.66
	n	3	11	4	4	7	17
Cd (ppm)	minimum	2.75	0.22	1.04	0.84	0.90	0.25
	maximum	2.75	1.50	1.37	2.07	1.37	2.31
	median	2.75	0.76	1.21	1.57	1.09	0.85
	mean	2.75	0.80	1.21	1.51	1.12	0.88
	S.D.	-	0.40	0.23	0.60	0.24	0.56
	n	1	11	2	4	3	17
Cr (ppm)	minimum	39	-	40	-	30	6
	maximum	88	-	52	-	51	17
	median	46	-	47	-	36	12
	mean	58	-	46	-	38	12
	S.D.	27	-	5	-	7	8
	n	3	0	4	0	7	2
Cu (ppm)	minimum	156	66	100	67	59	17
	maximum	380	459	156	221	299	279
	median	321	126	127	139	86	55
	mean	285	167	127	142	113	73
	S.D.	116	131	24	65	85	62
	n	3	11	4	4	7	17

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (cont'd)

		The Narrows		Wrights Cove		Bedford Bay	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Hg (ppb)	minimum	1078	910	650	440	207	150
	maximum	1810	2630	1349	1650	2654	2190
	median	1282	1360	789	1480	565	570
	mean	1390	1417	894	1263	797	643
	S.D.	378	515	330	559	855	520
	n	3	11	4	4	7	15
Li (ppm)	minimum	24	16	33	49	34	43
	maximum	36	53	44	61	51	107
	median	28	35	37	57	41	71
	mean	29	34	38	56	42	73
	S.D.	6	11	5	6	7	18
	n	3	11	4	4	7	17
Pb (ppm)	minimum	161	135	45	105	55	18
	maximum	241	432	213	1142	138	169
	median	180	207	187	196	74	116
	mean	194	254	158	410	82	99
	S.D.	42	109	78	490	26	51
	n	3	11	4	4	7	17
Zn (ppm)	minimum	748	150	258	178	231	111
	maximum	4019	718	482	724	600	472
	median	816	301	361	289	285	226
	mean	1861	379	366	370	323	238
	S.D.	1869	202	92	244	129	100
	n	3	11	4	4	7	17

Table 5.4 Comparison of summarized geochemical data from sediment grab samples collected in 2008 – 2009 and 1986 – 1988 (cont'd)

		The Narrows		Wrights Cove		Bedford Bay	
		2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988	2008 – 2009	1986 – 1988
Ni (ppm)	minimum	28	9	23	17	18	11
	maximum	52	73	30	37	33	37
	median	36	31	27	23	28	27
	mean	39	31	27	25	28	25
	S.D.	12	17	3	9	5	8
	n	3	11	4	4	7	17
Fe (wt. %)	minimum	2.76	2.86	3.18	2.59	1.85	2.05
	maximum	3.55	4.63	3.74	5.17	4.03	5.03
	median	3.11	3.66	3.38	4.34	3.41	4.33
	mean	3.14	3.62	3.42	4.11	3.29	3.88
	S.D.	0.40	0.51	0.25	1.09	0.75	0.96
	n	3	11	4	4	7	17
Mn (ppm)	minimum	309	437	342	300	271	500
	maximum	357	1030	492	663	554	864
	median	354	605	419	590	450	656
	mean	340	621	418	536	451	650
	S.D.	27	147	69	161	93	76
	n	3	11	4	4	7	17

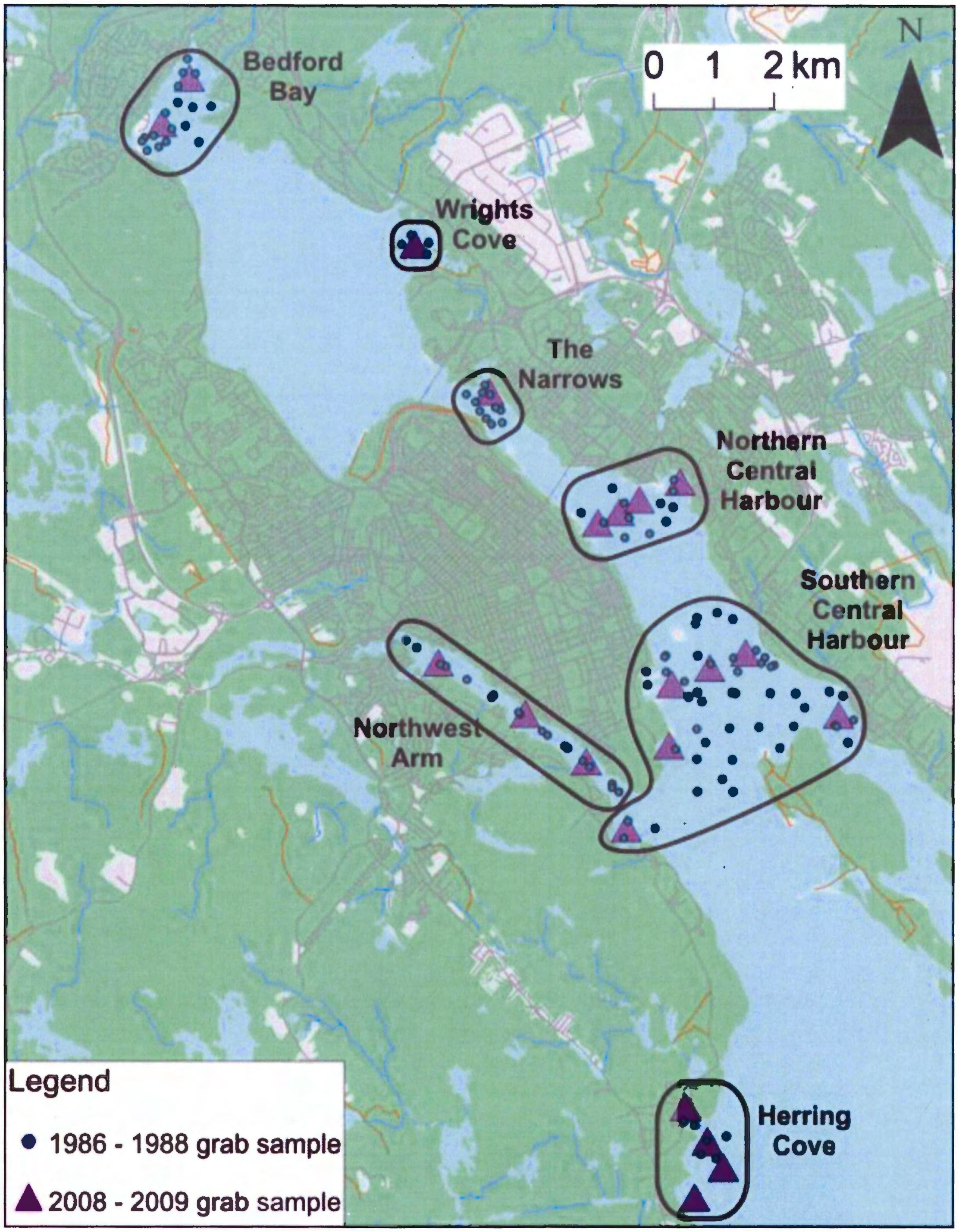


Figure 5.4 Map showing the locations of grab samples collected in 1986 – 1988 and 2008 – 2009. Also shown are the geographic locations used to describe the data and the grab samples which comprise them.

geographic location (Figure 5.4) to allow summary statistics to be calculated across the two sampling projects. Summary statistics for the 1986 – 1988 sampling project were calculated from raw data presented by Winters et al. (1991). In general, these results indicate that concentrations of lead, copper, and zinc in surface sediments have not changed substantially in the last 20 years.

Sediment grab samples collected by Tay et al. (1992) contained similar concentrations of lead and copper to the present study and Winters et al. (1991), but anomalously high concentrations of zinc (5580 – 13,584 ppm) and mercury (1600 – 22,900 ppb) in the two samples collected near Tufts Cove and anomalously high concentrations of zinc (600 ppm) in the sample collected in the southern portion of Central Harbour (near 2008 – 2009 sampling site *D3*). For comparison, concentrations of zinc and mercury in samples collected near Tufts Cove ranged from 1078 – 1810 ppb mercury and 748 – 4019 ppm zinc for the present study and 910 – 2630 ppb mercury and 150 – 718 ppm zinc in Winters et al. (1991). Median and mean concentrations of zinc and mercury in sediments collected near Tufts Cove were also higher in the present study than the 1986 – 1988 study. These results suggest that Tufts Cove is a particularly contaminated area of the harbour, which exhibits substantial variation in concentrations of zinc and mercury. Buckley and Hargrave (1989) attributed the high concentrations of lead, zinc, mercury, and copper to the influx of wastewater from the Tufts Cove outfall. Buckley and Winters (1992) also highlight the presence of the Tufts Cove Generating Station as a possible source of contaminants.

Differences in mean and median concentrations of chromium, lithium, iron, and manganese between 1986 – 1988 and 2008 – 2009 sediment grab samples can be attributed to differing dissolution procedures as discussed in Section 5.4. As previously mentioned, chromium concentrations in most areas of the harbour are at or just above background concentration suggesting that chromium contamination in the harbour is minimal. Lithium, iron, and manganese are commonly found in insoluble silicates, particularly lithium and iron. As such, highs observed in chromium, lithium, iron and manganese concentrations in sediments collected in 1986 – 1988 can likely be attributed to the release of elements during the dissolution of insoluble silicates using HF.

Mean and median mercury concentrations from samples collected in Outer Harbour, Northwest Arm, and Wrights Cove during the 1986 – 1988 sampling study are higher than those collected during the 2008 – 2009 sampling study. This difference in concentrations between these two sampling studies may reflect stricter controls on mercury emissions from hospitals and dentist offices and a decrease in the use of mercury in consumer products. However, it is surprising that similar differences were not observed in Bedford Bay, the Narrows, or Central Harbour. In fact, median and mean concentrations of mercury are higher in the northern portion of Central Harbour than they were 20 years ago. This difference may be the result of greater mixing in Bedford Bay, the Narrows, and Central Harbour.

In several areas of the harbour, multiple types of samples were collected in the same area (within 10 m) in an effort to compare different sampling methods. The results from these comparisons (sediment grab samples and the tops of cores (0 – 2 cm)) are summarized in Table 5.5. Unfortunately the different types of samples were collected at different times over a two year period making the distinction between differences resulting from temporal variation and method variation difficult to distinguish. However, in Herring Cove where a grab sample (*HC*) and slow core (9) were collected within 10 m of each other, variation in metals concentrations observed between the grab sample and the slow core was generally less than the variation observed between grab sampling events. This suggests that there is little to no difference between grab sampling and slow coring. Differences were observed in the OC concentrations in slow core 8 and vibracore 7 collected in the mouth of Northwest Arm, but again this may simply encompass the natural variation in harbour sediments. No differences in mercury concentrations were observed between slow core 8 and vibracore 7.

In Table 5.6 background concentrations, sediment quality guidelines, and median concentrations ranges in sediment grab samples from two different areas of the harbour

Table 5.5 Geochemical comparison of different sampling methods

Area	Sample Type	Cruise	Stn. No.	Sed. depth (cm)	OC (wt. %)	Cr (ppm)	Cu (ppm)	Hg (ppb)	Ni (ppm)	Pb (ppm)	Zn (ppm)	ΣPAH (ppm)	Cop.[b] (ppm)
Herring Cove	Slow core	2009-060	9	0 – 1	6.32	26	37	220	34	61	146	23.594	2.830
	Slow core	2009-060	9	1 – 2	6.56	22	115	300	40	89	141	-	-
	Grab sample[a]	-	HC	0 – 2	4.05	18	66	254	13	110	197	47.107	1.690
Bedford Bay	Vibracore	2008-053	2	0 – 2	6.88	-	30	222	31	51	103	2.606	0.363
	Slow core	2009-060	1	0 – 1	6.49	39	68	431	-	99	231	4.366	2.083
	Slow core	2009-060	1	1 – 2	4.64	29	58	503	-	92	193	-	-
Mouth of Northwest Arm	Slow core	2009-060	8	0 – 1	5.55	-	-	675	-	-	-	-	-
	Slow core	2009-060	8	1 – 2	5.66	-	-	875	-	-	-	-	-
	Vibracore	2008-053	7	0 – 2	4.30	-	-	794	-	-	-	-	-

[a] Median concentrations of OC and metals for all four sampling events are shown

[b] Coprostanol

Table 5.6 Comparison of background concentrations, sediment quality values, and median sediment grab sample concentrations

	Background concentration	ISQG	PEL	Median grab sample concentration	
				Outer Harbour	Northern Central Harbour
Cadmium (ppm)	0.1 – 0.8	0.7	4.2	0.04	0.5
Copper (ppm)	5 – 38	18.7	108	10	121
Chromium (ppm)	15 – 35	52.3	160	9	37
Mercury (ppb)	<25	130	700	24	1657
Nickel (ppm)	1 – 30	15.9[a]	42.8[b]	9	26
Lead (ppm)	10 – 30	30.2	112	15	159
Zinc (ppm)	40 – 80	124	271	43	208

[a] threshold effects level (NOAA 2008)

[b] (NOAA 2008)

are listed. It is important to note that although the relatively clean sediments from Outer Harbour do not exceed the SQVs, expected background concentration ranges of cadmium, copper, and nickel do exceed the ISQG. Background concentrations in Outer Harbour are lower than what would be expected in other parts of the harbour because of the abundance of shell hash and low concentrations of organic carbon in this area. Expected background concentrations of lead are also very near the ISQG for lead. These results highlight the importance of taking care when applying SQVs as a blanket approach to determining toxicity of sediments and anthropogenic contamination input.

In the summer of 2008, fecal coliform counts in the waters of Halifax Harbour were sufficiently low to allow beaches to reopen for the first time in decades. Although water quality had improved sufficiently to allow beaches to open, concentrations of metals in sediments remained above the PEL for some areas of the harbour. This difference between water and sediment quality highlights the need for the addition of sediment quality monitoring to the sampling program conducted by HRM to evaluate source reduction as a result of increased wastewater treatment.

5.5.2 Spatial Variations in Organic Contaminants

The highest concentrations of OC in sediment grab samples were observed near Tufts Cove (*TC*), Mill Cove (*MC*), the Dartmouth Yacht Club (*DYC*) and the Armdale Yacht Club (*AYC*). Buckley and Winters (1992) also observed high concentrations of OC in Bedford Bay, Northwest Arm, and near Tufts Cove, which they attributed to the presence of major wastewater outfalls. Similar to metal contaminants, there appears to be no change in the concentration of OC with time in surficial samples when the concentrations of OC from each of the nine sites that were sampled during all four sampling events are examined (Figure 5.3).

Summary statistics for concentrations of OC in sediment grab samples from the present-day sampling events and from previous sampling efforts conducted from 1986 to 1988 are shown in Table 5.4. As previously discussed, sampling sites were grouped according to general geographic location (Figure 5.4). Summary statistics for the 1986 – 1988 sampling effort were calculated from raw data presented by Winters et al. (1991). In general, these results indicate that concentrations of OC in surface sediments have not changed substantially in the last 20 years. Median and mean concentrations of OC in sediments collected near Tufts Cove were higher in the present study than the 1986 – 1988 study. As noted earlier, Tufts Cove displays substantial variation in levels of contamination which can be attributed to wastewater outfalls in the area (which receive input from the Burnside Business Park) and the presence of the Tufts Cove Generating Station.

Total PAHs previously analyzed in Halifax Harbour sediments were highest in the Northwest Arm and the Narrows (>48 ppm) (Hellou et al. 2002a), while concentrations of total PAHs in this study were highest in Herring Cove (*HC*: 47 ppm), near the Armdale Yacht Club in Northwest Arm (*AYC*: 35 ppm) and in Central Harbour (*EE3*: 21 ppm). The level of parental combustion products (as defined in Section 5.4.3) determined by Gearing et al. (1991) at a depth of 2.5 cm (20.4 ppm) is similar to the level of combustion products determined in the sediment grab sample collected near the Armdale Yacht Club (*AYC*: 21.3 ppm). Hellou et al. (2002a) also found similar levels of PAHs in the Northwest Arm. Tay et al. (1992) examined parental PAHs in the top 30 cm of surficial sediments. Their concentrations of total parental PAHs from two samples collected from Tufts Cove (3.32 – 25.4 ppm) are similar to the concentrations of total parental PAHs determined in the single sample collected near Tufts Cove (*TC*) from this study (7.93 ppm). Concentrations of parental PAHs from Tay et al.'s (1991) Eastern Passage sample (9.41 ppm) are substantially higher than the concentrations of parental PAHs determined in the present study's sample collected near the Shearwater Yacht Club (*SYC*: 2.88 ppm). However, Tay et al.'s (1991) Eastern Passage sample is closer to the outfall for the Eastern Passage WWTF and was taken over a much larger depth interval than the *SYC* sediment grab sample. Concentrations of parental PAHs in Halifax Harbour are high, but within the range of concentrations observed in several other localities including the western Mediterranean Sea and St. John (New Brunswick) (Hellou et al. 2002 and references therein). Concentrations of parental PAHs are slightly higher in the more contaminated areas of Boston Harbour (Dahlen et al. 2006), but within the range of Halifax Harbour parental PAH levels.

The parental PAHs which displayed the highest concentrations in sediment grab samples were the same as those observed in sediment cores (benzo[b&j&k]fluoranthene, fluoranthene, and pyrene). Hellou et al. (2002a) determined that fluoranthene, pyrene, and phenanthrene were the most abundant parental PAHs in all grab samples collected. This difference in parental PAHs between the two studies may reflect the greater sampling density in the Hellou et al. (2002a) study, which included multiple samples from Bedford Basin and the northern portion of Outer Harbour (areas which were not sampled for PAHs). Retene, a PAH indicative of the pyrolysis of conifers (e.g. Wakeham et al. 1980) was the most abundant parental PAH in a single sediment grab sample collected near Black Rock Beach (*BRB*). The highest concentrations of dibenzothiophene were observed near the Armdale Yacht Club (*AYC*). This site is near the site of a previous coal foundry (ca. 1860) (Watts and Raymond 2003), which may explain the high concentrations of dibenzothiophene found at that site.

Hellou et al. (2002a) observed lower concentrations of alkylated PAHs relative to parental PAHs (% alkylated: 14.9 – 28.9%, mean: 23.1%, S.D.: 3.6%). In the present study, similar results were observed. Parental PAHs in sediment grab samples were more abundant than alkylated PAHs (% alkylated: 19 – 45%, mean: 36%, S.D.: 8%) suggesting that pyrogenic sources are the principal sources of PAHs in Halifax Harbour sediments. The degree of alkylation in sediment cores was similar to what was observed in sediment grab samples. The lower concentrations of alkylated PAHs relative to parental PAHs observed by Hellou et al. (2002a) may have resulted from decreases in petrogenic contributions relative to pyrogenic contributions over the sediment interval they sampled.

The ISQG for eleven parental PAHs was exceeded in seven of eleven sediment grab samples. The PEL for at least six of the eleven parental PAHs was exceeded in four of those sediment grab samples (*EE3*, *HC*, *AYC*, and *DC*). All sites sampled for organic contaminants had concentrations of at least one PAH greater than the ISQG.

Table 5.7 Sediment grab sample diagnostic PAH ratios

Cruise	Station	Lab ID	AN/ AN+PA	FL/ FL+PY	BA/ BA+CH	IP/ IP+BP	PA+AN+PY+FL/ CH+BA+BF+BaP+IP+DBA+BP	PA/AN	FL/PY
Apr. 09	BRB	20090200	0.27	0.53	0.43	0.56	1.03	2.68	1.14
Apr. 09	EE3	20090202	0.30	0.52	0.42	0.54	0.83	2.39	1.07
Apr. 09	HP3	20090203	0.25	0.55	0.42	0.50	1.02	2.95	1.24
Apr. 09	HP2	20090207	0.66	0.52	0.42	0.56	0.24	0.53	1.06
Apr. 09	HC	20090209	0.49	0.60	0.34	0.55	0.56	1.03	1.52
Apr. 09	AYC	20090210	0.26	0.54	0.44	0.56	1.01	2.87	1.16
Apr. 09	EE1	20090211	0.23	0.52	0.42	0.55	0.93	3.27	1.08
Apr. 09	HP1	20090213	0.39	0.53	0.40	0.51	0.80	1.59	1.12
Apr. 09	TC	20090215	0.22	0.54	0.42	0.53	1.07	3.52	1.17
Apr. 09	DC	20090216	0.23	0.53	0.42	0.54	0.74	3.32	1.15
Apr. 09	SYC	20090217	0.28	0.52	0.37	0.54	0.86	2.55	1.07

Diagnostic ratios of parental PAHs in sediment grab samples (Table 5.7) suggest that the majority of parental PAHs are from pyrogenic sources with the exception of samples collected near Black Rock Beach (*BRB*), Tufts Cove (*TC*), Herring Cove (*HP3*) and the Armdale Yacht Club (*AYC*), which have ratios suggestive of both pyrogenic and petrogenic sources. Hellou et al. (2002a) reached similar conclusions, indentifying the major sources of PAHs in harbour sediments as combustion dominated. They reported FL/PY and PA/AN ratios of 1.08 – 1.30 (mean: 1.19, S.D.: 0.8) and 2.65 – 4.08 (mean: 3.23, S.D.: 0.40), respectively. The FL/PY and the PA/AN ratios obtained for the present study have a wider range of values (FL/PY: 1.02 – 1.52, mean: 1.15, S.D.: 0.13; PA/AN: 0.53 – 3.52, mean: 2.44, S.D.: 0.93). However, Hellou et al. (2002a) did not analyze samples from in or around Herring Cove. If the Herring Cove samples (*HC*, *HP1*, *HP2*, and *HP3*) are removed from the present analysis, the range of values for FL/PY (1.02 – 1.17) and PA/AN (2.39 – 3.52) ratios are more similar to those of Hellou et al. (2002a). The FL/PY and PA/AN ratios from all sediment grab samples in the present study are suggestive of wood burning emissions, car soot, and Nova Scotia soils.

Hellou et al. (2002a) noted lower concentrations of HMW alkylated PAHs (PAHa) relative to parental PAHs (PAHp) (PAHa:PAHp 0.14 – 0.21, mean: 0.16, S.D.: 0.03) and higher ratios of LMW alkylated PAHs to parental PAHs (PAHa:PAHp 0.42 – 1.09, mean: 0.82, S.D.: 0.17). Similarly, in the present study lower ratios of alkylated to parental PAHs were observed when examining HMW PAHs (PAHa:PAHp 0.16 – 0.44, mean: 0.22, S.D.: 0.08) than LMW PAHs (PAHa:PAHp 0.77 – 4.31, mean: 2.23, S.D.: 1.00) (Tables D.1 and D.2). However, the ratios of alkylated to parental LMW PAHs are higher in the present study than those observed by Hellou et al. (2002a).

Highs observed in total PAHs in the Herring Cove sediment grab sample (*HC*) are higher than concentrations of total PAHs in the Herring Cove core. All Herring Cove samples are suggestive of a greater input of parental PAHs relative to alkylated PAHs (19 – 35% alkylation), suggesting combustion dominated sources. Similar highs were not seen in metal (Table B.1) or coprostanol concentrations (Table D.3) in samples from Herring Cove, suggesting that PAHs are the major contaminants in Herring Cove.

Coprostanol concentrations in sediment grab samples collected in Central Harbour, Northwest Arm, and Herring Cove ranged from 0.29 – 18.0 ppm. Low concentrations of coprostanol were observed near Herring Cove (0.29 – 0.45 ppm), likely due to the high proportion of shell hash, low concentration of organic carbon, and the non-depositional nature of this area. The single sample collected in Herring Cove (*HC*) contained the lowest concentration of coprostanol suggesting that this area is fairly uncontaminated by wastewater effluents. The highest concentrations were observed in Central Harbour (2.49 – 18.0 ppm), highlighting the effect sewage effluents have had on this area of the harbour. Previously collected data examining coprostanol in Central Harbour sediments showed concentrations ranging from 2.9 – 20.7 ppm (Hellou et al. 2008), suggesting that the 2009 samples do not show evidence of the initiation of wastewater treatment in that area. However, as previously mentioned, samples collected during the April 2009 sampling expedition may not be representative of the top 0 – 2 cm of surficial sediments. The sample collected near the Eastern Passage WWTF (*SYC*) had fairly low concentrations of coprostanol (2.76 ppm) relative to samples collected near previously untreated outfalls in the northern portion of Central Harbour (5.20 – 18.0 ppm). However while no additional sediment data were available for coprostanol concentrations in grab samples collected from Bedford Basin or Bedford Bay, concentrations of coprostanol in the top 1 cm of slow cores collected in that area range from 0.632 – 27.213 ppm. The highest concentration of coprostanol was observed nearest the outfall (<75 m), but fell rapidly (2.083 ppm) within 150 m of the outfall.

Diagnostic steroid ratios in Halifax Harbour sediment grab samples are summarized in Table 5.8. These ratios suggest that the majority of Halifax Harbour has been subjected to contamination by wastewater effluents. Samples collected near Herring Cove (*HP1* and *HP3*) are the only samples which can be described as uncontaminated by sewage effluents based on diagnostic ratios. However, these samples are composed mainly of shell hash and minimal organic carbon. Samples collected near Black Rock Beach (*BRB*) and Herring Cove (*HP2*) had only one ratio indicative of fecal origins.

Samples collected in Herring Cove provided a unique opportunity to compare the effect different methods of sampling have on concentrations of organic contaminants. Concentrations of organic contaminants were higher in the grab sample (*HC*) than in slow core 9 with the exception of coprostanol. However, it is difficult to determine if this difference is related to differences in sampling techniques or if it simply capturing the natural variation in sediment chemistry as additional samples were not available for comparison.

Table 5.8 Sediment grab sample diagnostic steroid ratios

Cruise	Station	Lab ID	coprostanol/ coprostanol + cholestanol	coprostanol/ cholesterol
Apr. 09	**BRB**	**20090200**	**0.75**	**0.31**
Apr. 09	**EE3**	**20090202**	**0.83**	**1.81**
Apr. 09	**HP3**	**20090203**	**0.70**	**0.04**
Apr. 09	**HP2**	**20090207**	**0.69**	**0.22**
Apr. 09	**HC**	**20090209**	**0.61**	**0.68**
Apr. 09	**AYC**	**20090210**	**0.72**	**0.43**
Apr. 09	**EE1**	**20090211**	**0.88**	**1.81**
Apr. 09	**HP1**	**20090213**	**0.58**	**0.08**
Apr. 09	**TC**	**20090215**	**0.79**	**2.09**
Apr. 09	**DC**	**20090216**	**0.86**	**0.87**
Apr. 09	**SYC**	**20090217**	**0.73**	**0.73**

5.6 SUMMARY

1. Background concentrations of metals calculated in this study (chromium, mercury, and zinc) are lower than background concentrations determined in previous studies likely due to differences in instrumentation, dissolution procedures, and previously collected inadequate lengths of cores. The current study highlights the importance of not indiscriminately applying SQVs as background concentrations of cadmium, copper, and nickel exceed the ISQG in Halifax Harbour in some parts of the harbour.

2. Pore water analyses confirm the reducing nature of harbour sediments in most areas of the harbour. Decreasing contributions of organic matter as a result of wastewater treatment may eventually lead to more oxic conditions in some areas of the harbour (particularly the mouth of Northwest Arm) which in turn may change the mobility and bioavailability of particulate-bound metals and the rate at which organic contaminants degrade.

3. In general, concentrations of metals in surficial sediments have not changed substantially since previous studies were conducted in the late 1980s. Mercury concentrations in surficial sediments are slightly lower which may be attributed to increased controls on mercury emissions (hospitals and dentist offices) and a decrease in the use of mercury in consumer products. Differences observed in concentrations of chromium, lithium, iron, and manganese are likely due to the less aggressive dissolution procedures used in the present study as compared to the 1986 – 1988 study. Central Harbour, particularly near Tufts Cove and Dartmouth Cove, remains the most contaminated area of the harbour. In examining concentrations of metals in surficial sediments collected while the WWTFs were brought online no change was evident, suggesting that insufficient

time has passed to see substantial changes in sediment chemistry as a result of increased wastewater treatment.

4. While absolute concentrations of PAHs in surficial sediments have not changed since the late 1990s, the relative proportion of alkylated to parental PAHs has changed which may reflect increased input from petrogenic sources. Herring Cove, an area of the harbour not previous analyzed, contains sediments with some of the highest concentrations of PAHs in the harbour.

5. Similar to the results observed in previous studies, most metals in sediments in Central Harbour reach maximum concentrations at depths corresponding to between 1940 and 1980. In general, concentrations of metal contaminants in near surface sediments in all areas of the harbour are decreasing. Concentrations of total PAHs in Central Harbour peak around 1965. A previous study in Northwest Arm had determined peaks in parental PAHs in sediments dated between 1940 and 1960, which was attributed to a subsequent decrease in wood and coal burning and the presence of the coal foundry in that area. Subsurface peaks in total PAHs were also observed in undated cores from Herring Cove and the mouth of Northwest Arm.

6. While fecal coliform levels in harbour waters decreased as a result of increased wastewater treatment sufficiently to allow beaches to open in the summer of 2008, a similar improvement in sediment quality was not observed, highlighting the need for the inclusion of sediment monitoring in harbour quality screening programs. Fecal contamination is evident in all areas of the harbour studied with the exception of Outer Harbour.

CHAPTER 6: EFFECTS OF WASTEWATER TREATMENT PRACTICES ON MARINE SEDIMENT CHEMISTRY NEAR MILL COVE, BEDFORD

Cores collected near Mill Cove, Bedford provide a unique opportunity to examine how wastewater treatment affects sediment chemistry and are used as a model system for predicting how increased wastewater treatment may affect sediment chemistry in other areas of Halifax Harbour. One would expect increased wastewater treatment to reduce the amount of wastewater sourced contaminants. Chapter 6 provides a detailed discussion of the inorganic and organic chemical characteristics of sediments near Mill Cove. It begins with establishing present-day and average sediment accumulation rates in Section 6.1. The effects of wastewater treatment on sediment chemistry will then be examined in Sections 6.2 and 6.3. In Section 6.4 these results are used to anticipate the effects of upgrading to secondary levels of wastewater treatment at all HRM WWTFs over the next 10 – 30 years as required by the new Wastewater Systems Effluent Regulations proposed by the CCME in March 2010.

6.1 AVERAGE AND PRESENT-DAY SEDIMENT ACCUMULATION RATES

To interpret changes in sediment chemistry and to link them to changes in wastewater treatment and source control measures, two slow cores collected near Mill Cove were dated using two different methods (radiometric dating and pore water analyses). Figure 3.5 shows the locations of cores collected near Mill Cove and Figure 6.1 shows the locations of cores collected near Mill Cove relative to the Mill Cove WWTF outfall. ^{210}Pb and ^{137}Cs profiles for slow cores 1 and 2 are shown in Figure G.1 and pore water profiles showing present-day sediment accumulation rates can be found in Figure 6.2. Dating results from ^{210}Pb and ^{137}Cs analyses of slow core 1 indicate mixing in the upper 5 cm and a sedimentation rate of 0.26 cm/year. The present-day sediment accumulation rate determined using pore water analyses was 0.05 cm/year. Similar results were obtained for slow core 2. Radiometric dating methods provide an estimate of 0.32 cm/year for the average sediment accumulation rate, while pore water analyses provide an estimate of 0.05 cm/year for the present-day sediment accumulation rate. The slightly higher average sedimentation rate calculated for slow core 2 likely reflects its proximity to the wastewater treatment outfall. There was no evidence of mixing in slow core 2. Previously determined average sedimentation rates from ^{210}Pb and ^{137}Cs dating of cores in Bedford Bay yielded a sedimentation rate of 0.19 cm/year (Buckley et al. 1995), while the previously determined present-day sedimentation rate using pore water methodologies was 0.10 cm/yr (Cranston 1994). The decrease in present-day sedimentation rate may reflect the expansion of the Mill Cove WWTF in 1997 and the addition of a surge/flow equalization tank which prevents direct by-passing to Bedford Basin without treatment. As discussed in Section 5.3, Cranston (1999) compared present-day sediment accumulation rates using pore water methodologies and average sedimentation rates determined using conventional dating methods and found agreement between the two methods within an order of magnitude. As Cranston (1999) states there is no perfect method for determining sediment accumulation rates. The best estimates of sediment

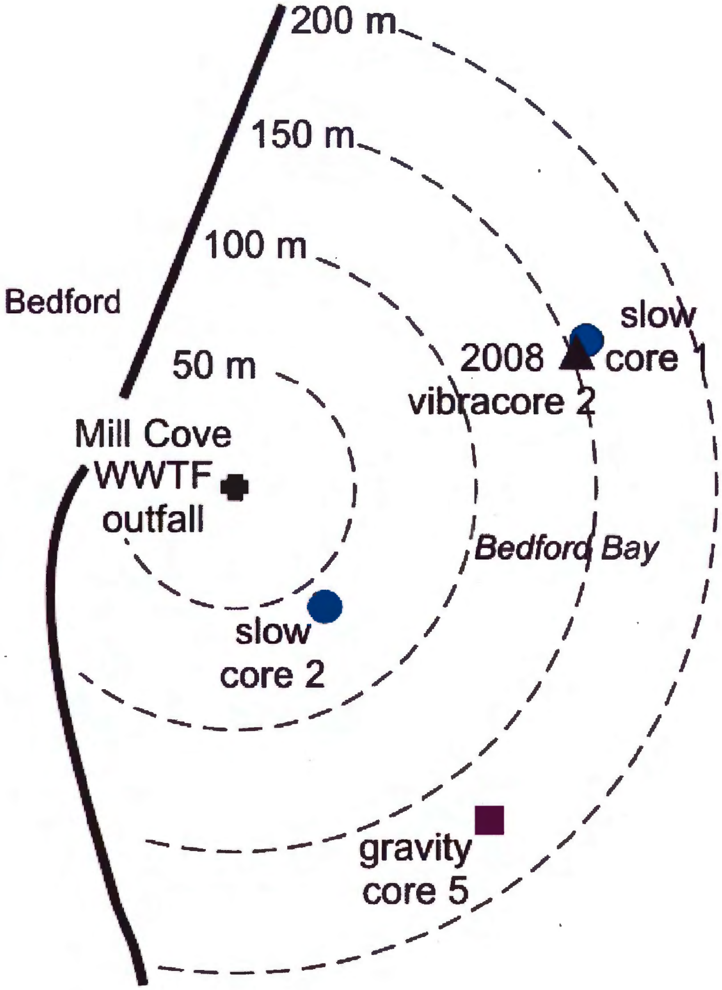


Figure 6.1 Map showing the locations of cores collected near Mill Cove relative to the Mill Cove WWTF outfall.

accumulation rates involve using multiple methods. Gravity core 5 was not dated, but pore water analyses from this core revealed a present-day sediment accumulation rate of 0.03 cm/year, which is slightly lower than the estimates of present-day sediment accumulation rates in the other cores collected near Mill Cove (slow cores 1 and 2). This suggests that the sediment regime in the area where gravity core 5 was collected may be different than areas where slow cores 1 and 2 were collected.

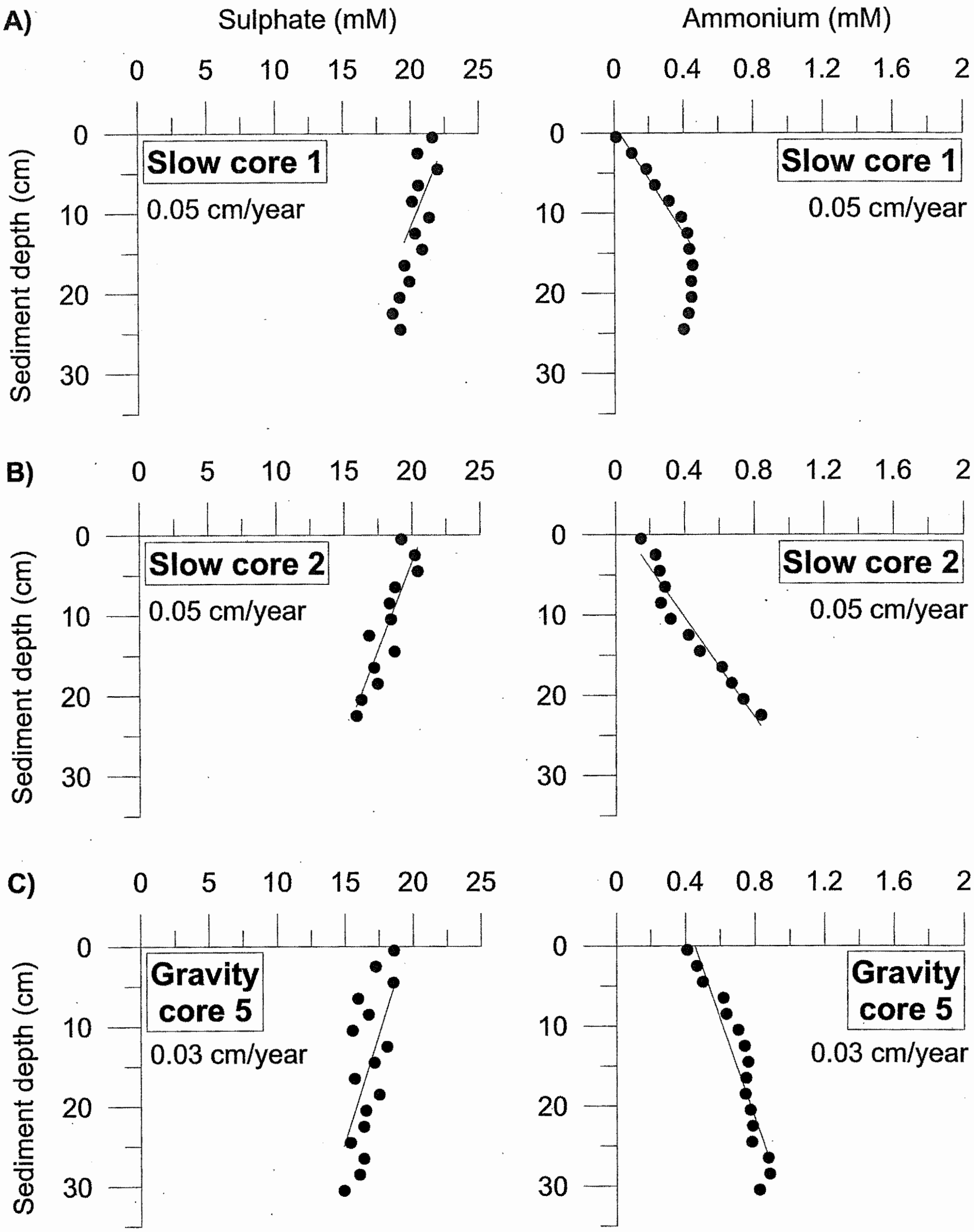


Figure 6.2 Pore water profiles of cores collected near Mill Cove. Lines shown are representative of sulphate and ammonium gradients used to calculate present-day sedimentation rates. Correlation coefficients for sulphate/depth and ammonium/depth were significant at a probability of $p < 0.05$.

6.2 VARIATIONS IN INORGANIC CONTAMINANTS NEAR MILL COVE

The concentrations of inorganic contaminants near Mill Cove were examined to determine the extent of contamination before and after the onset of wastewater treatment in 1970, and to assess the effects of wastewater treatment on metal concentrations over time. Slow core 1 and 2008 vibracore 2 were collected within 10 m of each other and were expected to have similar core profiles based on their proximity. However, when 2008 vibracore 2 was first examined concentrations in the top of the core were surprisingly low given the core's proximity to the Mill Cove WWTF outfall and the presence of higher concentrations of contaminants in slow core 1. Figure 6.3 shows geochemical profiles of 2008 vibracore 2 shifted down 22 cm and slow core 1. When 2008 vibracore 2 is shifted down 22 cm, there is a much better fit between the sediment chemistry of the two cores. Live foraminifera were not found in 2008 vibracore 2, unlike 2008 vibracores 5 and 8 (S. Mohamed, Dalhousie University, personal communication 2010). In general, foraminifera live in the top 1 cm of sediments (Phleger 1960), although some studies have found live foraminifera as deep as 16 cm (Boltovskoy 1966). The absence of live foraminifera in 2008 vibracore 2 also suggests loss of sediment at the top of this core, perhaps as a result of sediment disturbance during vibracoring operations.

The geochemical sediment core profiles of gravity core 5 are substantially different from slow cores 1 and 2 (Figures E.13 – E.16 and E.21 – E.22). Concentrations of mercury and lead are higher in the near surface in gravity core 5 and OC concentrations are fairly consistent down core, unlike slow cores 1 and 2. The large increases and drops observed in most metals in slow cores 1 and 2 are absent in gravity core 5. Concentrations of most metals in gravity core 5 show an increasing trend all the way up the core. Additionally, concentrations of copper, mercury, lead, and zinc all reach background levels between 13.5 and 21.5 cm, while only background concentrations of copper are reached in slow core 1 (20.5 cm depth) and slow core 2 (21.5 cm depth). Attempts were made to collect a

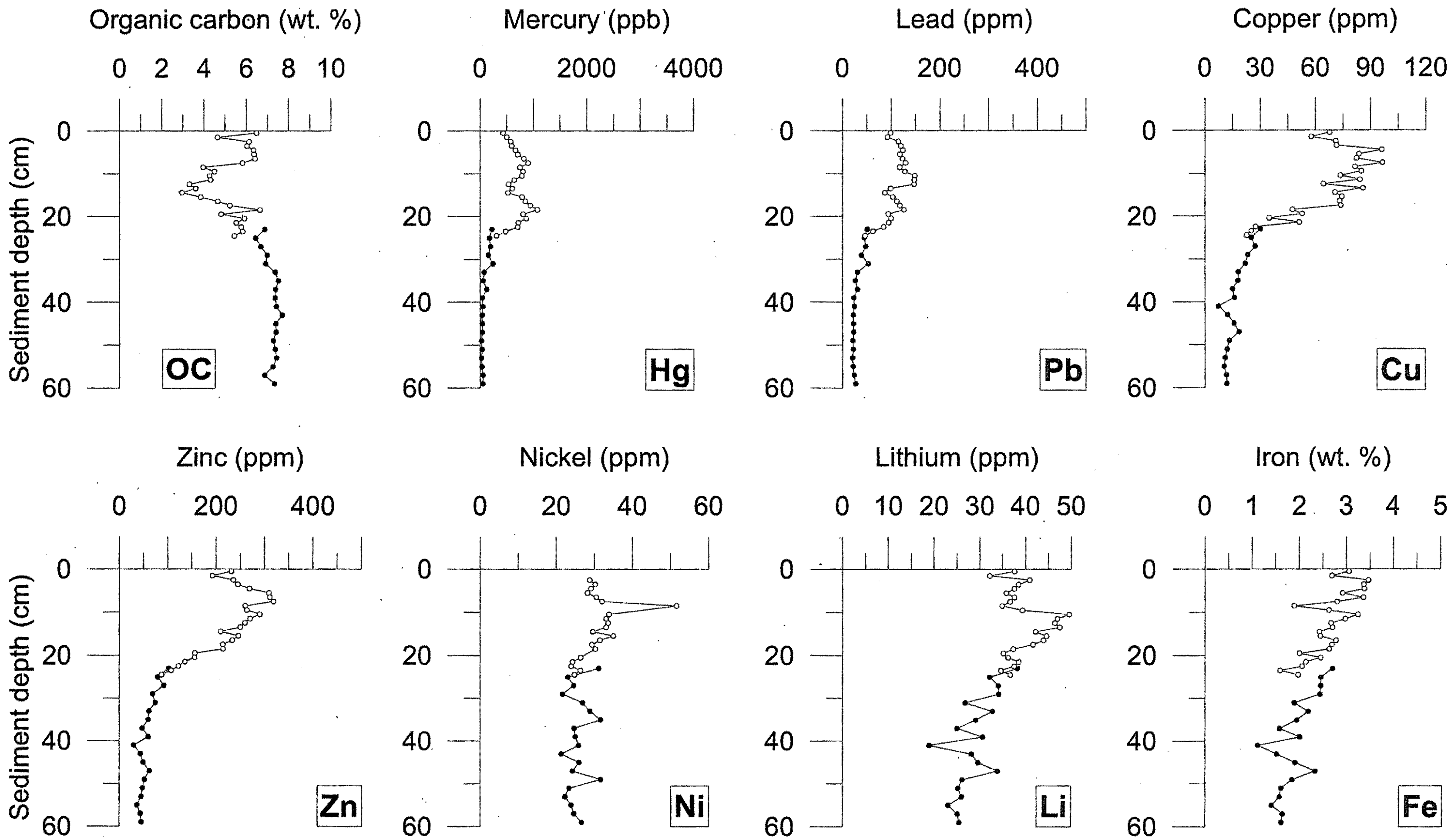


Figure 6.3 Geochemical sediment core profiles of 2008 vibracore 2 (black circles) and slow core 1 (white circles). Note the close match between the two profiles at depth, suggesting that approximately 22 cm of sediment is missing from the top of 2008 vibracore 2.

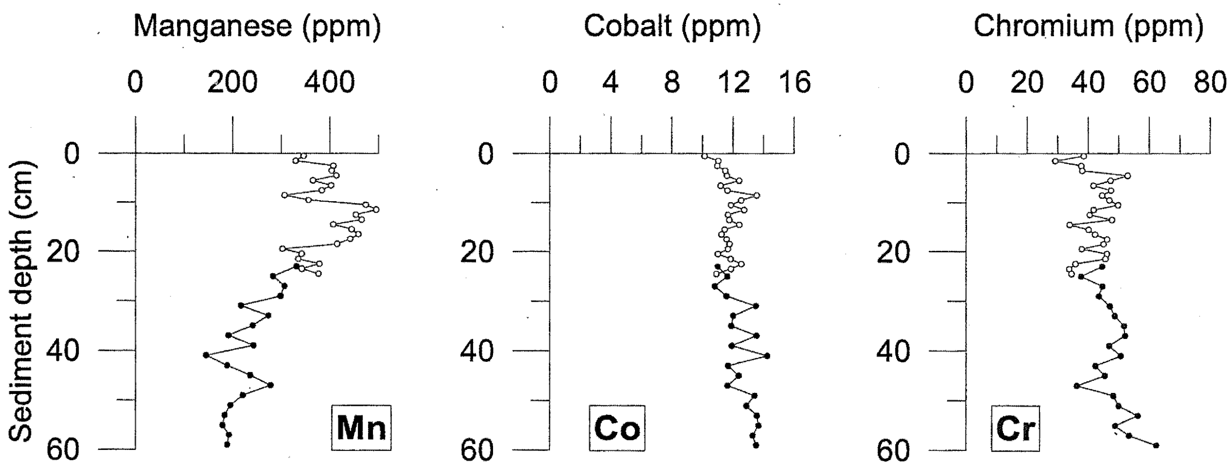


Figure 6.3 (cont'd) Geochemical sediment core profile of 2008 vibracore 2 (black circles) and slow core 1 (white circles).

slow core at the site where gravity core 5 was collected. However, the seafloor was too hard to allow the slow corer to penetrate the sediment. These observations suggest that the depositional regime is different at the site where gravity core 5 was collected relative to the slow core sites, perhaps as a result of recent changes in bottom currents due to infilling activities. Additionally, estimates of present-day sediment accumulation rates in gravity core 5 (0.03 cm/year) were lower than in slow cores 1 and 2 (0.05 cm/year) (Figure 6.2), further supporting a non-depositional environment at the gravity core 5 site. It is unlikely that significant amounts of sediment were lost during collection of gravity core 5 based on observation of a very thin oxidized layer near the top of this core during sampling. However, it is also possible that sediment at the gravity core 5 site was removed in the recent past as a result of dredging or scouring related to ongoing coastal development in the area.

Figures 6.4 – 6.7 show the dated geochemical sediment core profiles of slow cores 1 and 2. In general, the shapes of geochemical profiles of slow cores 1 and 2 are similar. However, peaks in the concentrations of metals are higher in slow core 2 than slow core 1, reflecting slow core 2's proximity to the Mill Cove WWTF outfall. Changes in the concentrations of some elements (e.g. lithium, zinc, OC, mercury, and manganese) occur earlier in the sediment record in slow core 1 than slow core 2, which may reflect mixing in slow core 1 or variable sedimentation rates in slow core 2.

Changes in the concentrations of lithium, manganese, and cobalt in slow core 2 may be related to dilution from the release of effluents as high concentrations of these elements are not expected to be found in wastewater. Concentrations of lead in 2008 vibracore 8 have dropped substantially in the last 40 years (Figure 5.1), likely as a result of source control. Decreases observed in lead in sediments near Mill Cove are also likely the result of increased source control as well as wastewater treatment. As demonstrated by Dalziel et al. (1991) nickel, cadmium, zinc, and copper were mostly found in the dissolved phase in harbour waters, while lead, iron, and manganese are generally found in the particulate phase. Because lead has a stronger affinity for particulate matter than either copper or zinc (Stumm and Morgan 1996), it is more likely to be removed through primary

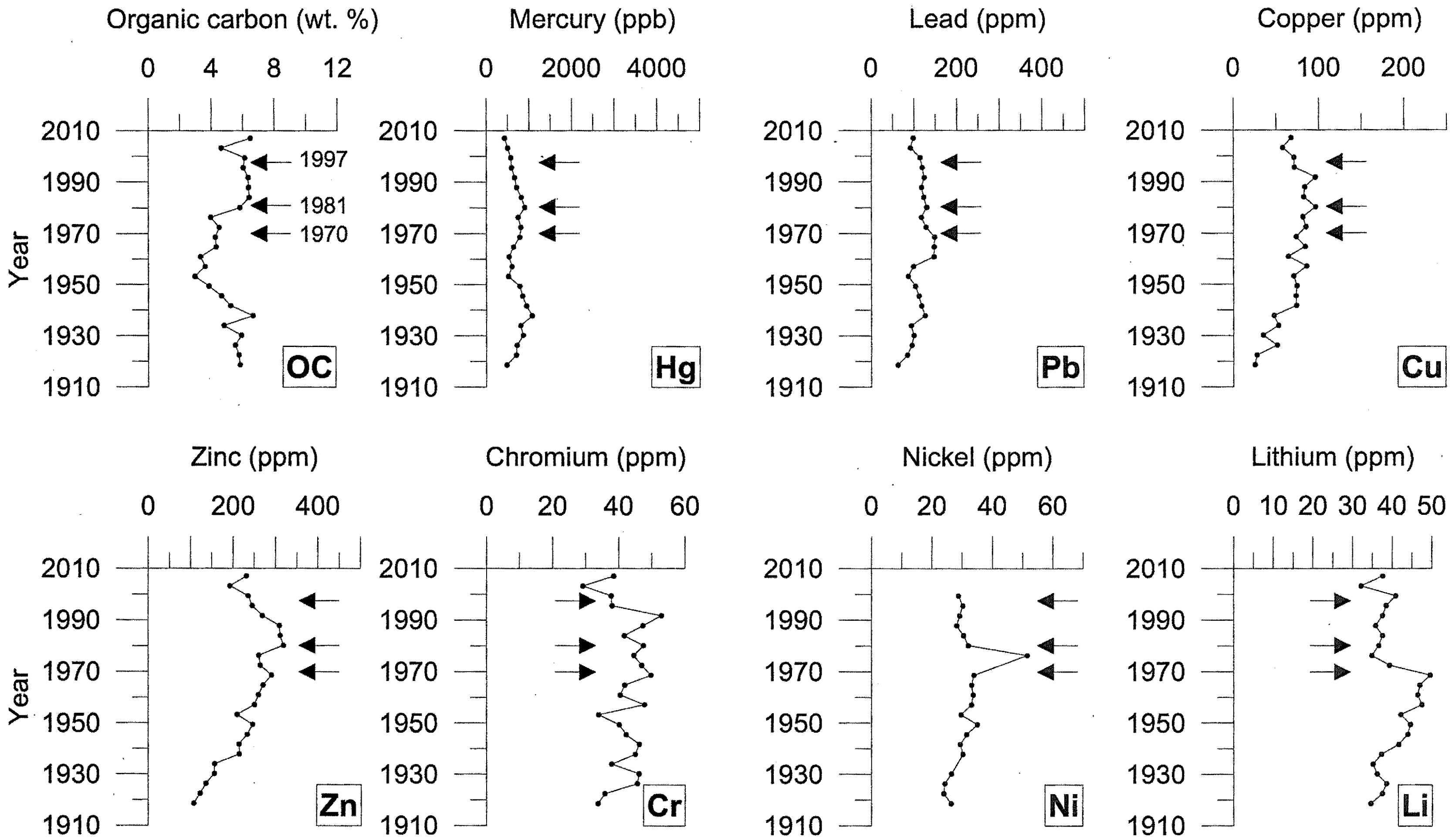


Figure 6.4 Temporal changes in the geochemistry of sediments in slow core 1 (near Mill Cove, Figure 3.5). Arrows denote significant changes in wastewater treatment. The Mill Cove WWTF opened in 1970 and was subsequently upgraded in 1981 and 1997.

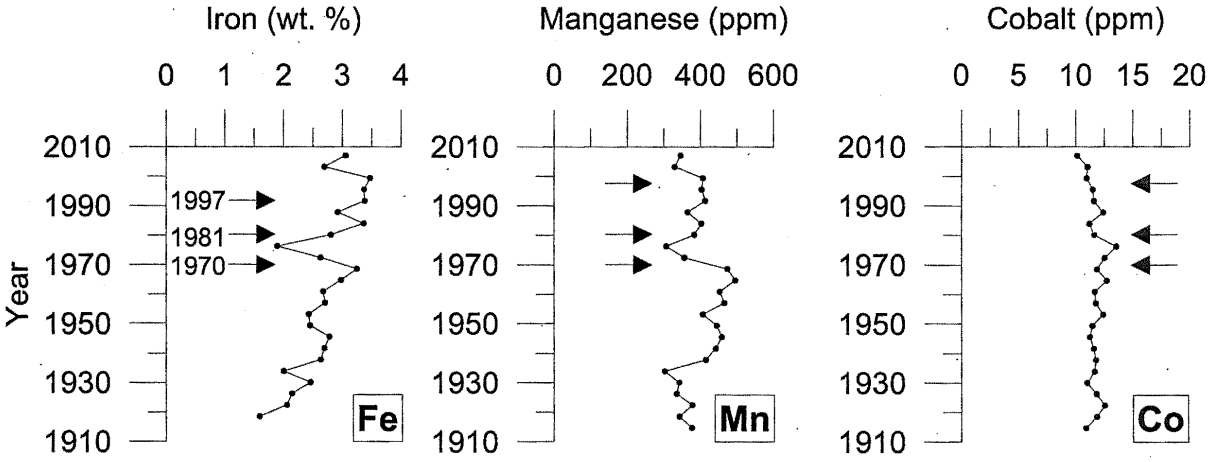


Figure 6.5 Temporal changes in the geochemistry of sediments in slow core 1 (near Mill Cove, Figure 3.5). Arrows denote significant changes in wastewater treatment. The Mill Cove WWTF opened in 1970 and was subsequently upgraded in 1981 and 1997.

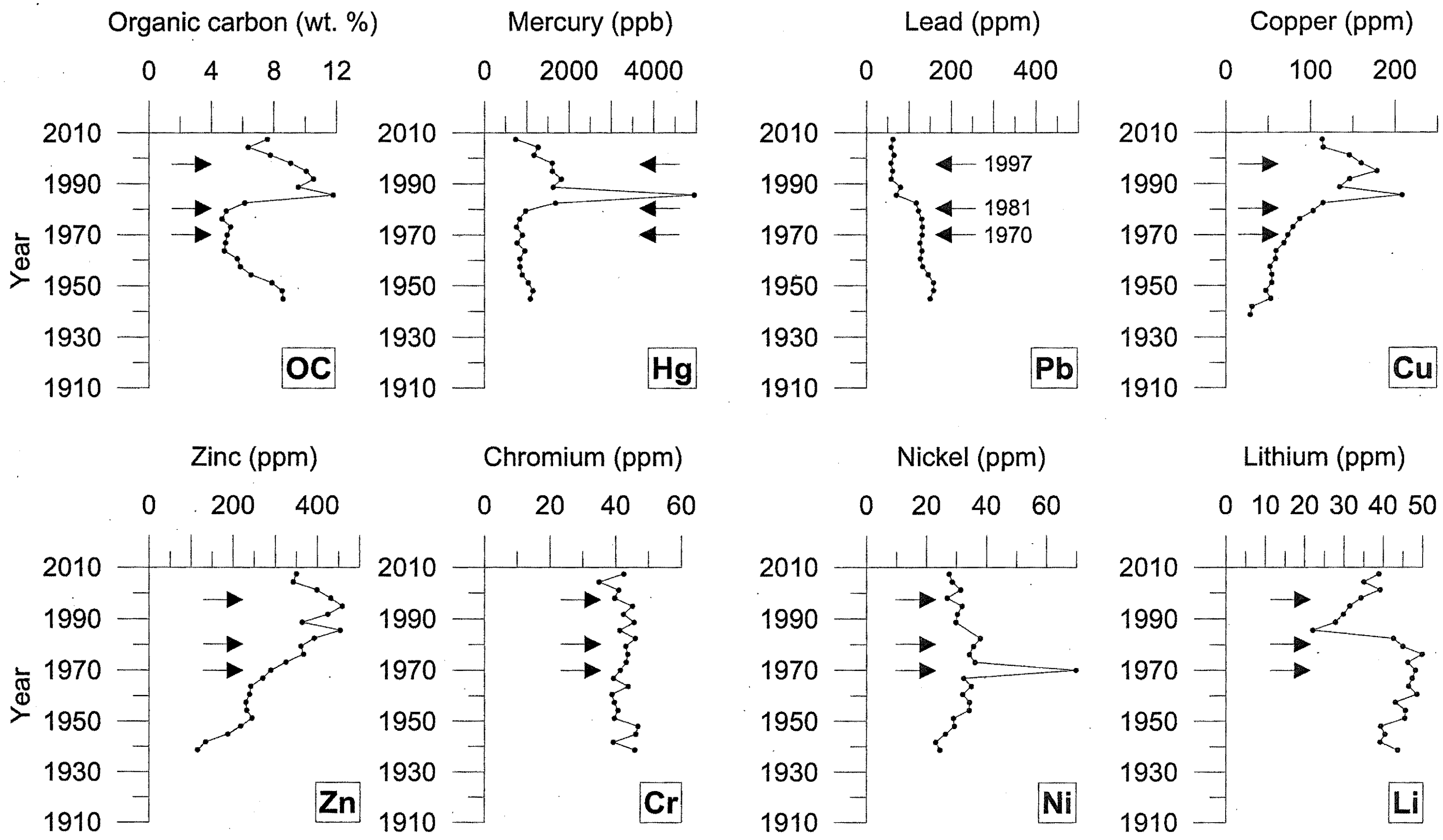


Figure 6.6 Temporal changes in the geochemistry of sediments in slow core 2 (near Mill Cove, Figure 3.5). Arrows denote significant changes in wastewater treatment. The Mill Cove WWTF opened in 1970 and was subsequently upgraded in 1981 and 1997.

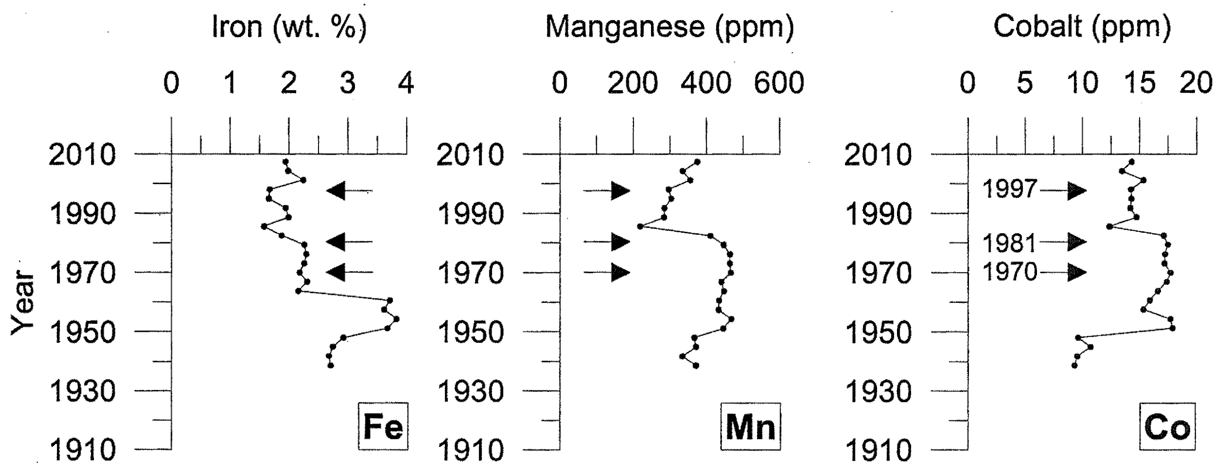


Figure 6.7 Temporal changes in the geochemistry of sediments in slow core 2 (near Mill Cove, Figure 3.5). Arrows denote significant changes in wastewater treatment. The Mill Cove WWTF opened in 1970 and was subsequently upgraded in 1981 and 1997.

sedimentation. Removal efficiencies for both lead and mercury are ≥65% at Mill Cove WWTF (Table 2.2). Decreases observed in mercury concentrations in slow cores 1 and 2 are also likely related to both source control and wastewater treatment. The mercury peak observed in slow core 2 at depths corresponding to 1985 is likely due to increased concentrations of OC at that depth, as mercury has a high affinity for OC. A smaller increase in OC is also observable in slow core 1 at depths corresponding to 1980 with a small peak in mercury also detectable. Highs in OC are likely attributable to changes in wastewater treatment processes, as previous studies have shown that the major source of OC in the harbour is wastewater (Buckley and Winters 1992). In general, the higher concentrations of metals in slow core 2 relative to slow core 1 point to a wastewater source for the majority of these metals. Wastewater is likely not the predominant source of lead, nickel, and chromium in sediments near Mill Cove, as those metals are either higher in slow core 1 or have similar concentrations in both cores. Changes in copper and zinc concentrations, particularly zinc concentrations are more likely related to source control as they are not removed as efficiently through wastewater treatment as mercury and lead (Table 2.2).

Concentrations of most metals in sediments near Mill Cove are decreasing. Substantial drops in mercury, lead, copper, and zinc are observable in slow cores 1 and 2 from approximately 1990 through to the present. Concentrations of metals in gravity core 5 appear to be decreasing in the very near surface, but still exceed the PEL for mercury and lead and the ISQG for copper and zinc. Mercury, copper, and zinc concentrations in the near surface of slow core 1 exceed the ISQG, while concentrations of mercury, lead, copper, and zinc exceed the PEL in the near surface of slow core 2 reflecting its proximity to the Mill Cove WWTF outfall.

By applying the sedimentation rate estimated for slow core 1 (0.26 cm/year) to 2008 vibracore 2, the timing of increases in contaminant concentrations above background levels in Bedford Bay may be determined. Using this estimate of sedimentation rate, concentrations of mercury began to rise above background levels in sediments corresponding to the mid 1800s, while concentrations of lead, zinc, and copper began to rise above background levels in sediments corresponding to the late 1800s. It is somewhat surprising that the observed increase in mercury does not correspond with the opening of the tannery and paper mill and that the increase in lead, zinc, and copper is not correlated with the increase in shipping in the mid 1800s (see Section 2.2.1). However, as previously discussed sedimentation rates in Bedford Bay have likely changed in the last 200 years due to wastewater treatment, increased population, infilling, and dredging, meaning that the sedimentation rate in 2008 vibracore 2 is likely lower than what was calculated in slow core 1, making applying the slow core 1 sedimentation rate to 2008 vibracore 2 ill advised.

6.3 VARIATIONS IN ORGANIC CONTAMINANTS NEAR MILL COVE

Hellou et al. (2002a) observed a correlation between total PAHs and OC in surficial sediments in Halifax Harbour with the exception of a single site in Bedford Bay, near the Mill Cove WWTF, which had relatively high concentrations of OC (4.8%) and relatively low concentrations of total PAHs (8.16 ppm). A grab sample collected near the Eastern Passage WWTF by Hellou et al. (2002a) contained relatively low concentrations of OC and total PAHs. Correlations between OC and total PAHs in this study were not significant. However, slow cores collected near the Mill Cove WWTF had fairly high concentrations of OC (5.23 – 7.59%) in the top 1 cm of sediment and similarly low concentrations of total PAHs (4.37 – 12.8 ppm). As shown in Table 2.1, removal efficiencies of PAHs for secondary treatment levels are greater than 85%, which may account for the observed lack of correlation between OC and total PAHs in Bedford Bay sediments collected by Hellou et al. (2002a). It is also possible that sources of PAHs in Bedford Bay do not include wastewater and since the source of OC in Mill Cove is overwhelmingly wastewater.

Figure 6.8 shows the dated organic geochemical sediment core profiles of slow cores 1 and 2. Subsurface maximums in combustion PAHs (as defined in Section 5.4.2) and total PAHs were observed in slow cores 1 and 2 at depths corresponding to 1930 and 1945, respectively. However, it is difficult to determine where the peak in PAH levels is actually located in the sediment given the low sampling density in slow cores 1 and 2. It may be better to describe peak PAH levels as occurring between 1920 – 1965 in slow core 1 and between 1940 – 1975 in slow core 2. As discussed in Section 5.4.2, recent decreases in the levels of combustion PAHs can likely be ascribed to a decline in wood and coal burning. Maximum concentrations of combustion parental PAHs were observed in the near surface of gravity core 5, likely reflecting either a non-depositional environment for gravity core 5 or missing sediment as discussed in Section 6.2. It is

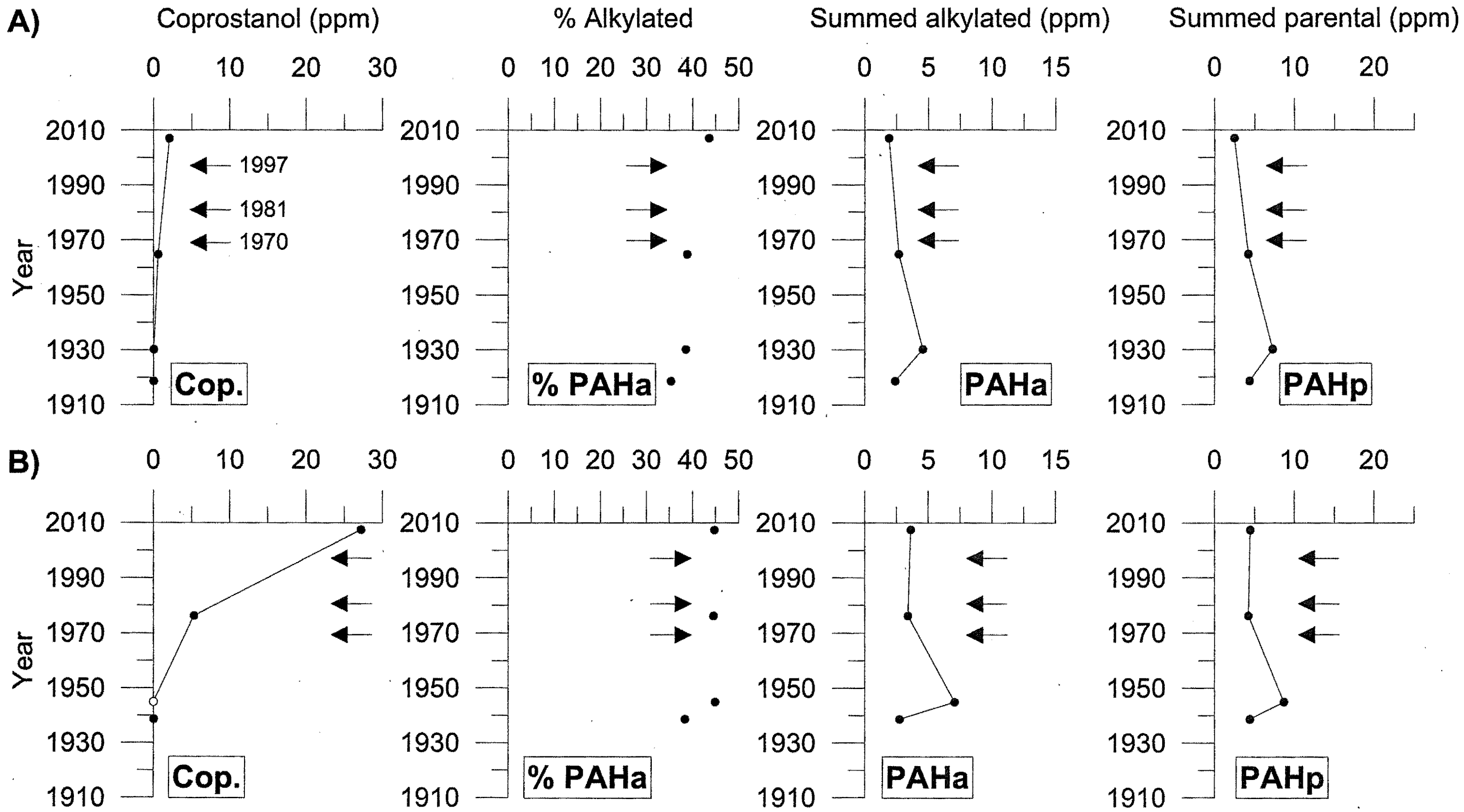


Figure 6.8 Temporal changes in the organic geochemistry of sediments in slow cores 1 and 2 (near Mill Cove, Figure 3.5). A) slow core 1. B) slow core 2. Open symbols denote samples with concentrations below the detection limit of the analyte. Arrows denote significant changes in wastewater treatment. The Mill Cove WWTF opened in 1970 and was subsequently upgraded in 1981 and 1997.

difficult to evaluate the effect wastewater treatment has had on PAH levels in Bedford Bay sediments as the sampling resolution of slow cores 1 and 2 does not allow a definitive evaluation to be made. Following the initiation of wastewater treatment a slight decrease in PAH levels is observable. However, similar decreases were observed in 2008 vibracore 8 from Central Harbour, suggesting that decreases may be unrelated to the initiation of wastewater treatment. The highest concentrations of dibenzothiophene in slow cores 1 and 2 were found at the same depths as the highest concentrations of combustion parental PAHs, strengthening the supposition that decreases in combustion PAHs are a result of a decline in the use of wood and coal burning. Similarly, maximum concentrations of dibenzothiophene were observed in the near surface of gravity core 5, as were maximum concentrations of combustion PAHs.

The ISQG for most PAHs is exceeded down the entire length of slow cores 1 and 2. Concentrations of PAHs are greater than the ISQG for most PAHs in the top 5 cm of 2008 vibracore 2 and the entire length of gravity core 5 with the exception of the sample collected at 20.5 cm depth. Although concentrations of PAHs near Mill Cove are not as high as concentrations observed in Central Harbour or Herring Cove, they are still high enough to warrant concern and would be considered contaminated down to depths of at least 30 cm.

Coprostanol concentrations in the near surface of slow core 2 are the highest of any core collected in the harbour, which can likely be attributed to the proximity of slow core 2 to the Mill Cove WWTF outfall. Concentrations in slow core 1 and gravity core 5 are substantially lower. Only one of the two steroid ratios indicated fecal contamination in the top 0 – 10 cm of cores collected near Mill Cove (slow core 1, slow core 2, and gravity core 5) (Table 5.3), below which coprostanol concentrations were at background levels. Concentrations of coprostanol in 2008 vibracore 2 remain below background levels for the entire length of the core. Using the average sedimentation rates determined in this study of 0.26 and 0.32 cm/year for slow cores 1 and 2, a 35 – 45 year time scale for steroid degradation in Bedford Bay can be estimated. However, the initiation of wastewater treatment at Mill Cove WWTF in 1970 may confound this deduction as it is not known where wastewater outfalls in Bedford Bay were previously located. The appearance of coprostanol at depths corresponding to 35 – 45 years could be a result of the release of treated wastewater near Mill Cove or could be a result of degradation below these depths. Additionally, it is difficult to determine the actual depth at which coprostanol concentrations go to background as the sampling density in both slow cores is so low.

6.4 ANTICIPATED EFFECTS OF WASTEWATER TREATMENT

As discussed in Section 2.4.5, municipalities in Canada will be soon required to ensure that wastewater is treated to a level equivalent to secondary treatment levels in the next 10 – 30 years. HRM will eventually need to upgrade their newly built advanced primary WWTFs to secondary treatment levels. One of the goals of this study was to try and anticipate the effects upgrading would have on sediment chemistry based on changes observed in sediment chemistry following the initiation of wastewater treatment in Bedford Bay in 1970.

Interpretations of analyses from slow cores 1 and 2 were confounded by several factors. Concentrations of metals have likely changed as a result of wastewater treatment, increased population, and stricter controls on sources of most metal contaminants, making it difficult to delineate which has had the greater impact. Additionally, wastewater is not the sole source of contaminants in the harbour. The average sedimentation rate of slow core 2 was based on the assumption that sedimentation rates have been constant for the last 100 years. However, this is almost certainly not the case given slow core 2's proximity to the wastewater outfall and the increased urbanization of Bedford in the last 50 years. Mixing in slow core 1 makes interpreting the sediment record even more challenging.

Based on observations made in this study, comparisons between removal efficiencies in the Mill Cove WWTF (Table 2.2), and a pilot study conducted by Hunt et al. (1995), the greatest changes in concentrations of contaminants as a result of upgrading from advanced primary to secondary treatment levels will likely be those contaminants in the dissolved form (e.g. copper, zinc, LMW PAHs). As discussed above, mercury and lead are generally found in particulate forms in circumneutral wastewaters and are more likely to be removed through primary sedimentation with or without the addition of flocculants.

Similarly, HMW PAHs are more hydrophobic than LMW PAHs and are more likely to be removed through primary sedimentation and flocculation. The change to activated sludge treatment (secondary treatment) will likely have a greater impact on the removal efficiencies of dissolved species (Chipasa 2003). It is important to note that this does not mean that removal efficiencies of lead, mercury, or HMW PAHs will not increase with secondary treatment, but that the relative increase in removal efficiency is expected to be greater for zinc, copper and LMW PAHs than for mercury, lead, and HMW PAHs.

It is difficult to predict how changes in wastewater treatment will affect biota in the harbour. As previously discussed, decreasing the input of organic matter is likely to result in increasingly oxic conditions in near-surface sediments. However, this may simply increase the exposure of benthic organisms to some contaminants. It is possible that some organisms currently avoiding the most reducing, most contaminated areas of the harbour, will begin to inhabit these areas as a result of changing redox conditions before the contaminants have been buried as has occurred in Boston Harbour (Section 1.1.2). It is important to underscore that wastewater treatment is not remediation; it is simply a source reduction. Sediments that are contaminated at present will remain contaminated until enough clean sediment has accumulated to bury them. As already observed following the initiation of wastewater treatment in 2008, improvements in contaminant concentrations will occur much more rapidly in the water column than in the sediments. In the long term, however, wastewater treatment will decrease concentrations of some contaminants making the harbour increasingly inhabitable for both pelagic and benthic species.

Examination of slow cores 1 and 2 epitomizes what can be expected in Central Harbour as a result of wastewater treatment at any level. Because wastewater was previously released into the harbour through several major outfalls the contamination in the harbour was widespread. With the release of effluent generally confined to two outfalls into Central Harbour (with the exception of overflow events), one would expect the distribution of contaminants in the harbour to change. As seen in Bedford Bay, concentrations of contaminants with wastewater sources will be highest near the outfalls and become lower as the distance to the outfall is increased. However, wastewater is not the only source of contaminants in the harbour and as such improvements in the levels of some contaminants (e.g. PAHs) may not be as dramatic as others (e.g. mercury). Additionally, concentrations of contaminants in the harbour are not going to return to pre-industrial concentrations due to the influx of contaminants from sources other than wastewater and the limitations in wastewater treatment capabilities

6.5 SUMMARY

1. Results from this study and a literature review indicate that concentrations of LMW PAHs, copper, and zinc would be expected to decrease to a greater extent relative to concentrations of HMW PAHs, mercury, and lead as a result of upgrading from advanced primary to secondary levels of wastewater treatment. Wastewater treatment is likely to change the distribution of contaminants in the harbour not only as a result of the actual wastewater treatment, but also as a result of the consolidation of outfalls. Wastewater sourced contaminants will now have two point sources in Central Harbour near which concentrations will be highest with concentrations generally decreasing away from these outfalls. Because there are sources of contaminants additional to wastewater in the harbour, there will not be a substantial decrease in the concentrations of all contaminants. Only concentrations of contaminants with predominantly wastewater sources are likely to change dramatically.

2. Concentrations of lead, copper, mercury, zinc, and PAHs in sediments near Mill Cove are decreasing, but remain above the ISQG (and in some instances above the PEL) in the near surface.

3. Present-day and average sediment accumulation rates in Bedford Bay estimated through pore water (0.03 – 0.05 cm/year) and conventional dating (0.26 – 0.32 cm/year) analyses, respectively, yield sediment accumulation rates within an order of magnitude of each other. Sediment accumulation rates determined in the present study correspond well to estimates determined by Buckley et al. (1995) and Cranston (1994) (0.04 – 1.2 cm/year).

CHAPTER 7: CONCLUSIONS

7.1 SUMMARY OF CONCLUSIONS

1. Concentrations of most metals in surficial sediments throughout Halifax Harbour have not changed substantially in the last 20 years. However, mercury concentrations are slightly lower in some areas of the harbour which can likely be attributed to increased source control and a reduction in the use of mercury. Decreases in the concentrations of chromium, lithium, iron, and manganese can be ascribed to different dissolution procedures. Not enough time has passed for any changes in sediment chemistry resulting from increased wastewater treatment to be apparent yet given the relatively low sedimentation rates in the harbour and the recent difficulties with operations of the Halifax WWTF (Section 2.4.3). While concentrations of PAHs have remained at the same levels for the last 10 years, there is an apparent increase in the proportion of alkylated PAHs relative to parental PAHs. This change can likely be ascribed to increased input from petrogenic sources. With the exception of Outer Harbour sediments which contain abundant shell material, sediments in the near surface of Halifax Harbour show evidence of fecal contamination.

2. Differences in instrumentation, methodology, and inadequate core lengths are likely the explanation for higher background concentrations of some metals (chromium, mercury, and zinc) in harbour sediments when data from this study are compares to those determined in previous studies. Background concentrations of cadmium, copper, and nickel exceed the CCME's ISQG or NOAA's threshold effects level, underscoring the importance of taking care when applying SQVs.

3. Sediments in most areas of the harbour are reducing at the sediment-water interface, which has a strong control on the speciation of metals and degradation of organic contaminants. Increased wastewater treatment in the harbour is likely to result in sediments becoming increasingly oxic, which may lead to changes in

the mobility and bioavailability of some sediment-bound metals and increase degradation rates of organic contaminants.

4. Removal efficiencies of contaminants generally found in the dissolved state (e.g. copper, zinc, and LMW PAHs) are likely to be impacted to a greater extent by upgrading from advanced primary to secondary treatment levels than removal efficiencies of contaminants generally bound to particulate matter (e.g. mercury, lead, HMW PAHs). Additionally, results from this study suggest that decreases in concentrations of contaminants will likely be limited to areas away from wastewater outfalls and that only contaminants with predominantly wastewater sources will see a substantial decrease in concentration following increased wastewater treatment.

5. While no evidence of improvements to marine sediment quality were observed as a result of increased wastewater treatment during this study, water quality improved sufficiently to open Halifax beaches for the first time in 30 years. This disconnect between sediment and water quality underscores the need to include sediment quality monitoring as part of harbour quality screening programs.

7.2 SUGGESTIONS FOR FUTURE RESEARCH

The results in this thesis provide researchers and regulators with pre-industrial background concentrations and near-surface contaminant concentrations in Halifax Harbour sediments at the commencement of wastewater treatment in 2009 – 2010. Establishing these baselines is essential for measuring the success of the HSP and future wastewater treatment projects. The following research projects should be implemented as a follow-up to the current study:

1. While water quality screening is currently undertaken on a biweekly basis, changes in sediment quality are not reflected this rapidly. Instead, implementing sediment quality monitoring every five years would allow sufficient time for sediments to accumulate (1 – 2 cm) such that any improvements in sediment chemistry as a result of increased wastewater treatment would be apparent.

2. Redox conditions have a strong control on the speciation of metals and degradation rates of PAHs and coprostanol, changing the bioavailability and mobility of contaminants. Because changes in organic matter input as a result of increased wastewater treatment are likely to affect redox conditions, pore water chemistry should also be examined every five years. *In situ* methods of measuring pore water chemistry (e.g. thin film techniques, peepers, microelectrodes) are recommended to provide the most accurate data for changes in sediment redox conditions.

3. While monitoring changes in water quality and sediment quality can provide evidence as to the effectiveness of wastewater treatment, it is the environmental impact of contaminants on biota that is of primary concern. Biological monitoring

studies should be conducted every 2 years and should include studies of both pelagic and benthic biota.

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APPENDIX A: SAMPLING SUMMARY

Table A.1 Sampling summary

Cruise	Station No.	Longitude (dec. deg.)	Latitude (dec. deg.)	Sample Type	Water Depth (m)	Core Length (cm)	Date (yr/mo/da)
93Secunda	2	-63.5517	44.6378	Vibracore	20.5	512	93/08/22
93Secunda	9	-63.5393	44.6088	Vibracore	27.0	600	93/08/22
93Secunda	10	-63.5532	44.6382	Vibracore	20.5	512	93/08/22
-	D3	-63.5452	44.6385	Grab	23.8	-	08/03/21
-	D2	-63.5527	44.6362	Grab	27.1	-	08/03/21
-	HP3	-63.5552	44.5573	Grab	8.2	-	08/03/21
-	HP2	-63.5492	44.5618	Grab	33.8	-	08/03/21
-	HP1	-63.5526	44.5657	Grab	NA	-	08/03/21
-	HC	-63.5572	44.5707	Grab	4.9	-	08/03/21
-	BRB	-63.5611	44.6247	Grab	11.0	-	08/03/21
-	EE1	-63.5765	44.6577	Grab	21.3	-	08/03/21
-	EE2	-63.5720	44.6593	Grab	20.4	-	08/03/21
-	EE3	-63.5678	44.6612	Grab	10.4	-	08/03/21
-	TC	-63.5994	44.6771	Grab	4.9	-	08/03/21
-	DYC	-63.6152	44.6989	Grab	10.7	-	08/03/21
-	BST	-63.6686	44.7166	Grab	14.9	-	08/03/21
-	PC	-63.5700	44.6123	Grab	7.9	-	08/03/21
-	RNSYS	-63.5785	44.6222	Grab	14.3	-	08/03/21
-	AYC	-63.6096	44.6367	Grab	12.8	-	08/03/21
-	HC	-63.5572	44.5707	Grab	4.0	-	08/07/15
-	PC	-63.5700	44.6123	Grab	7.6	-	08/07/15
-	RNSYS	-63.5785	44.6222	Grab	13.7	-	08/07/15
-	AYC	-63.6096	44.6367	Grab	22.9	-	08/07/15
-	BRB	-63.5611	44.6247	Grab	11.0	-	08/07/15
-	D1	-63.5607	44.6338	Grab	18.3	-	08/07/15
-	D3	-63.5452	44.6385	Grab	21.0	-	08/07/15
-	EE1	-63.5765	44.6577	Grab	21.3	-	08/07/15
-	EE2	-63.5720	44.6593	Grab	18.6	-	08/07/15
-	EE3	-63.5678	44.6612	Grab	9.0	-	08/07/15
-	DYC	-63.6152	44.6989	Grab	12.0	-	08/07/15
-	DC	-63.5592	44.6639	Grab	5.8	-	08/07/15
-	DS1	-63.6686	44.7166	Grab	12.8	-	08/07/15
-	HP2	-63.5492	44.5618	Grab	33.2	-	08/07/15
-	HP3	-63.5552	44.5573	Grab	25.0	-	08/07/15
-	BYC	-63.6629	44.7234	Grab	9.1	-	08/07/15
-	ST5	-63.5914	44.6292	Grab	18.3	-	08/07/15
-	SYC	-63.5255	44.6294	Grab	16.2	-	08/07/15

Table A.1 Sampling summary cont'd

Cruise	Station No.	Longitude (dec. deg.)	Latitude (dec. deg.)	Sample Type	Water Depth (m)	Core Length (cm)	Date (yr/mo/da)
-	AYC	-63.6096	44.6367	Grab	10.7	-	08/10/21
-	RNSYS	-63.5785	44.6222	Grab	13.4	-	08/10/21
-	PC	-63.5700	44.6123	Grab	8.5	-	08/10/21
-	HC	-63.5572	44.5707	Grab	4.0	-	08/10/21
-	BRB	-63.5611	44.6247	Grab	13.7	-	08/10/21
-	BB1	-63.6686	44.7107	Grab	10.4	-	08/10/21
-	BYC	-63.6629	44.7234	Grab	11.3	-	08/10/21
-	DYC	-63.6152	44.6989	Grab	12.8	-	08/10/21
-	TC	-63.5994	44.6771	Grab	7.0	-	08/10/21
-	DC	-63.5592	44.6639	Grab	7.9	-	08/10/21
-	EE2	-63.5720	44.6593	Grab	20.7	-	08/10/21
-	EE3	-63.5678	44.6612	Grab	14.3	-	08/10/21
-	D1	-63.5607	44.6338	Grab	19.5	-	08/10/21
-	D2	-63.5527	44.6362	Grab	24.1	-	08/10/21
-	D3	-63.5452	44.6385	Grab	22.9	-	08/10/21
-	SYC	-63.5255	44.6294	Grab	17.4	-	08/10/21
2008-053	2	-63.6686	44.7160	Vibracore	13.7	293	08/11/12
2008-053	3	-63.6641	44.7129	Vibracore	17.1	271	08/11/12
2008-053	5	-63.5526	44.5643	Vibracore	30.0	171	08/11/12
2008-053	6	-63.5384	44.6098	Vibracore	21.3	407	08/11/12
2008-053	7	-63.5707	44.6171	Vibracore	12.5	402	08/11/12
2008-053	8	-63.5710	44.6521	Vibracore	20.1	362	08/11/12
2008-053	9	-63.5601	44.6632	Vibracore	6.4	230	08/11/12
-	BRB	-63.5611	44.6247	Grab	12.2	-	09/04/08
-	MC	-63.6696	44.7166	Grab	14.3	-	09/04/08
-	EE3	-63.5678	44.6612	Grab	NA	-	09/04/08
-	HP3	-63.5552	44.5573	Grab	29.3	-	09/04/08
-	D1	-63.5607	44.6338	Grab	21.6	-	09/04/08
-	DYC	-63.6152	44.6989	Grab	13.7	-	09/04/08
-	D3	-63.5452	44.6385	Grab	23.2	-	09/04/08
-	HP2	-63.5492	44.5618	Grab	34.4	-	09/04/08
-	BYC	-63.6629	44.7234	Grab	11.6	-	09/04/08
-	HC	-63.5572	44.5707	Grab	4.9	-	09/04/08
-	AYC	-63.6096	44.6367	Grab	9.8	-	09/04/08
-	EE1	-63.5765	44.6577	Grab	21.0	-	09/04/08
-	PC	-63.5700	44.6123	Grab	8.5	-	09/04/08
-	HP1	-63.5526	44.5657	Grab	32.6	-	09/04/08

Table A.1 Sampling summary cont'd

Cruise	Station No.	Longitude (dec. deg.)	Latitude (dec. deg.)	Sample Type	Water Depth (m)	Core Length (cm)	Date (yr/mo/da)
-	EE2	-63.5720	44.6593	Grab	18.6	-	09/04/08
-	TC	-63.5994	44.6771	Grab	6.1	-	09/04/08
-	DC	-63.5592	44.6639	Grab	7.6	-	09/04/08
-	SYC	-63.5255	44.6294	Grab	16.8	-	09/04/08
2009-060	1	-63.6686	44.7161	Slow core	16.2	25	09/04/30
2009-060	2	-63.6699	44.7151	Slow core	15.0	23	09/04/30
2009-060	5	-63.6691	44.7143	Gravity core	16.1	32	09/04/30
2009-060	8	-63.5705	44.6172	Slow core	15.5	35	09/04/30
2009-060	9	-63.5573	44.5707	Slow core	4.5	30	09/04/30

APPENDIX B: SEDIMENT GEOCHEMICAL RESULTS

Table B.1 Grab sample geochemical data

Cruise	Station	Lab ID	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Mar. 08	D3	20080001	2.83	0.26	9	27	30	2.86	463	33	420	21	73	78
Mar. 08	D2	20080002	3.73	0.34	10	27	45	2.70	410	29	348	22	64	102
Mar. 08	HP3	20080003	0.29	0.04	6	<10	8	1.42	22	38	281	6	30	43
Mar. 08	HP2	20080004	0.42	0.04	5	11	8	1.00	13	13	253	11	16	30
Mar. 08	HP1	20080005	0.52	0.03	5	<10	9	0.87	30	25	159	10	16	43
Mar. 08	HC	20080006	4.68	0.87	8	13	74	1.64	203	23	231	14	49	147
Mar. 08	BRB	20080007	4.56	0.55	11	32	66	3.37	481	36	389	24	69	142
Mar. 08	EE1	20080008	4.30	0.47	10	33	100	3.35	1884	30	360	27	426	155
Mar. 08	EE2	20080009	5.03	0.50	11	40	117	3.19	1019	30	369	32	87	202
Mar. 08	EE3	20080010	6.76	0.65	10	36	137	4.78	2442	33	341	24	148	225
Mar. 08	TC	20080011	11.10	2.75	11	88	380	2.76	1810	36	309	52	180	4019
Mar. 08	DYC	20080012	7.17	1.04	12	44	136	3.27	651	33	342	30	45	371
Mar. 08	MC	20080013	5.81	1.09	14	33	86	3.87	565	37	435	31	77	285
Mar. 08	PC	20080014	5.70	0.55	9	88	72	3.48	759	35	368	22	76	156
Mar. 08	RNSYS	20080015	5.81	0.99	9	62	78	3.82	1628	35	333	21	91	205
Mar. 08	AYC	20080016	6.09	0.91	11	83	92	4.20	1025	36	391	26	84	193
July 08	HC	20080214	5.12	1.38	7	29	87	1.89	211	27	226	15	135	257
July 08	PC	20080215	5.25	0.70	9	35	77	2.89	652	40	364	26	166	157
July 08	RNSYS	20080216	5.24	0.86	10	36	80	2.89	947	42	372	26	231	183
July 08	AYC	20080217	5.75	0.92	12	43	109	3.54	1009	46	352	31	183	227
July 08	BRB	20080218	4.52	0.57	11	33	66	2.93	502	38	371	28	91	168
July 08	D1	20080219	3.17	0.87	-	-	-	-	-	-	-	-	175	-
July 08	D3	20080220	3.27	0.31	11	31	55	3.40	543	32	390	23	102	131
July 08	EE1	20080221	3.08	0.58	13	39	106	3.62	1111	43	440	33	324	271
July 08	EE2	20080222	4.54	0.45	12	41	120	2.91	1026	36	379	31	139	200
July 08	EE3	20080223	4.68	0.32	10	35	121	3.16	2585	40	333	22	187	203
July 08	DYC	20080224	6.03	1.37	14	52	156	3.74	928	44	492	30	208	351
July 08	DC	20080225	4.76	1.77	10	42	192	2.86	2699	29	290	24	426	360

Table B.1 Grab sample geochemical data (cont'd)

Cruise	Station	Lab ID	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
July 08	MC	20080226	3.04	1.37	17	42	120	3.70	768	51	511	33	138	360
July 08	HP2	20080227	0.66	0.14	7	12	11	1.26	24	17	318	14	8	50
July 08	HP3	20080228	0.08	<0.01	5	<10	2	1.37	<5	54	271	7	8	44
July 08	BYC	20080229	5.08	0.90	16	36	67	2.83	207	41	419	28	55	260
July 08	ST5	20080230	5.34	0.59	11	38	82	3.27	892	43	384	28	135	176
July 08	SYC	20080234	3.31	0.34	11	31	51	3.62	516	34	437	27	59	131
Oct. 08	AYC	20080240	6.46	-	11	40	111	3.42	1136	44	360	27	142	215
Oct. 08	RNSYS	20080241	5.63	-	11	35	85	3.12	1023	42	402	25	192	196
Oct. 08	PC	20080242	5.77	-	11	33	232	3.04	743	39	393	24	111	207
Oct. 08	HC	20080243	3.42	-	9	24	58	1.90	535	30	264	12	164	227
Oct. 08	BRB	20080244	4.17	-	12	31	63	3.01	557	41	402	26	90	172
Oct. 08	MC	20080245	13.87	-	11	51	299	1.85	2654	34	271	18	71	600
Oct. 08	BYC	20080246	3.35	-	17	32	59	3.34	234	50	517	32	73	236
Oct. 08	DYC	20080247	6.55	-	12	50	117	3.48	1349	39	457	25	213	482
Oct. 08	TC	20080248	8.21	-	12	46	156	3.55	1282	28	357	36	241	748
Oct. 08	DC	20080249	5.87	-	12	48	246	3.26	1820	33	355	28	945	547
Oct. 08	EE2	20080250	4.92	-	12	31	75	3.00	1495	38	379	23	171	203
Oct. 08	EE3	20080251	4.09	-	11	33	91	3.29	996	39	381	25	100	163
Oct. 08	D1	20080252	4.06	-	12	28	85	2.88	673	31	361	27	100	233
Oct. 08	D2	20080253	3.89	-	11	30	65	3.14	426	32	457	26	73	148
Oct. 08	D3	20080254	3.36	-	10	32	53	3.58	478	32	506	31	82	143
Oct. 08	SYC	20080255	2.80	-	11	32	53	3.55	344	30	477	21	61	148
Apr. 09	BRB	20090200	2.12	-	8	20	36	2.55	205	28	350	18	48	118
Apr. 09	MC	20090201	6.15	-	14	39	100	3.41	819	42	450	26	85	290
Apr. 09	EE3	20090202	5.62	-	11	38	141	3.54	2770	29	391	30	148	230
Apr. 09	HP3	20090203	0.82	-	7	<10	11	1.42	24	29	270	8	20	45
Apr. 09	D1	20090204	3.89	-	11	26	66	2.91	518	29	397	23	95	158

Table B.1 Grab sample geochemical data (cont'd)

Cruise	Station	Lab ID	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Apr. 09	DYC	20090205	6.54	-	11	40	100	3.18	650	35	380	23	167	258
Apr. 09	D3	20090206	3.20	-	11	24	42	3.12	386	30	454	20	81	104
Apr. 09	HP2	20090207	0.84	-	7	11	13	1.67	35	15	351	9	15	43
Apr. 09	BYC	20090208	3.59	-	16	30	59	4.03	330	37	554	27	74	231
Apr. 09	HC	20090209	2.70	-	9	12	45	1.81	296	22	224	13	85	167
Apr. 09	AYC	20090210	6.35	-	11	25	99	3.91	1216	36	362	23	214	219
Apr. 09	EE1	20090211	2.22	-	12	19	75	3.38	437	31	435	25	72	137
Apr. 09	PC	20090212	5.28	-	9	23	65	3.14	603	35	386	24	94	148
Apr. 09	HP1	20090213	0.63	-	6	<10	11	1.24	49	15	272	7	13	36
Apr. 09	EE2	20090214	5.05	-	13	28	121	3.20	1454	32	402	28	134	214
Apr. 09	TC	20090215	7.28	-	10	39	321	3.11	1078	24	354	28	161	816
Apr. 09	DC	20090216	5.48	-	12	45	181	3.53	2741	33	393	25	1517	315
Apr. 09	SYC	20090217	3.19	-	11	29	61	3.28	341	34	436	21	57	127

Table B.2 Sediment core geochemical data

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	2	20080031	0.5	3.20	0.30	8	33	35	3.03	2831	30	378	22	67	119
93SECUNDA	2	20080032	2.5	3.64	0.40	9	31	102	2.70	1009	29	392	24	104	123
93SECUNDA	2	20080033	3.5	3.78	0.42	9	32	35	2.96	567	31	402	25	136	125
93SECUNDA	2	20080034	5.5	3.79	0.33	9	29	56	2.55	491	27	364	23	135	121
93SECUNDA	2	20080035	7.5	3.35	0.38	9	28	66	2.72	523	27	386	35	149	114
93SECUNDA	2	20080036	9.5	3.60	0.85	11	27	76	2.51	485	25	388	41	205	117
93SECUNDA	2	20080037	11.5	8.02	0.51	7	23	71	2.51	527	29	369	27	91	108
93SECUNDA	2	20080038	13.5	3.25	0.86	10	25	61	2.56	648	26	364	26	157	116
93SECUNDA	2	20080039	15.5	3.81	0.67	11	27	59	2.52	531	25	349	27	130	109
93SECUNDA	2	20080040	17.5	3.67	-	9	29	46	2.78	451	30	362	30	383	180
93SECUNDA	2	20080041	19.5	4.49	-	11	27	63	2.72	528	27	362	22	131	117
93SECUNDA	2	20080042	21.5	4.39	0.89	11	25	70	2.74	528	27	367	35	130	121
93SECUNDA	2	20080043	23.5	4.14	0.50	10	26	86	2.22	690	26	312	26	107	106
93SECUNDA	2	20080044	25.5	3.49	0.30	9	26	39	2.49	476	27	326	23	73	91
93SECUNDA	2	20080045	27.5	3.52	0.17	10	24	24	3.01	502	32	385	26	98	105
93SECUNDA	2	20080046	29.5	3.03	0.28	10	25	34	2.44	234	27	344	28	72	93
93SECUNDA	2	20080047	41.5	2.23	0.48	8	30	18	2.69	11	27	374	27	12	53
93SECUNDA	2	20080048	51.5	2.15	0.35	10	30	18	2.45	11	27	374	29	11	55
93SECUNDA	2	20080049	61.5	2.26	0.38	9	29	17	2.47	11	28	376	29	11	56
93SECUNDA	2	20080050	71.5	2.06	0.37	8	28	19	2.32	16	27	371	26	11	54
93SECUNDA	2	20080051	81.5	1.77	0.13	9	23	18	2.39	16	26	355	20	12	56
93SECUNDA	2	20080052	91.5	2.13	0.30	9	27	15	2.51	15	27	382	26	12	56
93SECUNDA	2	20080053	101.5	2.09	0.34	6	25	15	2.55	13	26	386	26	13	56
93SECUNDA	2	20080054	111.5	2.16	0.33	8	29	16	2.63	11	27	395	28	13	61
93SECUNDA	2	20080055	121.5	2.15	0.38	9	34	18	2.93	9	32	436	25	13	66
93SECUNDA	2	20080056	131.5	2.11	0.14	9	29	17	2.79	9	29	431	22	10	62
93SECUNDA	2	20080057	141.5	2.12	0.60	8	29	16	2.77	9	31	428	28	9	62
93SECUNDA	2	20080058	151.5	1.98	0.55	9	33	19	3.02	13	31	467	29	12	65
93SECUNDA	2	20080059	161.5	2.02	0.55	9	35	16	2.84	9	32	440	28	10	67

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	2	20080060	171.5	1.99	0.33	8	27	17	2.91	9	29	407	27	11	62
93SECUNDA	2	20080061	181.5	1.75	0.11	8	28	15	2.74	9	30	439	23	11	65
93SECUNDA	2	20080062	191.5	1.90	0.60	9	29	19	2.80	10	31	393	23	12	65
93SECUNDA	2	20080063	201.5	1.99	0.49	8	31	22	2.86	10	30	368	29	28	66
93SECUNDA	2	20080064	211.5	1.89	0.43	9	29	17	2.80	9	30	410	27	10	60
93SECUNDA	2	20080065	221.5	1.90	-	10	26	19	2.73	9	30	394	24	15	59
93SECUNDA	2	20080066	231.5	1.75	0.18	10	26	16	2.63	9	31	423	25	10	59
93SECUNDA	2	20080067	241.5	2.02	0.34	11	29	18	2.79	9	31	442	30	11	64
93SECUNDA	2	20080068	251.5	2.01	0.61	10	31	18	2.77	9	31	454	27	13	62
93SECUNDA	2	20080069	261.5	1.93	0.13	9	31	18	2.77	12	31	413	20	10	57
93SECUNDA	2	20080070	271.5	1.91	0.46	11	24	17	2.72	10	30	386	31	14	62
93SECUNDA	2	20080071	281.5	1.80	0.08	9	32	15	3.01	10	29	388	22	-	56
93SECUNDA	2	20080072	291.5	2.05	0.36	11	27	18	2.98	11	33	476	31	-	65
93SECUNDA	2	20080073	301.5	1.88	0.74	8	30	16	2.79	10	36	458	27	-	66
93SECUNDA	9	20080074	2.5	1.36	0.45	10	24	30	2.38	224	28	435	23	49	92
93SECUNDA	9	20080075	4.5	1.71	0.59	9	22	28	2.29	179	27	395	23	47	82
93SECUNDA	9	20080076	6.5	1.46	0.43	9	23	26	2.16	188	26	390	22	50	82
93SECUNDA	9	20080077	11.5	1.54	0.50	9	21	28	2.49	191	26	394	20	50	85
93SECUNDA	9	20080078	16.5	1.83	0.47	8	23	28	2.19	171	26	370	23	56	75
93SECUNDA	9	20080079	21.5	1.69	0.41	10	23	30	2.37	159	29	415	22	65	87
93SECUNDA	9	20080080	26.5	1.88	0.73	10	24	29	2.44	154	29	390	23	57	88
93SECUNDA	9	20080081	31.5	1.85	0.72	8	23	26	2.36	126	28	395	24	49	78
93SECUNDA	9	20080082	36.5	2.45	0.70	9	26	35	2.38	282	28	387	24	75	85
93SECUNDA	9	20080083	41.5	2.44	0.84	9	26	34	2.64	259	32	435	25	78	92
93SECUNDA	9	20080084	46.5	2.49	0.65	12	26	34	2.51	334	32	424	25	70	98
93SECUNDA	9	20080085	51.5	3.87	0.77	10	27	32	2.46	401	30	403	24	94	101
93SECUNDA	9	20080086	56.5	1.83	0.47	9	23	25	2.52	197	31	428	23	63	84

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	9	20080087	61.5	2.72	0.91	10	30	29	2.65	322	31	442	27	106	87
93SECUNDA	9	20080088	66.5	2.38	0.63	8	23	25	2.44	291	31	430	22	87	81
93SECUNDA	9	20080089	71.5	1.95	0.33	8	19	19	2.08	237	26	343	18	59	57
93SECUNDA	9	20080090	76.5	1.93	0.86	6	20	16	1.89	187	25	330	18	48	60
93SECUNDA	9	20080091	81.5	1.97	0.63	8	17	17	2.02	112	26	356	22	41	56
93SECUNDA	9	20080092	86.5	1.76	0.43	8	17	15	2.05	67	26	365	18	27	48
93SECUNDA	9	20080093	91.5	1.62	0.42	9	17	16	2.37	33	27	390	15	20	43
93SECUNDA	9	20080094	96.5	1.48	0.34	7	16	32	1.87	35	23	317	17	22	42
93SECUNDA	9	20080095	101.5	1.70	0.44	8	19	16	2.17	16	25	383	14	14	52
93SECUNDA	9	20080096	111.5	1.93	0.64	7	20	16	2.34	14	25	358	21	12	55
93SECUNDA	9	20080097	122.5	1.64	0.42	9	21	17	2.37	13	25	383	23	13	52
93SECUNDA	9	20080098	131.5	1.86	0.74	9	26	18	2.52	11	29	412	24	15	55
93SECUNDA	9	20080099	141.5	1.85	0.55	8	18	16	2.23	9	26	369	18	15	49
93SECUNDA	9	20080100	151.5	1.37	0.31	8	19	16	2.14	9	24	406	17	14	49
93SECUNDA	9	20080101	161.5	1.90	0.71	7	20	17	2.42	11	26	405	23	9	54
93SECUNDA	9	20080102	171.5	1.97	0.14	10	21	18	2.60	10	28	426	22	13	54
93SECUNDA	9	20080103	181.5	2.15	0.74	8	21	17	2.31	9	26	369	20	15	53
93SECUNDA	9	20080104	191.5	2.47	0.58	13	21	17	2.41	10	27	385	23	11	53
93SECUNDA	9	20080105	201.5	2.21	0.36	10	22	16	2.56	10	24	411	22	11	50
93SECUNDA	9	20080106	211.5	2.64	-	11	26	20	0.01	10	30	<15	28	13	62
93SECUNDA	9	20080107	221.5	2.33	-	11	26	21	0.01	11	30	<15	27	12	61
93SECUNDA	9	20080108	231.5	2.87	0.79	11	21	20	<0.01	9	29	<15	22	10	61
93SECUNDA	9	20080109	241.5	2.41	0.76	10	22	17	0.01	9	28	<15	28	14	56
93SECUNDA	9	20080110	251.5	2.19	0.32	9	19	18	<0.01	9	26	<15	20	12	53
93SECUNDA	9	20080111	261.5	23.60	-	<3	<10	5	<0.01	9	4	<15	4	1	15
93SECUNDA	9	20080112	272.5	12.40	0.58	4	<10	8	<0.01	16	19	<15	10	2	27
93SECUNDA	9	20080113	281.5	2.64	0.26	8	21	17	<0.01	9	27	<15	17	12	50
93SECUNDA	9	20080114	291.5	1.30	0.23	7	20	13	1.97	14	23	347	14	9	52
93SECUNDA	9	20080115	301.5	1.95	0.20	7	21	16	2.09	9	26	373	20	12	48

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	9	20080181	309.5	1.85	-	10	22	19	2.35	9	28	392	23	11	51
93SECUNDA	9	20080182	321.5	1.49	-	8	23	16	2.31	8	27	405	20	11	48
93SECUNDA	9	20080183	331.5	1.71	-	8	23	18	2.27	8	27	394	12	11	47
93SECUNDA	9	20080184	341.5	1.45	-	8	20	16	2.25	7	26	412	5	11	46
93SECUNDA	9	20080185	351.5	1.10	-	8	19	14	2.01	6	24	388	18	9	44
93SECUNDA	9	20080186	361.5	1.75	-	9	23	17	2.31	8	27	416	9	11	49
93SECUNDA	9	20080187	371.5	1.71	-	8	22	18	2.37	8	27	412	9	11	51
93SECUNDA	9	20080188	381.5	1.35	-	9	22	17	2.22	7	27	403	9	10	49
93SECUNDA	9	20080189	391.5	1.32	-	8	23	17	2.39	7	26	419	9	10	47
93SECUNDA	9	20080190	401.5	1.46	-	8	23	16	2.44	7	27	423	5	9	46
93SECUNDA	9	20080191	411.5	1.67	-	8	24	18	2.42	8	27	413	7	10	47
93SECUNDA	9	20080192	421.5	1.77	-	8	26	18	2.43	8	29	430	11	11	49
93SECUNDA	9	20080193	431.5	1.91	-	8	27	19	2.68	9	29	439	10	11	51
93SECUNDA	9	20080194	441.5	1.73	-	9	25	19	2.54	10	29	430	15	10	50
93SECUNDA	9	20080195	451.5	1.58	-	6	24	19	2.58	8	29	460	9	11	51
93SECUNDA	9	20080196	461.5	1.66	-	7	23	18	2.45	8	29	433	-	11	50
93SECUNDA	9	20080197	471.5	1.50	-	5	24	17	2.27	7	27	397	8	9	47
93SECUNDA	9	20080198	481.5	1.30	-	6	23	16	2.19	7	25	406	7	8	44
93SECUNDA	9	20080199	491.5	1.43	-	8	22	19	2.34	7	28	398	4	9	48
93SECUNDA	9	20080200	501.5	1.57	-	7	21	18	2.42	7	28	435	13	10	44
93SECUNDA	9	20080201	511.5	1.85	-	7	25	19	2.44	8	28	394	4	10	49
93SECUNDA	9	20080202	521.5	1.56	-	9	23	18	2.37	7	28	440	17	9	50
93SECUNDA	9	20080203	531.5	1.68	-	8	25	17	2.30	7	27	414	22	9	49
93SECUNDA	9	20080204	541.5	1.56	-	8	23	16	2.27	7	29	415	17	10	50
93SECUNDA	9	20080205	551.5	1.56	-	9	26	18	2.35	7	30	412	22	9	56
93SECUNDA	9	20080206	561.5	1.83	-	10	27	20	2.79	9	33	469	22	11	59
93SECUNDA	9	20080207	571.5	1.63	-	10	24	19	2.30	8	29	414	18	9	52
93SECUNDA	9	20080208	581.5	1.66	-	10	25	16	2.41	7	29	423	29	9	53
93SECUNDA	9	20080209	591.5	1.37	-	9	23	16	2.32	7	28	436	19	9	49

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	9	20080210	598.5	1.46	-	9	24	18	2.34	7	30	392	22	10	55
93SECUNDA	10	20080116	1.5	3.16	0.15	8	26	30	2.58	309	30	316	21	89	77
93SECUNDA	10	20080117	3.5	2.85	0.17	8	27	32	2.93	300	29	352	22	90	79
93SECUNDA	10	20080118	5.5	2.85	0.15	7	22	27	2.64	295	27	338	21	68	71
93SECUNDA	10	20080119	7.5	3.87	0.13	6	22	26	2.60	309	27	337	20	83	69
93SECUNDA	10	20080120	9.5	2.77	0.15	6	23	24	2.85	331	27	360	20	88	69
93SECUNDA	10	20080121	11.5	3.01	0.14	6	23	24	2.62	290	26	352	22	75	67
93SECUNDA	10	20080122	13.5	2.70	0.12	5	26	26	2.96	293	26	358	19	78	66
93SECUNDA	10	20080123	15.5	2.82	0.12	3	25	24	2.65	294	28	337	23	41	67
93SECUNDA	10	20080124	17.5	2.61	0.10	6	25	24	2.70	224	28	330	27	47	71
93SECUNDA	10	20080125	19.5	2.64	0.12	6	25	23	2.60	255	26	354	22	38	59
93SECUNDA	10	20080126	21.5	2.78	0.12	8	22	23	2.42	200	25	326	23	55	57
93SECUNDA	10	20080127	23.5	2.73	0.11	7	25	27	2.63	109	27	366	24	46	65
93SECUNDA	10	20080128	25.5	2.46	0.11	5	25	26	2.70	101	28	398	27	51	66
93SECUNDA	10	20080129	27.5	2.34	0.14	5	24	23	2.80	110	25	359	23	46	59
93SECUNDA	10	20080130	29.5	2.17	-	5	24	23	2.54	106	27	359	29	49	62
93SECUNDA	10	20080131	31.5	2.33	0.19	5	25	20	2.53	154	25	398	24	65	58
93SECUNDA	10	20080132	33.5	2.56	-	4	23	17	2.63	117	25	423	25	38	62
93SECUNDA	10	20080133	35.5	2.46	1.22	6	22	18	2.34	27	25	354	34	15	73
93SECUNDA	10	20080134	37.5	2.40	0.57	5	22	18	2.38	17	27	388	29	16	77
93SECUNDA	10	20080135	39.5	2.59	0.30	4	24	20	2.68	37	29	395	31	19	73
93SECUNDA	10	20080136	41.5	2.57	0.30	4	24	17	2.43	31	26	372	24	18	62
93SECUNDA	10	20080137	43.5	2.64	0.20	9	24	19	2.53	99	26	395	19	29	66
93SECUNDA	10	20080138	45.5	3.24	0.31	8	23	23	2.58	163	26	427	21	62	81
93SECUNDA	10	20080139	47.5	2.63	0.33	8	23	18	2.83	65	28	431	23	21	78
93SECUNDA	10	20080140	49.5	3.26	0.28	9	27	33	2.70	531	31	414	28	96	89
93SECUNDA	10	20080141	61.5	2.64	0.17	9	29	21	2.69	39	30	390	25	21	112
93SECUNDA	10	20080142	71.5	2.47	0.15	9	31	19	2.77	26	29	390	21	19	108

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	10	20080143	81.5	2.42	0.11	9	28	19	2.75	26	30	387	22	25	79
93SECUNDA	10	20080144	91.5	2.64	0.13	7	27	18	2.87	25	28	443	19	12	63
93SECUNDA	10	20080145	101.5	2.76	0.40	9	28	19	2.82	35	28	383	19	18	85
93SECUNDA	10	20080146	111.5	2.53	0.20	9	28	18	2.71	17	27	408	21	16	65
93SECUNDA	10	20080147	121.5	2.37	0.56	9	27	17	2.67	14	28	371	22	14	64
93SECUNDA	10	20080148	131.5	2.26	0.48	9	33	19	2.74	15	29	384	22	15	69
93SECUNDA	10	20080149	141.5	2.22	0.40	7	28	18	2.72	18	29	378	21	15	63
93SECUNDA	10	20080150	151.5	2.25	0.45	8	29	19	2.72	17	30	394	23	18	75
93SECUNDA	10	20080151	161.5	2.14	0.44	8	27	17	2.65	20	27	393	18	14	59
93SECUNDA	10	20080152	171.5	2.20	0.36	8	28	17	2.52	18	28	382	19	14	58
93SECUNDA	10	20080153	181.5	2.12	0.37	7	25	17	2.46	11	28	390	20	17	57
93SECUNDA	10	20080154	191.5	2.13	0.27	7	27	18	2.71	9	30	428	22	13	60
93SECUNDA	10	20080155	201.5	1.96	0.36	7	29	17	3.11	9	28	357	22	11	61
93SECUNDA	10	20080156	211.5	2.18	0.14	7	22	17	2.28	11	27	389	21	12	53
93SECUNDA	10	20080157	221.5	2.03	0.34	7	20	15	2.38	9	27	366	21	14	52
93SECUNDA	10	20080158	231.5	2.08	0.05	7	21	15	2.48	9	27	350	17	14	51
93SECUNDA	10	20080159	241.5	2.06	0.26	7	20	15	2.31	8	27	362	14	14	52
93SECUNDA	10	20080160	251.5	1.91	0.11	7	20	14	2.21	9	27	373	21	13	49
93SECUNDA	10	20080161	261.5	2.05	0.41	6	20	16	2.38	10	28	374	20	14	52
93SECUNDA	10	20080162	271.5	1.89	0.32	7	20	16	2.47	9	29	357	22	15	53
93SECUNDA	10	20080163	281.5	1.97	0.27	10	28	19	2.82	9	36	400	30	13	62
93SECUNDA	10	20080164	291.5	1.87	0.33	10	29	19	2.62	9	36	420	22	13	62
93SECUNDA	10	20080165	301.5	1.84	0.22	11	26	18	2.62	9	36	403	23	15	59
93SECUNDA	10	20080166	311.5	1.76	0.23	11	28	18	2.68	9	34	379	23	14	57
93SECUNDA	10	20080167	321.5	1.81	0.24	13	28	18	2.85	9	36	388	25	17	59
93SECUNDA	10	20080168	331.5	1.69	0.35	14	25	19	2.75	8	36	391	23	17	58
93SECUNDA	10	20080169	341.5	1.84	0.27	14	26	18	2.70	9	34	387	23	14	59
93SECUNDA	10	20080170	351.5	1.92	0.33	14	28	19	2.68	11	36	417	30	16	61
93SECUNDA	10	20080171	359.5	2.02	-	14	32	19	2.76	9	34	387	22	12	56

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
93SECUNDA	10	20080172	371.5	1.75	0.10	12	34	24	2.98	9	38	419	26	13	62
93SECUNDA	10	20080173	381.5	1.85	0.11	12	27	19	2.83	10	37	438	22	15	61
93SECUNDA	10	20080174	391.5	1.37	0.31	12	23	15	2.50	7	34	521	24	12	58
93SECUNDA	10	20080175	401.5	1.72	0.15	10	24	18	3.15	9	39	519	29	16	62
2008-053	2	20080300	23	6.88	-	11	45	30	2.71	222	38	332	31	51	103
2008-053	2	20080301	25	6.45	-	12	38	25	2.46	175	32	283	23	45	79
2008-053	2	20080302	27	6.70	-	11	45	27	2.45	195	34	307	25	48	92
2008-053	2	20080303	29	7.00	-	12	44	23	2.44	156	34	299	22	39	69
2008-053	2	20080304	31	6.92	-	14	47	22	1.89	242	27	218	27	53	74
2008-053	2	20080305	33	7.37	-	12	49	18	2.19	75	33	274	29	31	61
2008-053	2	20080306	35	7.53	-	12	52	18	1.95	58	29	242	32	26	60
2008-053	2	20080307	37	7.39	-	14	52	15	1.58	127	25	192	25	31	48
2008-053	2	20080308	39	7.37	-	12	47	16	2.01	44	31	243	25	23	60
2008-053	2	20080309	41	7.43	-	14	51	7	1.11	54	19	146	26	24	30
2008-053	2	20080310	43	7.71	-	12	42	12	1.52	40	28	189	21	22	44
2008-053	2	20080311	45	7.40	-	12	45	16	1.91	43	30	236	26	23	49
2008-053	2	20080312	47	7.41	-	12	36	19	2.34	41	34	278	24	23	62
2008-053	2	20080313	49	7.28	-	13	48	13	1.84	26	26	221	32	21	52
2008-053	2	20080314	51	7.38	-	13	50	12	1.61	40	25	196	23	22	48
2008-053	2	20080315	53	7.43	-	14	56	11	1.58	26	26	184	22	20	45
2008-053	2	20080316	55	7.27	-	14	49	10	1.41	35	23	179	24	22	36
2008-053	2	20080317	57	6.87	-	13	53	12	1.64	56	25	193	25	24	44
2008-053	2	20080318	59	7.34	-	14	62	12	1.62	51	25	189	27	27	45
2008-053	2	20080319	61	7.23	-	13	53	15	2.01	37	30	255	19	24	56
2008-053	2	20080320	63	7.19	-	14	51	12	1.60	41	25	203	17	25	47
2008-053	2	20080321	65	6.94	-	14	50	10	1.63	42	25	203	23	23	48
2008-053	2	20080322	67	6.90	-	14	49	7	1.34	39	21	163	21	25	34
2008-053	2	20080323	69	6.63	-	13	51	9	1.51	59	23	191	25	27	39

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	2	20080324	71	6.59	-	15	49	7	1.38	52	20	184	16	26	37
2008-053	2	20080325	77	6.40	-	14	54	7	1.32	64	22	184	23	28	38
2008-053	2	20080326	82	6.33	-	13	50	7	1.38	37	22	191	23	25	39
2008-053	2	20080327	87	6.46	-	13	42	12	1.95	25	27	260	22	23	55
2008-053	2	20080328	92	6.15	-	14	46	6	1.25	27	18	184	20	24	33
2008-053	2	20080329	97	6.18	-	15	48	7	1.52	22	24	204	23	23	41
2008-053	2	20080330	102	5.91	-	14	42	4	1.13	23	19	179	15	22	31
2008-053	2	20080331	107	5.87	-	12	39	10	1.66	24	27	244	22	26	50
2008-053	2	20080332	112	5.84	-	15	48	4	1.15	24	20	185	8	-	31
2008-053	2	20080333	117	6.22	-	15	62	6	1.25	26	22	197	23	-	38
2008-053	2	20080334	122	6.27	-	14	42	6	1.30	27	23	202	17	-	39
2008-053	2	20080335	132	6.86	-	-	-	-	-	25	-	-	-	-	-
2008-053	2	20080336	142	10.09	-	-	-	-	-	26	-	-	-	-	-
2008-053	2	20080337	152	10.86	-	-	-	-	-	34	-	-	-	-	-
2008-053	2	20080338	162	8.09	-	-	-	-	-	30	-	-	-	-	-
2008-053	2	20080339	172	10.05	-	-	-	-	-	41	-	-	-	-	-
2008-053	2	20080340	182	12.46	-	-	-	-	-	52	-	-	-	-	-
2008-053	2	20080341	192	15.01	-	-	-	-	-	62	-	-	-	-	-
2008-053	2	20080342	202	12.25	-	-	-	-	-	69	-	-	-	-	-
2008-053	2	20080343	212	0.15	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080344	222	0.20	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080345	232	0.12	-	-	-	-	-	7	-	-	-	-	-
2008-053	2	20080346	242	0.19	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080347	252	0.04	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080348	262	0.04	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080349	272	0.08	-	-	-	-	-	<5	-	-	-	-	-
2008-053	2	20080350	282	0.03	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080351	1	3.22	-	-	-	-	-	453	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	3	20080352	3	3.38	-	-	-	-	-	384	-	-	-	-	-
2008-053	3	20080353	5	4.14	-	-	-	-	-	543	-	-	-	-	-
2008-053	3	20080354	7	3.29	-	-	-	-	-	434	-	-	-	-	-
2008-053	3	20080355	9	1.71	-	-	-	-	-	237	-	-	-	-	-
2008-053	3	20080356	11	1.29	-	-	-	-	-	103	-	-	-	-	-
2008-053	3	20080357	13	1.08	-	-	-	-	-	68	-	-	-	-	-
2008-053	3	20080358	15	0.88	-	-	-	-	-	20	-	-	-	-	-
2008-053	3	20080359	17	1.05	-	-	-	-	-	11	-	-	-	-	-
2008-053	3	20080360	19	1.25	-	-	-	-	-	48	-	-	-	-	-
2008-053	3	20080361	21	1.30	-	-	-	-	-	21	-	-	-	-	-
2008-053	3	20080362	23	0.36	-	-	-	-	-	6	-	-	-	-	-
2008-053	3	20080363	25	0.32	-	-	-	-	-	7	-	-	-	-	-
2008-053	3	20080364	27	0.53	-	-	-	-	-	8	-	-	-	-	-
2008-053	3	20080365	29	0.42	-	-	-	-	-	7	-	-	-	-	-
2008-053	3	20080366	31	0.37	-	-	-	-	-	8	-	-	-	-	-
2008-053	3	20080367	33	0.37	-	-	-	-	-	11	-	-	-	-	-
2008-053	3	20080368	35	0.20	-	-	-	-	-	9	-	-	-	-	-
2008-053	3	20080369	37	0.37	-	-	-	-	-	14	-	-	-	-	-
2008-053	3	20080370	39	0.18	-	-	-	-	-	7	-	-	-	-	-
2008-053	3	20080371	41	0.35	-	-	-	-	-	11	-	-	-	-	-
2008-053	3	20080372	43	0.64	-	-	-	-	-	8	-	-	-	-	-
2008-053	3	20080373	45	0.57	-	-	-	-	-	12	-	-	-	-	-
2008-053	3	20080374	47	0.40	-	-	-	-	-	6	-	-	-	-	-
2008-053	3	20080375	49	0.58	-	-	-	-	-	8	-	-	-	-	-
2008-053	3	20080376	55	0.46	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080377	60	1.23	-	-	-	-	-	9	-	-	-	-	-
2008-053	3	20080378	65	0.58	-	-	-	-	-	10	-	-	-	-	-
2008-053	3	20080379	70	0.12	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080380	75	0.07	-	-	-	-	-	27	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	3	20080381	80	0.14	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080382	85	0.11	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080383	90	0.36	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080384	95	0.81	-	-	-	-	-	8	-	-	-	-	-
2008-053	3	20080385	100	0.23	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080386	110	0.67	-	-	-	-	-	7	-	-	-	-	-
2008-053	3	20080387	120	0.10	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080388	130	0.12	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080389	140	0.12	-	-	-	-	-	9	-	-	-	-	-
2008-053	3	20080390	150	0.19	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080391	160	0.07	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080392	170	0.06	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080393	180	0.08	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080394	190	0.06	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080395	200	0.04	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080396	210	0.01	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080397	220	0.02	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080398	230	0.03	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080399	240	0.03	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080400	250	0.07	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080401	260	0.02	-	-	-	-	-	<5	-	-	-	-	-
2008-053	3	20080402	270	0.06	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080403	1	0.21	-	6	25	5	0.33	9	14	61	13	26	22
2008-053	5	20080404	3	0.15	-	5	22	10	0.32	9	15	56	<3	26	21
2008-053	5	20080405	5	0.11	-	5	20	4	0.36	8	19	58	10	21	20
2008-053	5	20080406	7	0.21	-	5	21	6	0.32	9	17	59	8	24	18
2008-053	5	20080407	9	0.12	-	6	18	5	0.26	11	13	52	5	24	16
2008-053	5	20080408	11	0.12	-	5	16	4	0.44	8	29	77	5	21	25

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	5	20080409	13	0.18	-	5	16	5	0.40	13	18	66	7	22	21
2008-053	5	20080410	15	0.35	-	5	22	6	0.37	20	15	67	5	26	24
2008-053	5	20080411	17	0.31	-	4	18	6	0.39	17	17	71	4	26	21
2008-053	5	20080412	19	0.23	-	3	22	6	0.42	14	20	79	7	26	27
2008-053	5	20080413	21	0.25	-	5	21	6	0.65	14	43	139	<3	32	33
2008-053	5	20080414	23	0.26	-	5	19	6	0.35	15	11	61	-	25	18
2008-053	5	20080415	25	0.19	-	4	17	7	0.68	14	26	122	4	24	27
2008-053	5	20080416	27	0.65	-	4	19	9	0.60	16	21	99	8	22	35
2008-053	5	20080417	29	0.29	-	3	20	7	0.57	8	19	98	7	22	24
2008-053	5	20080418	31	0.22	-	4	18	6	0.65	<5	21	118	9	21	29
2008-053	5	20080419	33	0.49	-	<3	15	6	0.75	<5	17	148	9	17	24
2008-053	5	20080420	35	0.44	-	3	18	6	0.69	<5	26	136	16	16	28
2008-053	5	20080421	37	0.39	-	<3	10	6	0.82	<5	33	150	13	11	26
2008-053	5	20080422	39	0.33	-	<3	11	5	0.91	<5	27	176	6	11	26
2008-053	5	20080423	41	0.68	-	<3	12	6	1.01	<5	27	187	10	11	29
2008-053	5	20080424	43	0.20	-	<3	11	5	0.81	<5	27	151	11	10	25
2008-053	5	20080425	45	0.17	-	<3	<10	6	0.88	<5	29	175	12	10	28
2008-053	5	20080426	47	0.65	-	<3	10	8	1.15	<5	27	212	6	13	29
2008-053	5	20080427	49	0.34	-	<3	10	5	0.98	<5	32	172	8	11	28
2008-053	5	20080428	55	0.21	-	<3	<10	5	0.99	<5	28	194	11	9	25
2008-053	5	20080429	60	0.30	-	<3	11	5	0.99	<5	29	198	14	12	27
2008-053	5	20080430	65	0.24	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080431	70	0.23	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080432	75	0.24	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080433	80	0.42	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080434	85	0.44	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080435	90	0.27	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080436	95	0.31	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080437	100	0.32	-	-	-	-	-	<5	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	5	20080438	105	0.37	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080439	110	0.55	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080440	115	0.42	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080441	120	0.67	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080442	125	0.48	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080443	130	0.33	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080444	135	0.30	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080445	140	0.33	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080446	145	0.29	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080447	150	0.28	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080448	155	0.27	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080449	160	0.27	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080450	165	0.25	-	-	-	-	-	<5	-	-	-	-	-
2008-053	5	20080451	170	0.37	-	-	-	-	-	<5	-	-	-	-	-
2008-053	6	20080452	1	2.57	-	-	-	-	-	133	-	-	-	-	-
2008-053	6	20080453	3	2.81	-	-	-	-	-	127	-	-	-	-	-
2008-053	6	20080454	5	2.59	-	-	-	-	-	125	-	-	-	-	-
2008-053	6	20080455	7	2.34	-	-	-	-	-	125	-	-	-	-	-
2008-053	6	20080456	9	2.58	-	-	-	-	-	155	-	-	-	-	-
2008-053	6	20080457	11	2.41	-	-	-	-	-	177	-	-	-	-	-
2008-053	6	20080458	13	2.27	-	-	-	-	-	205	-	-	-	-	-
2008-053	6	20080459	15	2.33	-	-	-	-	-	179	-	-	-	-	-
2008-053	6	20080460	17	2.03	-	-	-	-	-	149	-	-	-	-	-
2008-053	6	20080461	19	2.12	-	-	-	-	-	247	-	-	-	-	-
2008-053	6	20080462	21	1.92	-	-	-	-	-	195	-	-	-	-	-
2008-053	6	20080463	23	2.23	-	-	-	-	-	219	-	-	-	-	-
2008-053	6	20080464	25	2.13	-	-	-	-	-	258	-	-	-	-	-
2008-053	6	20080465	27	2.48	-	-	-	-	-	315	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	6	20080466	29	2.23	-	-	-	-	-	287	-	-	-	-	-
2008-053	6	20080467	31	1.84	-	-	-	-	-	326	-	-	-	-	-
2008-053	6	20080468	33	2.51	-	-	-	-	-	400	-	-	-	-	-
2008-053	6	20080469	35	2.60	-	-	-	-	-	391	-	-	-	-	-
2008-053	6	20080470	37	2.11	-	-	-	-	-	250	-	-	-	-	-
2008-053	6	20080471	39	1.72	-	-	-	-	-	193	-	-	-	-	-
2008-053	6	20080472	41	2.37	-	-	-	-	-	249	-	-	-	-	-
2008-053	6	20080473	43	2.29	-	-	-	-	-	299	-	-	-	-	-
2008-053	6	20080474	45	2.53	-	-	-	-	-	331	-	-	-	-	-
2008-053	6	20080475	47	2.38	-	-	-	-	-	313	-	-	-	-	-
2008-053	6	20080476	49	2.26	-	-	-	-	-	353	-	-	-	-	-
2008-053	6	20080477	55	1.63	-	-	-	-	-	140	-	-	-	-	-
2008-053	6	20080478	60	1.69	-	-	-	-	-	104	-	-	-	-	-
2008-053	6	20080479	65	1.62	-	-	-	-	-	43	-	-	-	-	-
2008-053	6	20080480	70	1.56	-	-	-	-	-	19	-	-	-	-	-
2008-053	6	20080481	75	1.46	-	-	-	-	-	13	-	-	-	-	-
2008-053	6	20080482	80	1.44	-	-	-	-	-	7	-	-	-	-	-
2008-053	6	20080483	85	1.69	-	-	-	-	-	8	-	-	-	-	-
2008-053	6	20080484	90	1.59	-	-	-	-	-	8	-	-	-	-	-
2008-053	6	20080485	95	1.51	-	-	-	-	-	8	-	-	-	-	-
2008-053	6	20080486	100	1.43	-	-	-	-	-	8	-	-	-	-	-
2008-053	6	20080487	110	1.35	-	-	-	-	-	<5	-	-	-	-	-
2008-053	6	20080488	115	1.51	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080489	120	1.56	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080490	130	1.72	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080491	140	1.25	-	-	-	-	-	<5	-	-	-	-	-
2008-053	6	20080492	150	1.74	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080493	160	1.48	-	-	-	-	-	<5	-	-	-	-	-
2008-053	6	20080494	170	1.73	-	-	-	-	-	<5	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	6	20080495	180	1.39	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080496	190	1.84	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080497	200	2.07	-	-	-	-	-	9	-	-	-	-	-
2008-053	6	20080498	210	1.88	-	-	-	-	-	7	-	-	-	-	-
2008-053	6	20080499	220	1.87	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080500	230	1.75	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080501	240	1.84	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080502	250	2.16	-	-	-	-	-	7	-	-	-	-	-
2008-053	6	20080503	260	1.86	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080504	270	1.82	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080505	280	-	-	-	-	-	-	-	-	-	-	-	-
2008-053	6	20080506	290	1.67	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080507	300	1.59	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080508	310	1.80	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080509	320	1.67	-	-	-	-	-	5	-	-	-	-	-
2008-053	6	20080510	330	1.59	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080511	340	1.81	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080512	350	1.60	-	-	-	-	-	6	-	-	-	-	-
2008-053	6	20080513	360	1.53	-	-	-	-	-	8	-	-	-	-	-
2008-053	6	20080514	370	2.00	-	-	-	-	-	7	-	-	-	-	-
2008-053	6	20080515	380	1.97	-	-	-	-	-	9	-	-	-	-	-
2008-053	6	20080516	390	1.81	-	-	-	-	-	7	-	-	-	-	-
2008-053	6	20080517	400	1.58	-	-	-	-	-	7	-	-	-	-	-
2008-053	7	20080518	1	4.30	-	-	-	-	-	794	-	-	-	-	-
2008-053	7	20080519	3	3.95	-	-	-	-	-	971	-	-	-	-	-
2008-053	7	20080520	5	4.27	-	-	-	-	-	889	-	-	-	-	-
2008-053	7	20080521	7	3.50	-	-	-	-	-	790	-	-	-	-	-
2008-053	7	20080522	9	3.09	-	-	-	-	-	556	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	7	20080523	11	3.37	-	-	-	-	-	631	-	-	-	-	-
2008-053	7	20080524	13	3.05	-	-	-	-	-	293	-	-	-	-	-
2008-053	7	20080525	15	3.14	-	-	-	-	-	412	-	-	-	-	-
2008-053	7	20080526	17	3.35	-	-	-	-	-	187	-	-	-	-	-
2008-053	7	20080527	19	3.44	-	-	-	-	-	58	-	-	-	-	-
2008-053	7	20080528	21	3.30	-	-	-	-	-	50	-	-	-	-	-
2008-053	7	20080529	23	3.45	-	-	-	-	-	14	-	-	-	-	-
2008-053	7	20080530	25	3.69	-	-	-	-	-	14	-	-	-	-	-
2008-053	7	20080531	27	3.76	-	-	-	-	-	29	-	-	-	-	-
2008-053	7	20080532	29	4.24	-	-	-	-	-	40	-	-	-	-	-
2008-053	7	20080533	31	4.38	-	-	-	-	-	32	-	-	-	-	-
2008-053	7	20080534	33	3.95	-	-	-	-	-	31	-	-	-	-	-
2008-053	7	20080535	35	4.39	-	-	-	-	-	18	-	-	-	-	-
2008-053	7	20080536	37	4.29	-	-	-	-	-	21	-	-	-	-	-
2008-053	7	20080537	39	4.38	-	-	-	-	-	22	-	-	-	-	-
2008-053	7	20080538	41	4.37	-	-	-	-	-	17	-	-	-	-	-
2008-053	7	20080539	43	4.43	-	-	-	-	-	15	-	-	-	-	-
2008-053	7	20080540	45	3.90	-	-	-	-	-	13	-	-	-	-	-
2008-053	7	20080541	47	3.81	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080542	49	3.81	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080543	55	3.61	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080544	60	3.77	-	-	-	-	-	10	-	-	-	-	-
2008-053	7	20080545	65	2.37	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080546	70	3.36	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080547	75	3.21	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080548	80	3.47	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080549	85	3.35	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080550	90	3.28	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080551	95	3.09	-	-	-	-	-	9	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	7	20080552	100	3.07	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080553	110	2.99	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080554	120	3.00	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080555	130	3.09	-	-	-	-	-	7	-	-	-	-	-
2008-053	7	20080556	140	3.30	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080557	150	3.57	-	-	-	-	-	7	-	-	-	-	-
2008-053	7	20080558	160	3.40	-	-	-	-	-	7	-	-	-	-	-
2008-053	7	20080559	170	3.00	-	-	-	-	-	7	-	-	-	-	-
2008-053	7	20080560	180	3.24	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080561	190	3.08	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080562	200	3.22	-	-	-	-	-	10	-	-	-	-	-
2008-053	7	20080563	210	3.27	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080564	220	3.13	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080565	230	3.27	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080566	240	3.03	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080567	250	3.48	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080568	260	3.12	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080569	270	2.87	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080570	280	2.81	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080571	290	2.90	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080572	300	2.71	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080573	310	2.69	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080574	320	2.74	-	-	-	-	-	8	-	-	-	-	-
2008-053	7	20080575	330	2.50	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080576	340	2.44	-	-	-	-	-	9	-	-	-	-	-
2008-053	7	20080577	350	2.24	-	-	-	-	-	10	-	-	-	-	-
2008-053	7	20080578	360	2.34	-	-	-	-	-	10	-	-	-	-	-
2008-053	7	20080579	370	2.57	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080580	380	2.73	-	-	-	-	-	11	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	7	20080581	390	2.55	-	-	-	-	-	11	-	-	-	-	-
2008-053	7	20080582	400	2.74	-	-	-	-	-	12	-	-	-	-	-
2008-053	8	20080583	1	4.66	-	10	46	133	3.42	1829	38	369	35	155	250
2008-053	8	20080584	3	4.79	-	12	42	113	3.65	880	37	383	32	151	257
2008-053	8	20080585	5	4.44	-	14	47	112	3.61	1199	41	390	34	181	271
2008-053	8	20080586	7	4.36	-	14	41	113	3.81	1021	41	422	35	210	269
2008-053	8	20080587	9	4.22	-	14	42	112	3.59	1009	41	411	35	198	271
2008-053	8	20080588	11	5.29	-	13	39	116	4.71	2360	42	350	26	-	401
2008-053	8	20080589	13	5.95	-	12	51	129	4.08	2485	35	476	36	262	273
2008-053	8	20080590	15	5.57	-	12	48	-	4.02	1953	-	440	35	282	284
2008-053	8	20080591	17	6.27	-	13	49	107	3.94	2242	34	418	30	274	285
2008-053	8	20080592	19	7.40	-	13	48	146	3.86	2757	37	395	36	300	307
2008-053	8	20080593	21	6.48	-	13	48	119	3.94	2472	41	399	35	337	307
2008-053	8	20080594	23	6.35	-	12	40	103	4.19	1961	41	408	33	289	274
2008-053	8	20080595	25	5.73	-	13	32	92	4.41	1930	34	358	28	270	232
2008-053	8	20080596	27	5.57	-	10	28	110	4.04	2005	35	416	27	274	233
2008-053	8	20080597	29	5.18	-	12	32	101	3.32	1789	33	355	21	337	280
2008-053	8	20080598	31	5.52	-	11	31	101	3.24	2259	35	359	27	395	261
2008-053	8	20080599	33	5.51	-	12	32	100	3.46	2001	38	385	28	350	264
2008-053	8	20080600	35	7.05	-	11	31	94	3.51	2305	37	374	29	340	309
2008-053	8	20080601	37	9.07	-	12	32	111	3.52	3273	36	369	31	364	272
2008-053	8	20080602	39	6.07	-	10	26	81	3.37	2420	44	395	28	381	204
2008-053	8	20080603	41	6.86	-	11	31	75	3.94	2337	42	431	26	-	210
2008-053	8	20080604	43	5.72	-	10	31	85	3.51	2441	41	390	47	303	234
2008-053	8	20080605	45	5.51	-	12	33	70	3.37	2167	46	397	26	398	271
2008-053	8	20080606	47	6.65	-	9	32	56	3.23	1911	35	370	16	287	202
2008-053	8	20080607	49	6.29	-	10	29	58	3.20	2508	41	380	18	253	187
2008-053	8	20080608	55	6.54	-	9	27	52	3.77	2394	22	446	14	180	144

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	8	20080609	60	3.92	-	11	31	36	2.99	1179	27	383	18	266	135
2008-053	8	20080610	65	4.59	-	10	33	44	3.44	885	38	397	23	249	130
2008-053	8	20080611	70	4.08	-	9	29	26	2.88	499	27	363	16	170	91
2008-053	8	20080612	75	3.82	-	10	30	17	4.70	460	22	774	-	116	72
2008-053	8	20080613	80	4.09	-	8	42	23	2.79	460	28	379	-	80	81
2008-053	8	20080614	85	3.66	-	8	31	21	2.80	277	29	408	15	104	69
2008-053	8	20080615	90	3.61	-	10	33	22	4.09	535	30	456	15	-	75
2008-053	8	20080616	95	3.89	-	8	29	25	2.84	305	37	424	17	122	81
2008-053	8	20080617	100	3.50	-	8	29	13	2.87	414	22	409	11	53	69
2008-053	8	20080618	110	3.72	-	7	29	15	2.95	156	28	418	11	47	78
2008-053	8	20080619	120	3.49	-	8	29	13	2.79	95	28	412	9	29	70
2008-053	8	20080620	130	3.52	-	8	30	14	2.88	12	29	416	13	21	70
2008-053	8	20080621	140	3.18	-	7	30	17	2.52	11	32	360	17	21	67
2008-053	8	20080622	150	3.18	-	8	28	10	2.64	13	24	373	11	21	70
2008-053	8	20080623	160	3.09	-	10	26	20	2.70	14	38	381	25	21	72
2008-053	8	20080624	170	3.17	-	9	29	22	2.80	10	41	393	25	22	73
2008-053	8	20080625	180	3.14	-	8	28	15	2.66	10	33	395	24	21	74
2008-053	8	20080626	190	3.04	-	8	30	13	2.56	12	27	357	13	25	72
2008-053	8	20080627	200	3.00	-	7	25	12	2.73	9	28	394	-	22	72
2008-053	8	20080628	210	3.17	-	9	36	21	3.99	10	36	511	26	11	66
2008-053	8	20080629	220	2.85	-	10	32	20	4.07	9	36	506	24	11	65
2008-053	8	20080630	230	2.97	-	10	-	20	-	9	36	-	23	2	65
2008-053	8	20080631	240	2.81	-	10	31	21	4.01	9	36	506	25	12	67
2008-053	8	20080632	250	2.99	-	10	33	21	4.24	10	36	526	26	12	66
2008-053	8	20080633	260	3.16	-	10	32	21	4.02	10	36	497	24	11	67
2008-053	8	20080634	270	3.01	-	11	32	20	3.93	10	36	535	25	11	66
2008-053	8	20080635	280	3.03	-	10	33	20	4.12	10	36	514	24	11	66
2008-053	8	20080636	290	2.85	-	11	34	19	3.95	12	38	543	27	11	66
2008-053	8	20080637	300	2.58	-	11	33	19	4.36	10	40	506	27	12	70

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	8	20080638	310	2.51	-	11	31	19	4.30	9	39	538	29	12	70
2008-053	8	20080639	320	2.53	-	11	33	20	3.96	10	39	511	27	13	70
2008-053	8	20080640	330	2.48	-	10	-	18	-	11	38	-	27	4	66
2008-053	8	20080641	340	2.26	-	10	34	19	4.32	11	38	496	20	18	66
2008-053	8	20080642	350	2.18	-	10	33	21	4.06	10	32	490	20	17	108
2008-053	8	20080643	360	1.55	-	8	24	17	3.80	8	42	455	18	13	109
2008-053	9	20080644	1	6.53	-	-	-	-	-	2449	-	-	-	-	-
2008-053	9	20080645	3	6.89	-	-	-	-	-	2365	-	-	-	-	-
2008-053	9	20080646	5	9.53	-	-	-	-	-	3739	-	-	-	-	-
2008-053	9	20080647	7	7.81	-	-	-	-	-	2377	-	-	-	-	-
2008-053	9	20080648	9	6.96	-	-	-	-	-	2498	-	-	-	-	-
2008-053	9	20080649	11	6.63	-	-	-	-	-	2089	-	-	-	-	-
2008-053	9	20080650	13	7.33	-	-	-	-	-	1812	-	-	-	-	-
2008-053	9	20080651	15	6.66	-	-	-	-	-	1451	-	-	-	-	-
2008-053	9	20080652	17	7.41	-	-	-	-	-	1277	-	-	-	-	-
2008-053	9	20080653	19	5.27	-	-	-	-	-	960	-	-	-	-	-
2008-053	9	20080654	21	5.60	-	-	-	-	-	908	-	-	-	-	-
2008-053	9	20080655	23	5.03	-	-	-	-	-	942	-	-	-	-	-
2008-053	9	20080656	25	6.66	-	-	-	-	-	1087	-	-	-	-	-
2008-053	9	20080657	27	6.31	-	-	-	-	-	116	-	-	-	-	-
2008-053	9	20080658	29	6.33	-	-	-	-	-	39	-	-	-	-	-
2008-053	9	20080659	31	6.57	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080660	33	6.49	-	-	-	-	-	26	-	-	-	-	-
2008-053	9	20080661	35	6.35	-	-	-	-	-	25	-	-	-	-	-
2008-053	9	20080662	37	4.63	-	-	-	-	-	18	-	-	-	-	-
2008-053	9	20080663	39	5.29	-	-	-	-	-	19	-	-	-	-	-
2008-053	9	20080664	41	6.05	-	-	-	-	-	42	-	-	-	-	-
2008-053	9	20080665	43	5.79	-	-	-	-	-	43	-	-	-	-	-

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2008-053	9	20080666	45	6.16	-	-	-	-	-	36	-	-	-	-	-
2008-053	9	20080667	47	6.29	-	-	-	-	-	24	-	-	-	-	-
2008-053	9	20080668	49	6.33	-	-	-	-	-	21	-	-	-	-	-
2008-053	9	20080669	55	6.46	-	-	-	-	-	39	-	-	-	-	-
2008-053	9	20080670	60	6.84	-	-	-	-	-	31	-	-	-	-	-
2008-053	9	20080671	65	6.84	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080672	70	7.36	-	-	-	-	-	23	-	-	-	-	-
2008-053	9	20080673	75	7.96	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080674	80	7.68	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080675	85	7.77	-	-	-	-	-	13	-	-	-	-	-
2008-053	9	20080676	90	7.51	-	-	-	-	-	13	-	-	-	-	-
2008-053	9	20080677	95	7.49	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080678	100	7.24	-	-	-	-	-	16	-	-	-	-	-
2008-053	9	20080679	110	6.69	-	-	-	-	-	14	-	-	-	-	-
2008-053	9	20080680	120	7.28	-	-	-	-	-	17	-	-	-	-	-
2008-053	9	20080681	130	5.74	-	-	-	-	-	17	-	-	-	-	-
2008-053	9	20080682	140	7.27	-	-	-	-	-	17	-	-	-	-	-
2008-053	9	20080683	150	6.95	-	-	-	-	-	30	-	-	-	-	-
2008-053	9	20080684	160	5.79	-	-	-	-	-	22	-	-	-	-	-
2008-053	9	20080685	170	6.42	-	-	-	-	-	18	-	-	-	-	-
2008-053	9	20080686	180	7.08	-	-	-	-	-	21	-	-	-	-	-
2008-053	9	20080687	190	7.97	-	-	-	-	-	20	-	-	-	-	-
2008-053	9	20080688	200	7.74	-	-	-	-	-	20	-	-	-	-	-
2008-053	9	20080689	210	6.26	-	-	-	-	-	21	-	-	-	-	-
2008-053	9	20080690	220	5.84	-	-	-	-	-	21	-	-	-	-	-
2009-060	1	20090061	0.5	6.49	-	10	39	68	3.06	431	38	346	-	99	231
2009-060	1	20090062	1.5	4.64	-	11	29	58	2.69	503	32	330	-	92	193
2009-060	1	20090063	2.5	6.14	-	11	38	71	3.47	576	41	407	29	115	236

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	1	20090064	3.5	6.04	-	11	38	72	3.37	593	38	404	30	120	245
2009-060	1	20090065	4.5	6.35	-	12	53	96	3.38	665	38	413	29	124	269
2009-060	1	20090066	5.5	6.37	-	12	47	84	2.92	711	36	366	28	118	309
2009-060	1	20090067	6.5	6.42	-	11	42	82	3.36	823	38	403	31	123	311
2009-060	1	20090068	7.5	5.83	-	12	47	96	2.80	903	37	383	32	130	319
2009-060	1	20090069	8.5	3.97	-	14	45	82	1.89	748	35	307	52	117	261
2009-060	1	20090070	9.5	4.50	-	13	47	85	2.63	808	39	356	-	128	264
2009-060	1	20090071	10.5	4.27	-	12	50	74	3.25	786	50	474	34	148	291
2009-060	1	20090072	11.5	4.32	-	13	42	84	2.98	641	47	495	33	147	271
2009-060	1	20090073	12.5	3.32	-	12	40	64	2.67	533	46	454	34	147	260
2009-060	1	20090074	13.5	3.61	-	12	48	86	2.71	604	47	466	33	99	250
2009-060	1	20090075	14.5	2.97	-	12	34	71	2.43	523	42	407	30	87	210
2009-060	1	20090076	15.5	3.85	-	11	40	74	2.45	788	45	445	35	103	246
2009-060	1	20090077	16.5	4.66	-	11	42	73	2.78	850	44	459	32	112	234
2009-060	1	20090078	17.5	5.23	-	12	46	74	2.69	944	42	442	29	118	214
2009-060	1	20090079	18.5	6.66	-	12	45	48	2.63	1075	37	415	30	126	215
2009-060	1	20090080	19.5	4.82	-	12	38	53	2.01	807	35	303	-	94	157
2009-060	1	20090081	20.5	5.92	-	11	46	35	2.46	866	36	342	26	100	156
2009-060	1	20090082	21.5	5.53	-	12	46	51	2.14	720	39	335	24	95	136
2009-060	1	20090083	22.5	5.76	-	13	36	27	2.06	704	38	379	24	84	122
2009-060	1	20090084	23.5	5.84	-	12	34	25	1.59	480	35	343	26	63	108
2009-060	1	20090085	24.5	5.44	-	11	35	23	1.98	308	37	377	25	46	88
2009-060	2	20090087	0.5	7.59	-	14	42	114	1.94	740	39	375	28	63	350
2009-060	2	20090088	1.5	6.37	-	13	35	115	1.99	1270	35	335	29	58	343
2009-060	2	20090089	2.5	7.78	-	15	41	146	2.24	1175	39	356	31	65	399
2009-060	2	20090090	3.5	9.08	-	14	40	160	1.67	1603	34	297	27	58	432
2009-060	2	20090091	4.5	10.08	-	14	45	179	1.66	1606	31	304	32	62	459
2009-060	2	20090092	5.5	10.54	-	14	42	146	1.94	1820	30	285	30	58	424

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	2	20090093	6.5	9.57	-	15	46	134	1.99	1627	28	284	30	81	364
2009-060	2	20090094	7.5	11.80	-	12	41	208	1.57	4956	22	219	-	71	454
2009-060	2	20090095	8.5	6.13	-	17	46	115	1.87	1682	43	411	38	118	393
2009-060	2	20090096	9.5	4.95	-	17	43	103	2.26	976	45	447	36	123	361
2009-060	2	20090097	10.5	4.69	-	17	44	87	2.29	833	50	464	34	131	367
2009-060	2	20090098	11.5	5.23	-	17	43	79	2.26	760	46	464	36	132	326
2009-060	2	20090099	12.5	5.02	-	18	41	73	2.18	899	48	466	70	131	290
2009-060	2	20090100	13.5	4.91	-	17	39	69	2.31	774	47	441	32	126	270
2009-060	2	20090101	14.5	4.84	-	17	44	59	2.16	956	46	448	35	131	242
2009-060	2	20090102	15.5	5.66	-	16	39	59	3.71	840	49	435	32	127	239
2009-060	2	20090103	16.5	5.86	-	15	40	52	3.62	843	43	433	34	133	230
2009-060	2	20090104	17.5	6.53	-	18	41	54	3.82	894	46	468	34	146	232
2009-060	2	20090105	18.5	7.88	-	18	40	54	3.67	1039	45	446	29	159	245
2009-060	2	20090106	19.5	8.54	-	10	47	47	2.92	1147	39	367	29	159	218
2009-060	2	20090107	20.5	8.59	-	11	46	53	2.74	1086	40	371	26	150	188
2009-060	2	20090108	21.5	7.71	-	10	39	31	2.68	742	39	334	23	121	135
2009-060	2	20090109	22.5	7.49	-	9	46	29	2.71	595	44	371	24	100	116
2009-060	8	20090111	0.5	5.55	-	9	33	72	3.52	675	35	412	25	90	153
2009-060	8	20090112	1.5	5.66	-	9	32	68	2.63	875	32	299	26	88	144
2009-060	8	20090113	2.5	5.63	-	9	36	67	2.64	791	31	274	27	104	142
2009-060	8	20090114	3.5	5.02	-	9	32	85	2.82	697	34	314	26	62	156
2009-060	8	20090115	4.5	4.64	-	10	31	77	2.84	768	32	307	25	54	162
2009-060	8	20090116	5.5	3.82	-	8	25	85	2.39	543	28	250	23	37	126
2009-060	8	20090117	6.5	5.28	-	10	28	76	2.53	729	29	271	28	42	138
2009-060	8	20090118	7.5	5.71	-	9	26	76	2.79	1457	34	302	30	44	165
2009-060	8	20090119	8.5	5.32	-	9	21	95	2.65	711	31	289	27	41	151
2009-060	8	20090120	9.5	5.33	-	9	18	99	2.83	707	33	314	27	43	156
2009-060	8	20090121	10.5	5.51	-	9	14	64	2.56	726	33	280	27	37	137

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	8	20090122	11.5	5.17	-	9	15	81	3.13	789	36	351	28	24	163
2009-060	8	20090123	12.5	5.33	-	9	14	78	2.99	959	35	327	27	56	169
2009-060	8	20090124	13.5	5.26	-	9	14	80	3.05	1099	34	331	28	52	179
2009-060	8	20090125	14.5	4.87	-	10	11	82	3.49	1013	36	366	29	43	185
2009-060	8	20090126	15.5	4.80	-	9	11	81	3.27	1137	35	342	28	36	179
2009-060	8	20090127	16.5	4.72	-	10	11	94	3.08	1709	39	349	29	29	187
2009-060	8	20090128	17.5	4.71	-	10	10	68	3.21	1158	36	349	27	21	188
2009-060	8	20090129	18.5	4.82	-	9	<10	168	3.32	2031	36	353	27	27	194
2009-060	8	20090130	19.5	4.31	-	9	11	63	3.22	1086	39	349	27	19	173
2009-060	8	20090131	20.5	4.27	-	9	15	56	3.01	1058	37	333	26	24	162
2009-060	8	20090132	21.5	4.48	-	8	14	57	2.96	1014	37	332	27	29	166
2009-060	8	20090133	22.5	4.47	-	9	13	55	2.73	950	34	303	27	24	157
2009-060	8	20090134	23.5	3.82	-	9	12	45	2.69	777	39	304	28	28	136
2009-060	8	20090135	24.5	3.73	-	10	10	45	3.08	648	41	352	28	25	133
2009-060	8	20090136	25.5	3.78	-	7	13	40	2.67	629	36	315	27	23	117
2009-060	8	20090137	26.5	3.55	-	8	12	35	2.61	555	38	296	26	22	107
2009-060	8	20090138	27.5	3.71	-	8	11	38	2.48	598	37	274	26	21	108
2009-060	8	20090139	28.5	3.07	-	6	<10	29	2.81	467	32	323	25	23	86
2009-060	8	20090140	29.5	2.87	-	7	12	26	2.48	343	36	308	24	19	80
2009-060	8	20090141	30.5	2.88	-	7	14	26	2.91	290	36	331	25	23	83
2009-060	8	20090142	31.5	2.75	-	6	14	25	2.68	221	37	331	23	21	72
2009-060	8	20090143	32.5	3.12	-	7	13	27	2.77	262	35	346	24	23	83
2009-060	8	20090144	33.5	3.25	-	7	12	23	2.72	125	32	348	26	25	74
2009-060	8	20090145	34.5	3.19	-	8	15	22	2.79	59	37	349	26	18	67
2009-060	9	20090031	0.5	6.32	-	10	26	37	3.33	220	36	409	34	61	146
2009-060	9	20090032	1.5	6.56	-	10	22	115	2.76	300	34	417	40	89	141
2009-060	9	20090033	2.5	5.49	-	10	22	41	3.26	255	36	433	42	101	139
2009-060	9	20090034	3.5	4.52	-	11	25	70	3.20	418	39	453	45	115	151

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	9	20090035	4.5	3.99	-	11	22	86	3.34	673	37	462	52	133	156
2009-060	9	20090036	5.5	4.08	-	12	29	103	3.01	443	35	435	55	178	169
2009-060	9	20090037	6.5	3.74	-	12	22	90	3.18	534	46	461	49	79	153
2009-060	9	20090038	7.5	3.71	-	11	23	79	2.88	595	37	441	57	151	152
2009-060	9	20090039	8.5	3.74	-	13	24	83	3.34	733	37	482	57	129	149
2009-060	9	20090040	9.5	4.10	-	13	24	60	3.37	861	43	481	52	415	253
2009-060	9	20090041	10.5	4.54	-	12	22	83	3.25	575	36	458	45	133	150
2009-060	9	20090042	11.5	4.00	-	13	22	97	3.40	770	39	476	53	139	175
2009-060	9	20090043	12.5	5.31	-	12	22	116	3.07	550	36	462	48	91	163
2009-060	9	20090044	13.5	4.65	-	10	23	52	3.28	686	37	421	42	69	122
2009-060	9	20090045	14.5	4.04	-	10	20	37	3.78	600	44	480	22	86	134
2009-060	9	20090046	15.5	4.58	-	11	22	49	3.20	567	41	452	27	70	125
2009-060	9	20090047	16.5	4.49	-	10	20	23	3.03	626	38	435	33	17	69
2009-060	9	20090048	17.5	4.68	-	10	21	23	2.98	558	40	451	23	18	74
2009-060	9	20090049	18.5	5.04	-	10	22	24	2.88	675	41	466	33	18	80
2009-060	9	20090050	19.5	5.28	-	10	23	27	2.88	544	39	473	27	19	83
2009-060	9	20090051	20.5	4.59	-	10	21	25	3.11	577	38	474	33	19	90
2009-060	9	20090052	21.5	4.79	-	9	21	23	2.96	457	38	452	34	19	78
2009-060	9	20090053	22.5	3.37	-	10	17	23	3.07	378	38	451	35	19	75
2009-060	9	20090054	23.5	3.79	-	11	18	26	3.22	402	43	496	37	19	83
2009-060	9	20090055	24.5	5.05	-	10	20	24	3.06	637	41	456	43	20	79
2009-060	9	20090056	25.5	5.30	-	10	19	23	2.89	555	38	444	38	20	74
2009-060	9	20090057	26.5	6.42	-	11	22	22	3.01	615	41	474	45	19	77
2009-060	9	20090058	27.5	7.36	-	11	20	25	3.42	874	42	498	41	20	91
2009-060	9	20090059	28.5	4.29	-	11	19	22	3.22	652	44	496	37	18	77
2009-060	9	20090060	29.5	4.15	-	11	17	23	3.27	863	42	490	39	20	81
2009-060	5	20090147	0.5	5.23	-	13	32	71	3.80	885	41	431	28	139	226
2009-060	5	20090148	1.5	5.02	-	13	32	76	3.83	800	42	433	29	143	244

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	5	20090149	2.5	5.78	-	13	33	73	3.81	921	42	461	29	155	252
2009-060	5	20090150	3.5	5.50	-	8	20	47	2.11	769	30	511	19	95	152
2009-060	5	20090151	4.5	6.31	-	13	35	75	4.01	988	41	442	31	152	263
2009-060	5	20090152	5.5	5.67	-	9	22	49	2.56	714	33	422	20	102	163
2009-060	5	20090153	6.5	6.14	-	8	23	50	2.33	1022	32	381	20	94	159
2009-060	5	20090154	7.5	5.66	-	12	32	63	3.56	756	39	366	23	136	210
2009-060	5	20090155	8.5	6.08	-	11	31	65	3.42	769	39	354	27	118	215
2009-060	5	20090156	9.5	6.39	-	10	32	54	3.21	710	39	375	24	124	179
2009-060	5	20090157	10.5	5.72	-	10	27	54	2.64	677	35	326	21	96	177
2009-060	5	20090158	11.5	5.73	-	10	28	39	2.70	587	37	358	23	99	129
2009-060	5	20090159	12.5	6.50	-	9	27	41	2.59	503	35	332	22	81	129
2009-060	5	20090160	13.5	5.54	-	9	25	30	2.37	464	33	344	22	52	90
2009-060	5	20090161	14.5	6.17	-	9	29	33	2.60	305	35	342	23	61	99
2009-060	5	20090162	15.5	6.03	-	6	17	17	1.28	258	24	362	15	31	57
2009-060	5	20090163	16.5	6.73	-	7	23	20	1.42	139	29	345	19	34	66
2009-060	5	20090164	17.5	5.89	-	8	29	22	2.25	57	33	308	26	24	74
2009-060	5	20090165	18.5	6.88	-	6	17	12	1.04	22	21	311	14	13	41
2009-060	5	20090166	19.5	7.32	-	8	28	20	2.02	22	30	310	23	17	65
2009-060	5	20090167	20.5	7.25	-	8	27	23	1.99	80	29	253	23	25	76
2009-060	5	20090168	21.5	7.37	-	8	29	20	2.02	20	28	291	21	17	66
2009-060	5	20090169	22.5	7.58	-	8	39	26	2.69	24	35	277	27	19	81
2009-060	5	20090170	23.5	6.72	-	8	34	23	2.31	18	33	230	24	17	74
2009-060	5	20090171	24.5	7.20	-	7	30	21	2.06	21	30	290	20	16	69
2009-060	5	20090172	25.5	6.33	-	8	33	22	2.23	18	32	297	24	18	73
2009-060	5	20090173	26.5	6.85	-	6	24	15	1.43	21	25	275	17	14	53
2009-060	5	20090174	27.5	7.11	-	7	30	19	1.81	20	29	288	19	16	64
2009-060	5	20090175	28.5	6.17	-	6	26	17	1.63	29	25	299	15	16	59
2009-060	5	20090176	29.5	7.91	-	3	15	8	0.77	22	17	287	9	10	32
2009-060	5	20090177	30.5	7.27	-	4	18	13	0.94	190	19	274	9	20	47

Table B.2 Sediment core geochemical data (cont'd)

Cruise	Stn No	Lab ID	Sed. depth (cm)	Organic carbon (wt. %)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Fe (wt. %)	Hg (ppb)	Li (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
2009-060	5	20090178	31.5	5.85	-	4	19	14	1.07	140	20	291	12	18	49

Table B.3 Correlation coefficients (r) between inorganic contaminants and organic carbon in sediment core bottoms. Sample size for each analyte is in brackets. Coefficients in italics are significant at $p \leq 0.05$.

	Organic carbon (wt. %) (94)	Cd (ppm) (63)	Co (ppm) (86)	Cr (ppm) (84)	Cu (ppm) (86)	Fe (wt. %) (92)	Hg (ppb) (94)	Li (ppm) (86)	Mn (ppm) (92)	Ni (ppm) (86)	Pb (ppm) (91)	Zn (ppm) (94)
Organic carbon (wt. %) (94)	*1.00*											
Cd (ppm) (63)	-0.16	*1.00*										
Co (ppm) (86)	0.14	0.10	*1.00*									
Cr (ppm) (84)	*0.40*	0.02	*0.44*	1.00								
Cu (ppm) (86)	*-0.62*	-0.04	*0.29*	*0.40*	*1.00*							
Fe (wt. %) (92)	*-0.41*	-0.04	*0.52*	*0.71*	*0.68*	*1.00*						
Hg (ppb) (94)	0.12	-0.12	0.02	-0.05	*0.42*	-0.05	*1.00*					
Li (ppm) (86)	*-0.32*	-0.03	*0.55*	*0.74*	*0.62*	*0.94*	-0.03	*1.00*				
Mn (ppm) (92)	*-0.62*	-0.02	*0.54*	*0.60*	*0.77*	*0.91*	-0.01	*0.85*	*1.00*			
Ni (ppm) (86)	*-0.24*	0.25	*0.24*	*0.49*	*0.45*	*0.45*	0.05	*0.50*	*0.46*	*1.00*		
Pb (ppm) (91)	*0.32*	-0.12	-0.09	-0.07	*0.36*	-0.17	*0.89*	-0.17	-0.18	-0.03	*1.00*	
Zn (ppm) (94)	*-0.30*	-0.18	0.09	*0.41*	*0.74*	*0.51*	*0.29*	*0.51*	*0.52*	*0.39*	*0.33*	*1.00*

Table B.4 Correlation coefficients (r) between inorganic contaminants and organic carbon in the top 10 cm of sediment cores and grab samples. Sample size for each analyte is in brackets. Coefficients in italics are significant at $p \leq 0.05$.

	Organic carbon (wt. %) (143)	Cd (ppm) (48)	Co (ppm) (142)	Cr (ppm) (142)	Cu (ppm) (132)	Fe (wt. %) (142)	Hg (ppb) (142)	Li (ppm) (132)	Mn (ppm) (142)	Ni (ppm) (121)	Pb (ppm) (143)	Zn (ppm) (137)
Organic carbon (wt. %) (143)	*1.00*											
Cd (ppm) (48)	*0.75*	*1.00*										
Co (ppm) (142)	*0.53*	*0.52*	*1.00*									
Cr (ppm) (142)	*0.63*	*0.64*	*0.51*	*1.00*								
Cu (ppm) (132)	*0.73*	*0.87*	*0.40*	*0.61*	*1.00*							
Fe (wt. %) (142)	*0.33*	*0.33*	*0.50*	*0.44*	0.14	*1.00*						
Hg (ppb) (142)	*0.63*	*0.39*	*0.34*	*0.49*	*0.63*	*0.24*	*1.00*					
Li (ppm) (132)	*0.21*	0.28	*0.57*	*0.32*	0.13	*0.48*	0.05	*1.00*				
Mn (ppm) (142)	*0.18*	0.12	*0.59*	*0.22*	-0.08	*0.77*	0.04	*0.48*	*1.00*			
Ni (ppm) (121)	*0.49*	*0.65*	*0.63*	*0.39*	*0.46*	*0.50*	*0.30*	*0.41*	*0.57*	*1.00*		
Pb (ppm) (143)	0.15	*0.43*	*0.19*	*0.24*	*0.36*	*0.28*	*0.39*	0.11	0.17	*0.46*	*1.00*	
Zn (ppm) (137)	*0.48*	*0.72*	*0.22*	*0.52*	*0.68*	0.04	*0.30*	0.10	-0.06	*0.31*	0.13	*1.00*

APPENDIX C: GEOCHEMICAL SEDIMENT GRAB SAMPLE PLOTS AND MAPS

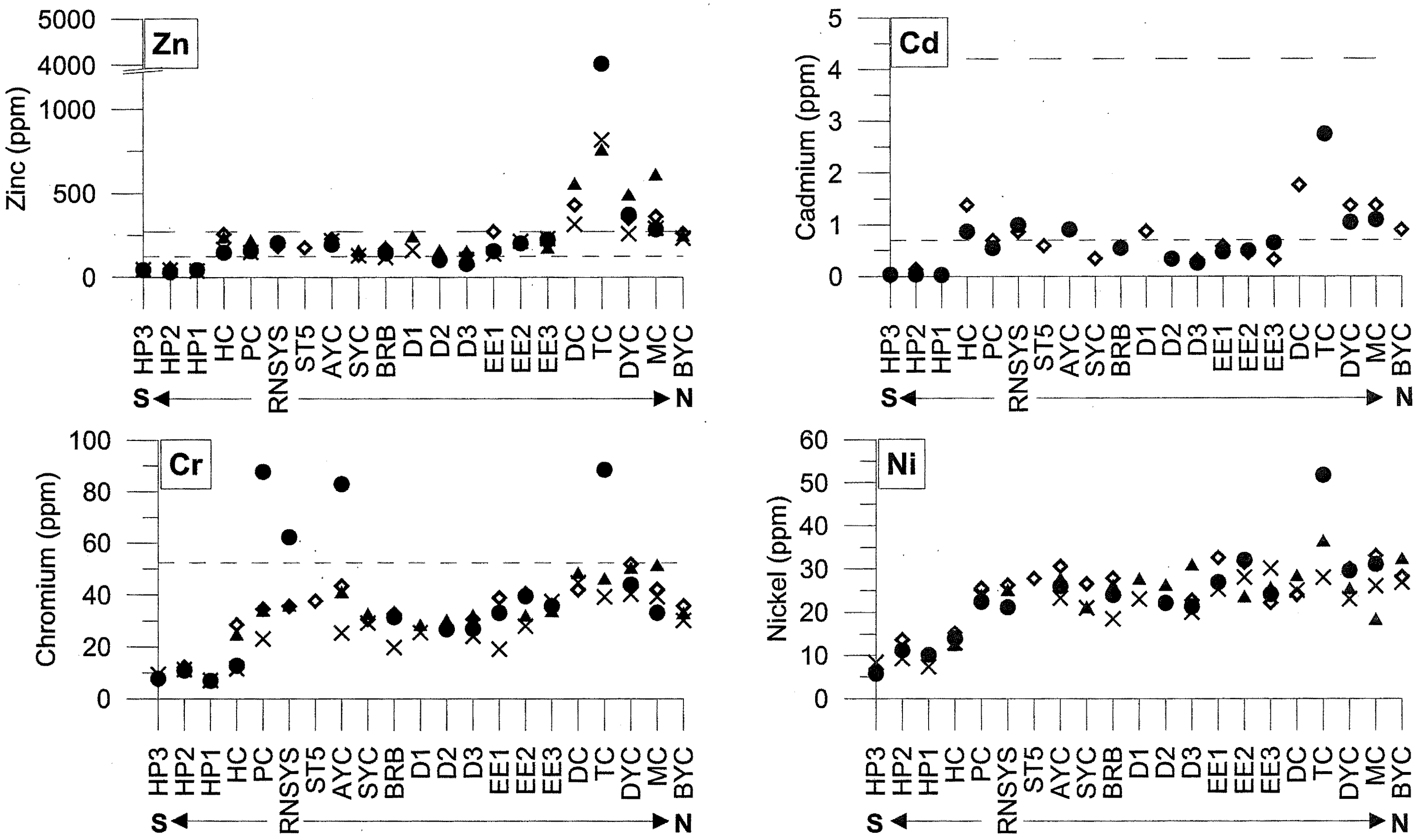

Figure C.1 Geochemical plots of sediment grab samples. Grab samples were collected at four different times over a 15 month period (● March 2008, ◇ July 2008, ▲ October 2008, × April 2009) and are arranged from south to north (Figure 3.6). The short dashed line represents the ISQG (CCME 2002), while the longer dashed line represents the PEL (CCME 2002).

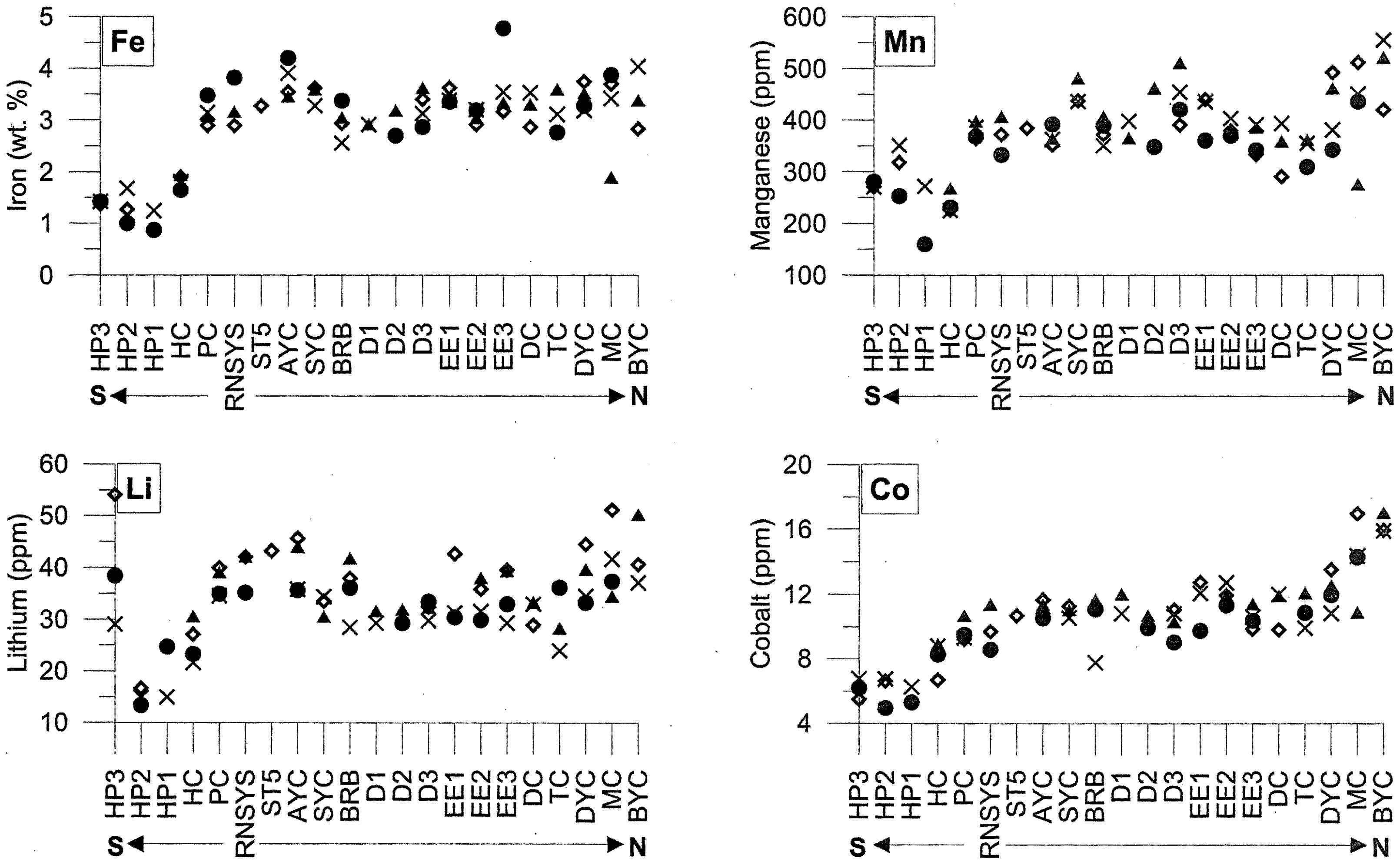

Figure C.2 Geochemical plots of sediment grab samples. Grab samples were collected at four different times over a 15 month period (● March 2008, ◇ July 2008, ▲ October 2008, × April 2009) and are arranged from south to north (Figure 3.6).

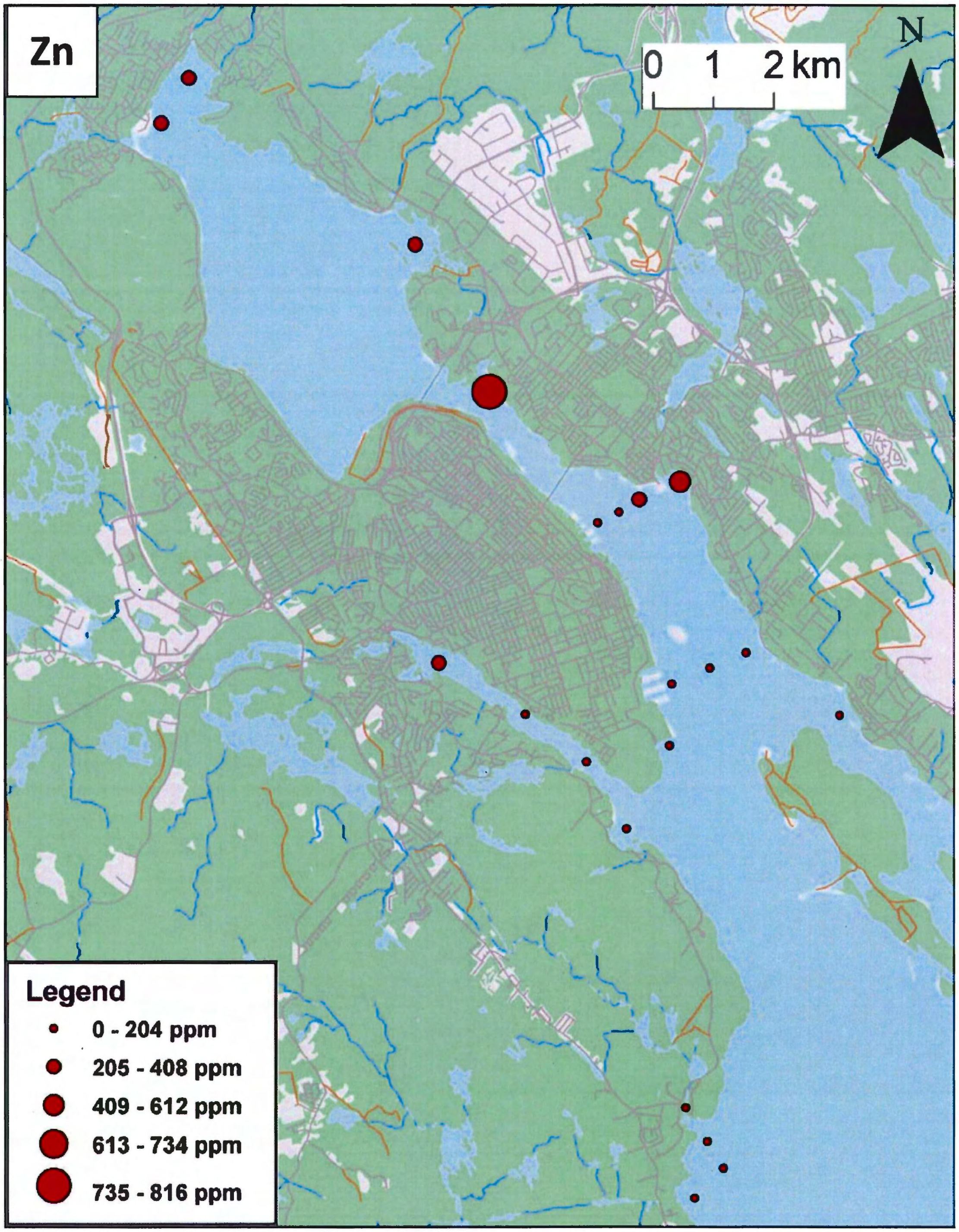

Figure C.3 Proportional dot size map of median zinc concentrations (ppm) in sediment grab samples collected during all four sampling events.

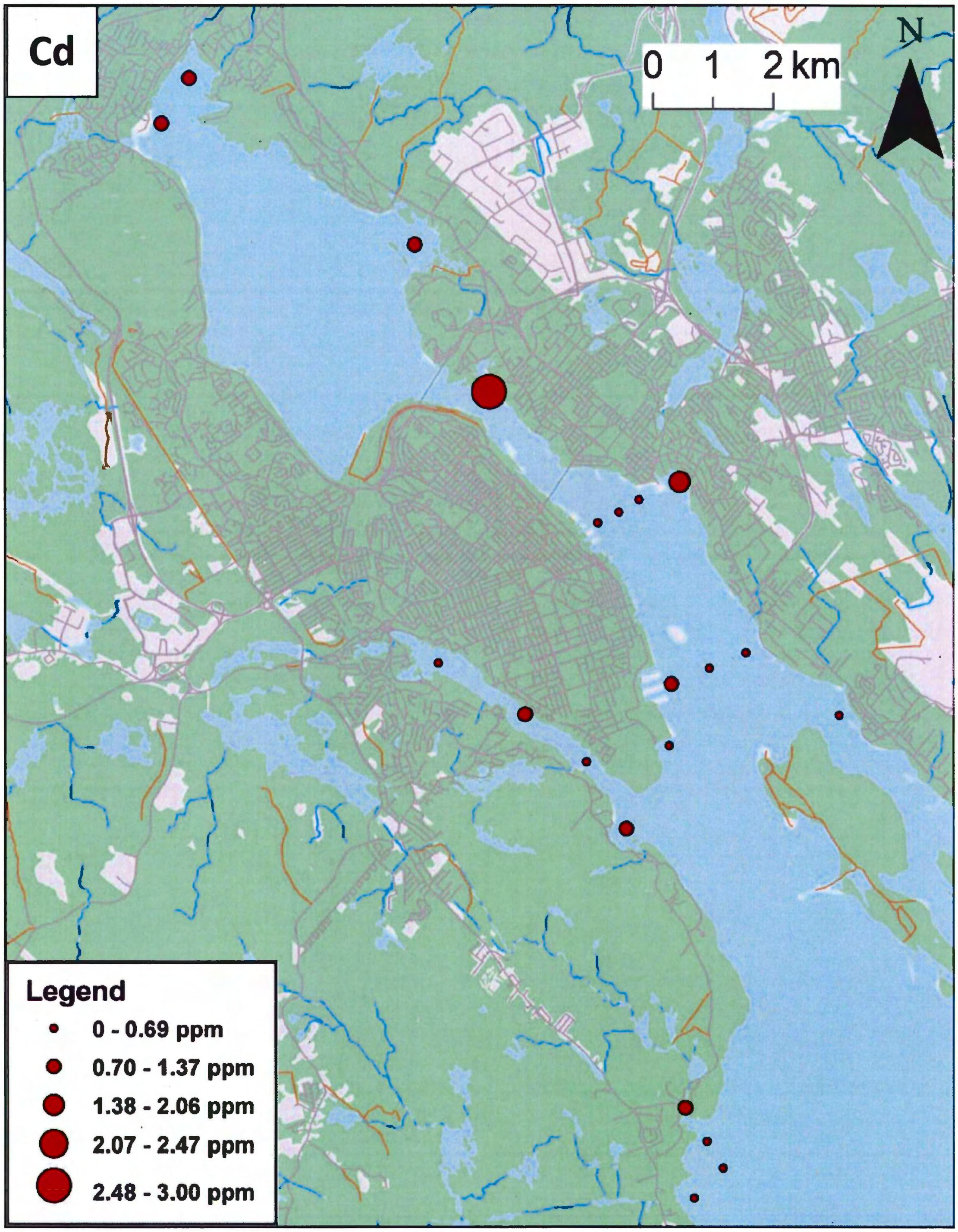

Figure C.4 Proportional dot size map of median cadmium concentrations (ppm) in sediment grab samples collected during all four events.

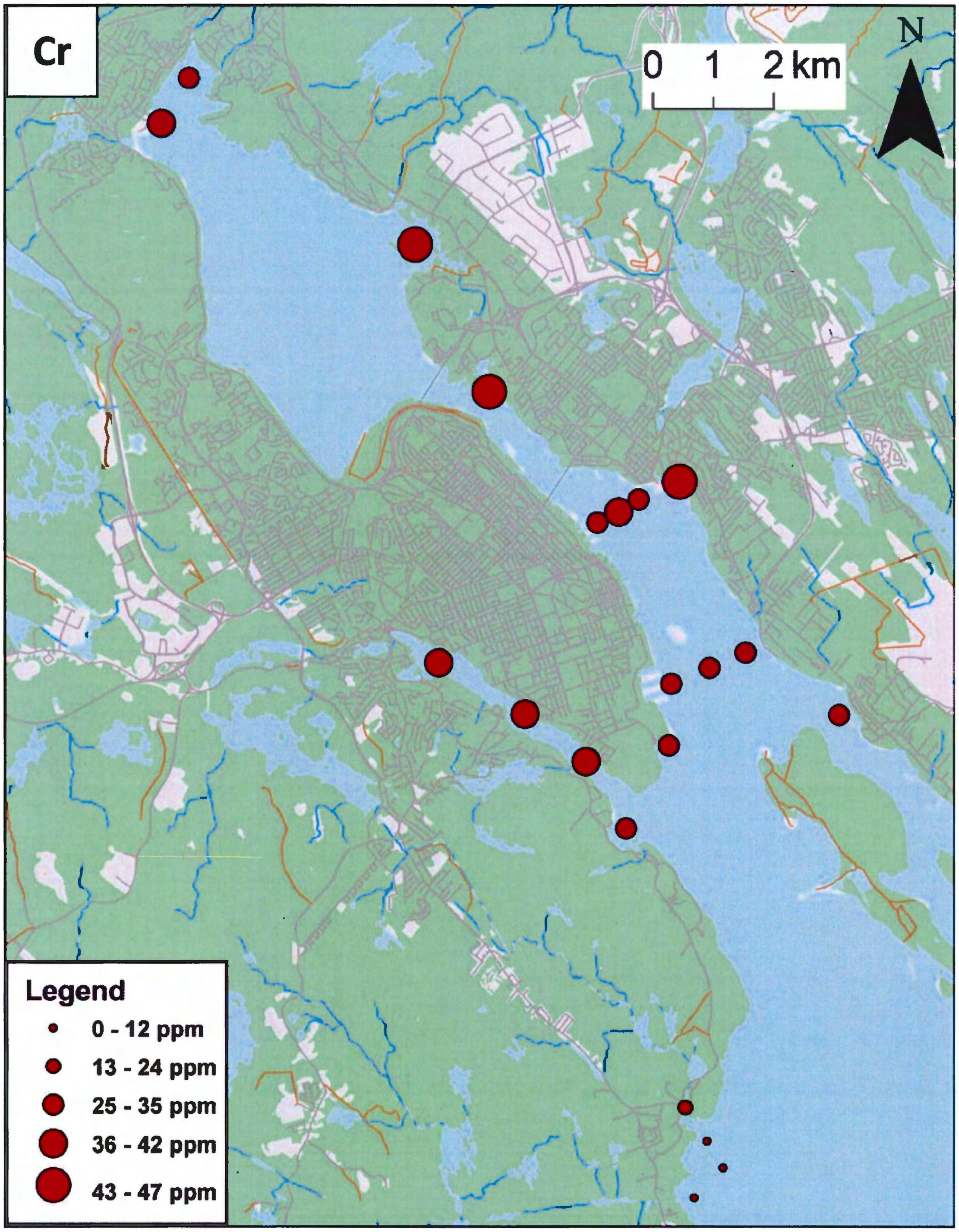

Figure C.5 Proportional dot size map of median chromium concentrations (ppm) in sediment grab samples collected during all four sampling events.

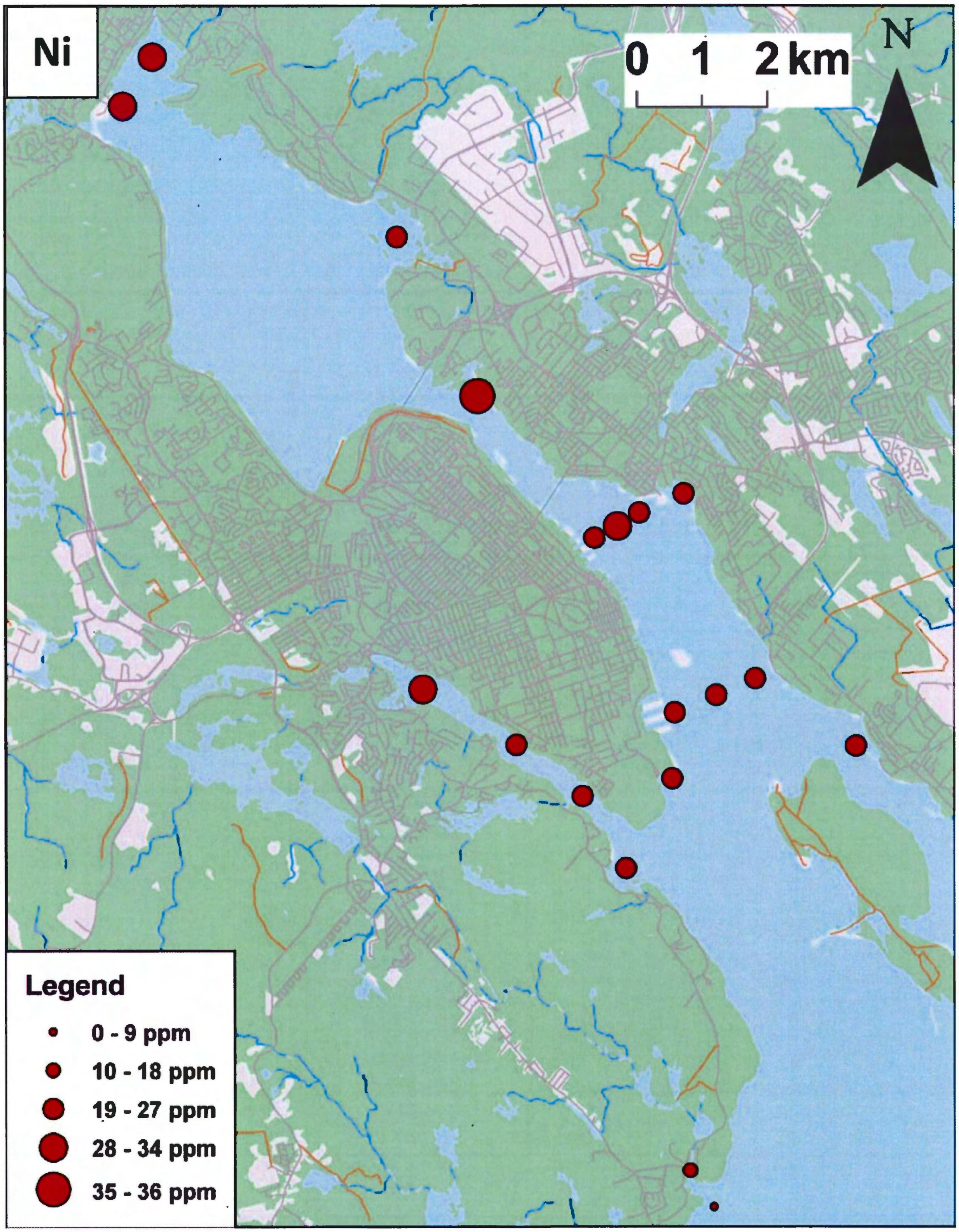

Figure C.6 Proportional dot size map of median nickel concentrations (ppm) in sediment grab samples collected during all four sampling events.

APPENDIX D: SEDIMENT PAH AND STEROID RESULTS

Table D.1 Sediment grab sample parental PAH results

Cruise	Station No.	Lab ID	Sed. depth (cm)	Ay (ppm)	Ac (ppm)	Fl (ppm)	DBT (ppm)	PA (ppm)	AN (ppm)	FL (ppm)	PY (ppm)
April 09	BRB	20090200	1	0.086	0.086	0.133	0.059	0.848	0.317	0.978	0.854
April 09	EE3	20090202	1	0.139	0.160	0.216	0.126	1.442	0.604	1.956	1.824
April 09	HP3	20090203	1	<0.002	0.007	0.009	0.004	0.049	0.016	0.059	0.048
April 09	HP2	20090207	1	0.004	0.004	0.006	0.003	0.031	0.060	0.051	0.048
April 09	HC	20090209	1	0.121	0.167	0.297	0.117	2.120	2.050	5.630	3.700
April 09	AYC	20090210	1	0.456	0.271	0.398	0.221	2.952	1.030	4.167	3.600
April 09	EE1	20090211	1	0.033	0.067	0.088	0.050	0.558	0.171	0.732	0.681
April 09	HP1	20090213	1	0.003	0.009	0.010	0.006	0.060	0.038	0.094	0.085
April 09	TC	20090215	1	0.040	0.114	0.162	0.094	1.010	0.287	1.423	1.217
April 09	DC	20090216	1	0.058	0.144	0.182	0.120	1.321	0.399	1.928	1.681
April 09	SYC	20090217	1	<0.04	<0.04	<0.04	0.032	0.314	0.123	0.462	0.432

Table D.1 Sediment grab sample parental PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	BA (ppm)	CH (ppm)	BF (ppm)	BaP (ppm)	IP (ppm)	BP (ppm)	DBA (ppm)	Ret (ppm)
April 09	BRB	20090200	1	0.443	0.596	0.931	0.457	0.225	0.177	0.074	2.283
April 09	EE3	20090202	1	1.059	1.471	2.416	1.103	0.464	0.397	0.146	0.341
April 09	HP3	20090203	1	0.025	0.035	0.053	0.025	0.013	0.013	0.005	0.077
April 09	HP2	20090207	1	0.206	0.284	0.174	0.072	0.031	0.024	0.010	0.008
April 09	HC	20090209	1	3.729	7.314	7.457	2.971	1.178	0.982	0.277	0.236
April 09	AYC	20090210	1	1.758	2.258	3.718	1.848	0.988	0.792	0.277	0.121
April 09	EE1	20090211	1	0.278	0.381	0.691	0.338	0.294	0.243	0.086	0.176
April 09	HP1	20090213	1	0.055	0.082	0.096	0.048	0.030	0.028	0.007	0.008
April 09	TC	20090215	1	0.479	0.656	1.142	0.548	0.389	0.348	0.119	0.381
April 09	DC	20090216	1	1.015	1.388	2.154	1.091	0.727	0.627	0.210	0.935
April 09	SYC	20090217	1	0.160	0.276	0.498	0.232	0.174	0.146	0.058	0.108

Table D.2 Sediment grab sample alkylated PAH results

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 NA (ppm)	C2 NA (ppm)	C3 NA (ppm)	C1 FL/PY (ppm)	C1 Ac (ppm)	C1 Fl (ppm)	C2 Fl (ppm)	C3 Fl (ppm)
April 09	BRB	20090200	1	0.250	0.583	0.374	0.625	<0.08	<0.08	<0.08	<0.08
April 09	EE3	20090202	1	0.409	0.875	0.514	1.103	0.103	0.094	<0.012	<0.012
April 09	HP3	20090203	1	0.019	0.031	0.025	0.051	<0.008	<0.008	<0.008	<0.008
April 09	HP2	20090207	1	0.019	0.036	0.023	0.246	<0.004	<0.004	<0.004	<0.004
April 09	HC	20090209	1	0.127	0.316	0.249	3.657	0.083	<0.08	0.112	0.226
April 09	AYC	20090210	1	0.324	0.903	0.584	1.970	0.171	0.168	0.148	0.103
April 09	EE1	20090211	1	0.126	0.271	0.151	0.298	0.038	0.034	0.034	0.077
April 09	HP1	20090213	1	0.019	0.040	0.024	0.064	<0.004	<0.004	0.006	0.006
April 09	TC	20090215	1	0.236	0.493	0.283	0.563	0.062	0.067	0.087	0.138
April 09	DC	20090216	1	0.286	0.628	0.371	1.043	0.082	0.077	0.143	0.103
April 09	SYC	20090217	1	0.138	0.430	0.172	0.243	0.027	0.032	0.054	0.087

Table D.2 Sediment grab sample alkylated PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 DBT (ppm)	C2 DBT (ppm)	C3 DBT (ppm)	C1 PA/AN (ppm)	C2 PA/AN (ppm)	C3 PA/AN (ppm)	C1 BA/CH (ppm)
April 09	BRB	20090200	1	<0.08	0.114	<0.08	0.926	0.675	0.654	0.458
April 09	EE3	20090202	1	0.160	0.200	0.129	1.544	0.954	0.632	1.086
April 09	HP3	20090203	1	<0.008	<0.008	<0.008	0.059	0.053	0.039	0.031
April 09	HP2	20090207	1	<0.004	0.007	<0.004	0.151	0.091	0.054	0.149
April 09	HC	20090209	1	<0.08	0.111	0.120	1.440	0.666	0.423	1.814
April 09	AYC	20090210	1	0.237	0.253	0.166	2.467	1.333	0.785	1.621
April 09	EE1	20090211	1	0.044	0.059	0.070	0.447	0.317	0.206	0.275
April 09	HP1	20090213	1	<0.004	<0.004	<0.004	0.054	0.030	0.023	0.042
April 09	TC	20090215	1	0.072	0.135	0.219	0.777	0.541	0.433	0.479
April 09	DC	20090216	1	0.123	0.210	0.244	1.064	0.796	0.536	1.010
April 09	SYC	20090217	1	0.052	0.087	0.154	0.374	0.339	0.230	0.247

Table D.3 Sediment grab sample steroid results

Cruise	Station	Lab ID	Coprostanol (ppm)	Epi-coprostanol (ppm)	Cholesterol (ppm)	Cholestanol (ppm)
April 09	BRB	20090200	2.490	0.219	7.923	0.829
April 09	EE3	20090202	18.000	1.120	9.970	3.810
April 09	HP3	20090203	0.446	0.032	11.696	0.193
April 09	HP2	20090207	0.321	0.030	1.461	0.141
April 09	HC	20090209	1.690	0.146	2.500	1.060
April 09	AYC	20090210	2.000	0.168	4.608	0.769
April 09	EE1	20090211	5.200	0.490	2.880	0.734
April 09	HP1	20090213	0.292	0.052	3.730	0.210
April 09	TC	20090215	5.460	0.574	2.610	1.420
April 09	DC	20090216	14.900	1.090	17.200	2.360
April 09	SYC	20090217	2.760	0.294	3.780	1.010

Table D.4 Sediment core parental PAH results

Cruise	Station No.	Lab ID	Sed. depth (cm)	Ay (ppm)	Ac (ppm)	Fl (ppm)	DBT (ppm)	PA (ppm)	AN (ppm)	FL (ppm)	PY (ppm)	BA (ppm)
2008-053	2	20080300	23	0.021	0.016	0.028	0.016	0.158	0.043	0.195	0.205	0.102
2008-053	2	20080302	27	0.012	0.015	0.024	0.015	0.137	0.034	0.168	0.172	0.084
2008-053	2	20080312	47	<0.005	<0.005	<0.005	<0.005	0.029	<0.005	0.025	0.024	0.010
2008-053	2	20080317	57	<0.005	<0.005	<0.005	<0.005	0.020	<0.005	0.020	0.021	0.009
2008-053	2	20080320	63	<0.005	<0.005	<0.005	<0.005	0.016	<0.005	0.017	0.018	0.007
2008-053	2	20080322	67	<0.007	<0.007	<0.007	<0.007	0.022	0.008	0.027	0.028	0.013
2008-053	2	20080324	71	0.005	<0.005	0.008	<0.005	0.044	0.016	0.060	0.062	0.031
2008-053	2	20080334	122	<0.007	<0.007	<0.007	<0.007	0.038	<0.007	0.022	0.028	<0.007
2008-053	2	20080339	172	<0.01	<0.01	0.015	<0.01	0.067	<0.01	0.044	0.053	<0.01
2008-053	2	20080344	222	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
2008-053	2	20080349	272	<0.002	<0.002	<0.002	<0.002	0.008	<0.002	0.004	0.005	<0.002
2008-053	5	20080403	1	<0.002	<0.002	<0.002	<0.002	0.003	<0.002	0.005	0.005	0.007
2008-053	5	20080405	5									
2008-053	5	20080418	31	<0.003	<0.003	<0.003	<0.003	0.007	<0.003	0.004	0.006	0.029
2008-053	5	20080420	35									
2008-053	8	20080583	1	0.120	0.320	0.380	0.200	2.680	0.960	3.520	3.230	1.730
2008-053	8	20080585	5	0.100	0.170	0.230	0.120	1.610	0.590	2.240	2.310	1.090
2008-053	8	20080588	11	0.270	0.610	1.100	0.480	6.860	2.280	6.160	5.700	2.580
2008-053	8	20080590	15	0.150	0.330	0.420	0.250	2.790	1.090	3.620	3.780	1.680
2008-053	8	20080593	21	0.150	0.430	0.510	0.240	3.590	1.270	4.440	4.170	2.160
2008-053	8	20080595	25	0.197	0.309	0.436	0.261	3.180	1.220	3.990	4.430	1.930
2008-053	8	20080598	31	0.283	0.347	0.515	0.332	3.679	1.382	4.842	5.368	2.291
2008-053	8	20080600	35	1.100	1.110	2.140	1.250	15.60	6.734	24.56	21.77	11.09
2008-053	8	20080607	49	0.278	0.443	0.557	0.352	3.459	1.222	3.778	4.270	2.446
2008-053	8	20080617	100	0.012	<0.004	0.010	0.007	0.047	0.023	0.084	0.092	0.058
2008-053	8	20080632	250	<0.003	<0.003	<0.003	<0.003	0.013	0.004	0.007	0.009	<0.003
2008-053	8	20080637	300	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
2008-053	8	20080642	350	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.003	0.003	<0.002

Table D.4 Sediment core parental PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	Ay (ppm)	Ac (ppm)	Fl (ppm)	DBT (ppm)	PA (ppm)	AN (ppm)	FL (ppm)	PY (ppm)	BA (ppm)
2009-060	1	20090061	0.5	0.080	0.020	0.024	0.010	0.193	0.128	0.396	0.348	0.193
2009-060	1	20090072	11.5	0.104	0.032	0.045	0.028	0.368	0.181	0.596	0.617	0.342
2009-060	1	20090081	20.5	0.202	0.050	0.081	0.045	0.622	0.300	0.992	1.084	0.574
2009-060	1	20090084	23.5	0.083	0.033	0.053	0.026	0.382	0.208	0.655	0.671	0.373
2009-060	2	20090087	0.5	0.148	0.033	0.054	<0.01	0.354	0.208	0.658	0.580	0.381
2009-060	2	20090097	10.5	0.110	0.026	0.046	0.030	0.319	0.184	0.630	0.568	0.375
2009-060	2	20090107	20.5	0.237	0.064	0.115	0.065	0.792	0.359	1.185	1.242	0.726
2009-060	2	20090109	22.5	0.098	0.031	0.051	0.025	0.397	0.169	0.641	0.656	0.402
2009-060	5	20090147	0.5	0.219	0.055	0.089	0.047	0.688	0.372	0.996	1.023	0.605
2009-060	5	20090157	10.5	0.139	0.041	0.067	0.029	0.477	0.223	0.755	0.774	0.513
2009-060	5	20090167	20.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2009-060	5	20090177	30.5	0.036	0.015	0.028	<0.01	0.192	0.082	0.289	0.298	0.160
2009-060	8	20090111	0.5	0.313	0.078	0.149	0.075	1.215	0.552	1.612	1.385	0.773
2009-060	8	20090121	10.5	0.305	0.106	0.172	0.085	1.242	0.681	2.000	1.719	0.987
2009-060	8	20090131	20.5	0.937	0.159	0.364	0.149	2.329	1.071	3.103	2.971	1.485
2009-060	8	20090141	30.5	0.049	0.022	0.033	0.016	0.282	0.124	0.423	0.411	0.248
2009-060	9	20090031	0.5	0.144	0.056	0.168	0.055	1.385	1.321	2.567	2.119	1.543
2009-060	9	20090041	10.5	0.482	0.081	0.156	0.090	1.115	1.110	1.662	2.706	1.839
2009-060	9	20090051	20.5	0.368	0.158	0.249	0.118	1.704	0.912	2.881	2.985	1.885
2009-060	9	20090060	29.5	0.302	0.069	0.162	0.083	1.183	1.040	1.824	2.162	1.738

Table D.4 Sediment core parental PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	CH (ppm)	BF (ppm)	BaP (ppm)	IP (ppm)	BP (ppm)	DBA (ppm)	Ret (ppm)	Per (ppm)
2008-053	2	20080300	23	0.134	0.198	0.105	0.095	0.098	0.024	0.049	-
2008-053	2	20080302	27	0.110	0.157	0.084	0.072	0.073	0.019	0.044	-
2008-053	2	20080312	47	0.014	0.013	0.009	0.005	0.005	<0.005	0.006	-
2008-053	2	20080317	57	0.010	0.017	0.009	0.008	0.008	<0.005	0.006	-
2008-053	2	20080320	63	0.010	0.010	0.007	0.007	0.006	<0.005	0.005	-
2008-053	2	20080322	67	0.020	0.027	0.013	0.007	0.013	<0.007	0.007	-
2008-053	2	20080324	71	0.040	0.058	0.031	0.020	0.020	0.005	0.008	-
2008-053	2	20080334	122	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	0.014	-
2008-053	2	20080339	172	0.010	<0.01	<0.01	<0.01	<0.01	<0.01	0.031	-
2008-053	2	20080344	222	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	-
2008-053	2	20080349	272	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.003	-
2008-053	5	20080403	1	0.017	0.004	0.003	<0.002	<0.002	<0.002	0.003	-
2008-053	5	20080405	5								
2008-053	5	20080418	31	0.102	<0.003	<0.003	<0.003	<0.003	<0.003	0.045	-
2008-053	5	20080420	35								
2008-053	8	20080583	1	2.300	3.190	1.680	1.110	1.020	0.300	0.212	-
2008-053	8	20080585	5	1.580	2.310	1.220	0.790	0.710	0.220	0.186	-
2008-053	8	20080588	11	3.390	4.730	2.590	1.500	1.280	0.420	0.352	-
2008-053	8	20080590	15	2.360	3.350	1.830	1.535	1.324	0.437	0.437	-
2008-053	8	20080593	21	3.010	4.340	2.380	1.855	1.697	0.513	0.355	-
2008-053	8	20080595	25	3.150	4.840	2.330	1.871	1.600	0.564	0.443	-
2008-053	8	20080598	31	3.266	5.354	2.835	1.741	1.479	0.486	0.536	-
2008-053	8	20080600	35	13.42	20.00	11.19	5.938	4.846	1.529	1.138	-
2008-053	8	20080607	49	3.000	4.045	2.400	1.658	1.462	0.438	1.387	-
2008-053	8	20080617	100	0.066	0.088	0.052	0.029	0.031	0.010	2.034	-
2008-053	8	20080632	250	0.004	<0.003	<0.003	<0.003	<0.003	<0.003	0.011	-
2008-053	8	20080637	300	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	-
2008-053	8	20080642	350	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	-

Table D.4 Sediment core parental PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	CH (ppm)	BF (ppm)	BaP (ppm)	IP (ppm)	BP (ppm)	DBA (ppm)	Ret (ppm)	Per (ppm)
2009-060	1	20090061	0.5	0.204	0.375	0.188	0.142	0.139	0.029	0.023	0.045
2009-060	1	20090072	11.5	0.340	0.671	0.328	0.270	0.244	0.056	0.034	0.095
2009-060	1	20090081	20.5	0.567	1.136	0.588	0.495	0.444	0.105	0.096	0.142
2009-060	1	20090084	23.5	0.346	0.662	0.348	0.257	0.231	0.056	0.085	0.091
2009-060	2	20090087	0.5	0.370	0.753	0.342	0.281	0.251	0.056	0.212	0.089
2009-060	2	20090097	10.5	0.368	0.719	0.314	0.254	0.225	0.059	0.069	0.086
2009-060	2	20090107	20.5	0.766	1.352	0.657	0.515	0.481	0.125	0.181	0.146
2009-060	2	20090109	22.5	0.391	0.677	0.336	0.258	0.213	0.064	0.158	0.082
2009-060	5	20090147	0.5	0.622	1.107	0.522	0.434	0.357	0.107	0.126	0.110
2009-060	5	20090157	10.5	0.475	0.840	0.400	0.338	0.296	0.081	0.164	0.092
2009-060	5	20090167	20.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.019
2009-060	5	20090177	30.5	0.149	0.325	0.165	0.120	0.123	0.025	0.037	0.048
2009-060	8	20090111	0.5	0.712	1.351	0.730	0.475	0.399	0.109	0.079	0.160
2009-060	8	20090121	10.5	0.881	1.632	0.882	0.578	0.487	0.127	0.062	0.194
2009-060	8	20090131	20.5	1.436	2.673	1.606	1.062	0.849	0.237	0.140	0.314
2009-060	8	20090141	30.5	0.217	0.384	0.224	0.141	0.127	0.033	0.234	0.052
2009-060	9	20090031	0.5	1.967	2.869	1.295	0.816	0.740	0.187	0.069	0.282
2009-060	9	20090041	10.5	1.677	3.037	1.513	0.913	0.840	0.218	0.365	0.366
2009-060	9	20090051	20.5	1.531	2.861	1.513	1.025	0.879	0.214	0.773	0.390
2009-060	9	20090060	29.5	1.240	2.105	1.009	0.654	0.575	0.165	0.322	0.222

Table D.5 Sediment core alkylated PAH results

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 NA (ppm)	C2 NA (ppm)	C3 NA (ppm)	C1 FL/PY (ppm)	C1 Ac (ppm)	C1 Fl (ppm)	C2 Fl (ppm)	C3 Fl (ppm)
2008-053	2	20080300	23	0.073	0.252	0.114	0.132	<0.04	<0.04	<0.04	<0.04
2008-053	2	20080302	27	0.053	0.185	0.082	0.105	<0.028	<0.028	<0.028	<0.028
2008-053	2	20080312	47	0.007	0.056	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2008-053	2	20080317	57	0.006	0.050	0.022	<0.02	<0.02	<0.02	<0.02	<0.02
2008-053	2	20080320	63	0.011	0.058	0.021	0.022	<0.02	<0.02	<0.02	<0.02
2008-053	2	20080322	67	0.008	0.137	0.032	<0.028	<0.028	<0.028	<0.028	<0.028
2008-053	2	20080324	71	0.018	0.097	0.029	0.043	<0.02	<0.02	<0.02	<0.02
2008-053	2	20080334	122	0.009	0.058	0.034	<0.028	<0.028	<0.028	<0.028	<0.028
2008-053	2	20080339	172	0.028	0.857	0.101	<0.04	<0.04	<0.04	<0.04	<0.04
2008-053	2	20080344	222	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
2008-053	2	20080349	272	0.005	0.011	0.011	<0.008	<0.008	<0.008	<0.008	<0.008
2008-053	5	20080403	1	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
2008-053	5	20080405	5								
2008-053	5	20080418	31	0.013	0.040	0.046	<0.012	<0.012	<0.012	<0.012	<0.012
2008-053	5	20080420	35								
2008-053	8	20080583	1	0.490	1.250	0.700	1.870	<0.28	<0.28	<0.28	<0.28
2008-053	8	20080585	5	0.390	0.730	0.530	1.340	<0.28	<0.28	<0.28	<0.28
2008-053	8	20080588	11	0.950	1.720	1.130	2.910	0.360	0.320	<0.28	<0.28
2008-053	8	20080590	15	0.770	1.420	1.040	2.050	0.220	0.290	<0.20	<0.20
2008-053	8	20080593	21	0.560	1.050	0.700	2.490	0.230	<0.20	<0.20	<0.20
2008-053	8	20080595	25	0.838	1.530	1.120	2.820	0.210	0.200	<0.20	<0.20
2008-053	8	20080598	31	0.867	1.420	1.040	3.253	0.244	0.269	<0.12	<0.12
2008-053	8	20080600	35	1.920	3.460	2.540	10.354	0.600	0.710	<0.12	<0.12
2008-053	8	20080607	49	0.899	1.522	1.306	2.308	0.261	0.226	<0.012	<0.012
2008-053	8	20080617	100	0.078	0.196	0.151	0.128	<0.016	<0.016	<0.016	<0.016
2008-053	8	20080632	250	0.013	0.037	0.020	<0.012	<0.012	<0.012	<0.012	<0.012
2008-053	8	20080637	300	0.014	0.057	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016
2008-053	8	20080642	350	0.008	0.031	0.011	<0.008	<0.008	<0.008	<0.008	<0.008

Table D.5 Sediment core alkylated PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 NA (ppm)	C2 NA (ppm)	C3 NA (ppm)	C1 FL/PY (ppm)	C1 Ac (ppm)	C1 Fl (ppm)	C2 Fl (ppm)	C3 Fl (ppm)
2009-060	1	20090061	0.5	0.146	0.569	0.211	0.203	<0.04	<0.04	<0.04	0.075
2009-060	1	20090072	11.5	0.165	0.554	0.221	0.378	<0.04	<0.04	<0.04	<0.04
2009-060	1	20090081	20.5	0.291	0.609	0.416	0.686	<0.04	0.069	<0.04	0.169
2009-060	1	20090084	23.5	0.130	0.396	0.209	0.363	<0.04	<0.04	<0.04	0.079
2009-060	2	20090087	0.5	0.143	0.970	0.326	0.382	<0.04	<0.04	<0.04	0.246
2009-060	2	20090097	10.5	0.160	0.746	0.212	0.398	<0.04	<0.04	<0.04	0.162
2009-060	2	20090107	20.5	0.586	1.051	0.673	0.979	0.055	0.101	0.085	0.232
2009-060	2	20090109	22.5	0.140	0.460	0.238	0.432	<0.04	<0.04	<0.04	0.090
2009-060	5	20090147	0.5	0.425	1.034	0.506	0.726	<0.04	0.072	<0.04	0.225
2009-060	5	20090157	10.5	0.210	0.655	0.331	0.547	<0.04	<0.04	<0.04	0.113
2009-060	5	20090167	20.5	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
2009-060	5	20090177	30.5	0.102	0.424	0.132	0.189	<0.04	<0.04	<0.04	<0.04
2009-060	8	20090111	0.5	0.185	0.553	0.324	0.833	<0.04	0.096	0.076	0.227
2009-060	8	20090121	10.5	0.232	0.537	0.398	1.035	0.068	0.108	0.088	0.232
2009-060	8	20090131	20.5	0.371	0.842	0.663	2.015	0.103	0.230	0.209	0.457
2009-060	8	20090141	30.5	0.051	0.157	0.113	0.257	<0.02	<0.02	<0.02	0.043
2009-060	9	20090031	0.5	0.080	0.456	0.246	1.634	0.072	0.099	0.059	0.247
2009-060	9	20090041	10.5	0.265	0.569	0.325	1.839	0.056	0.079	<0.04	0.251
2009-060	9	20090051	20.5	0.213	0.460	0.428	1.738	0.076	0.120	<0.04	0.239
2009-060	9	20090060	29.5	0.289	0.582	0.408	1.677	0.052	0.103	0.060	0.253

Table D.5 Sediment core alkylated PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 DBT (ppm)	C2 DBT (ppm)	C3 DBT (ppm)	C1 PA/AN (ppm)	C2 PA/AN (ppm)	C3 PA/AN (ppm)	C1 BA/CH (ppm)
2008-053	2	20080300	23	<0.04	<0.04	<0.04	0.257	0.120	0.093	0.142
2008-053	2	20080302	27	<0.028	<0.028	<0.028	0.189	0.091	0.076	0.106
2008-053	2	20080312	47	<0.02	<0.02	<0.02	0.037	<0.02	<0.02	<0.02
2008-053	2	20080317	57	<0.02	<0.02	<0.02	0.025	<0.02	<0.02	<0.02
2008-053	2	20080320	63	<0.02	<0.02	<0.02	0.027	<0.02	<0.02	<0.02
2008-053	2	20080322	67	<0.028	<0.028	<0.028	0.060	<0.028	<0.028	<0.028
2008-053	2	20080324	71	<0.02	<0.02	<0.02	0.090	0.036	0.032	0.044
2008-053	2	20080334	122	<0.028	<0.028	<0.028	0.049	0.047	<0.028	<0.028
2008-053	2	20080339	172	<0.04	<0.04	<0.04	0.272	0.070	0.048	<0.04
2008-053	2	20080344	222	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
2008-053	2	20080349	272	<0.008	<0.008	<0.008	0.012	<0.008	<0.008	<0.008
2008-053	5	20080403	1	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
2008-053	5	20080405	5							
2008-053	5	20080418	31	<0.012	<0.012	<0.012	0.018	0.019	0.060	0.018
2008-053	5	20080420	35							
2008-053	8	20080583	1	<0.28	<0.28	<0.28	3.050	1.200	0.810	1.680
2008-053	8	20080585	5	<0.28	<0.28	<0.28	2.220	0.990	0.700	1.220
2008-053	8	20080588	11	0.360	0.370	<0.28	4.540	2.250	1.110	2.310
2008-053	8	20080590	15	0.300	0.410	<0.20	3.210	1.490	1.150	1.890
2008-053	8	20080593	21	0.250	0.310	0.480	2.890	1.440	1.090	2.220
2008-053	8	20080595	25	0.330	0.440	0.610	3.180	1.830	1.640	2.700
2008-053	8	20080598	31	0.333	0.449	0.577	4.382	1.842	1.724	2.823
2008-053	8	20080600	35	0.840	0.690	0.460	11.544	4.646	3.468	8.481
2008-053	8	20080607	49	0.333	0.239	<0.012	3.413	1.667	1.252	2.369
2008-053	8	20080617	100	<0.016	0.070	<0.016	0.411	0.105	0.589	0.157
2008-053	8	20080632	250	<0.012	<0.012	<0.012	0.026	<0.012	<0.012	<0.012
2008-053	8	20080637	300	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016
2008-053	8	20080642	350	<0.008	<0.008	<0.008	0.015	<0.008	<0.008	<0.008

Table D.5 Sediment core alkylated PAH results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	C1 DBT (ppm)	C2 DBT (ppm)	C3 DBT (ppm)	C1 PA/AN (ppm)	C2 PA/AN (ppm)	C3 PA/AN (ppm)	C1 BA/CH (ppm)
2009-060	1	20090061	0.5	<0.04	<0.04	<0.04	0.249	0.204	0.104	0.146
2009-060	1	20090072	11.5	<0.04	0.071	<0.04	0.390	0.358	0.248	0.295
2009-060	1	20090081	20.5	0.067	0.092	<0.04	0.707	0.569	0.385	0.512
2009-060	1	20090084	23.5	<0.04	<0.04	<0.04	0.382	0.357	0.188	0.292
2009-060	2	20090087	0.5	0.064	0.266	0.166	<0.04	0.328	0.446	0.282
2009-060	2	20090097	10.5	<0.04	0.119	0.145	0.386	0.370	0.386	0.319
2009-060	2	20090107	20.5	0.089	0.147	0.112	0.955	0.758	0.530	0.721
2009-060	2	20090109	22.5	<0.04	<0.04	<0.04	0.454	0.347	0.221	0.363
2009-060	5	20090147	0.5	0.069	0.117	0.117	0.957	0.629	0.417	0.578
2009-060	5	20090157	10.5	<0.04	0.059	<0.04	0.540	0.409	0.269	0.432
2009-060	5	20090167	20.5	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
2009-060	5	20090177	30.5	<0.04	<0.04	<0.04	0.208	0.200	0.108	0.146
2009-060	8	20090111	0.5	0.084	0.118	0.067	1.015	0.687	0.373	0.521
2009-060	8	20090121	10.5	0.065	0.110	0.069	1.245	0.841	0.398	0.631
2009-060	8	20090131	20.5	0.143	0.189	0.153	2.250	1.437	0.679	1.170
2009-060	8	20090141	30.5	<0.02	0.029	<0.02	0.297	0.227	0.141	0.168
2009-060	9	20090031	0.5	<0.04	0.074	0.059	1.315	0.857	0.407	0.944
2009-060	9	20090041	10.5	0.051	0.119	0.155	1.226	0.866	0.772	<0.04
2009-060	9	20090051	20.5	0.073	0.103	0.076	1.627	1.025	0.670	1.020
2009-060	9	20090060	29.5	0.058	0.118	0.069	1.344	1.022	0.576	1.003

Table D.6 Sediment core steroid results

Cruise	Station No.	Lab ID	Sed. depth (cm)	Coprostanol (ppm)	Epi-coprostanol (ppm)	Cholesterol (ppm)	Cholestanol (ppm)
2008-053	2	20080300	23	0.363	1.330	1.130	0.781
2008-053	2	20080302	27	0.195	0.475	0.770	0.447
2008-053	2	20080312	47	<0.03	<0.03	0.210	0.061
2008-053	2	20080317	57	0.021	0.090	0.238	0.074
2008-053	2	20080320	63	<0.02	0.056	0.199	0.071
2008-053	2	20080322	67	0.056	0.121	0.314	0.145
2008-053	2	20080324	71	0.060	0.148	0.367	0.116
2008-053	2	20080334	122	<0.03	<0.03	0.418	0.044
2008-053	2	20080339	172	<0.05	<0.05	0.715	0.228
2008-053	2	20080344	222	<0.01	<0.01	0.036	<0.01
2008-053	2	20080349	272	<0.01	<0.01	0.098	<0.01
2008-053	5	20080403	1	0.038	<0.01	0.249	0.041
2008-053	5	20080405	5				
2008-053	5	20080418	31	<0.02	<0.02	0.166	0.016
2008-053	5	20080420	35				
2008-053	8	20080583	1	13.600	1.190	5.580	2.630
2008-053	8	20080585	5	3.137	0.382	1.222	1.061
2008-053	8	20080588	11	3.875	0.475	1.358	1.188
2008-053	8	20080590	15	1.780	0.231	0.681	0.646
2008-053	8	20080593	21	<0.30	<0.30	0.672	<0.30
2008-053	8	20080595	25	0.445	<0.20	1.038	0.493
2008-053	8	20080598	31	0.411	<0.20	0.908	0.429
2008-053	8	20080600	35	0.331	<0.20	0.524	0.351
2008-053	8	20080607	49	0.254	0.070	0.381	0.391
2008-053	8	20080617	100	0.082	<0.02	0.752	0.149
2008-053	8	20080632	250	<0.02	<0.02	0.133	0.033
2008-053	8	20080637	300	<0.02	<0.02	0.126	0.036
2008-053	8	20080642	350	<0.01	<0.01	0.063	0.034

Table D.6 Sediment core steroid results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	Coprostanol (ppm)	Epi-coprostanol (ppm)	Cholesterol (ppm)	Cholestanol (ppm)
2009-060	1	20090061	0.5	2.083	0.728	7.556	2.153
2009-060	1	20090072	11.5	0.617	0.327	1.372	0.982
2009-060	1	20090081	20.5	0.059	0.087	0.339	0.333
2009-060	1	20090084	23.5	0.042	0.107	0.329	0.222
2009-060	2	20090087	0.5	27.213	14.279	28.689	14.738
2009-060	2	20090097	10.5	5.324	2.352	3.155	4.535
2009-060	2	20090107	20.5	<0.10	0.186	0.554	0.604
2009-060	2	20090109	22.5	0.039	0.109	0.559	0.284
2009-060	5	20090147	0.5	0.632	0.488	1.895	1.207
2009-060	5	20090157	10.5	0.503	0.297	1.457	0.811
2009-060	5	20090167	20.5	<0.01	0.077	0.318	0.071
2009-060	5	20090177	30.5	<0.15	0.187	0.382	0.290
2009-060	8	20090111	0.5	4.340	0.483	6.370	1.540
2009-060	8	20090121	10.5	0.909	0.201	0.947	0.926
2009-060	8	20090131	20.5	0.133	<0.07	0.226	0.163
2009-060	8	20090141	30.5	0.013	0.024	0.083	0.045
2009-060	9	20090031	0.5	2.830	0.246	10.600	1.160
2009-060	9	20090041	10.5	<0.10	<0.10	0.427	0.287
2009-060	9	20090051	20.5	<0.08	<0.08	0.263	0.164
2009-060	9	20090060	29.5	<0.08	<0.08	0.352	0.275

Table D.7 Correlation coefficients (r) between PAHs, coprostanol, and organic carbon in sediment core tops and grab samples. Correlations in italics are significant at $p \leq 0.5$ (n = 18).

	ΣPAH (ppm)	ΣPAHp (ppm)	ΣPAHa (ppm)	% PAH	Coprostanol (ppm)	Organic carbon (wt. %)
ΣPAH (ppm)	*1.00*					
ΣPAHp (ppm)	*0.99*	*1.00*				
ΣPAHa (ppm)	*0.94*	*0.89*	*1.00*			
% PAH (ppm)	-0.28	-0.33	-0.13	*1.00*		
Coprostanol (ppm)	0.16	0.11	0.28	0.17	*1.00*	
Organic carbon (wt. %)	0.37	0.31	*0.52*	0.24	*0.53*	*1.00*

APPENDIX E: GEOCHEMICAL SEDIMENT CORE PROFILES

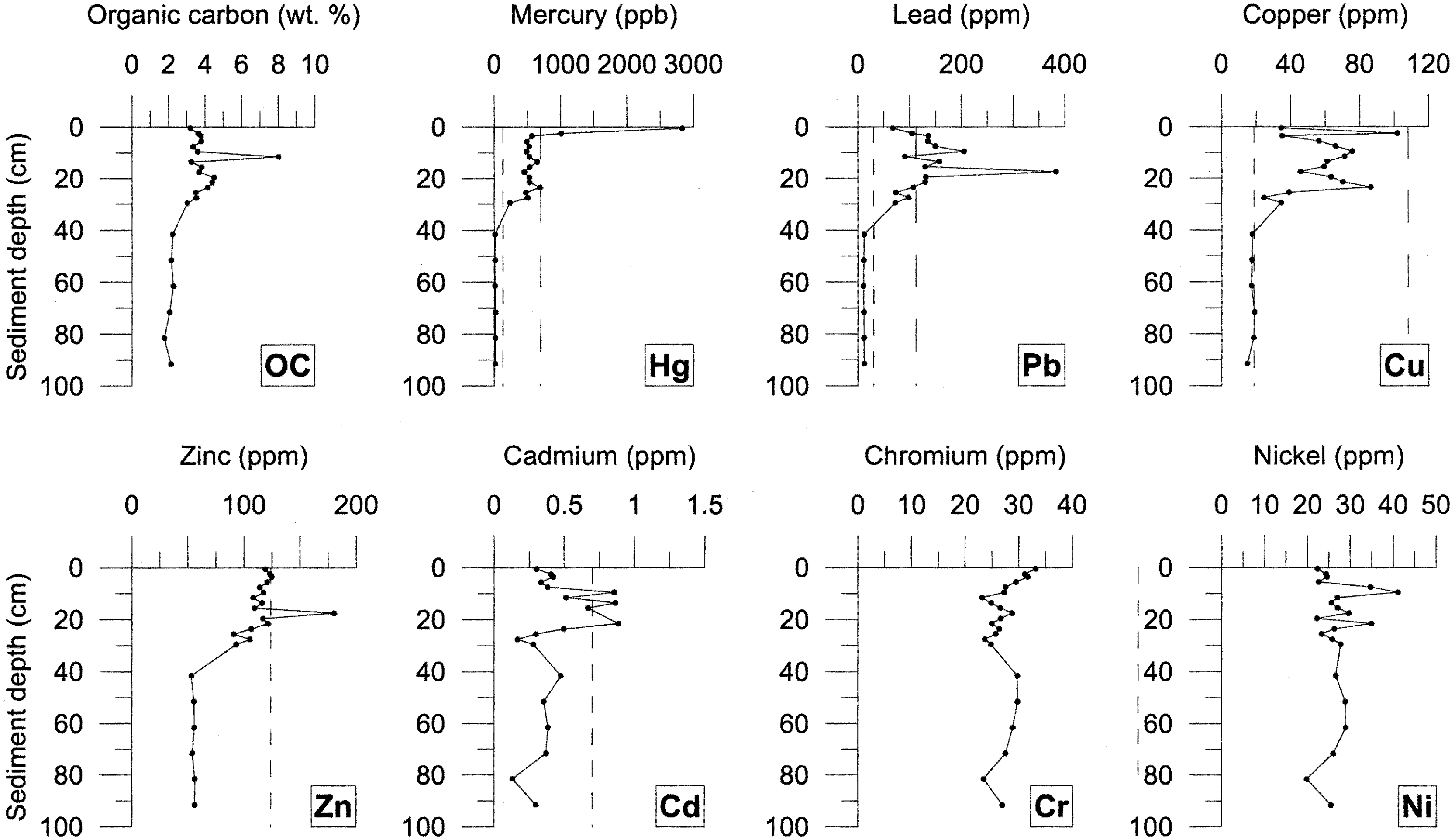

Figure E.1 Geochemical sediment core profiles of 1993 vibracore 2 (south of Georges Island, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

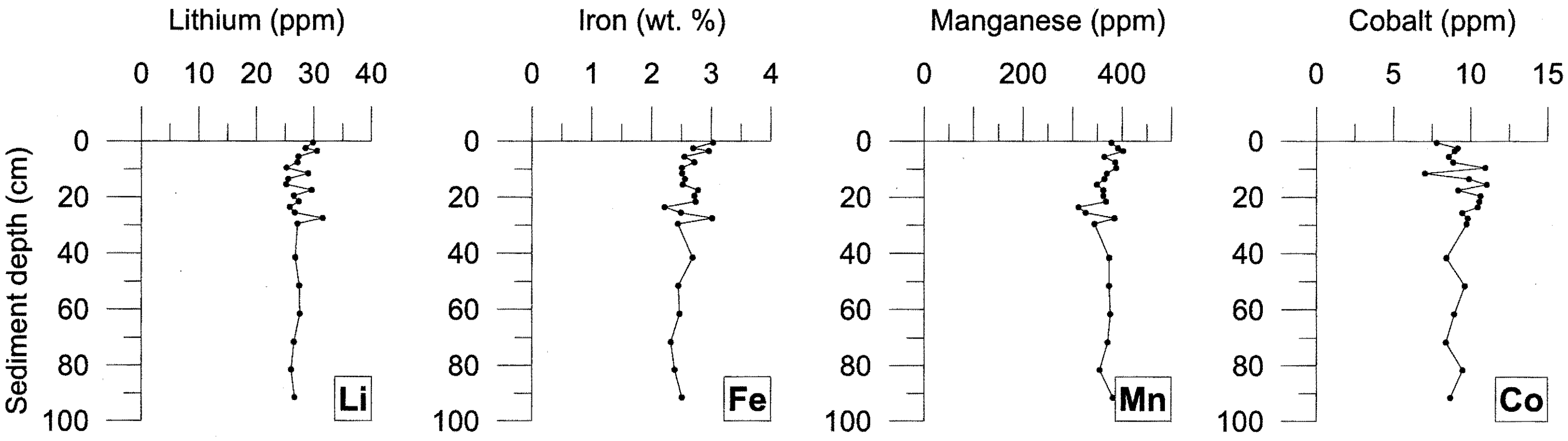

Figure E.2 Geochemical sediment core profiles of 1993 vibracore 2 (south of Georges Island, Figure 3.5).

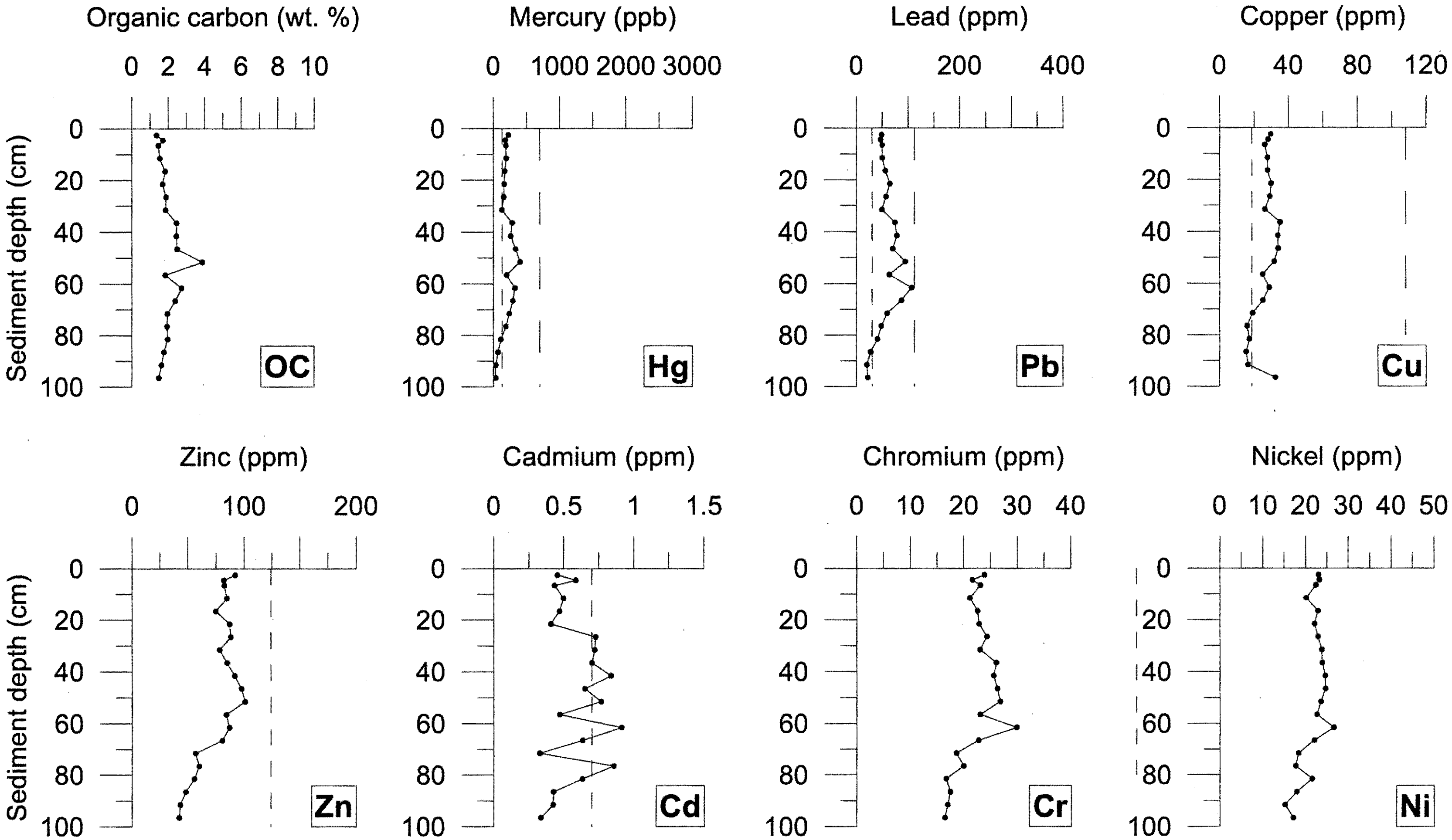

Figure E.3 Geochemical sediment core profiles of 1993 vibracore 9 (west of McNabs Island, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

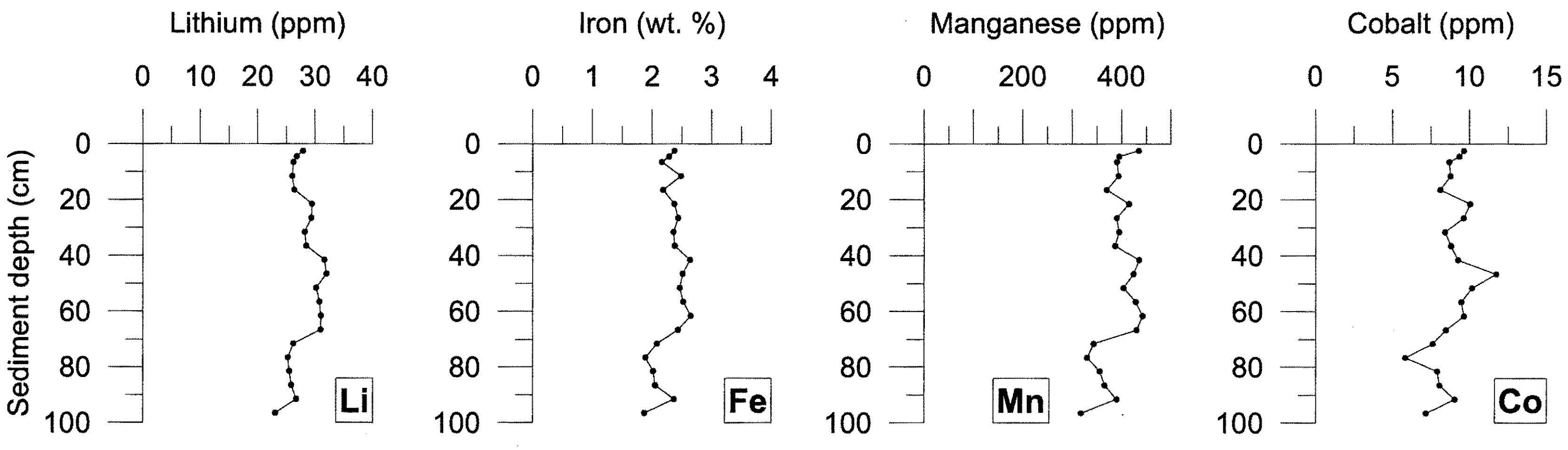

Figure E.4 Geochemical sediment core profiles of 1993 vibracore 9 (west of McNabs Island, Figure 3.5).

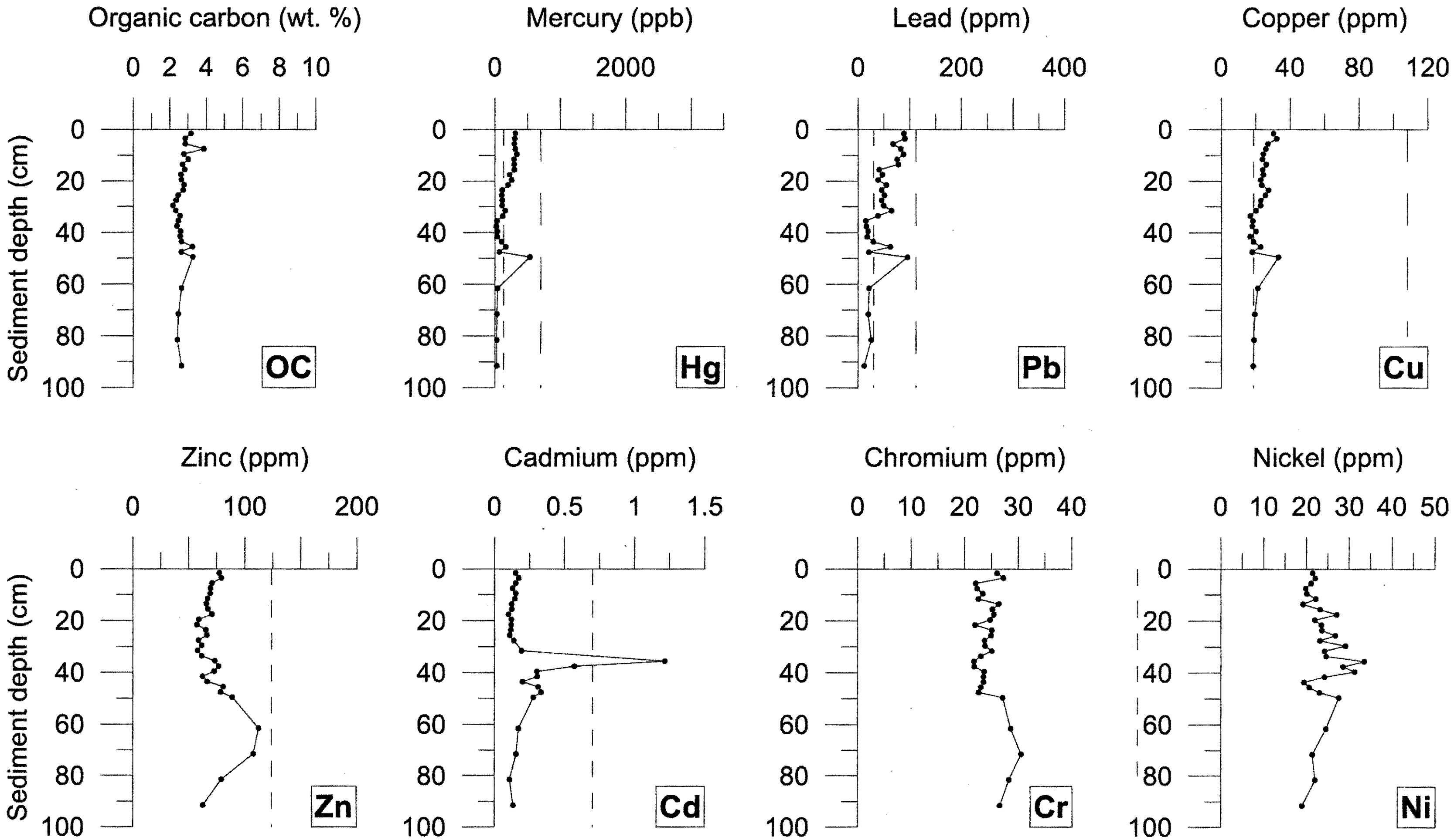

Figure E.5 Geochemical sediment core profiles of 1993 vibracore 10 (south of Georges Island, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

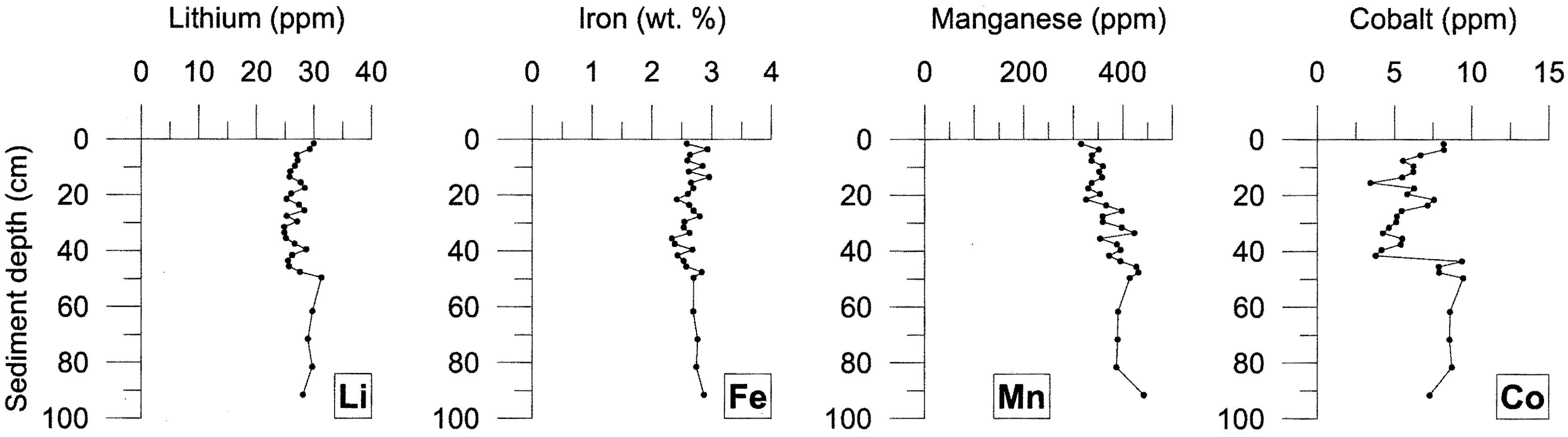

Figure E.6 Geochemical sediment core profiles of 1993 vibracore 10 (south of Georges Island, Figure 3.5).

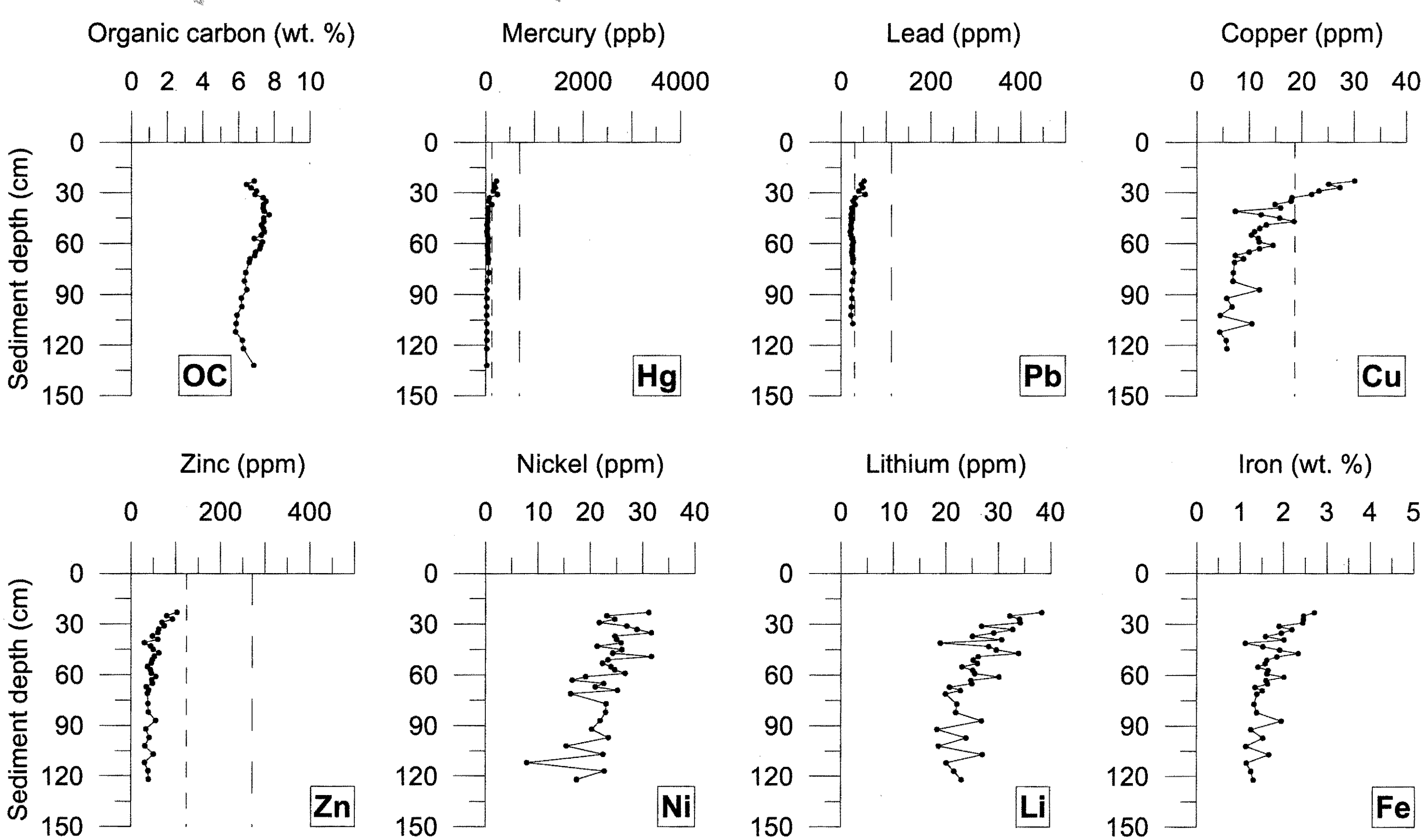

Figure E.7 Geochemical sediment core profiles of 2008 vibracore 2 (near Mill Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002). 2008 vibracore 2 has been shifted down 22 cm to reflect the missing sediment in this core. See Section 6.2 for further discussion.

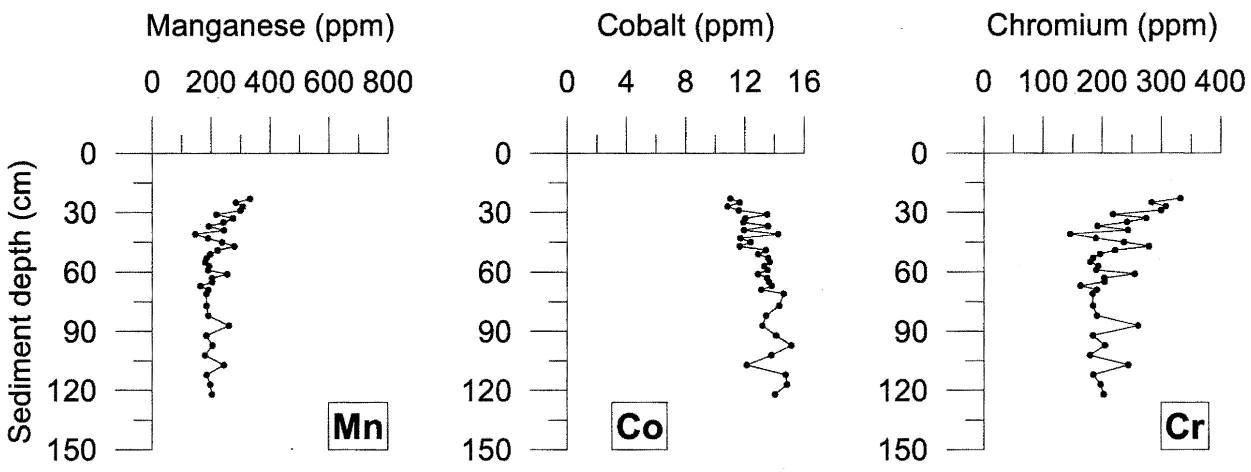

Figure E.8 Geochemical sediment core profiles of 2008 vibracore 2 (near Mill Cove, Figure 3.5). 2008 vibracore 2 has been shifted down 22 cm to reflect the missing sediment in this core. See Section 6.2 for further discussion.

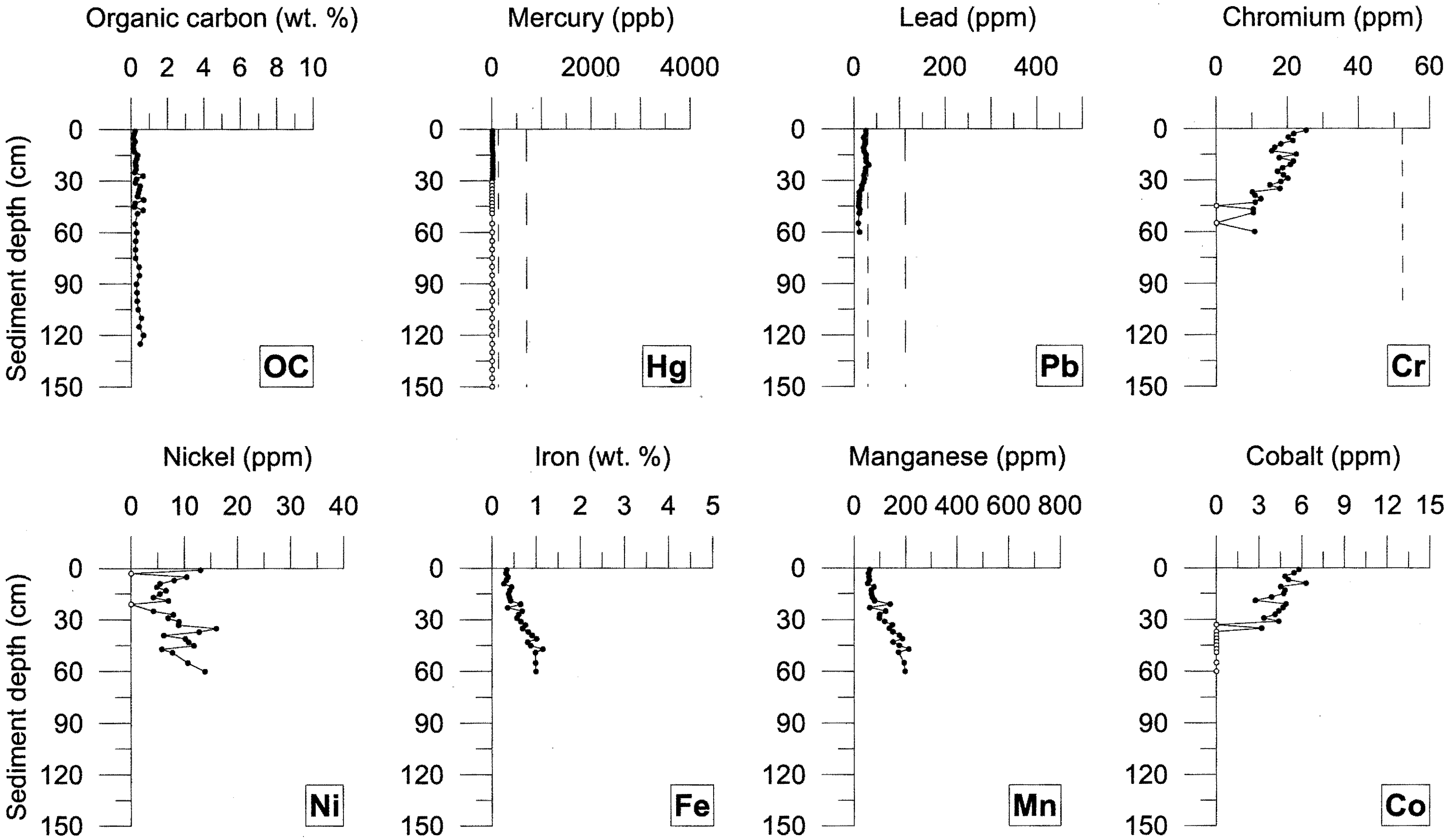

Figure E.9 Geochemical sediment core profiles of 2008 vibracore 5 (near Herring Cove, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte. The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

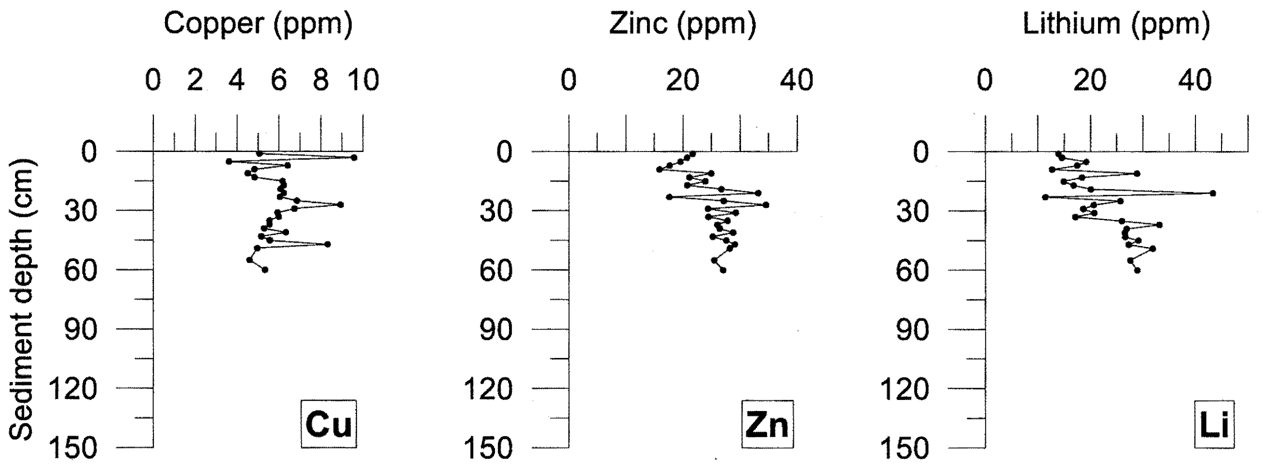

Figure E.10 Geochemical sediment core profiles of 2008 vibracore 5 (near Herring Cove, Figure 3.5).

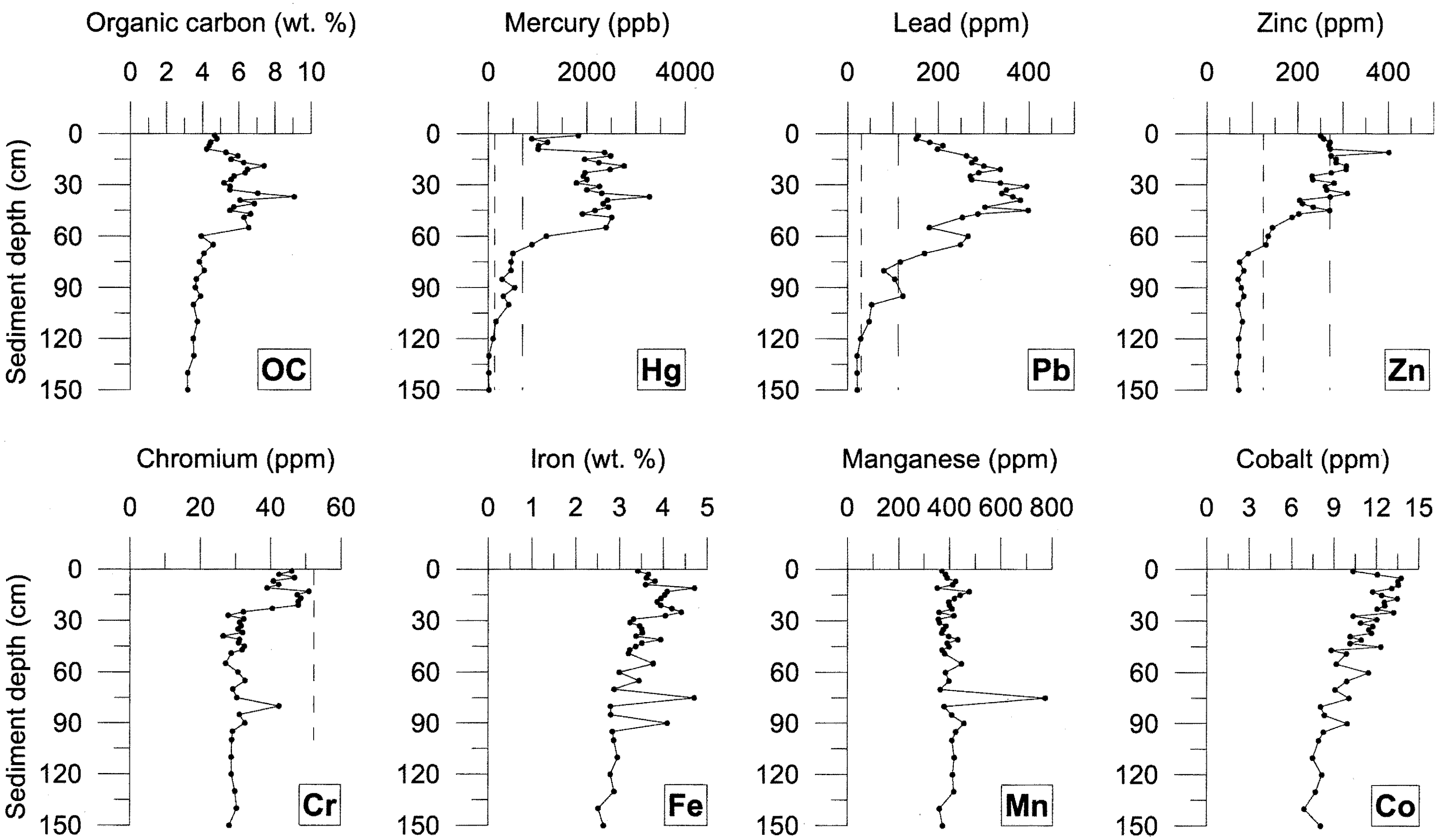

Figure E.11 Geochemical sediment core profiles of 2008 vibracore 8 (north of Georges Island, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

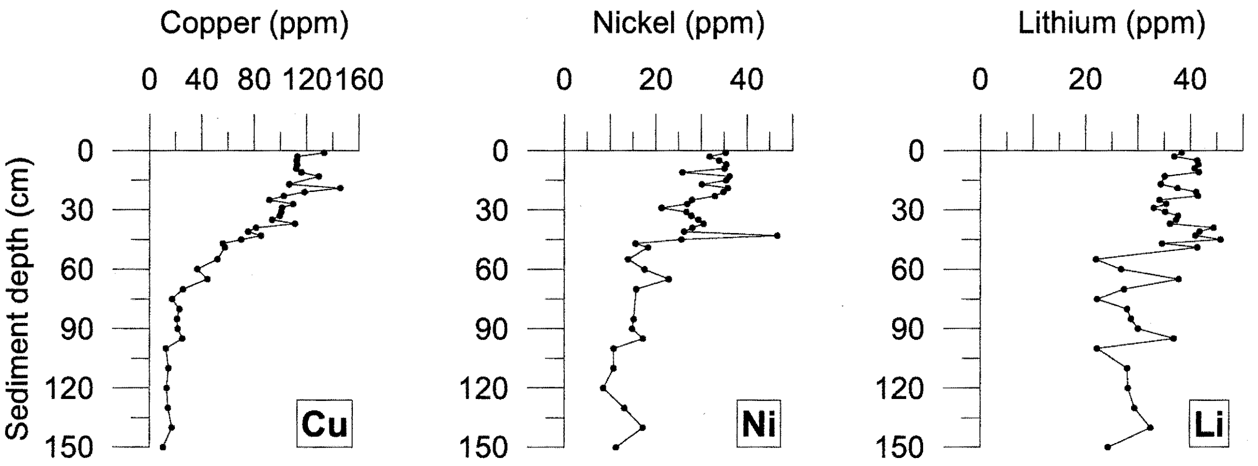

Figure E.12 Geochemical sediment core profiles of 2008 vibracore 8 (north of Georges Island, Figure 3.5).

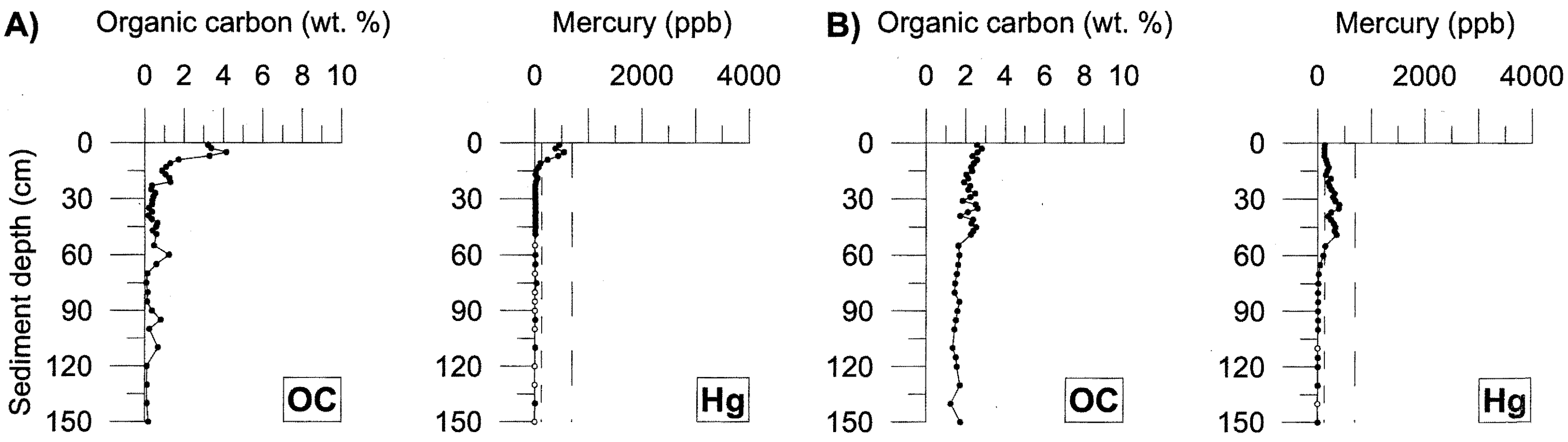

Figure E.13 Geochemical sediment core profiles of 2008 vibracore 3 and 2008 vibracore 6. A) 2008 vibracore 3 (Bedford Bay, Figure 3.5). B) 2008 vibracore 6 (west of McNabs Island, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte. The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

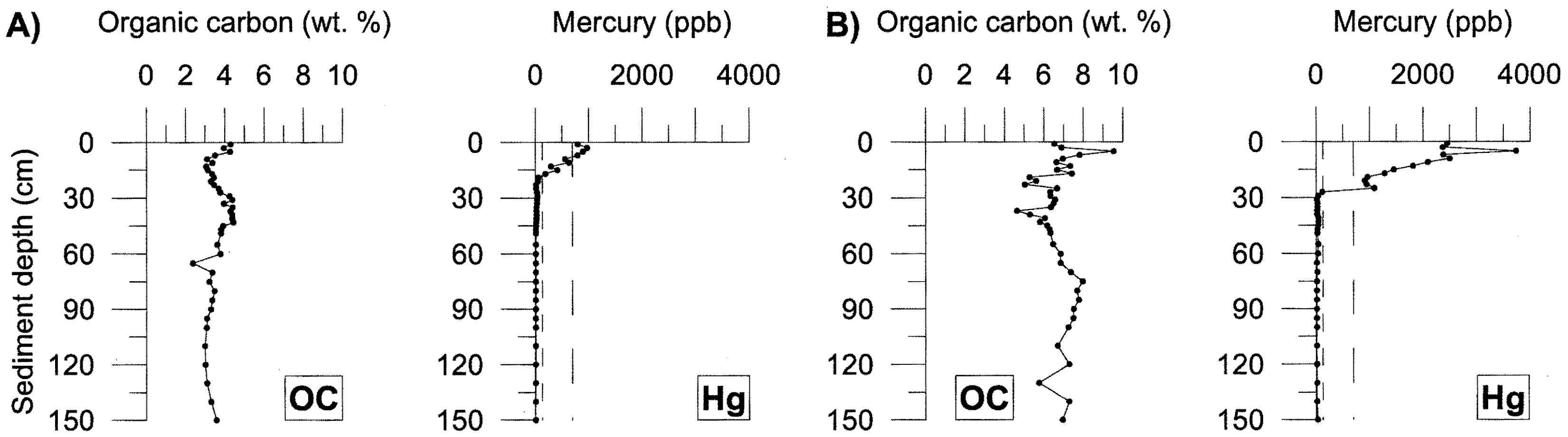

Figure E.14 Geochemical sediment core profiles of 2008 vibracore 7 and 2008 vibracore 9. A) 2008 vibracore 7 (mouth of Northwest Arm, Figure 3.5). B) 2008 vibracore 9 (Dartmouth Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

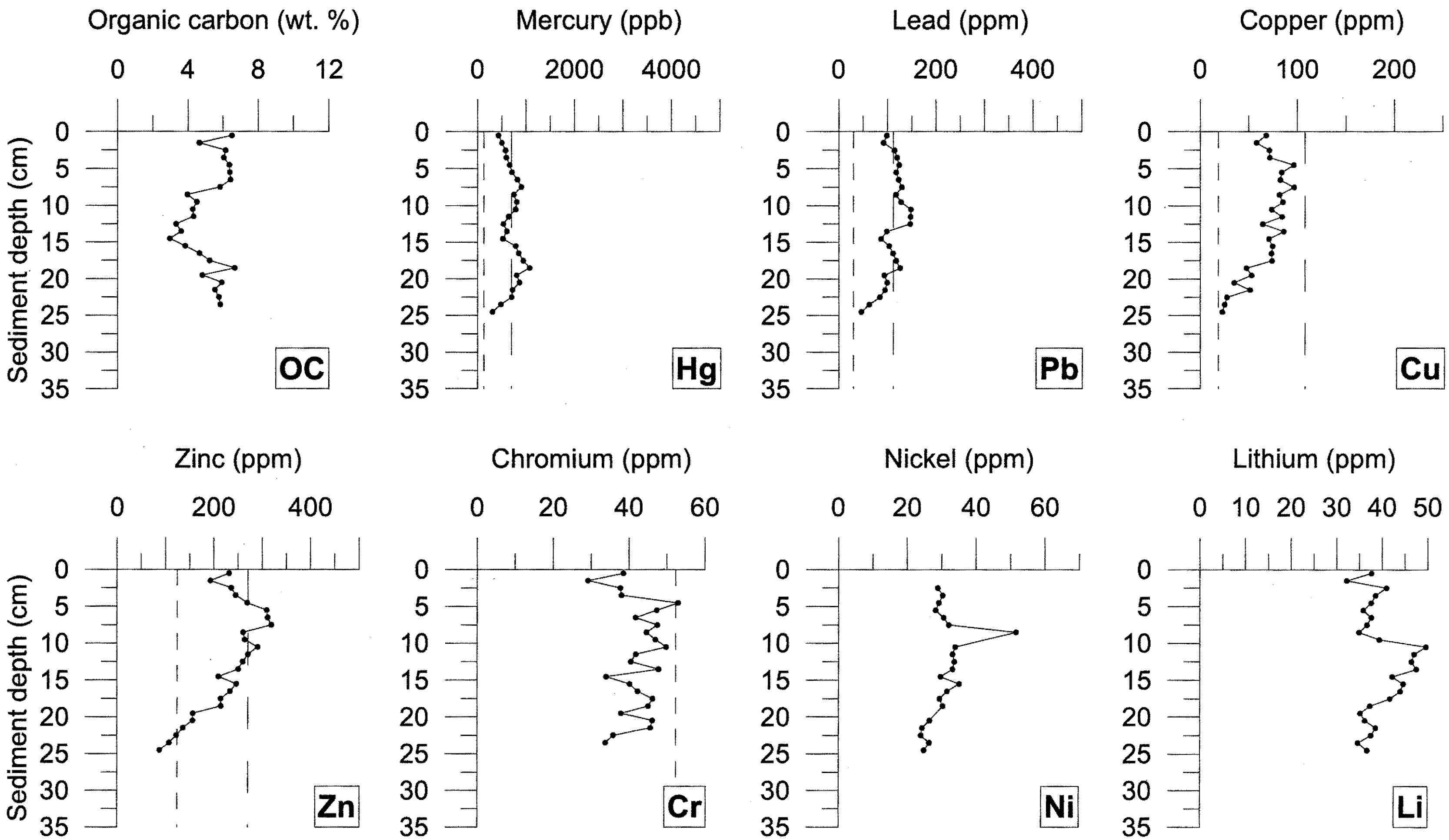

Figure E.15 Geochemical sediment core profiles of slow core 1 (near Mill Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

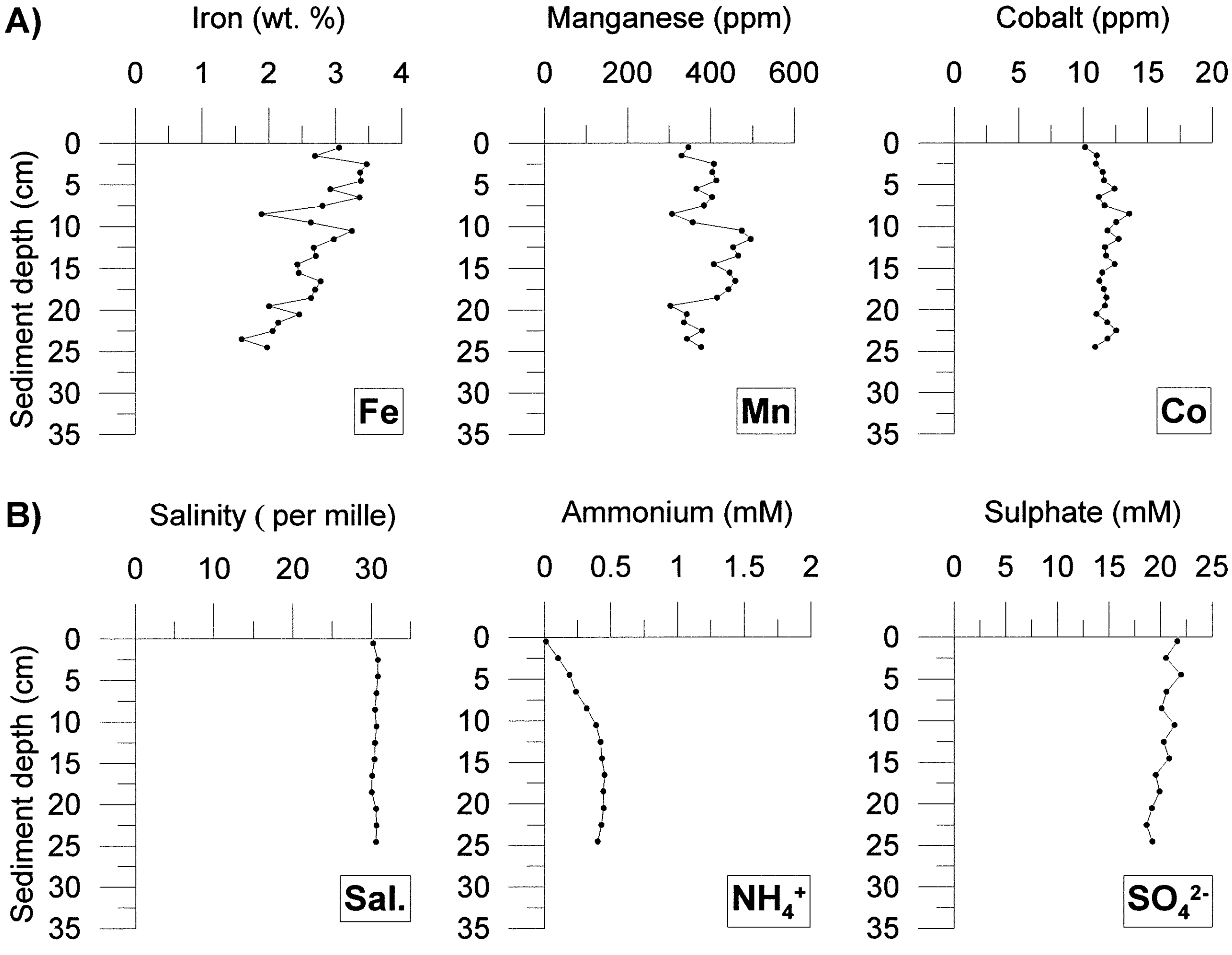

Figure E.16 Geochemical core profiles of slow core 1 (near Mill Cove, Figure 3.5). A) Geochemical sediment core profiles of slow core 1. B) Geochemical pore water profiles of slow core 1.

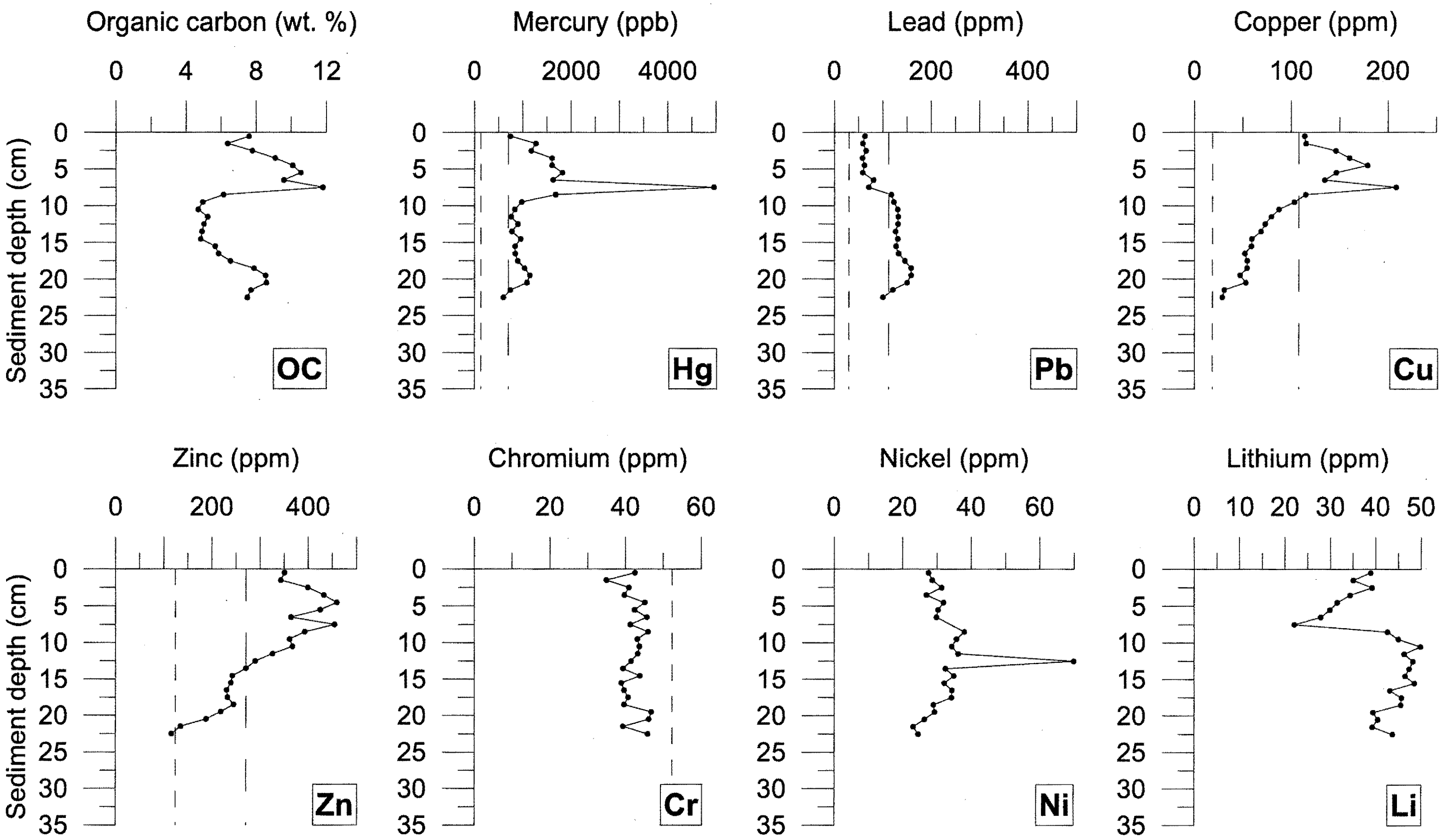

Figure E.17 Geochemical sediment core profiles of slow core 2 (near Mill Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

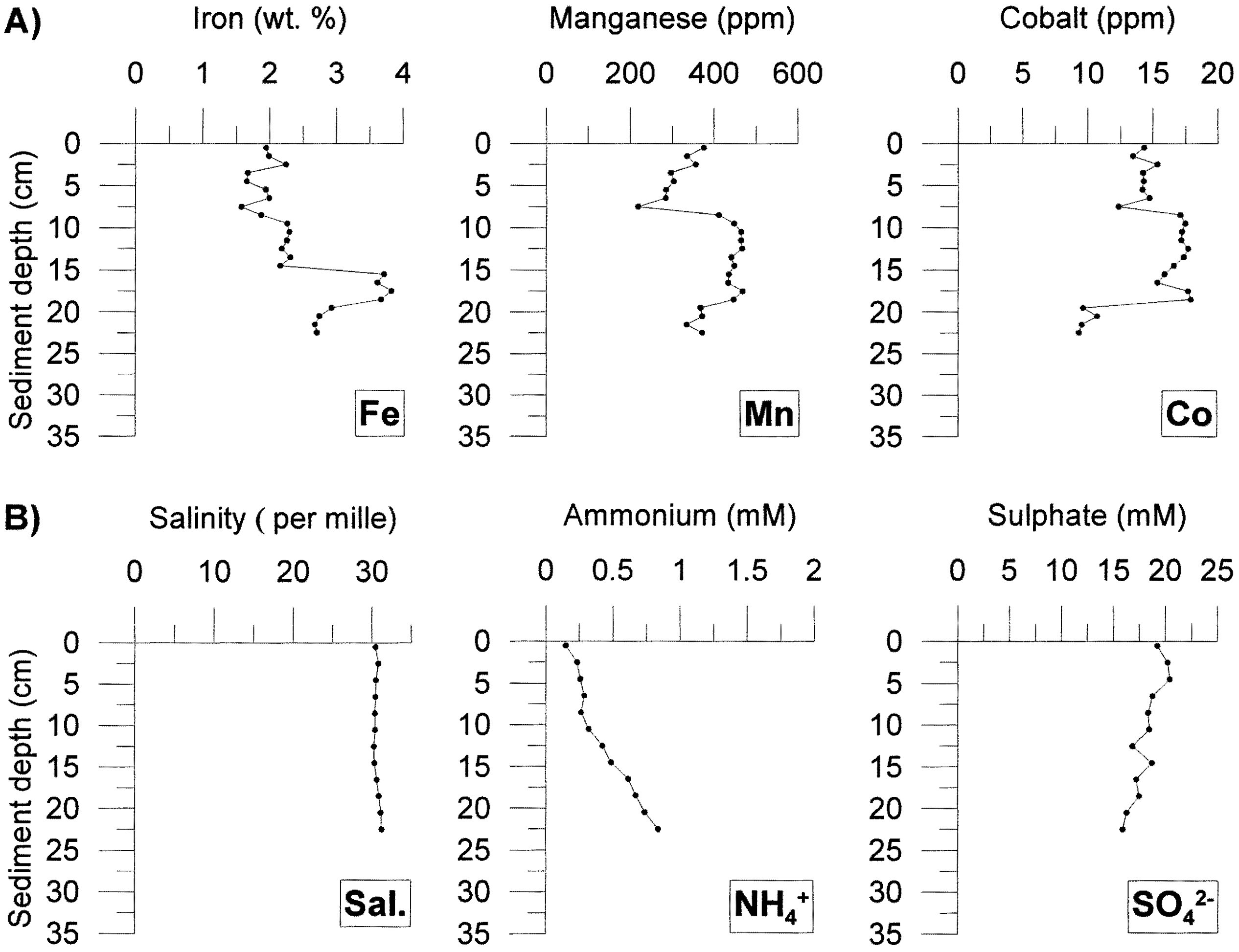

Figure E.18 Geochemical core profiles of slow core 2 (near Mill Cove, Figure 3.5). A) Geochemical sediment core profiles of slow core 2. B) Geochemical pore water profiles of slow core 2.

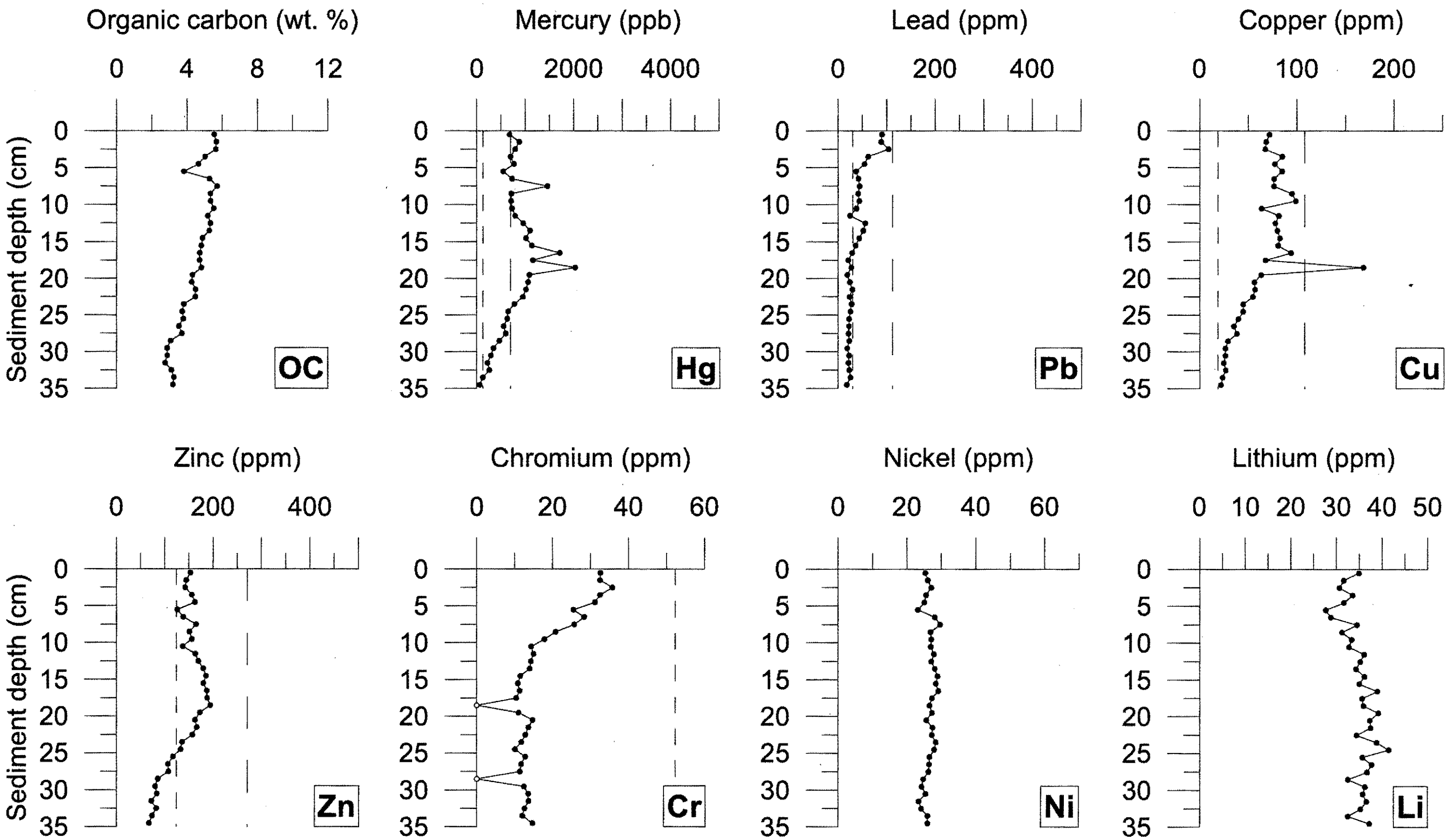

Figure E.19 Geochemical sediment core profiles of slow core 8 (mouth of Northwest Arm, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte. The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

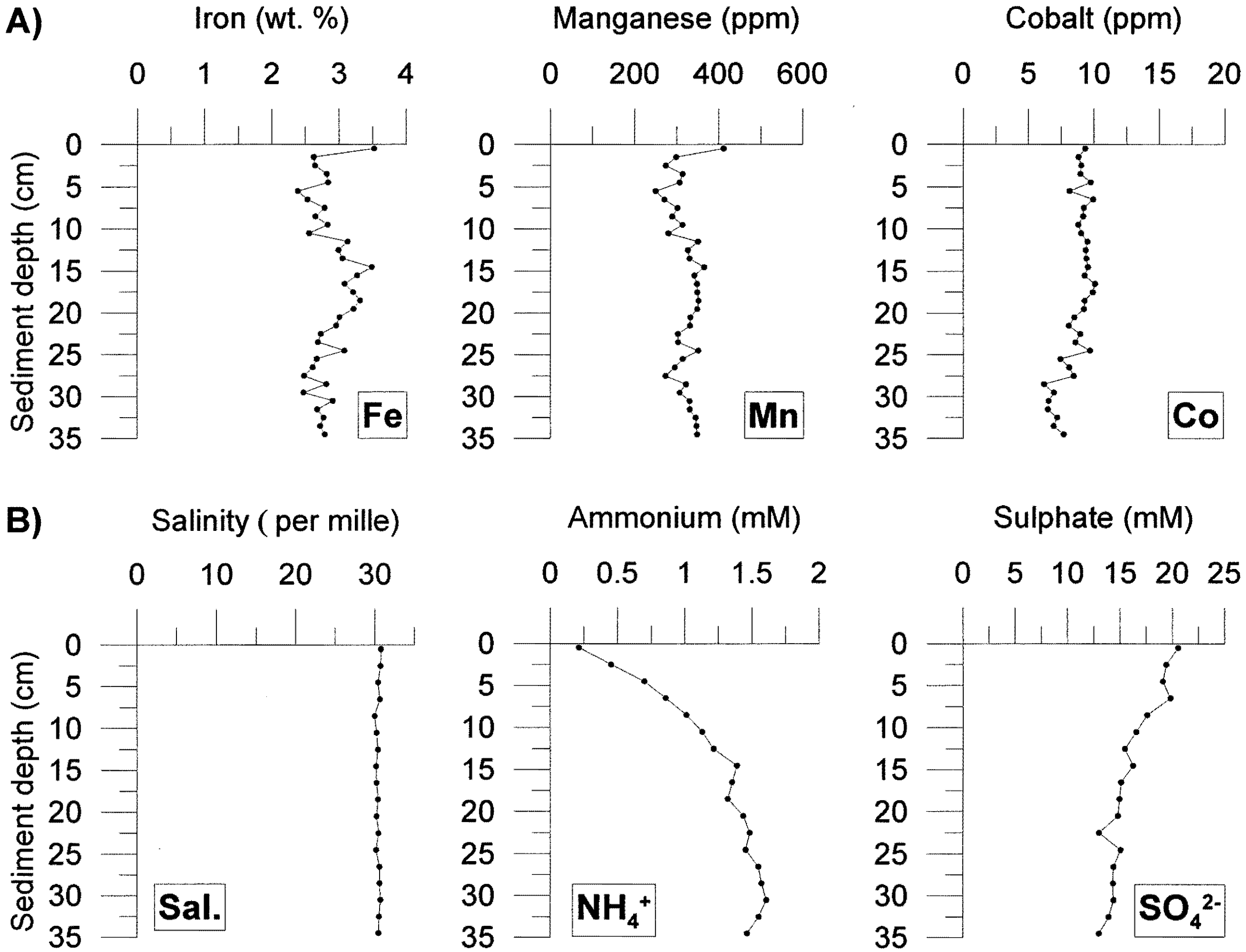

Figure E.20 Geochemical core profiles of slow core 8 (mouth of Northwest Arm, Figure 3.5). A) Geochemical sediment core profiles of slow core 8. B) Geochemical pore water profiles of slow core 8.

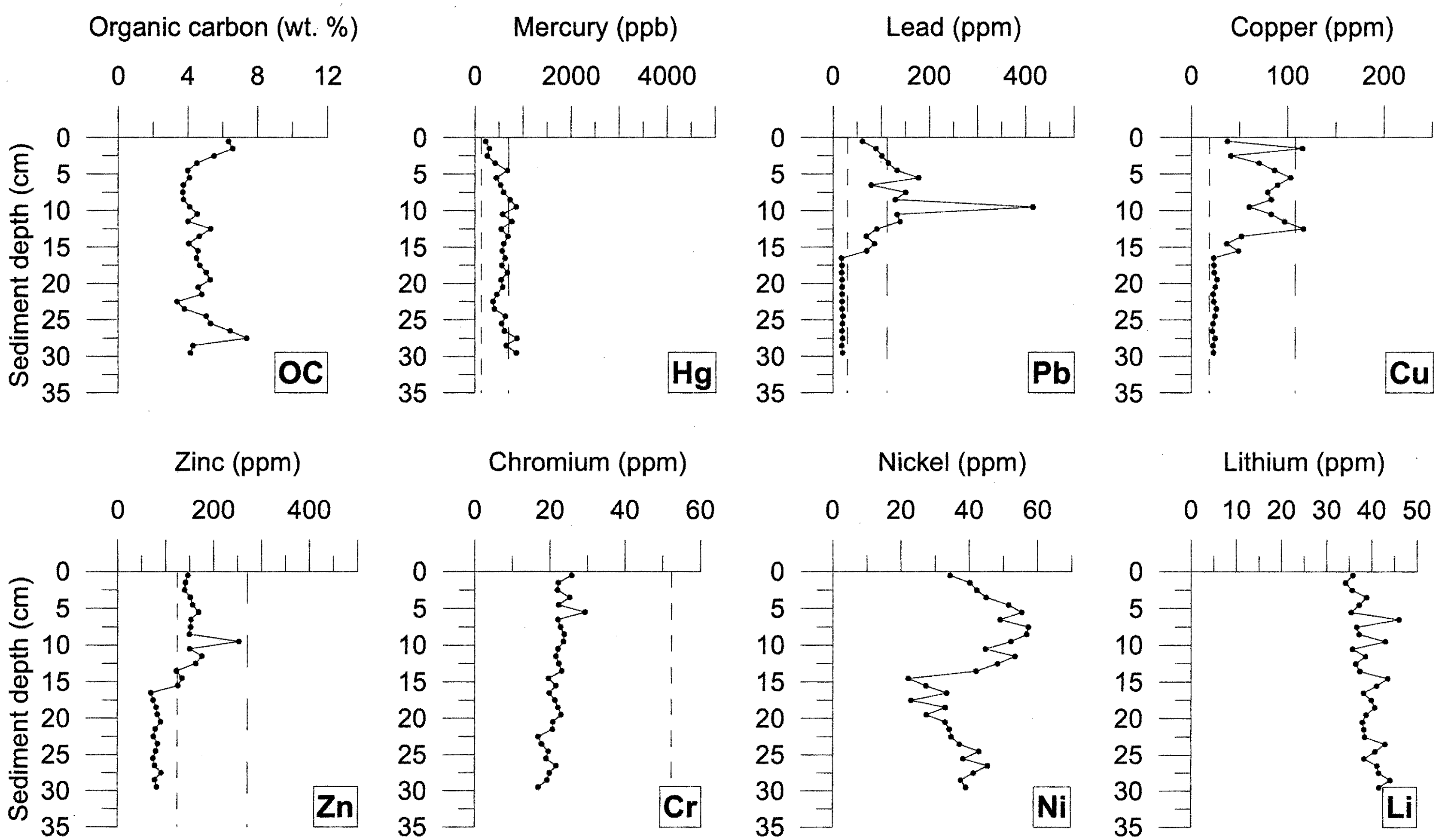

Figure E.21 Geochemical sediment core profiles of slow core 9 (Herring Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

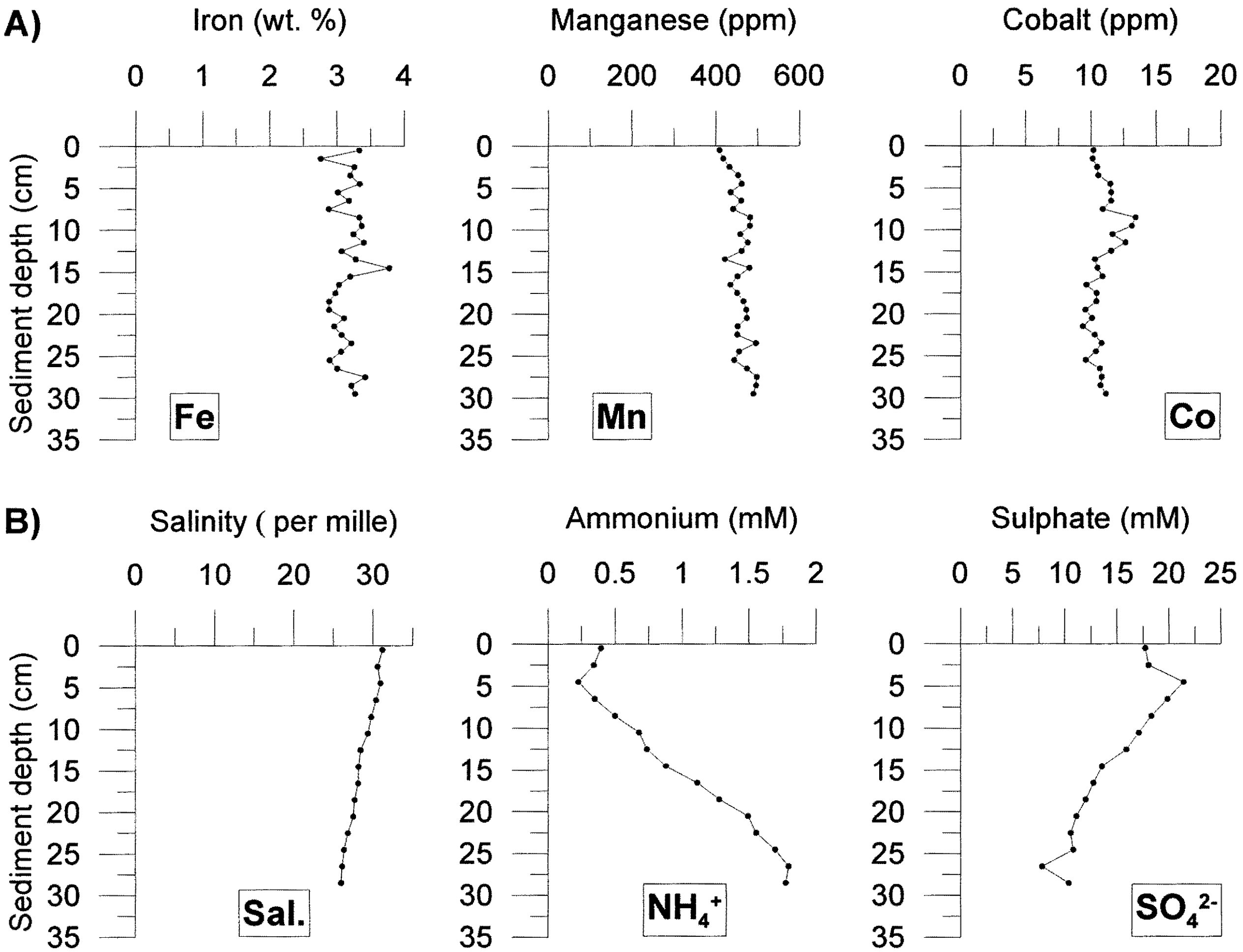

Figure E.22 Geochemical core profiles of slow core 9 (Herring Cove, Figure 3.5). A) Geochemical sediment core profiles of slow core 9. B) Geochemical pore water profiles of slow core 9.

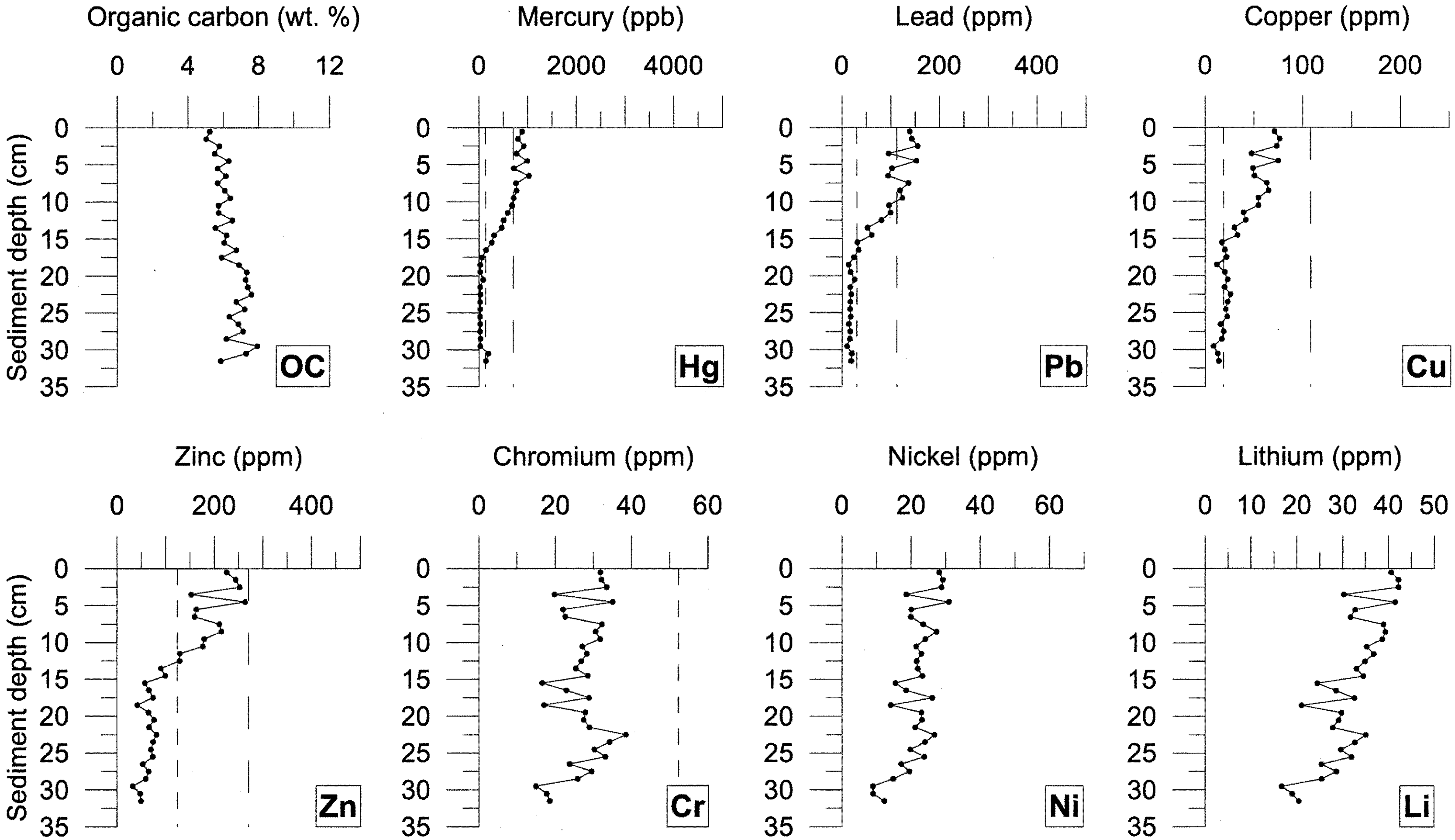

Figure E.23 Geochemical sediment core profiles of gravity core 5 (near Mill Cove, Figure 3.5). The short dashed line is representative of the ISQG (CCME 2002), while the long dashed line is representative of the PEL (CCME 2002).

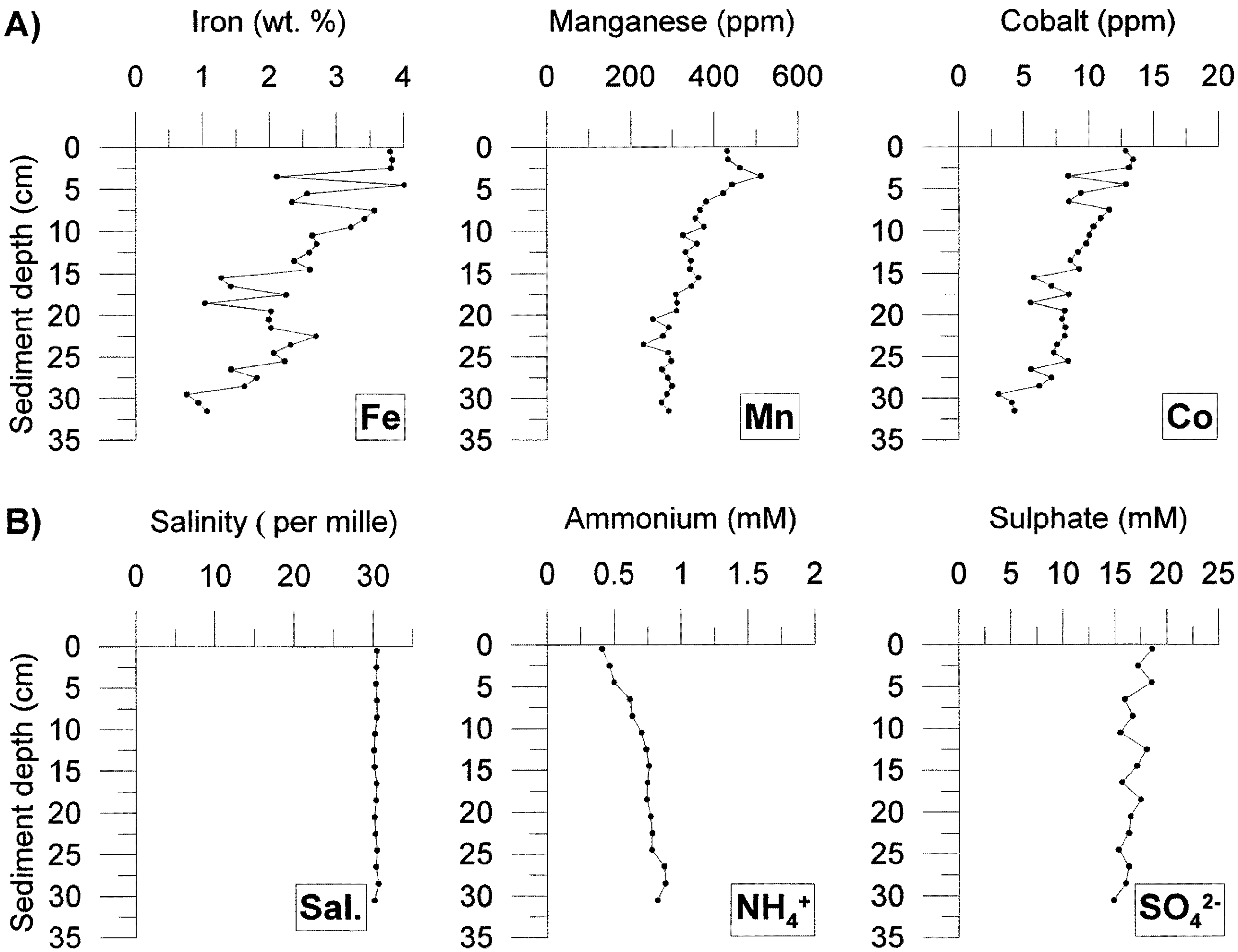

Figure E.24 Geochemical core profiles of gravity core 5 (near Mill Cove, Figure 3.5). A) Geochemical sediment core profiles of gravity core 5. B) Geochemical pore water profiles of gravity core 5.

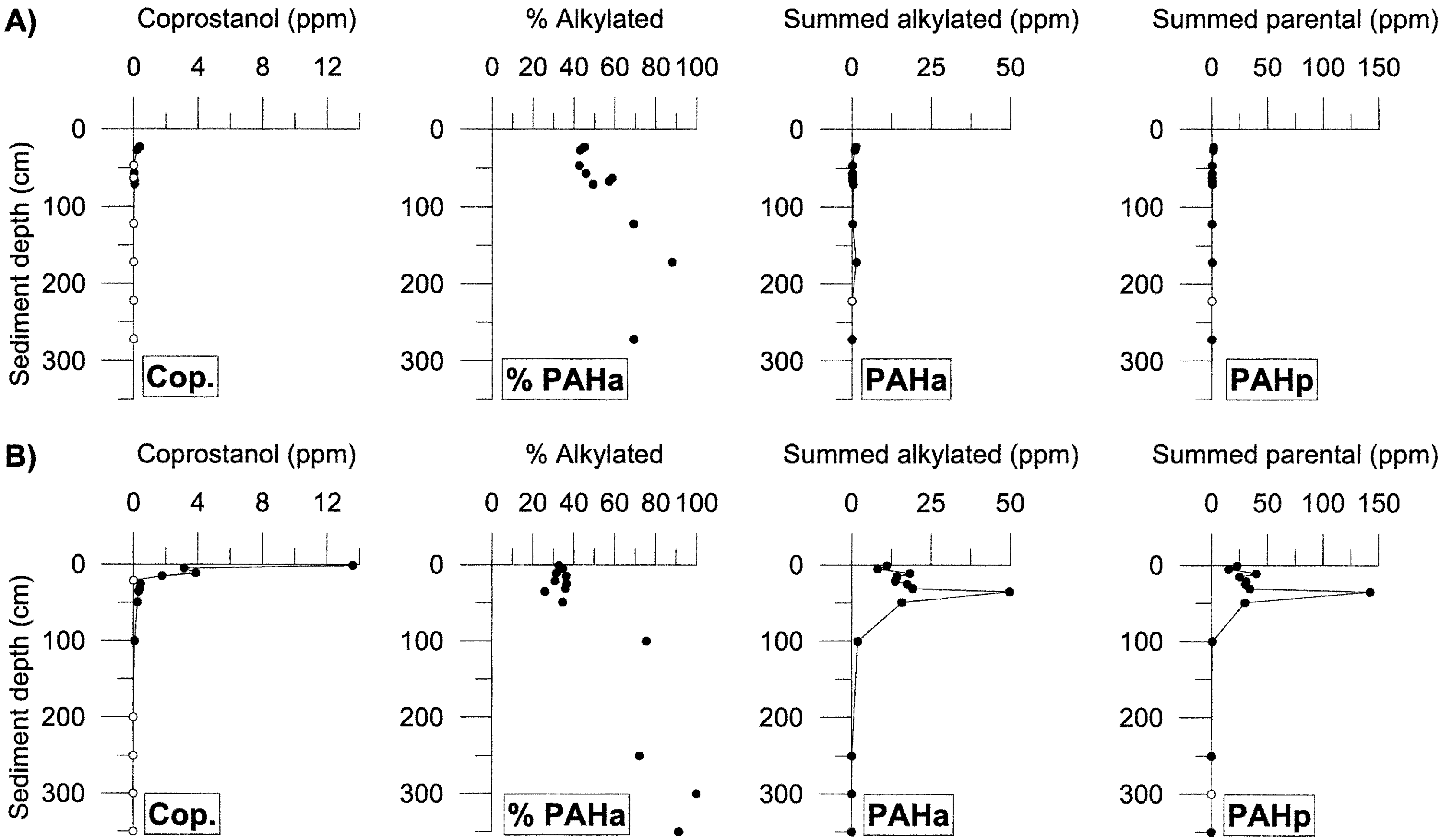

Figure E.25 Organic geochemical sediment core profiles of 2008 vibracore 2 and 2008 vibracore 8. A) 2008 vibracore 2 (near Mill Cove, Figure 3.5). B) 2008 vibracore 8 (north of Georges Island, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte.

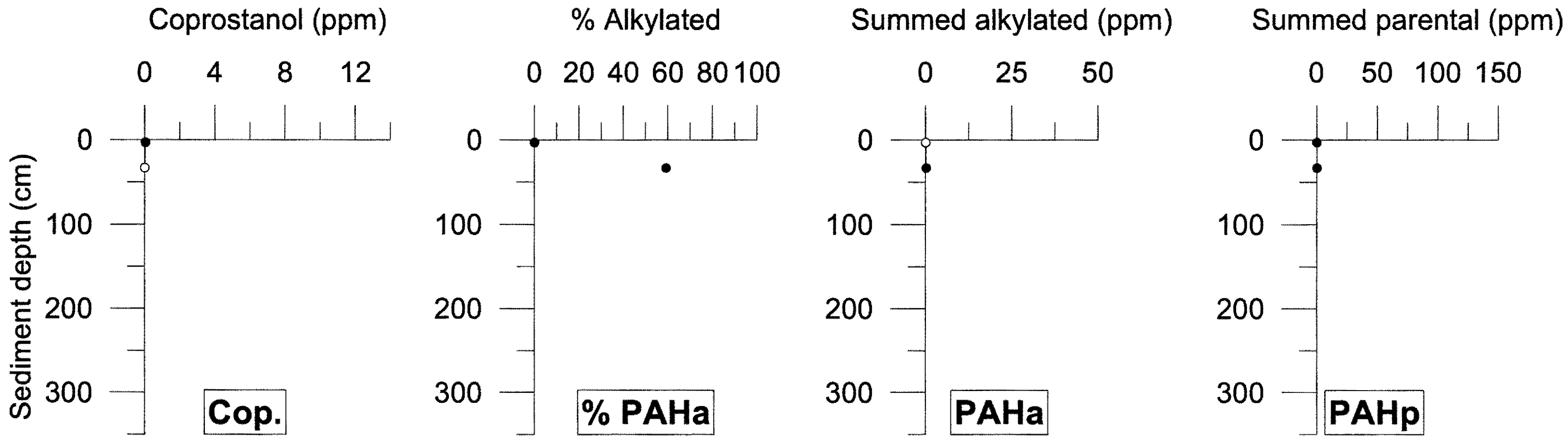

Figure E.26 Organic geochemical sediment core profiles of 2008 vibracore 5 (near Herring Cove, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte.

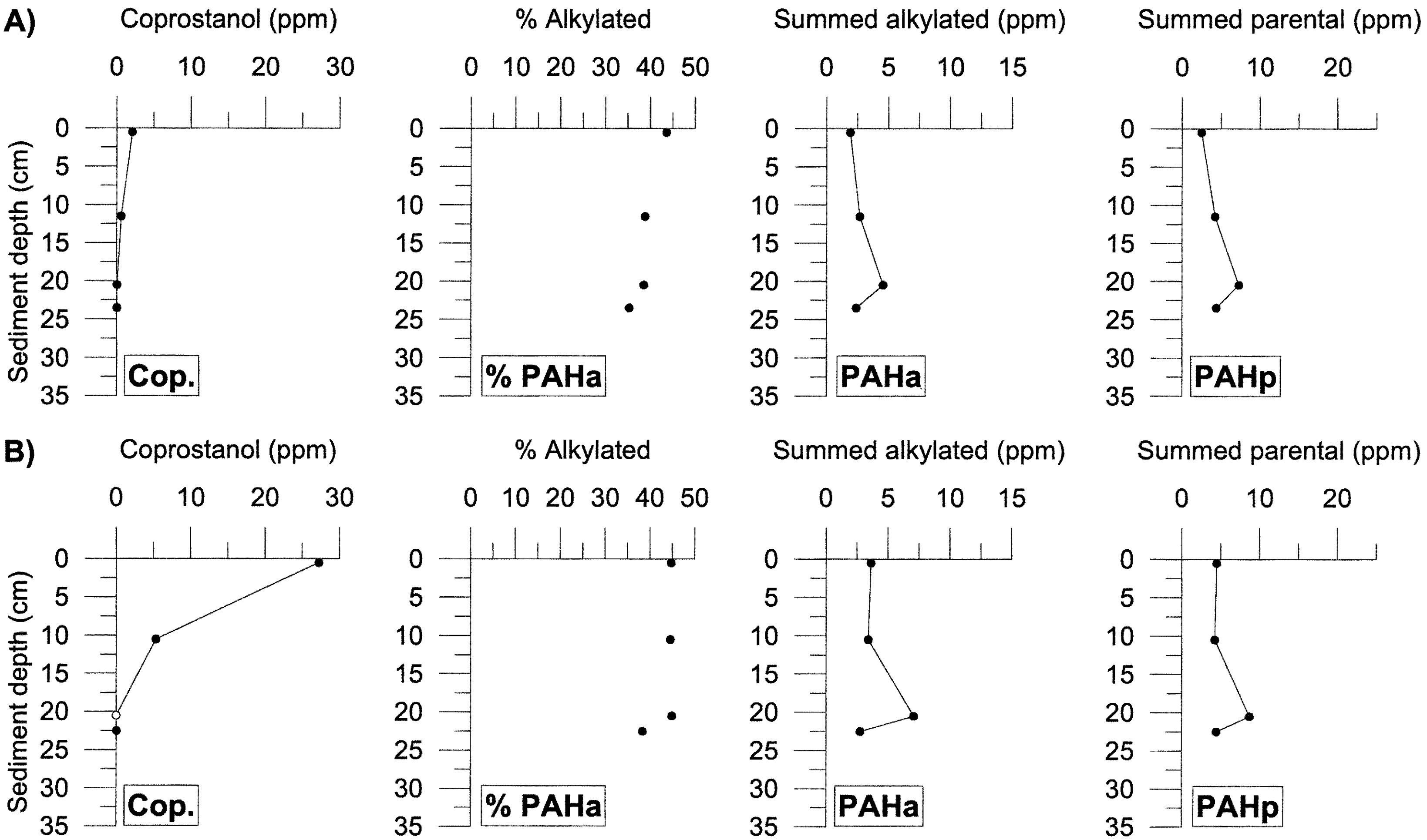

Figure E.27 Organic geochemical sediment core profiles of slow core 1 and slow core 2. A) slow core 1 (near Mill Cove, Figure 3.5). B) slow core 2 (near Mill Cove, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte.

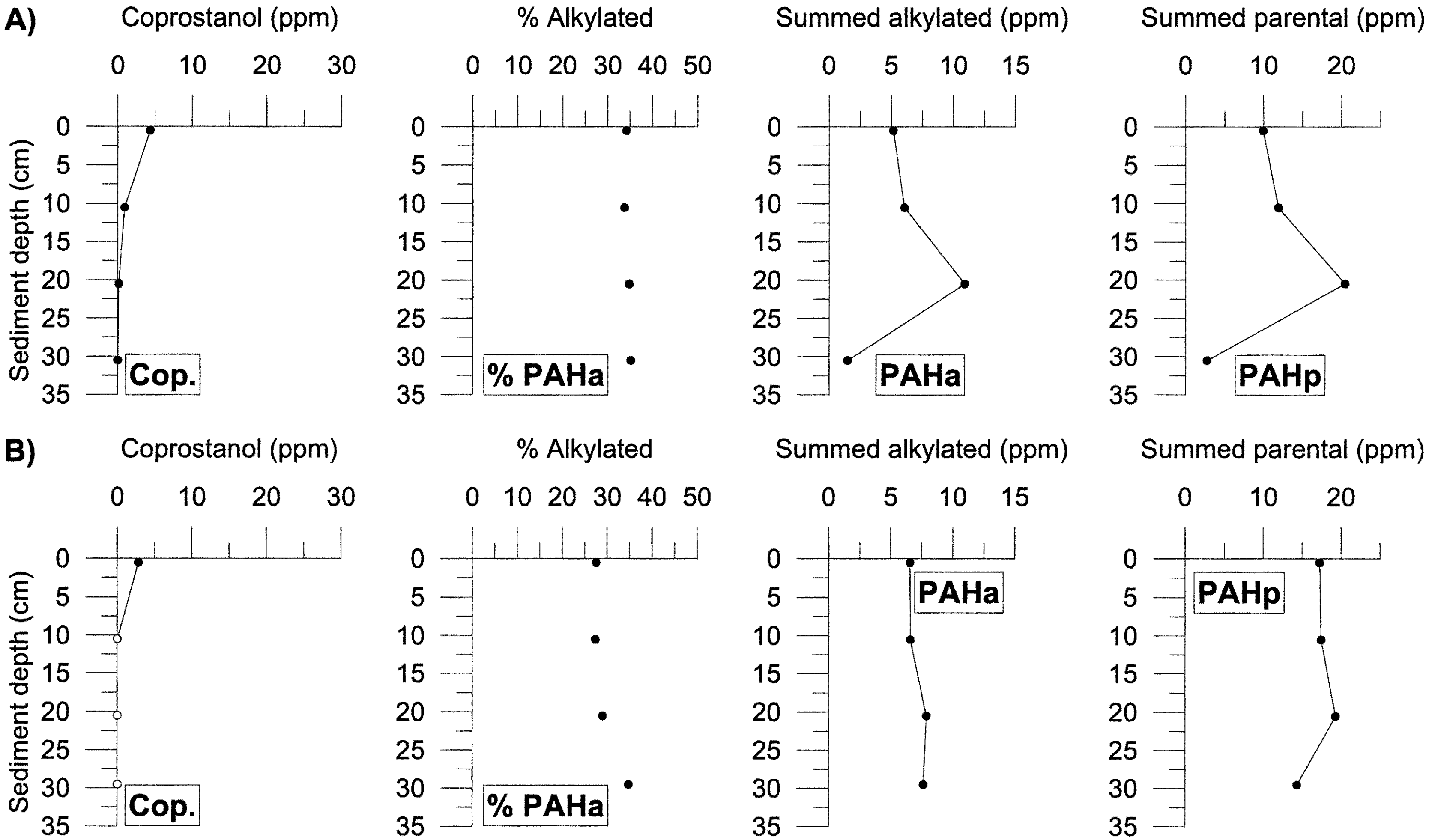

Figure E.28 Organic geochemical sediment core profiles of slow core 8 and slow core 9. A) slow core 8 (mouth of Northwest Arm, Figure 3.5). B) slow core 9 (Herring Cove, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte.

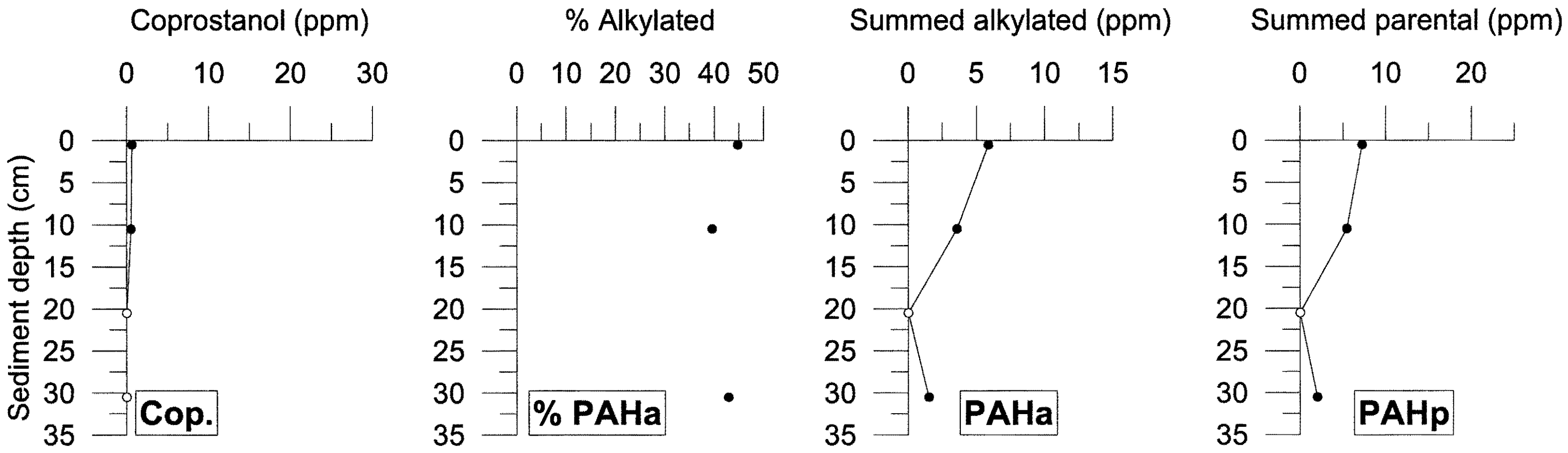

Figure E.29 Organic geochemical sediment core profiles of gravity core 5 (near Mill Cove, Figure 3.5). Open symbols denote samples with concentrations below the detection limit of the analyte.

APPENDIX F: PORE WATER RESULTS AND CORE PROFILES

Table F.1 Pore water geochemistry results

Cruise	Station No.	Lab ID	Sed. depth (cm)	Salinity (‰)	Ammonium (mM)	Sulphate (mM)
2009-060	1	20090061	0.5	30.2	0.01	22
2009-060	1	20090063	2.5	30.8	0.10	21
2009-060	1	20090065	4.5	30.8	0.19	22
2009-060	1	20090067	6.5	30.7	0.24	21
2009-060	1	20090069	8.5	30.5	0.32	20
2009-060	1	20090071	10.5	30.7	0.39	21
2009-060	1	20090073	12.5	30.5	0.42	20
2009-060	1	20090075	14.5	30.4	0.43	21
2009-060	1	20090077	16.5	30.1	0.45	20
2009-060	1	20090079	18.5	30.0	0.44	20
2009-060	1	20090081	20.5	30.6	0.45	19
2009-060	1	20090083	22.5	30.7	0.43	19
2009-060	1	20090085	24.5	30.6	0.40	19
2009-060	2	20090087	0.5	30.5	0.15	19
2009-060	2	20090089	2.5	30.8	0.23	20
2009-060	2	20090091	4.5	30.5	0.26	20
2009-060	2	20090093	6.5	30.5	0.29	19
2009-060	2	20090095	8.5	30.4	0.26	18
2009-060	2	20090097	10.5	30.4	0.32	18
2009-060	2	20090099	12.5	30.3	0.42	17
2009-060	2	20090101	14.5	30.4	0.49	19
2009-060	2	20090103	16.5	30.7	0.61	17
2009-060	2	20090105	18.5	30.9	0.67	17
2009-060	2	20090107	20.5	31.1	0.74	16
2009-060	2	20090109	22.5	31.3	0.84	16
2009-060	5	20090147	0.5	30.5	0.41	19
2009-060	5	20090149	2.5	30.4	0.46	17
2009-060	5	20090151	4.5	30.4	0.50	19
2009-060	5	20090153	6.5	30.5	0.62	16
2009-060	5	20090155	8.5	30.5	0.63	17
2009-060	5	20090157	10.5	30.2	0.70	16
2009-060	5	20090159	12.5	30.1	0.74	18
2009-060	5	20090161	14.5	30.2	0.76	17
2009-060	5	20090163	16.5	30.4	0.75	16
2009-060	5	20090165	18.5	30.4	0.74	18
2009-060	5	20090167	20.5	30.2	0.77	17
2009-060	5	20090169	22.5	30.3	0.78	16
2009-060	5	20090171	24.5	30.5	0.78	15
2009-060	5	20090173	26.5	30.4	0.87	16
2009-060	5	20090175	28.5	30.7	0.88	16
2009-060	5	20090177	30.5	30.2	0.82	15
2009-060	8	20090111	0.5	30.8	0.21	21
2009-060	8	20090113	2.5	30.7	0.45	19
2009-060	8	20090115	4.5	30.4	0.70	19

Table F.1 Pore water geochemistry results (cont'd)

Cruise	Station No.	Lab ID	Sed. depth (cm)	Salinity (‰)	Ammonium (mM)	Sulphate (mM)
2009-060	8	20090117	6.5	30.7	0.86	20
2009-060	8	20090119	8.5	30.0	1.01	18
2009-060	8	20090121	10.5	30.2	1.13	17
2009-060	8	20090123	12.5	30.4	1.22	15
2009-060	8	20090125	14.5	30.2	1.39	16
2009-060	8	20090127	16.5	30.2	1.35	15
2009-060	8	20090129	18.5	30.4	1.32	15
2009-060	8	20090131	20.5	30.2	1.44	15
2009-060	8	20090133	22.5	30.5	1.48	13
2009-060	8	20090135	24.5	30.2	1.45	15
2009-060	8	20090137	26.5	30.6	1.55	14
2009-060	8	20090139	28.5	30.6	1.57	14
2009-060	8	20090141	30.5	30.7	1.61	14
2009-060	8	20090143	32.5	30.5	1.55	14
2009-060	8	20090145	34.5	30.5	1.46	13
2009-060	9	20090031	0.5	31.2	0.39	18
2009-060	9	20090033	2.5	30.6	0.34	18
2009-060	9	20090035	4.5	31.0	0.22	21
2009-060	9	20090037	6.5	30.4	0.35	20
2009-060	9	20090039	8.5	29.8	0.50	18
2009-060	9	20090041	10.5	29.4	0.68	17
2009-060	9	20090043	12.5	28.5	0.74	16
2009-060	9	20090045	14.5	28.2	0.88	14
2009-060	9	20090047	16.5	28.2	1.11	13
2009-060	9	20090049	18.5	27.7	1.28	12
2009-060	9	20090051	20.5	27.5	1.49	11
2009-060	9	20090053	22.5	26.9	1.55	11
2009-060	9	20090055	24.5	26.4	1.69	11
2009-060	9	20090057	26.5	26.1	1.79	8
2009-060	9	20090059	28.5	26.0	1.77	10

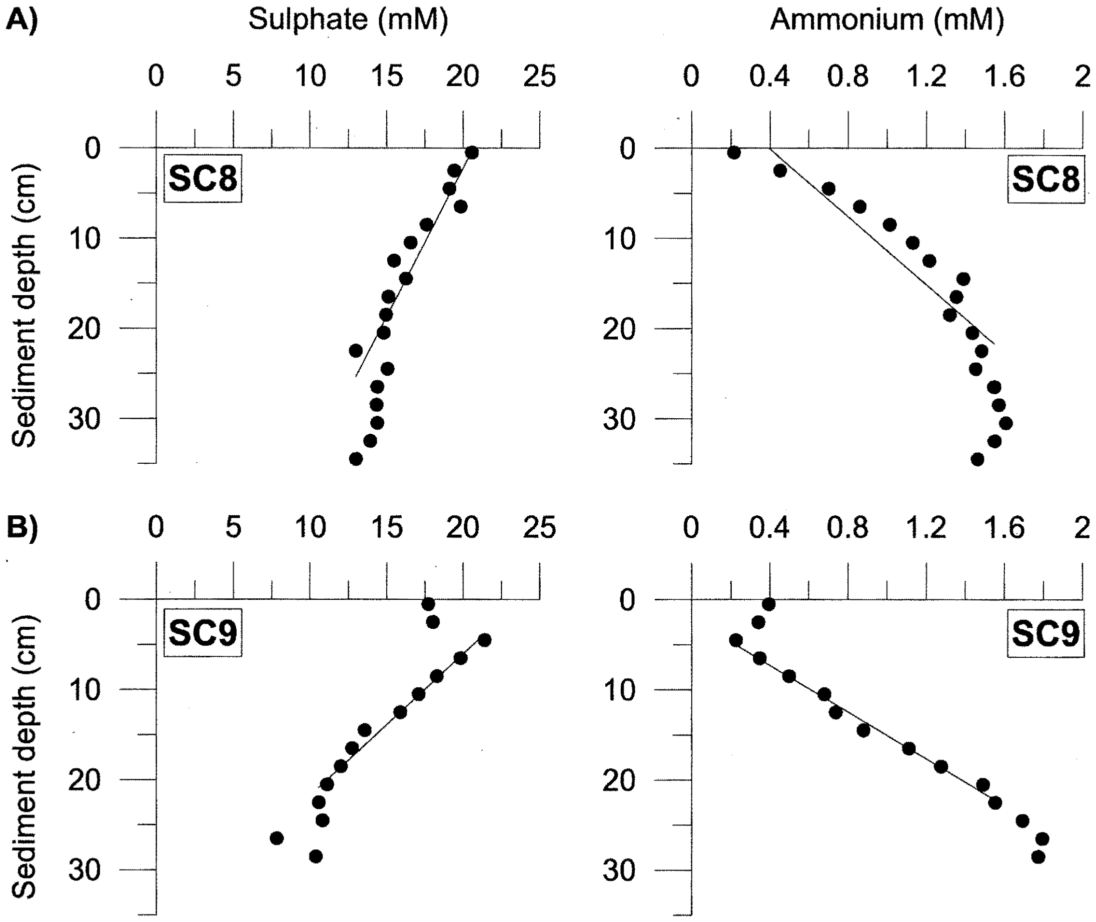

Figure F.1 Pore water profiles of cores from the mouth of Northwest Arm (slow core 8) and Herring Cove (slow core 9). Lines shown are representative of sulphate and ammonium gradients used to calculate present-day sedimentation rates. Present-day sedimentation rates for slow cores 8 and 9 were estimated to be 0.10 cm/year and 0.15 cm/year, respectively. Correlation coefficients for sulphate/depth and ammonium/depth were significant at a probability of $p < 0.05$. A) slow core 8. B) slow core 9.

APPENDIX G: ^{210}Pb AND ^{137}Cs RESULTS

Table G.1 Sediment core ^{210}Pb and ^{137}Cs results

Cruise	Stn. No.	Lab ID	Sed. depth (cm)	Total ^{210}Pb (dpm/g)	Total ^{210}Pb error (dpm/g)	^{137}Cs (Bq/kg)	^{137}Cs error (Bq/kg)
2009-060	1	20090061	0.5	13.69	0.58	-	-
2009-060	1	20090062	1.5	10.63	0.48	-	-
2009-060	1	20090063	2.5	11.68	0.50	-	-
2009-060	1	20090064	3.5	11.53	0.54	9.70	2.40
2009-060	1	20090065	4.5	12.19	0.50	11.10	2.00
2009-060	1	20090068	7.5	9.45	0.38	14.90	2.18
2009-060	1	20090070	9.5	7.85	0.33	12.78	1.50
2009-060	1	20090072	11.5	6.29	0.28	15.74	1.59
2009-060	1	20090074	13.5	9.12	0.56	15.71	2.30
2009-060	1	20090076	15.5	5.56	0.28	18.94	2.46
2009-060	1	20090078	17.5	4.82	0.27	14.00	2.44
2009-060	1	20090080	19.5	2.81	0.20	-	-
2009-060	1	20090085	24.5	2.51	0.17	<2.6	-
2009-060	2	20090087	0.5	15.35	0.60	4.89	1.85
2009-060	2	20090088	1.5	14.41	0.65	-	-
2009-060	2	20090089	2.5	13.87	0.58	6.69	1.30
2009-060	2	20090090	3.5	13.41	0.54	-	-
2009-060	2	20090091	4.5	13.38	0.56	25.20	2.18
2009-060	2	20090094	7.5	7.35	0.34	-	-
2009-060	2	20090096	9.5	8.45	0.39	15.73	2.00
2009-060	2	20090098	11.5	7.05	0.28	16.80	2.18
2009-060	2	20090100	13.5	6.47	0.35	18.42	1.54
2009-060	2	20090102	15.5	3.11	0.13	23.50	2.52
2009-060	2	20090104	17.5	4.98	0.20	21.26	3.00
2009-060	2	20090106	19.5	4.55	0.27	-	-
2009-060	2	20090109	22.5	-	-	<3.4	-
2009-060	8	20090111	0.5	10.97	0.46	-	
2009-060	8	20090112	1.5	9.43	0.38	2.93	1.61
2009-060	8	20090113	2.5	10.03	0.39	4.93	1.03
2009-060	8	20090114	3.5	9.75	0.34	3.86	1.00
2009-060	8	20090115	4.5	1.60	0.05	6.43	1.62
2009-060	8	20090116	5.5	1.50	0.04	2.82	0.85
2009-060	8	20090118	7.5	-	-	3.56	1.94
2009-060	8	20090119	8.5	1.62	0.05	3.95	1.28
2009-060	8	20090120	9.5	1.59	0.05	3.70	1.30
2009-060	9	20090031	0.5	15.55	0.48	4.58	1.42
2009-060	9	20090032	1.5	14.94	0.46	3.50	1.64
2009-060	9	20090033	2.5	12.93	0.42	3.68	1.73
2009-060	9	20090034	3.5	7.30	0.39	4.39	1.18
2009-060	9	20090035	4.5	5.46	0.30	3.97	1.18
2009-060	9	20090038	7.5	3.86	0.21	<1.6	-
2009-060	9	20090040	9.5	3.71	0.20	1.62	0.89

Table G.1 Sediment core ^{210}Pb and ^{137}Cs results (cont'd)

Cruise	Stn. No.	Lab ID	Sed. depth (cm)	Total ^{210}Pb (dpm/g)	Total ^{210}Pb error (dpm/g)	^{137}Cs (Bq/kg)	^{137}Cs error (Bq/kg)
2009-060	9	20090043	12.5	3.67	0.20	<1.5	-
2009-060	9	20090045	14.5	1.92	0.13	<1.5	-
2009-060	9	20090048	17.5	3.17	0.16	<1.0	-
2009-060	9	20090050	19.5	3.27	0.15	<2.7	-
2009-060	9	20090055	24.5	-	-	<1.6	-
2009-060	9	20090060	29.5	2.30	0.16	<1.9	-

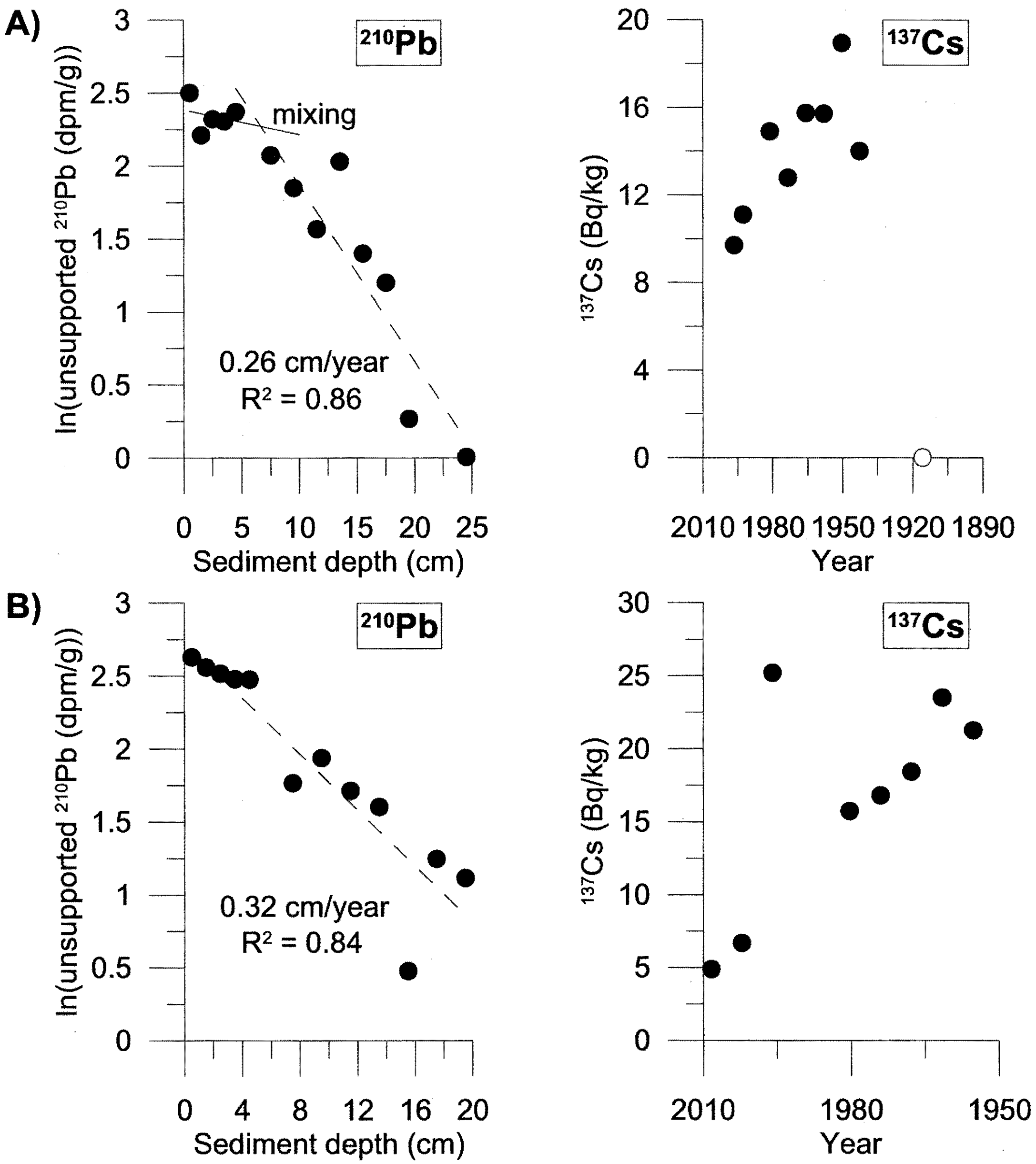

Figure G.1 The natural logarithm of unsupported ^{210}Pb versus sediment depth and ^{137}Cs geochronologies in slow core 1 and slow core 2. A) slow core 1 (near Mill Cove, Figure 3.5). The nearly horizontal activity profile indicated by the solid line is indicative of mixing in the upper 5 cm. A sediment accumulation rate of 0.26 cm/year was calculated using the slope defined by the dashed line. ^{137}Cs first appears at sediment depths corresponding to 1942 and an initial peaks at sediment depths corresponding to 1950 supporting mixing over 5 cm depth in this core. B) slow core 2 (near Mill Cove, Figure 3.5). A sediment accumulation rate of 0.32 cm/year was calculated using the slope defined by the dashed line. ^{137}Cs first appears at sediment depths corresponding to 1955 and an initial peak at sediment depths corresponding to 1962 supporting the estimated sediment accumulation rate.

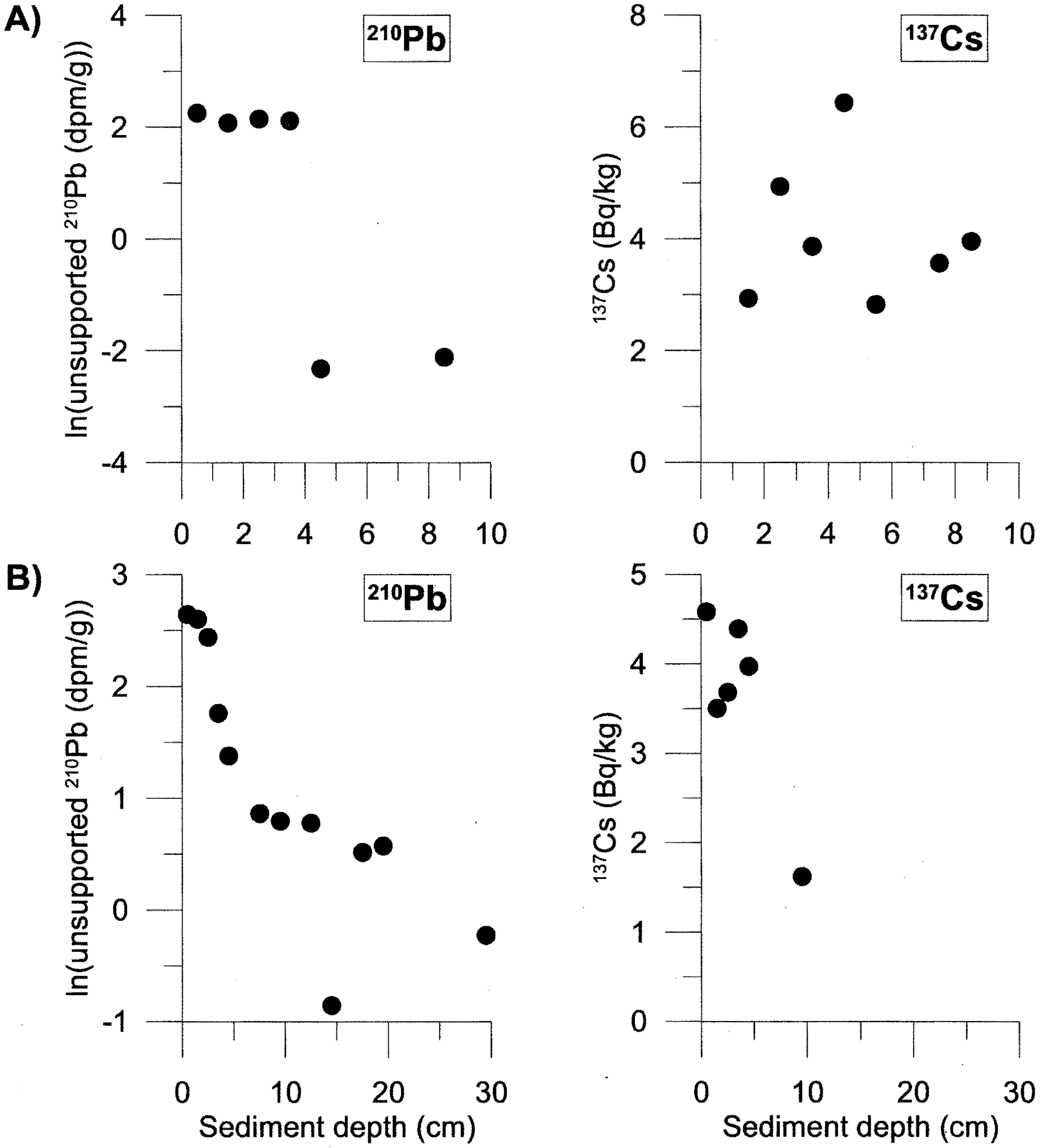

Figure G.2 The natural logarithm of unsupported ^{210}Pb versus sediment depth and ^{137}Cs versus sediment depth in slow core 8 and slow core 9. A) slow core 8. (mouth of Northwest Arm, Figure 3.5). The nearly horizontal ^{210}Pb activity profile near the surface of slow core 8 and the variation in ^{137}Cs activity throughout the core are suggestive of mixing. A sedimentation rate cannot be determined due to mixing and scouring. However, a low sedimentation rate (<0.2 cm/year) is indicated by the relationship between ^{210}Pb activity and sediment depth. B) slow core 9 (Herring Cove, Figure 3.5). The nearly horizontal ^{210}Pb activity profile in the top few cm of slow core 9 and the variation in ^{137}Cs activity down to 10 cm are suggestive of mixing in the top few cm. A sedimentation rate cannot be determined due to mixing. However, the steep slope of changing ^{210}Pb activity with depth is suggestive of a low sedimentation rate (<0.2 cm/year).

APPENDIX H: CORE DESCRIPTION LOGS AND PHOTOGRAPHS

Table H.1 Sediment core description of 1993 vibracore 2

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 30				BLACK ORGANIC MUD (AT 16 cm BANDED BLACK ORGANIC MUD)	SANDY MUD
30 – 199	GAS CRACKS		5Y/5/3	OLIVE, MASSIVE, SANDY MUD, SHELL BEARING	SANDY MUD
199 – 204	GAS CRACKS		5Y/5/3	OLIVE, MASSIVE, SANDY MUD, SHELL BEARING, LARGE SLATE COBBLE	SANDY MUD
204 – 333	GAS CRACKS		5Y/5/3	OLIVE, MASSIVE, SANDY MUD, BLACK MOTTLING, ABUNDANT SHELLS	SANDY MUD AND SHELLS
333 – 366			5Y/5/3	OLIVE, MASSIVE, SANDY MUD, BLACK MOTTLING, ABUNDANT SHELLS, GRADATIONAL CONTACT, INCREASING AMOUNTS OF PEBBLES, BECOMING CLAYEY?	SANDY MUD AND SHELLS
366 – 414			5Y/5/3	OLIVE GREY ORGANIC MUD	MUD
414 – 415				MEDIUM TO COARSE SAND	SAND
415 – 425				BROWNISH GREY CLAY, SLATE COBBLE AT 416 cm AND 424 cm	CLAY
425 – 430				OLIVE GREY, MASSIVE, SANDY MUD	SANDY MUD
430 – 435			2.5YR/6/0	BLUISH GREY CLAY, COBBLE AT 432 cm	CLAY
435 – 490	DEFORMED		7.5YR/6/2	INTERBEDDED BLACK ORGANIC MATERIAL AND BROWN SANDY MUD	SANDY MUD
490 – 512			7.5YR/6/2	BROWN CLAY, SILT, SAND, PEBBLES, LAMINATED, RHYTHMIC LAYERING	CLAY, SILT, SAND, AND PEBBLES

Table H.2 Sediment core description of 1993 vibracore 9

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 59	DISTURBED	SO		SOUPY, BLACK, ODORIFEROUS MUD	MUD
59 – 90				BLACK, ODORIFEROUS MUD, BECOMING COHERENT	MUD
90 – 100			5Y/5/1	DARK OLIVE GREEN ODORIFEROUS MUD	MUD
100–115			5Y/5/1	OLIVE–BLACK MUD	MUD
115 – 120				VOID	VOID
120 - 157			5Y/5/3	DARK OLIVE GREY SANDY MUD, SHELLY	SANDY MUD
157 – 170			5Y/5/2	LIGHT OLIVE GREY SANDY MUD, SHELLY	SANDY MUD
170 – 205			5Y/5/2	LIGHT OLIVE GREY SANDY MUD, SHELLY, BECOMING BANDED WITH BLACK LAYERS, LARGE SHELL AT 189 cm	SANDY MUD
205 – 258			5Y/3/1 AND 5Y/3/2	BANDED LIGHT OLIVE GREY SANDY MUD WITH DARK LAYERS	SANDY MUD
258 – 275				SHARP ERODED CONTACT, PEAT, SALT MARSH?	PEAT
275 – 300			5Y/3/1	OLIVE GREY MUDDY, FINE SAND WITH SHELLS, BIOTURBATED, ORGANIC LAYER AT 301–302 cm	MUDDY SAND
300 – 315			5Y/3/1	OLIVE GREY FINE SAND, MUDDY, BIOTURBATED	MUDDY SAND
315 – 400			5Y/3/1	OLIVE GREY SANDY MUD WITH A PEAT LENS AT 325 cm, BIOTURBATED, COBBLE AT 335 cm	SANDY MUD
400 – 535			5Y/3/1 AND 5Y/3/2	DARK OLIVE GREY SANDY MUD, BIOTURBATED, PEAT LENS AT 532–535 cm	SANDY MUD
535 – 600				LIGHT OLIVE GREY SANDY MUD, BIOTURBATED, PEAT AT 551 cm	SANDY MUD

Table H.3 Sediment core description of 1993 vibracore 10

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 34	DISTURBED			DISTURBED BLACK MUD, STRONG H_2S ODOUR	MUD
35 - 125			5Y/5/3	OLIVE GREY SANDY MUD, BLACK MOTTLING	SANDY MUD
125 – 213			5Y/5/3	OLIVE GREY SANDY MUD, MOTTLING DIMINISHES, SHELL BEARING	SANDY MUD
213 – 362			5Y/5/3	OLIVE GREY SANDY MUD AT SHELL LAYERS AT 304 cm, 307 cm, AND 347 cm, AND COBBLES AT 342 cm AND 358 cm	SANDY MUD
362 – 400			5Y/5/3	OLIVE GREY SAND MUD	SANDY MUD
400 – 450			5Y/5/3	OLIVE GREY SANDY MUD, SHELLY AT TOP OF INTERVAL, DIMINISHES DOWN INTERVAL	SANDY MUD
450 – 462				SHARP CONTACT, FIBROUS PEAT, SANDY LENS AT 455–460 cm	PEAT
462 – 512				GREY FAINTLY LAMINATED FINE SAND	SAND

Table H.4 Sediment core description of 2008 vibracore 2

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
22 – 32	DEFORMED	SO	GLEY/2.5/10Y	GREENISH BLACK, HIGHLY DISTURBED MUD WITH HIGH ORGANIC MATTER, COLOUR IS DARKER AT THE TOP	MUD
32 – 42	DEFORMED	SO	GLEY/3/10Y	VERY DARK GREENISH GREY, DISTURBED MUD WITH HIGH ORGANIC CONTENT	MUD
42 – 62		SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH HIGH ORGANIC CONTENT	MUD
62 – 72		SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH ORGANIC MATTER AND SHELL FRAGMENTS AT TOP OF INTERVAL	MUD
72 – 122		SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH HIGH ORGANIC CONTENT, PIECE OF WOOD AND SHELL AT 60 cm, PLANT LEAVES AT 91 cm	MUD
122 – 142		ST	GLEY/4/10Y	DARK GREENISH GREY MUD, NOT SOFT, BUT NOT MORE STIFF, PIECE OF WOOD AT 101 cm, SHELL FRAGMENTS AT 107 cm, BECOMING STIFFER AND DARKER NEAR THE BOTTOM OF THE INTERVAL, PLANT MATERIAL LAST 4 cm	MUD
142 – 144		ST	GLEY/2.5/10Y	GREENISH BLACK MUD, PLANT LEAF MATERIAL	MUD
144 – 147		ST	GLEY/5/10Y	GREENISH GREY MUD	MUD
147 – 196		ST	GLEY/3/10Y	VERY DARK GREENISH GREY MUD, LENSES OF LIGHTER MUD (6/5GY) AT 131 cm, 137 cm, AND 145 cm. PIECE OF WOOD AT 155 cm	MUD
196 – 204		SF	GLEY/2.5/N	BLACK PEAT, A BIT STICKY	PEAT
204 – 232		ST	GLEY/7/10BG	LIGHT GREEN, VERY FINE SAND BECOMING A LITTLE COARSER DOWN THE INTERVAL	SAND
232 – 257		ST	CHROMA/5/2	FINE GRAINED SAND BECOMING REDDISH IN COLOUR DOWN THE INTERVAL	SAND
257 – 293		ST	CHROMA/5/4	FINE TO MEDIUM GRAINED SAND	SAND

Table H.5 Sediment core description of 2008 vibracore 3

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 6		SF	GLEY/3/5PB	MUD WITH A LITTLE ORGANIC MATTER, A BIT STICKY	MUD
6 – 26		SF	GLEY/4/5PB	MUDDY SAND, THE PROPORTION OF MUD DECREASES DOWN CORE	MUDDY SAND
26 – 30		SF	GLEY/3/5BG	SAND	SAND
30 – 60		ST	GLEY/7/5PB	FINE TO MEDIUM GRAINED, LIGHT COLOURED SAND WITH SOME WOOD PIECES AND A LONG WORM BURROW NEAR THE BOTTOM	SAND
60 – 69		SF	GLEY/5/5GY	GREENISH GREY SANDY MUD WITH SOME WOOD PIECES. THE MUD BECOMES MORE SANDY TOWARDS THE BOTTOM	SANDY MUD
69 – 89		ST	GLEY/6/N	COARSE SAND WITH A LARGE PIECE OF WOOD AT 80 CM DEPTH	SAND
89 – 100		SF to ST		FINE TO MEDIUM SAND WITH A SMALL AMOUNT OF MUD WHICH INCREASES DOWN CORE	SAND TO MUDDY SAND
100 – 123		SF to ST	GLEY/6/N	FINE TO MEDIUM SAND	SAND
123 – 155		ST	GLEY/6/10Y	VERY COARSE, SUBANGULAR SAND WITH PEBBLES	SANDY WITH PEBBLES
155 – 271		ST	CHROMA/7.5YR/5/6	BROWN, MEDIUM TO COARSE GRAINED SAND WITH LARGE DARK GRAINS	SAND

Table H.6 Sediment core description of 2008 vibracore 5

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 8	DEFORMED	SF TO ST	10YR/4/6	DARK YELLOWISH BROWN, FINE TO COARSE GRAINED SAND WITH ABUNDANT SHELL FRAGMENTS UP TO 3 MM	SAND AND SHELL FRAGMENTS
8 – 20	DEFORMED	ST	10Y/2.5/1	GREENISH BLACK, FINE GRAINED SAND WITH ABUNDANT BLACK ORGANIC MATTER AND MODERATE SHELL FRAGMENTS UP TO 2 MM. LIMITED PARALLEL LAMINATIONS	SAND AND SHELL FRAGMENTS
20 – 26	DEFORMED	ST	5Y/3/2	DARK OLIVE GREY, FINE TO MEDIUM GRAINED SAND WITH MODERATE SHELL FRAGMENTS AND LIMITED SUBROUNDED PEBBLES	SAND
26 – 39	DEFORMED	ST	5Y/4/2	OLIVE GREY FINE TO COARSE GRAINED SAND WITH ABUNDANT PEBBLES UP TO 5 MM AND ABUNDANT SHELL FRAGMENTS UP TO 2 CM	SAND, PEBBLES, AND SHELL FRAGMENTS
39 – 44	DEFORMED	ST	5Y/4/2	OLIVE GREY FINE GRAINED SAND WITH LIMITED SHELL FRAGMENTS UP TO 3 MM	SAND
44 – 51	DEFORMED	ST	5Y/3/2	DARK OLIVE GREY FINE TO MEDIUM GRAINED SAND WITH ABUNDANT SHELL FRAGMENTS UP TO 2 CM AND LIMITED PEBBLES UP TO 1 CM	SAND AND SHELL FRAGMENTS
51 – 58	DEFORMED	ST	10Y/3/1	VERY DARK GREENISH GREY FINE TO MEDIUM GRAINED SAND WITH SOME SHELL FRAGMENTS, LIMITED WHOLE SHELLS AND SOME PEBBLES (UP TO 3 MM)	SAND
58 – 70	DEFORMED	ST	10Y/3/1	VERY DARK GREENISH GREY FINE TO MEDIUM GRAINED SAND WITH SOME PEBBLES AND LIMITED SHELL FRAGMENTS	SAND
70 – 81	DEFORMED	ST	5Y/3/2	DARK OLIVE GREY PEBBLES AND SOME SHELL FRAGMENTS	SAND
81 – 92		ST	5Y/4/2	OLIVE GREY SILT TO FINE GRAINED SAND WITH SOME SHELL FRAGMENTS AND LIMITED SUBROUNDED PEBBLES	SILT TO SAND
92 – 102		ST	5Y/3/2	DARK OLIVE GREY SILT OT FINE GRAINED SAND WITH LIMITED SHELL FRAGMENTS AND PEBBLES	SAND

Table H.6 Sediment core description of 2008 vibracore 5 (cont'd)

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
102 – 104		SF	5Y/3/2	DARK OLIVE GREY SILT OT FINE GRAINED SAND WITH LIMITED SHELL FRAGMENTS AND LIMITED PEBBLES	SAND
104 – 108		SF	5Y/3/2	DARK OLIVE GREY SILT OT FINE GRAINED SAND WITH LIMITED SHELL FRAGMENTS AND LIMITED PEBBLES AND BLACK MOTTLING (5Y/2.5/2)	SAND
108 – 113		SF	5Y/3/2	DARK OLIVE GREY SILT OT FINE GRAINED SAND WITH LIMITED SHELL FRAGMENTS AND LIMITED PEBBLES	SAND
113 – 123		SF TO ST	5Y/3/2	DARK OLIVE GREY SILT TO FINE GRAINED SAND WITH SOME SHELL FRAGMENTS, WHOLE SHELLS, AND SOME PEBBLES	SAND
123–143		SF TO ST	5Y/3/2	DARK OLIVE GREY SILT TO FINE GRAINED SAND WITH SOME SHELL FRAGMENTS AND LIMITED PEBBLES. 1 SUBANGULAR COBBLE AT 125 CM	SILT TO SAND
143 – 153		ST	5Y/3/2	DARK OLIVE GREY SILT TO FINE GRAINED SAND WITH SOME SHELL FRAGMENTS AND LIMITED PEBBLES. 1 SUBANGULAR COBBLE AT 125 CM	SILT TO SAND
153 – 157		ST	5Y/3/2	DARK OLIVE GREY SILT TO FINE GRAINED SAND, INCREASING SAND CONTENT OVER THE INTERVAL WITH SOME SHELL FRAGMENTS AND SOME MOTTLING	SILT TO SAND
157 – 171		ST	5Y/3/2	DARK OLIVE GREY FINE GRAINED SAND WITH SOME SILT AND SOME SHELL FRAGMENTS, LIMITED MOTTLING	SAND

Table H.7 Sediment core description of 2008 vibracore 6

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 17		SF	10Y/2/1	BLACK SILT WITH LIMITED ORGANIC CONTENT, LIGHTER MOTTLING (5Y/3/1)	SILT
17 – 27		SF	2.5/2.5/1	BLACK SILT WITH SOME CLAY, DISCONTINUOUS LAMINATIONS, INCREASED LIGHTER MOTTLING (5Y/3/1)	SILT
27 – 38		SF	2.5/2.5/1	BLACK SILT WITH SOME CLAY, LAMINATIONS, LIGHT MOTTLING (5Y/3/1)	SILT
38 – 50		SF	10Y/2/1	BLACK SILT WITH SOME CLAY, LAMINATIONS, SOME MOTTLING, INCREASING PROPORTION OF LIGHTER MOTTLING	SILT
50 – 61		SF TO ST	2.5Y/2.5/1	BLACK SILT WITH SOME CLAY, SOME MOTTLING (5Y/3/1), SINGLE WORM TUBE AT 52 cm	SILT
61 – 63	GAS CRACKING	SF TO ST	2.5Y/2.5/1	BLACK SILT WITH SOME CLAY, SOME MOTTLING (5Y/3/1), SINGLE WORM TUBE AT 52 cm	SILT
63 – 103	GAS CRACKING	SF TO ST	2.5Y/2.5/1	BLACK CLAY AND SILT, VERY SLIGHT LIGHTER MOTTLING, LIMITED SHELL FRAGMENTS	CLAY TO SILT
103 – 200		SF	GLEY/3/10Y	VERY DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD
200 – 240		SF	GLEY/3/0Y	VERY DARK GREENISH GREY MUD WITH SHELL FRAGMENTS AND A PIECE OF WOOD AT 203 cm DEPTH	MUD
240 – 250		SF TO ST	GLEY/3/0Y	VERY DARK GREENISH GREY MUD WITH SHELL FRAGMENTS AND A PIECE OF WOOD AT 203 cm DEPTH	MUD
250 – 304		SF TO ST	GLEY/3/10Y	VERY DARK GREENISH GREY MUD WITH FEW SHELL FRAGMENTS	MUD
304 – 400		SF TO ST	GLEY/3/10Y	VERY DARK GREENISH GREY MUD WITH SOME SHELL FRAGMENTS NEAR THE BOTTOM OF THE INTERVAL	MUD
400 – 407		SF TO ST	GLEY/3/10Y	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD

Table H.8 Sediment core description of 2008 vibracore 7

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 12		SO	GLEY/3/N	VERY DARK GREY MUD WITH HIGH ORGANIC CONTENT. SOUPY	MUD
12 – 40		SF	GLEY/3/10Y	VERY DARK GREENISH GREY MUD WITH SHELL FRAGMENTS, STICKY	MUD
40 – 80		SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD
80 – 100		SF TO ST	GLEY/4/10Y	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD
100 – 200		SF TO ST	GLEY/4/10Y	DARK GREENISH GREY MUD WITH SOME LEAF MATERIAL AND SHELL FRAGMENTS, BIT STICKY	MUD
200 – 250		SF TO ST	GLEY/4/10Y	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD AND SHELL FRAGMENTS
250 – 402		SF TO ST	GLEY/4/5GY	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS	MUD AND SHELL FRAGMENTS

Table H.9 Sediment core description of 2008 vibracore 8

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 12		SO	GLEY/2.5/N	BLACK SOUPY TO SOFT MUD WITH HIGH ORGANIC CONTENT	MUD
12 – 27		SF	GLEY/2.5/N	BLACK SOUPY TO SOFT MUD WITH HIGH ORGANIC CONTENT	MUD
27 – 37		SF	GLEY/3/10Y	VERY DARK GREENISH GREY MUD WITH ROCK FRAGMENTS AND PIECE OF WOOD	MUD
37 – 69		SF	GLEY/3/N	VERY DARK GREY MUD WITH PLANT ROOTS AND SHELL FRAGMENTS	MUD
69 – 100		SF	GLEY/3/10Y	VERY DARK GREENISH GREY STICKY MUD WITH ROCK FRAGMENTS AND COAL SEGMENT	MUD
100 – 200		SF TO ST	GLEY/4/10Y	DARK GREENISH GREY MUD WITH PLANT ROOTS, SHELLS, AND SHELL FRAGMENTS	MUD
200 – 300		SF TO ST	GLEY/4/10Y	DARK GREENISH GREY MUD WITH SHELL FRAGMENTS AND SMALL ROCK FRAGMENTS	MUD
300 – 362		SF TO ST	GLEY/4/10Y	MUD WITH SHELL FRAGMENTS AND ROCK FRAGMENTS (LARGE ONE AT BOTTOM OF INTERVAL)	MUD

Table H.10 Sediment core description of 2008 vibracore 9

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 27		SU	GLEY/2.5/N	BLACK SOUPY MUD WITH HIGH ORGANIC CONTENT AND A SMALL PIECE OF WOOD, SHELL FRAGMENTS IN LOWER PORTION OF INTERVAL	MUD
27 – 79		SU TO SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH ROCK FRAGMENTS AND LITTLE PIECES OF WOOD	MUD
79 – 100		SF	GLEY/4/10Y	DARK GREENISH GREY MUD WITH ROCK FRAGMENTS AND LITTLE PIECES OF WOOD	MUD
100 – 200		SF TO SY	GLEY/4/10Y	DARK GREENISH GREY MUD WITH VERY SMALL PIECES OF ROCK, WOOD, AND SHELL FRAGMENTS	MUD
200 – 230		SF TO SY	GLEY/4/10Y	DARK GREENISH GREY MUD WITH FRAGMENTS OF WOOD	MUD

Table H.11 Sediment core description of gravity core 5

Depth (cm)	Deformation	Consistency	Munsell Colour	Sedimentologic Description	Lithology
0 – 12		SO	10YR/2/1	SILTY CLAY, SOFT, BLACK, WITH A DARKER PATCH (10YR/2/1)	SILTY CLAY
12 – 17		SO	2.5Y/2.5/1	SILTY CLAY, SOFT, GREENISH BLACK	SILTY CLAY
17 – 32		SO	2.5Y/2.5/1	SILTY CLAY, SOFT, GREENISH BLACK WITH RARE SHELL FRAGMENTS	SILTY CLAY

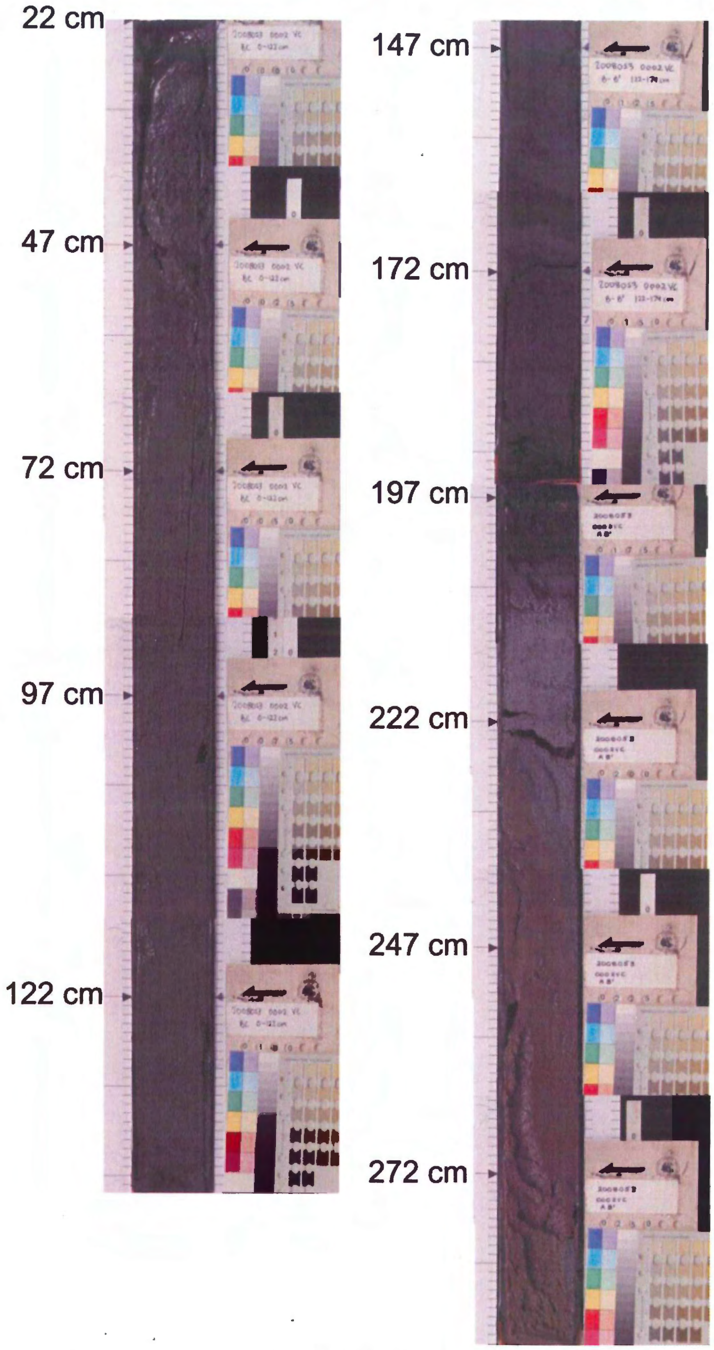

Figure H.1 Photograph of sediment core 2008 vibracore 2.

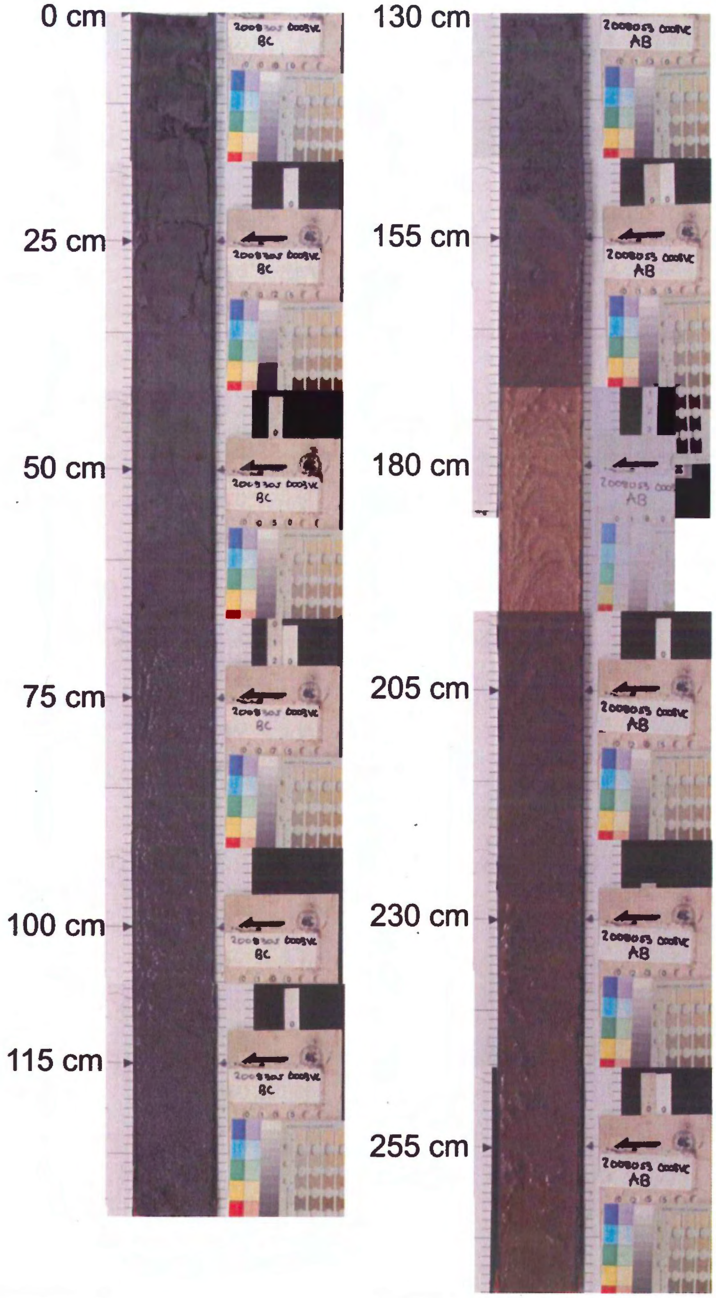

Figure H.2 Photograph of sediment core 2008 vibracore 3.

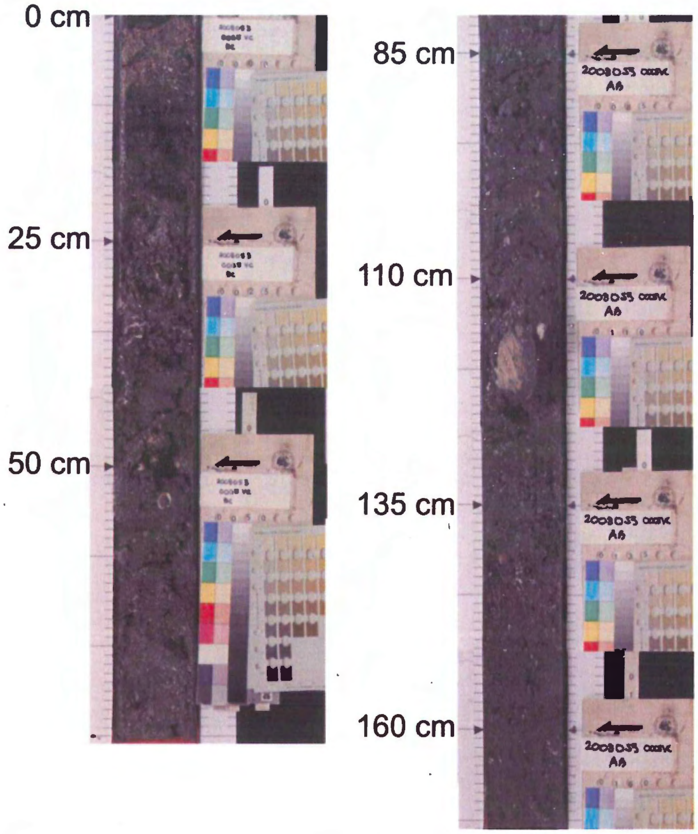

Figure H.3 Photograph of sediment core 2008 vibracore 5.

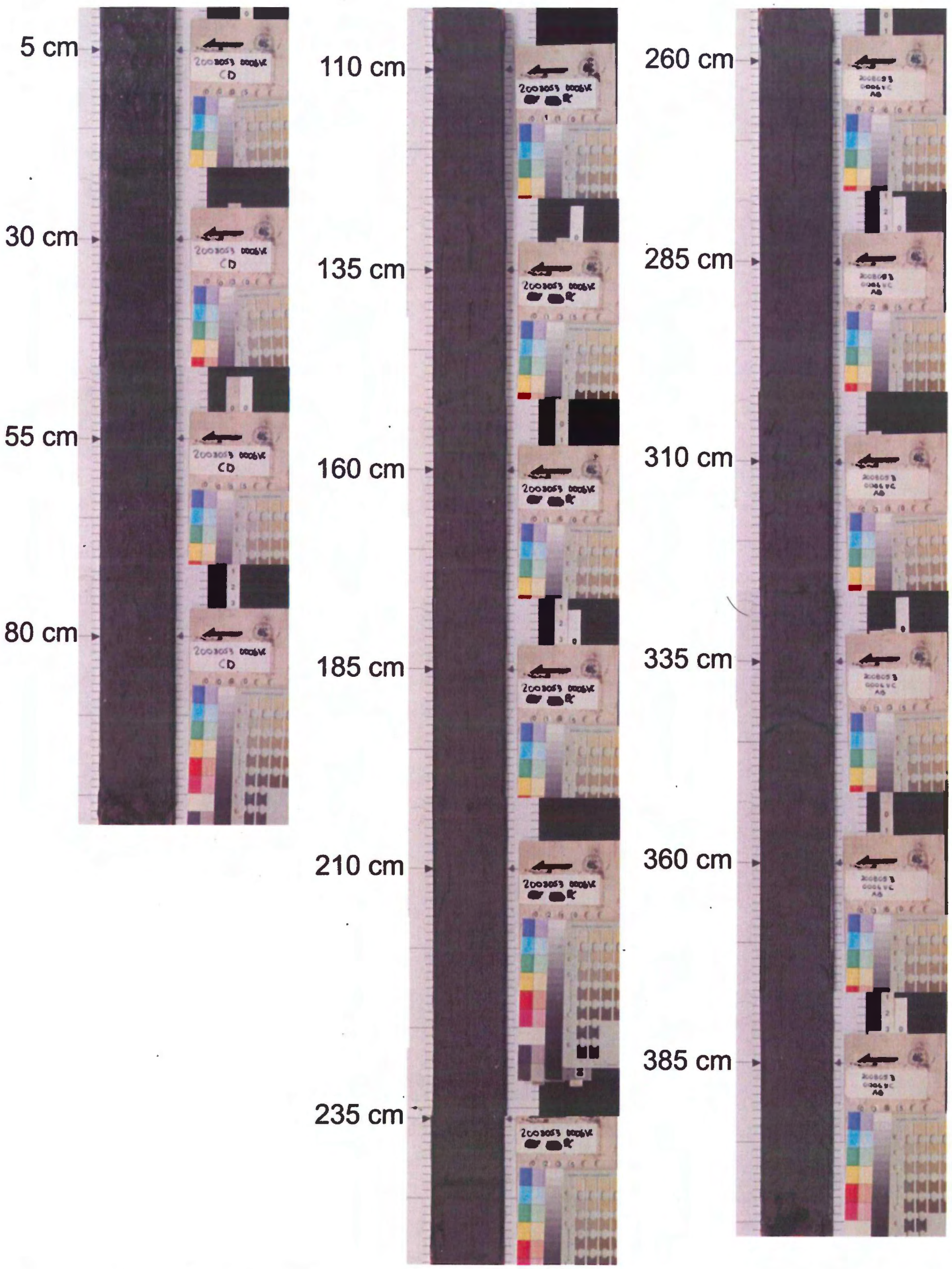

Figure H.4 Photograph of sediment core 2008 vibracore 6.

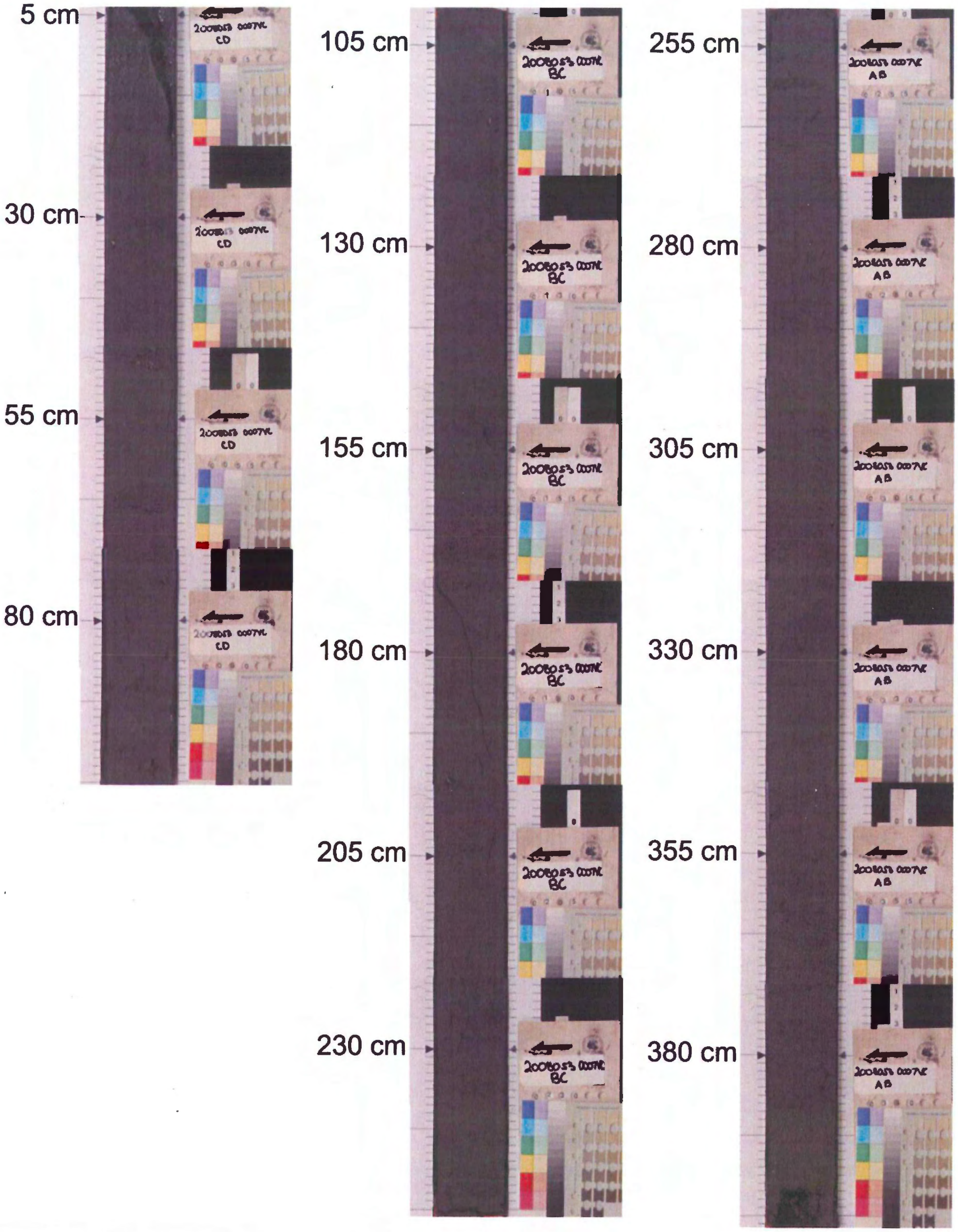

Figure H.5 Photograph of sediment core 2008 vibracore 7.

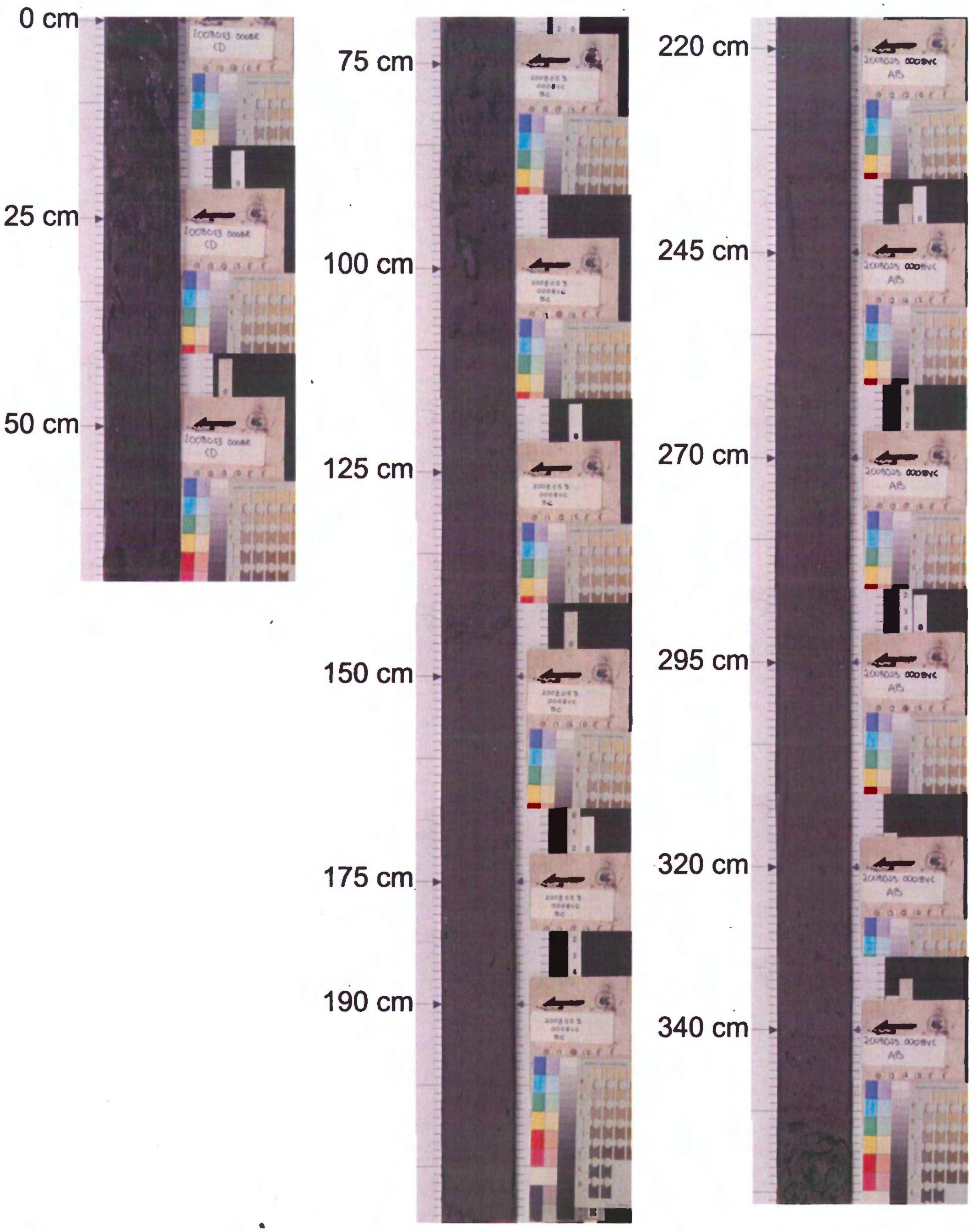

Figure H.6 Photograph of sediment core 2008 vibracore 8.

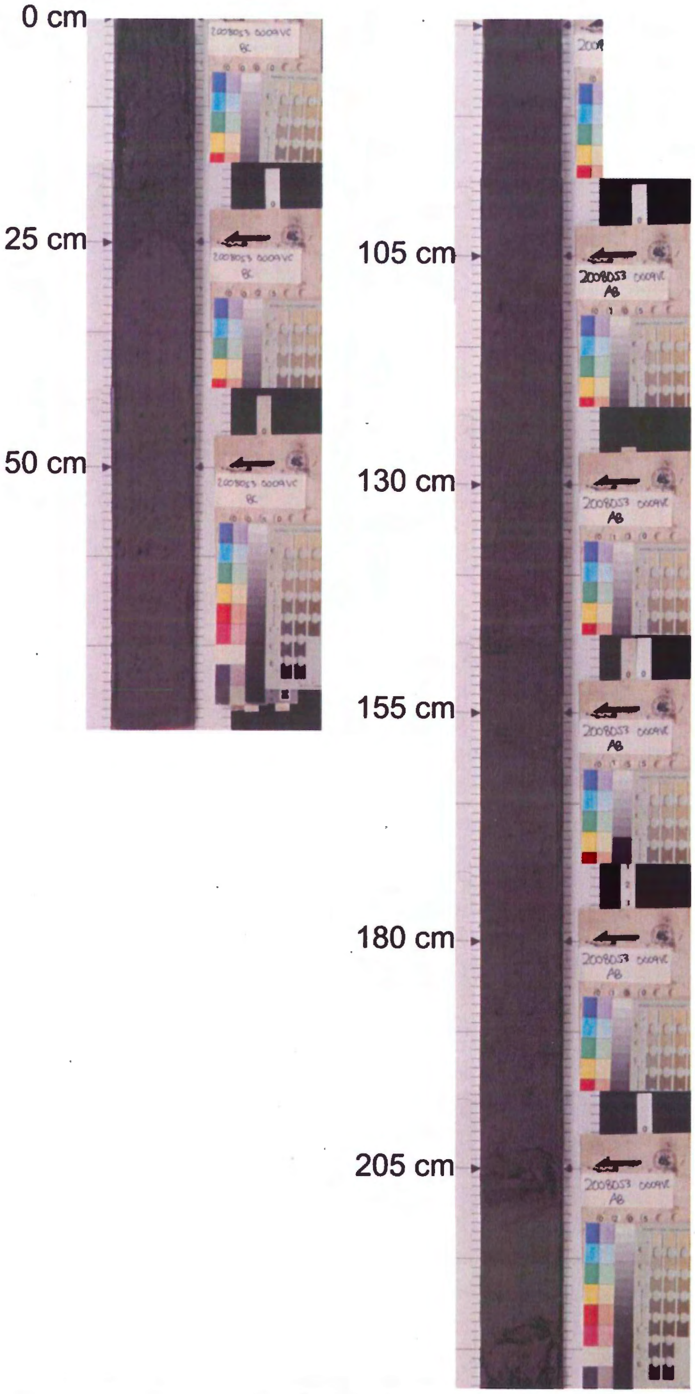

Figure H.7 Photograph of sediment core 2008 vibracore 9.