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Mercury Dynamics in Sediments of the St. Lawrence River Near Cornwall, Ontario

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MERCURY DYNAMICS IN SEDIMENTS OF THE ST. LAWRENCE RIVER NEAR CORNWALL, ONTARIO

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Thesis submitted to the
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ABSTRACT

The St. Lawrence River near Cornwall, Ontario was designated an Area of Concern by the International Joint Commission in 1985. Sediments from the Area of Concern have historically been contaminated with mercury (Hg), and although concentrations have decreased since the 1970s they still remain high. Several sediment cores were collected from three sites within the Area of Concern in 2004/05, to determine whether sediments act as a source or sink of mercury. The three sites were chosen based on their proximity to former Hg dischargers, including a chlor-alkali plant, a pulp and paper mill, and a textile mill. Sediment and pore water phases were analyzed for total mercury (THg) and methyl mercury (MeHg) and cores were dated using radioisotope analaysis to determine sedimentation and Hg accumulation rates, and to study the record of Hg contamination over the past half century. Total mercury in sediments from the three sites ranged from 0.7 to 60 $\mu g\ g^{-1}$ and methyl mercury ranged from 0.02 to 0.7 $\mu g\ g^{-1}$. Surface sediments had much lower Hg concentrations than deeper sediments, however they still exceeded sediment quality guidelines for the protection of aquatic organisms. The diffusional flux from the sediment to the overlying water ranged from 1.2 – 48.2 $ng\ cm^{-2}\ yr^{-1}$ for THg and 1.2 – 14.6 $ng\ cm^{-2}\ yr^{-1}$ for MeHg, but was small when compared to the flux of particulate bound mercury being deposited to the sediment (70 – 309 $ng\ cm^{-2}\ yr^{-1}$). These results showed that post-depositinal redistribution did not alter the Hg profile and trends in sediment Hg concentration corresponded well with source histories. Dated cores showed that mercury accumulation rates prior to 1970 were up to 60 times higher than current rates. Recent collections have indicated that fish from one specific site (Lamoureux Park) have higher Hg levels than fish collected from other sites along the Cornwall waterfront. This could not be explained by differences in the Hg flux or THg concentrations between sites however, the highest levels of sediment MeHg, the highest proportions of MeHg to THg in both sediment and pore water, and the highest rate of methane production in sediments were observed at the this site. At present, the contaminated sediments appear to act as a net sink for total mercury, yet they remain a potential source of MeHg to the food web and the river system.

RÉSUMÉ

Le Fleuve St-Laurent près de Cornwall (Ontario) a été désigné un 'secteur préoccupant' par la Commission mixte internationale (CMI) en 1985. Dans le passé, les sédiments de cette région ont été contaminés par le mercure (Hg) et bien que les concentrations aient diminué depuis les années 1970, elles sont toujours hautes. Plusieurs carottes de sédiments ont été recueillies à trois sites dans le secteur préoccupant en 2004/05, afin de déterminer si les sédiments agissent comme source ou puits de mercure. Les trois sites se trouvent à proximité d'anciens déchargeurs de Hg, y compris une usine de chlor-alcali, un moulin à papier et un moulin à textile. Le mercure total (THg) et le methyl-mercure (MeHg) ont été analysés dans les eaux interstitielles et dans les sédiments. De plus, l'analyse des radio-isotopes a été utilisée afin de déterminer l'âge des sédiments, ce qui permet aussi de déterminer le taux de sédimentation et le taux d'accumulation de Hg, et d'étudier les tendances d'accumulation de Hg au cours du dernier demi-siècle. La concentration de Hg dans les sédiments a varié de 0.7 à 60 $\mu g\ g^{-1}$ et le MeHg a varié de 0.02 à 0.7 $\mu g\ g^{-1}$. La concentration de Hg dans les sédiments de surface était beaucoup plus basse que celle dans les sédiments profonds, mais les concentrations observées demeurent supérieures aux recommandations canadiennes pour la qualité des sédiments. Le taux de diffusion de Hg provenant des sédiments a varié de 1.2 – 48.2 ng $cm^{-2}\ yr^{-1}$ pour le HgT et de 1.2 – 14.6 ng $cm^{-2}\ yr^{-1}$, pour le MeHg. Cependant, après comparaison au taux d'accumulation de Hg (70 – 309 ng $cm^{-2}\ yr^{-1}$), le taux de diffusion était faible. Ces résultats démontrent que la diagénèse n'a pas changé le profil de Hg dans les sédiments, et que les tendances de concentrations de Hg correspondent bien à l'historique des industries. D'après l'âge des sédiments, les taux d'accumulation de Hg avant les années 1970 était 60 fois plus élevé que les taux actuels. Par contre, des échantillons receuillis récemment ont démontré que leur concentration de Hg est plus élevée chez les poissons près du parc Lamoureux, par rapport aux autres sites. Ceci n'a pu être expliquer par une différence dans le taux d'accumulation ou de la concentration de Hg entre les sites. Cependant, les plus grandes concentrations de MeHg dans les sédiments, les plus grandes proportions de MeHg dans les sédiments et les eaux interstitielles, ainsi que les taux les plus élevés de production de méthane dans les sédiments ont été observé sur ce site. Actuellement, les sédiments contaminés semblent agir en tant que puits pour le HgT, tout en étant une source potentielle de MeHg pour le réseau alimentaire et le réseau fluvial.

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LIST OF ABBREVIATIONS

AOC	Area of Concern
AVS	Acid-Volatile Sulfide
CF/CS	Constant Flux / Constant Sedimentation
CIC	Constant Initial Concentration
CRS	Constant Rate of Supply
CV-AFS	Cold Vapour – Atomic Fluorescence Spectroscopy
EPA	Environmental Protection Agency
FID	Flame Ionization Detection
GC-AFS	Gas Chromatography – Atomic Fluorescence Spectrometry
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometer
IJC	International Joint Comission
LEL	Lowest Effect Level
LP	Lamoureux Park
MDL	Method Detection Limit
MOE	Ministry of the Environment
NEL	No Effect Level
PCB	Polychlorinated Biphenyls
PEL	Probable Effect Level
RAP	Remedial Action Plan
RF	Reference
RPD	Relative Percent Difference
SEL	Sever Effect Level
SLRIES	St. Lawrence River Institute of Environmental Sciences
SMART	Sources of Mercury Accumulating in Rivers and Tributaries
SQG	Sediment Quality Guideline
SRB	Sulfate Reducing Bacteria
TF	Tank Farm
WPCP	Water Pollution Control Plant
WPPI	Windmill Point to Pilon Island

CHAPTER 1

INTRODUCTION

1.1 Introduction

The presence and behaviour of mercury (Hg) in the environment is of critical interest and importance, primarily due to the tendency of its most toxic form, methyl mercury (MeHg), to bioaccumulate through all levels of the aquatic food web (Lindqvist *et al.* 1991). MeHg can accumulate in fish and piscivorous wildlife to levels that may reduce their reproductive success (Hammerschmidt *et al.* 2002; Wiener *et al.* 2002), and pose a threat to human health (Grandjean *et al.* 1997). Consumption of fish containing significant amounts of MeHg is the primary route of human MeHg exposure today. Our knowledge of the neurotoxic effects of MeHg began with the environmental disasters in Japan, Northern Iraq, Pakistan, Guatemala, and Yugoslavia in the 1950 – 1960s (Klein and Goldberg 1970; D'Itri and D'Itri 1974; Harada 1995) and in New Mexico, Iraq, and Ghana in the 1970s (Bakir *et al.* 1973; Derban 1974; Takizawa 1979). In these cases, human consumption of MeHg contaminated food resulted in the poisoning of whole communities, over ten thousand cases of neuropathy, and nearly a thousand fatalities (Bono 1997). Although extreme cases such as these are rare, mild adverse effects to chronic MeHg exposure are being reported. Recent epidemiological studies show that long term exposure to low levels of MeHg can cause neurological deficits (Ninomiya *et al.* 1995; Wheatley *et al.* 1997; Grandjean *et al.* 1998; Lebel *et al.* 1998; Dolbec *et al.* 2000). Due to the chronic and acute effects of prolonged exposure to MeHg, it is important to understand its origin, fate, and transport .

1.1.1 Sources and Fate of Mercury in the Environment

Distribution and transport of mercury in the environment depends on its chemical form. Emissions of Hg occur primarily as elemental Hg (Hg^0) which has a relatively long atmospheric residence time (0.5 – 3 years) and consequently, the potential for long range atmospheric transport (Schroeder and Munthe 1998). Mercury is also released as reactive gaseous and particulate Hg, both of which have shorter atmospheric residence times, contributing to local and regional Hg deposition. Once in the atmosphere, elemental Hg is oxidized to Hg^{2+}. Cycling of Hg^{2+} between the earth surface and atmosphere occurs by particle settling (dry deposition) or by rain scavenging (Iverfeldt 1991; Perry *et al.* 2005). Once it enters the aquatic environment, Hg binds with inorganic ligands (e.g. Cl-, OH-) or dissolved organic carbon (DOC), or sorbs to particulate matter. Hg can also be reduced microbially or abiotically to elemental Hg and then returned to the atmosphere by volatilization (Mason *et al.* 1994). A large proportion of Hg in the water column eventually ends up in the bottom sediments through particle settling (Lee *et al.* 1998), where it can form poorly soluble mercury sulfide (HgS) (Mikac *et al.* 1985), be incorporated with sulfide phases such as acid volatile sulfide (AVS) (Driscoll *et al.* 1994; Paquette and Helz 1995; Jay *et al.* 2000), or be converted to MeHg through microbial degradation. The major Hg and MeHg transfers in freshwater ecosystems are summarized in Figure 1-1.

Natural sources of Hg include volatilization from oceans, volcanic releases, weathering of rocks and soils, and hot spring activity (Nriagu 1989; Schroeder and Munthe 1998), while anthropogenic sources include combustion of fossil fuel and waste, metal works, chlor-alkali plants, and gold mining (Lee *et al.* 2001). Natural sources of Hg can be significant in the contamination of aquatic food chains. However, since the onset of industrialization in the late nineteenth century, anthropogenic Hg emissions have become significant (Mason *et al.* 1994; Hudson *et al.* 1995; Mierle 2001). Slemr and Langer (1992) measured atmospheric Hg over the Atlantic Ocean from 1977 to 1990 and found that it increased at a rate of about 1 – 2 %

per year. This realization led to the implementation of emission control measures in North America in the mid-1980s (e.g. OECD 1994; US EPA 1997; Pacyna *et al.* 2001). Subsequently, several studies have reported declines in atmospheric Hg (Engstrom and Swain 1997; Benoit *et al.* 1998A; Sunderland and Chmura 2000; Temme *et al.* 2003). Despite this, because of its persistent nature in the environment, there is little evidence of similar declines in the concentrations of Hg in the food chain (Evers *et al.* 1998; Chase *et al.* 2001). For this reason, Hg remains an international public health concern.

Mercury contamination of freshwater fish in Canada became apparent in the mid-1970s. Barbeau *et al.* (1976) detected fish MeHg concentrations of 4 $\mu g\ g^{-1}$ in areas of Quebec. Bishop and Neary (1976) recorded even higher concentrations of 24 $\mu g\ g^{-1}$ in fish from Wabigoon/English River system in northern Ontario. Indigenous communities were exposed to unacceptably high MeHg levels from eating fish in these areas (Wheatley, 1979). Currently in Ontario, 92.6 % of all consumption restrictions on sport fish from inland water bodies are as a result of Hg (MOE 2005).

Mechanisms regulating the initial incorporation of MeHg at the base of the food web, and its subsequent trophic transfer remain controversial (Watras *et al.* 1998). In many cases, Hg concentrations in fish vary from location to location and numerous studies have attempted to identify factors that might explain the spatial variability (Wren 1991; Rasmussen *et al.* 1998). This phenomenon has been linked to the role of sediments in the production of MeHg (Mierle 2001), which has led many to study sediments to investigate sources of Hg to the system and the processes that control its distribution. Sediments are a repository for natural and pollution-derived Hg (Gagnon *et al.* 1997; Bloom *et al.* 1999; Mason and Lawrence

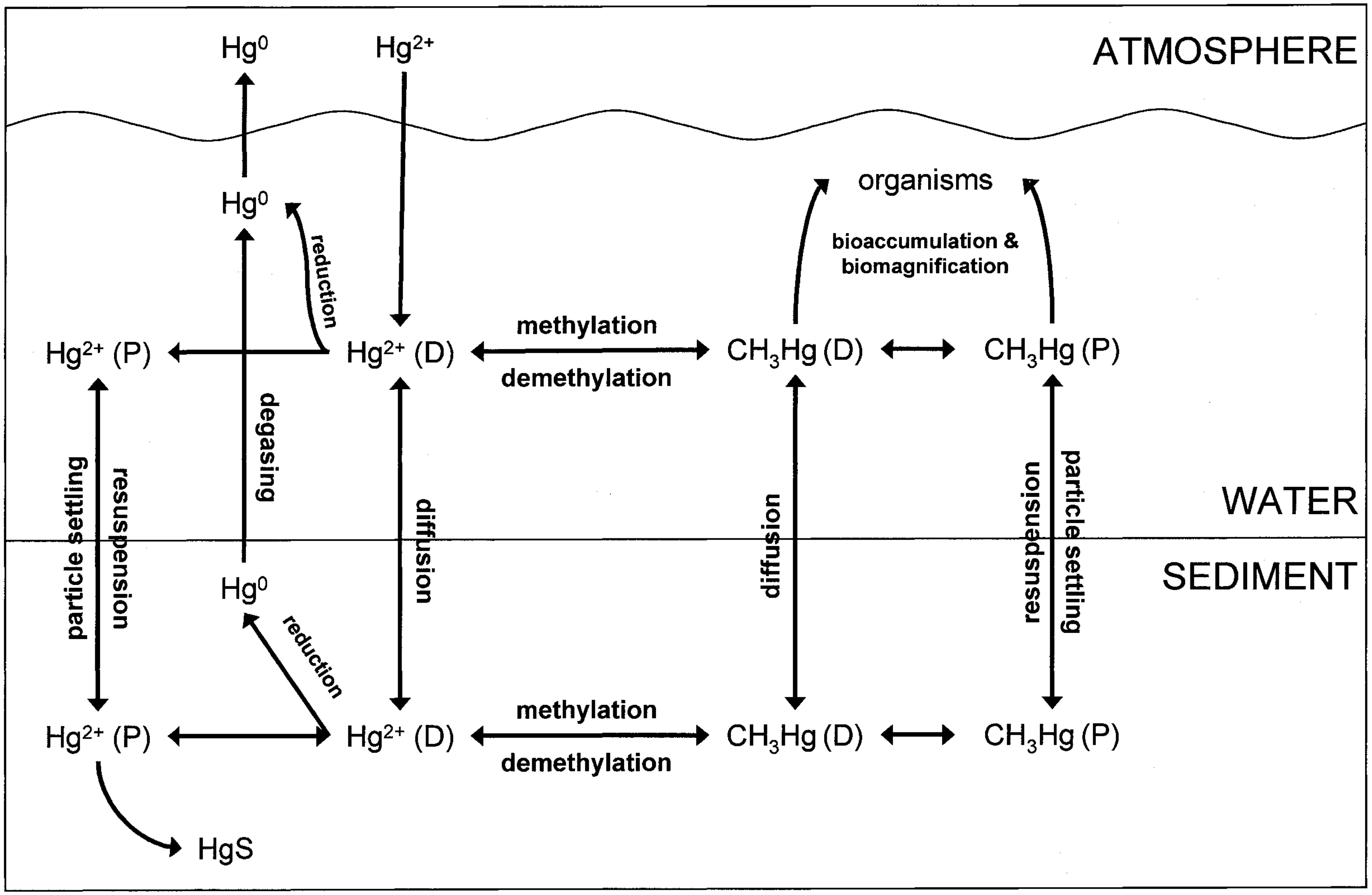

FIGURE 1-1 Mercury cycling in the environment: Hg^{2+}: inorganic Hg; Hg^{0}: elemental Hg; CH_3Hg: MeHg; (D): dissolved; (P): particulate (modified from Kim 2004).

1999; Conaway *et al.* 2003) and are a potentially significant source of MeHg to the food web, including fishes for human consumption (May *et al.* 1997; Benoit *et al.* 1998A; Hammerschmidt and Fitzgerald 2004). Understanding Hg dynamics in sediments becomes increasingly important in polluted areas where there is potential for bioaccumulation.

1.1.2 Mercury Contamination of the St. Lawrence River near Cornwall

The St. Lawrence River is considered a major world river (Milliman and Meade 1983). It has been subjected to several waves of anthropogenic disturbance (St. Lawrence Centre 1996) over the past century, resulting in localized degradation of water and bottom sediment quality (Reavie *et al.* 1998). This has been the case near Cornwall, Ontario, where local industrial facilities historically discharged significant quantities of contaminants to the river (Lepage *et al.* 2000). As a result, the stretch of river along the Cornwall waterfront was designated an Area of Concern (AOC) by the International Joint Commission (IJC) in 1985. Local point sources at the time of this study included Domtar Fine Papers Ltd. (pulp and paper mill), which closed in early 2006, and the city of Cornwall's Water Pollution Control Plant (WPCP). Former dischargers in Cornwall included Courtaulds Fibres (a rayon manufacturer) which closed in November 1992, Cornwall Chemicals (producers of sodium hydrosulfide, hydrochloric acid, carbon tetrachloride, and carbon disulfide), which closed in 1995, and ICI Forest Products (a mercury cell chlor-alkali plant), which closed in March 1995. Non-point sources to the river include agricultural run off, storm sewers, combined sewer overflows and atmospheric deposition (OMEE 1994).

Sediments from the Cornwall AOC have historically been contaminated with Hg. Mercury concentrations have decreased since the 1970s (Kauss *et al.* 1988), when industries began to alter their operating practices in response to new government regulations, limiting the amount of Hg discharged in liquid effluent (Environment Canada 1981). The subsequent closure of three major plants (Courtaulds, ICI, Cornwall Chemicals) in the early 1990s resulted in further decreases in Hg discharge to the river. Despite this, Hg concentrations in sediments of the Area of Concern remain high, and are a potential source of Hg to the river system and its food chain (Golder Associates 2004).

TABLE 1-1 Summary of Average Surface Sediment Hg Concentrations[a] (ug g^{-1}) in the Cornwall AOC

Year (sample depth)	LP site[b]	TF site	WPPI site	study
1970 (0 – 7 cm)	4.70 (0.85 – 14.5)		14.23 (1.24 – 35.9)	Anderson 1990
1975 (0 – 3 cm)	5.69 (0.05 – 18.2)		9.51 (0.62 – 44.0)	
1979 (0 – 3 cm)	6.80 (1.50 – 19.8)		5.40 (0.13 – 18.0)	
1985 (0 – 3 cm)	0.63		1.19 (0.13 – 4.4)	
1991 (0 – 3 cm)	3.26	0.56	1.73 (0.19 – 3.13)	OMEE 1994
1992 (0 – 2 cm)		0.25 (0.13 – 0.5)		MOE 1992
1997 (0 – 10 cm)	1.23 (0.79 – 1.71)		5.57 (1.67 – 19.5)	Richman 1999
1999 (grab)	2.10 (1.1 – 2.8)	4.51 (0.58 – 7.5)	1.50 (0.89 – 2.2)	SLRIES 1999
2001 (0 – 10 cm)	0.80 (0.38 – 1.65)	1.74 (0.61 – 2.88)	2.25 (0.42 – 5.57)	Grapentine *et al.* 2003

[a] Values in parentheses represent the ranges of Hg concentrations measured at each site.

[b] Locations of the Lamoureux Park (LP), Tank Farm (TF), and Windmill Point to Pilon Island (WPPI) sites can be found in Figure 1-2.

Several sediment studies were conducted from 1970 to 2001, showing the extent of the Hg contamination along the Cornwall waterfront (Table 1-1). Prior to 1985, average Hg concentrations at all sites exceeded the upper limit of the Sediment Quality Guidelines (SQGs) established by Environment Canada (CCME 2005) and the Ontario Ministry of the Environment (Persaud *et al.* 1993). A decrease in the average Hg concentration in sediment from 1985 to 2001 was observed, however, sediments still were not considered to be of acceptable quality based on national and provincial guidelines (see section *1.3.1.4* for SQGs). Currently, the Ontario Ministry of the Environment (MOE) has recommended consumption restrictions for large walleye in the area (Gaskin *et al.* 1979; NESCAUM *et al.* 1998). There is concern that the elevated Hg levels in walleye are the result of contaminated sediments.

1.1.3 Objectives of the Study

The processes underlying the cycling of Hg in freshwater sediments are crucial in understanding and preventing contamination of lakes, rivers, and their associated food webs. In order to better explain these processes in the Cornwall AOC, the Sources of Mercury Accumulating in Rivers and Tributaries (SMART) project was developed. This is a multi-disciplinary team that aims to develop a novel, integrated approach to the management of mercury contamination in large river ecosystems. The project aims to establish a large river conceptual model for Hg uptake into top predators. The fate of Hg in the sediments is central to this model. The present study will focus on Hg processes occurring within the sediments and at the sediment-water interface.

This study will determine the partitioning of THg and MeHg between the solid phase and pore water phase in sediments of the St. Lawrence River. Information from pore water analysis will also be used to determine concentration gradients in the sediment column and at the sediment-water interface, in order to calculate diffusional fluxes. This study will also use ^{210}Pb dating techniques to quantify current rates of mercury accumulation and to evaluate the impact of former industrial activities on mercury accumulation to the Cornwall Area of Concern.

The primary objectives of this project are: (1) to study the spatial and temporal patterns of Hg concentration and accumulation in Cornwall sediments; (2) to measure rates of Hg deposition to sediments and dissolution from sediments, and; (3) to determine whether these sediments are a source or a sink of Hg to the overlying water and its organisms. Three approaches were used: (1) sediment cores were collected from several locations to examine the spatial variability of THg and MeHg along the Cornwall waterfront; (2) dated cores from the contaminated sites were used to assess whether the deposition of Hg to the study site has changed over time, and; (3) Hg transport within the sediment column and diffusion at the sediment-water interface were calculated using the gradient of Hg concentration in pore water and surface water samples. It is predicted that (1) there are differences in Hg concentration between sites based on their location with respect to former mercury dischargers; and (2) there is a trend towards increasing Hg concentration with depth in contaminated sediments of the Cornwall AOC, corresponding to historical inputs from local industry.

The first chapter includes a description of the study site, followed by a discussion on the concentration, speciation, and transport of mercury in sediments and at the sediment-water interface. The use of sediment cores as records of historical contaminant loading is also discussed. In Chapter 2, accumulation and diffusion rates are used to create a Hg budget for the sediment-water interface and sediment MeHg concentrations are compared between sites. In Chapter 3, temporal trends in Hg concentrations are linked to the history of local industrial operations and factors affecting MeHg concentrations in sediments are examined. Chapter 4 is a thesis summary.

1.2 Study Site

The Cornwall Area of Concern includes a stretch of the St. Lawrence River approximately 80km long, from the Moses-Saunders power dam to the eastern outlet of Lake St. François in Quebec. Fine-grained sediments are concentrated in the area of the north shore of the River between Windmill Point and Pilon Island (0.83 km^2). Smaller deposits occur at the Tank Farm (0.06 km^2) and Lamoureux Park (0.16 km^2) sites. Contaminated fine-grained sediments in the reach are unlikely to be disturbed by sediment resuspension or transport because they are inshore of the active zone of sediment transport (Rukavina 1998).

The present study will focus on three zones located along the Cornwall waterfront of the North Channel (Figure 1-2). Lamoureux Park (LP) is the westernmost sampling location, located closest to the pulp and paper mill and former chlor-alkali plant. Windmill Point to Pilon Island (WPPI) is the largest and easternmost zone, stretching from the former Courtaulds textile mill to the western edge of Pilon Island. The Tank Farm (TF) is the smallest sampling site and is situated between LP and WPPI. In these three zones, Hg concentrations in sediments (Table 1-1) exceed background levels, and also exceed MOE sediment criteria for the protection of aquatic life (Golder Associates 2004).

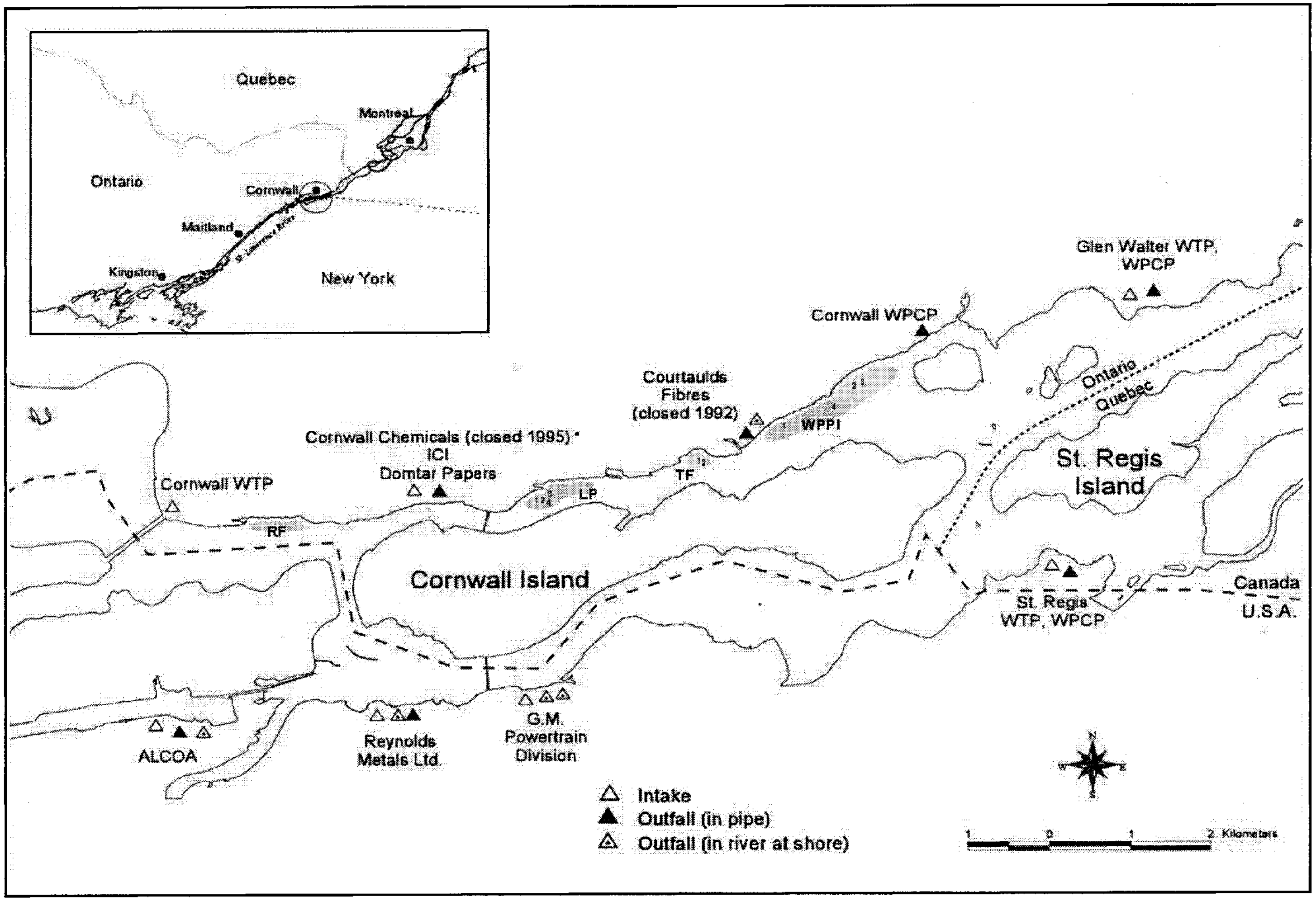

FIGURE 1-2 Location of sampling sites in the St. Lawrence River near Cornwall. Sampling was conducted in three zones designated as LP, Lamoureux Park (left); TF, Tank Farm (centre); and WPPI, Windmill Point to Pilon Island (right). An upstream site was used as a reference (RF). The coring sites are indicated by numbers (modified from St. Lawrence River RAP 1997).

1.3 Literature Review

1.3.1 Mercury Speciation in Freshwater Sediments

Bottom sediments play an important role in distributing and recycling Hg in freshwater systems (Parks *et al.* 1989; Ramalhosa *et al.* 2001; Kim *et al.* 2004). They are the main repositories of Hg in aquatic systems (Benoit *et al.* 1998B; Wang *et al.* 1998), and constitute an enriched pool potentially available to biota. Benthic organisms can be exposed to Hg and MeHg from the pore water, overlying water, and solid phase sediment. Since these organisms are an important source of energy to the aquatic food web, they have the potential to transfer the bioaccumulated MeHg from sediments to upper levels of the food chain (Gagnon and Fisher 1997; Wang *et al.*1998; Mason and Lawrence 1999). The bioavailability of sediment Hg to benthic organisms can be affected by factors such as organic content, iron and manganese (hydr)oxides, and sulfide content (Kim 2004). Mercury concentrations and the biogeochemistry governing its speciation within sediments are, therefore, of great interest in determining the fate and effects of mercury in freshwater systems.

1.3.1.1 Total Mercury in Sediments

The relative affinity of Hg for dissolved and particulate phases is measured by the distribution coefficient: $K_d = [Hg]_{particulate} / [Hg]_{dissolved}$, expressed in liters per kilogram. The distribution coefficients reported for THg are high (log K_d = 5 – 6), indicating a high affinity for the particulate phase (Coquery *et al.* 1997; Kroenke 2003). Consequently, over 90% of the Hg that enters the aquatic environment is eventually confined to the sediments (Kroenke 2003). Total mercury concentrations vary from parts per billion (ppb or ng g^{-1}) in clean sediment to parts per million (ppm or μg g^{-1}) in contaminated areas (Gobeil and Cossa 1993; Benoit *et al.* 1998B). In oxic sediments, Hg associates primarily with organic matter and iron/manganese oxides through adsorption and coprecipitation reactions, whereas in anoxic conditions, it is adsorbed onto and coprecipitated with sulfide minerals (Gobeil and Cossa 1993; Gagnon *et al.* 1997; Wang *et al.* 1998). In highly anoxic/sulfidric sediments, Hg may be complexed with dissolved sulfides forming soluble Hg-polysulfide species. This species is also available for methylation. Hg is released into pore water when metal oxides are reduced, or as a result of the microbial degradation of organic matter.

1.3.1.2 Methyl Mercury in Sediments

The observed MeHg concentrations present in the aquatic environment at any given time are a balance between methylation and demethylation processes. Biotic methylation of Hg occurs mainly in anoxic conditions near the sediment-water interface and is believed to be mediated by sulfate reducing bacteria (SRB) (Gilmour and Henry 1991). Both geochemical and microbial elements interrelate to influence rates of methylation and MeHg concentrations in sediments (Hammerschmidt and Fitzgerald 2004). Studies of MeHg levels in surface sediments have shown dependencies on inorganic Hg, organic matter, and sulfide content, as well as pH, Eh, and salinity (Mason and Lawrence 1999; Conaway *et al.* 2003; Hammerschmidt and Fitzgerald 2004). Although positive correlations have been recorded between MeHg and THg, the relationship is often weak due to the confounding effects of other factors. Concentrations of MeHg in sediments have been found to be positively correlated with the amount of organic matter present (Hammerschmidt and Fitzgerald 2004), while sulfides inhibit methylation due to precipitation of HgS and/or formation of charged

Hg-S complexes that are less likely to be taken up by diffusion into bacterial cells (Compeau and Bartha 1983; Mason *et al.* 1996; Gilmour *et al.* 1998; Benoit *et al.* 1999). Methyl mercury concentrations in sediments are typically less than 1 % of the THg concentration in less contaminated sites (< 500 ng g^{-1} THg) (Gagnon *et al.* 1996; Benoit *et al.* 2003; Conaway *et al.* 2003).

1.3.1.3 Background Concentrations

Estimates of background Hg concentrations in sediments are site-specific and range widely depending on the physical, geological, biological, and chemical characteristics of the river and its watershed. If estimates of background Hg concentrations can be made, the relative impact of humans on Hg cycling can be assessed. Background concentrations reported in the literature for Hg in freshwater sediments range from 0.02 to 0.20 μg g^{-1} (Table 1-2). To avoid the effect of modern increases in anthropogenic Hg emissions, most studies make a determination of background Hg concentrations based on concentrations found in deep core sediments.

TABLE 1-2 Range of Background Sediment Concentrations and Diffusional Fluxes of Total Hg

study site	concentration (μg g^{-1})	flux (μg m^{-2} yr^{-1})	study
Lake Tahoe, Nevada/California	0.02 – 0.04	38	Heyvaert *et al.* 2000
Central/Northern Canada (18 lakes)	0.02 – 0.13	1 – 114	Lockhart *et al.* 1998
Great Lakes Region, North America	0.03 – 0.08	14 – 135	Pirrone *et al.* 1998
Northern Quebec (12 lakes)	0.03 – 0.20	35 – 76	Lucotte *et al.* 1995
Minnesota and Wisconsin (7 lakes)	0.02 – 0.12	4 – 13	Engstrom *et al.* 1994

1.3.1.4 Sediment Quality Guidelines (SQG)

The Ontario Provincial Sediment Quality Guidelines (PSQGs) define three levels of eco-toxic effects and are based on the chronic, long-term effects of contaminants on benthic organisms (Persaud *et al.* 1993). The No Effect Level (NEL) is the level at which contaminants in sediments do not present a threat to water quality, benthic biota, wildlife or human health. The Lowest Effect Level (LEL) is the level at which actual eco-toxic effects become apparent. The Severe Effect Level (SEL) is the level at which contaminants could potentially eliminate most of the benthic organisms. The LEL for mercury is 0.2 $\mu g\ g^{-1}$ and the PEL is 2 $\mu g\ g^{-1}$ (Persaud *et al.* 1993).

Canadian Sediment Quality Guidelines for the protection of aquatic life have been established by Environment Canada (CCME 2005). For mercury, they consist of an interim Sediment Quality Guideline of 0.17 $\mu g\ g^{-1}$ and Probable Effect Level (PEL) of 0.486 $\mu g\ g^{-1}$. The national SQG and the PEL are used to define three ranges of chemical concentrations for a particular chemical, those that are rarely (<SQG), occasionally (between the SQG and the PEL), and frequently (>PEL) associated with adverse biological effects (MacDonald 1993; CCME 2005). Sediments with measured chemical concentrations that are equal to or lower than the national SQGs are considered to be of acceptable quality (CCME 2005).

1.3.2 Sediment Chronologies

Aquatic sediments are natural archives that can provide important information on the changing environment. They are important for dating events, as well as for calculating rates of sedimentation and element fluxes. Sediment chronology has been used to study changes in erosion rates (Van der Post *et al.* 1997), changes in water quality (Flower 1998), and to monitor contaminants (Fitzgerald *et al.* 1998; Yamashita *et al.* 2000). One of the most effective ways of dating sediments is by means of ^{210}Pb. With a half life of 22.3 years, this natural radioisotope is useful in dating on a time scale of 100 to 200 years (Oldfield and Appleby 1984). The technique was developed by Goldberg (1963) and has since been used in many studies of Hg contamination in aquatic systems (e.g. Engstrom and Swain 1997; Hermanson 1998; Frazier *et al.* 2000). In order to use this method effectively, it is important to understand the processes by which ^{210}Pb accumulates in sediments.

1.3.2.1 Geochemistry of ^{210}Pb

^{210}Pb is part of the ^{238}U decay series (Oldfield and Appleby 1984). The intermediate radioisotope ^{226}Ra decays to form ^{222}Rn, which in turn, through a number of short-lived isotopes, decays to ^{210}Pb. ^{226}Ra is present in most rocks, soils and sediments, supporting the *in situ* production of ^{210}Pb, also termed 'supported ^{210}Pb', which is typically in equilibrium with ^{226}Ra. ^{210}Pb can also reach sediments via an atmospheric pathway, whereby ^{226}Ra decays to ^{222}Rn, a gas which escapes into the atmosphere. It then decays to ^{210}Pb, which is scavenged from the air and deposited onto aquatic ecosystems, where it settles out of the water column. Once incorporated into the sediment, ^{210}Pb is generally resistant to diagenetic redistribution (Davis *et al.* 1984). This external supply is called 'unsupported ^{210}Pb' (Binford and Brenner 1986). Dating is based on the exponential decay of the unsupported ^{210}Pb fraction in sediments. The supported ^{210}Pb fraction is inferred from the ^{226}Ra concentration. The activity of unsupported ^{210}Pb, which is used for the calculation of sediment dates, and sedimentation rates, is easily obtained by subtracting the supported ^{210}Pb activity from the total ^{210}Pb activity (Oldfield and Appleby 1984).

1.3.2.2 Models

The ^{210}Pb dating technique has proved to be very effective, and several dating models have been developed; they are referred to as the constant flux/constant sedimentation rate (CF/CS), constant rate of supply (CRS), and constant initial concentration (CIC) models (Appleby and Oldfield 1978; Robbins 1978). Oldfield and Applefield (1984) describe the assumptions underlying these models. Where sedimentation rates are constant, the CF/CS model can be applied. The two remaining models are used in cases where sedimentation rates are variable. The CRS model assumes a constant flux of ^{210}Pb to the sediment, and is the preferred model for systems with variable rates of sediment accumulation. The CIC model assumes that sediments have a constant initial unsupported ^{210}Pb concentration. If the sedimentation rate changes, then the amount of ^{210}Pb scavenged from the water to the sediment changes proportionally.

1.3.3 Transport of Mercury at the Sediment-Water Interface

1.3.3.1 Accumulation

Establishing accurate sediment chronologies using ^{210}Pb dating techniques is required not only for calculating rates of sedimentation, but also for determining rates of Hg accumulation. A large portion of the Hg entering a lake may ultimately end up in the sediments, and measuring this flux is important in quantifying the dynamics of Hg in freshwater systems. The Hg accumulation rate for each dated stratum of a sediment core can be calculated as the product of the sediment accumulation rate and the Hg concentration in the stratum (Hermanson 1998; Heyvaert *et al.* 2000). Overall fluxes of THg to the sediments reported in the literature range between 1 and 135 μg m^{-2} yr^{-1} (Table 1-2). While the flux of THg is important in determining how and where Hg accumulates in the environment, it is the flux of MeHg that is important with respect to Hg accumulation in biota (Mierle 2001). Unfortunately, most studies to date have only measured accumulation rates of THg.

1.3.3.2 Diagenesis

Diagenesis refers to all the chemical, physical, and biological changes undergone by a sediment after its initial deposition. Diagenetic processes have the potential to reshape elemental profiles in sediments. For example, biomixing can displace a contaminant in the sediments giving a misleading date of entry or producing false peaks in the sediments (Boudreau 1997). For elements like manganese and iron, which are sensitive to redox conditions (Ridgeway and Price 1987; Gobeil *et al.* 1997), remobilization, upward diffusion and oxidation can significantly alter the sediment record of deposition (Lockhart *et al.* 2000). Accurate interpretation of sediment records assumes that diagenetic processes are insignificant and do not alter Hg distribution profiles in sediments over time. Since results from many studies are based on this assumption (Gobeil and Cossa 1993; Lockhart *et al.* 1998), determining its validity for mercury in this study is crucial.

The case *against* the alteration of Hg profiles by diagenetic redistribution of Hg in sediments has been made in several studies. For example, Hg profiles from many freshwater and marine systems have shown a pattern of increasing concentration in surface sediments from North American (Johnson *et al.* 1986; Johnson 1987; Rada *et al.* 1989; Swain *et al.* 1992;

Lockhart *et al.* 1993; Lucotte *et al.* 1995), and Scandinavian lakes (Johansson 1985; Verta *et al.* 1990). Not only is the timing of Hg increase synchronous among sites, but also the magnitude of the change is similar across a large geographic area (Fitzgerald *et al.* 1998), evidence that the surface enrichment is attributable to atmospheric deposition trends and not to diagenetic redistribution. The argument against post-depositional remobilization of Hg can also be made by studying Hg profiles for systems where Hg inputs are known. This was demonstrated in a study by Lockhart *et al.* (2000), where sediment core records were assembled from three lakes (Clay Lake, ON; Giauque Lake, NT; Stuart Lake, BC) for which the history of Hg loading was known. Mercury profiles derived from the cores agreed well with the history of inputs.

On the other hand, evidence *for* the diagenetic remobilization and alteration of Hg profiles is present throughout the literature. Gobeil *et al.* (1999) suggested that Hg profiles from Arctic basin cores were altered by redistribution during diagenesis because the strong similarities between Hg and iron profiles implied that a fraction of the THg co-precipitated with iron oxides. In addition, certain studies have shown marked gradients in sediment pore water profiles across the sediment-water interface (Bothner *et al.* 1980; Gobeil and Cossa 1993; Gagnon *et al.* 1996; Gagnon *et al.* 1997; Gill *et al.* 1999), leading to elevated fluxes of dissolved Hg from sediments to the water column (Matty and Long 1995). This process has the potential to reshape Hg profiles, if diffusion is fast enough, and sedimentation rates are low. Arguments for and against the diagenetic remobilization of Hg have been made in the literature (Rasmussen 1994; Fitzgerald *et al.* 1998). Therefore, sedimentary records of Hg should only be interpreted after considering the importance of diagenesis at a specific site.

In certain cases where evidence seems to indicate that Hg does undergo post-depositional remobilization, its effect on the shape of Hg profiles may not necessarily be significant. Gagnon *et al.* (1997) investigated the diagenetic behaviour of Hg in sediments of the Saguenay Fjord, in Canada. Despite evidence that Hg was being recycled with iron and manganese oxides at the redox boundary, the remobilization of Hg from deeper layers was too slow to account for the high surface concentrations, and it did not significantly alter the Hg profile. Although Hg remobilization may occur under certain conditions, it is important to recognize whether this process can produce significant Hg redistribution in sediments, or whether its effect is negligible. Where possible, obtaining the history of Hg inputs is useful for comparison of Hg sediment profiles. Comparing iron/manganese and pore water profiles to Hg profiles may also indicate whether or not there has been remobilization of Hg in the sediments. Unfortunately, recent studies arguing the importance of diagenetic processes on Hg profiles are often lacking in direct pore water measurements (Gobeil *et al.* 1999; Lockhart *et al.* 2000). Without this information, it is difficult to discount diffusion as a significant process in sediments.

1.3.3.3 Diffusion

The chemistry of pore waters is very important from a geochemical and toxicological perspective. This is because pore waters mediate the diffusional fluxes of metals at the sediment-water interface, and are a potentially important source of trace metals to biota living in the sediments and water column (Teasdale *et al.* 1995). Mercury concentrations in pore waters are not entirely controlled by exchange equilibrium between the solid phase and pore water phase (Bothner *et al.* 1980; Gagnon *et al.* 1997). For this reason, quantification of the dissolved Hg concentration gradient should not be inferred from solid-phase Hg; it is necessary to conduct pore water analyses.

As mentioned previously, the calculation of historic Hg accumulation rates to sediments requires that there has been no loss of Hg from the solid phase to pore waters, no transport within the sediment column, and no Hg transfer between the sediment pore water and water column (Fitzgeral *et al.* 1998). Significant loss as a result of diffusion from the sediments to the overlying water should be apparent from the presence of marked concentration gradients at the sediment-water interface (Carignan and Nriagu 1985). Thus, where pore water Hg concentrations exceed those in the water column, it is important to assess whether sediments are significant sources of Hg to the overlying water. Predicted diffusive fluxes can be calculated according to Fick's first law of diffusion (Berner 1980):

$$\mathrm{J} = -\,\Phi\, D_s\, (\,\delta C / \delta z\,) \tag{1}$$

where Φ is the porosity, D_s is the bulk sediment diffusion coefficient, and ($\delta C / \delta z$) is the concentration gradient across the sediment-water interface.

Gagnon *et al.* (1997) conducted pore water studies to determine the diagenetic mobility of anthropogenic Hg in coastal sediments. In this case, the presence of oxic surface sediments prevented significant diffusion of Hg to the overlying waters (Gagnon *et al.* 1997). In a similar study, Ramalhosa *et al.* (2001) calculated diffusion rates of Hg from marine sediments in Portugal and concluded that diffusive fluxes were not sufficiently high to significantly influence the Hg concentrations in the water column. In both cases, although a small diffusive flux was measured, sediments were found to act as a net sink, rather than a source of Hg.

1.4 Conclusion

This study provides data on current mercury concentrations, diffusion and accumulation rates in the St. Lawrence River Area of Concern near Cornwall. This information is intended to be used in predictive models of the cycling and bioaccumulation of mercury in river systems. Information about historic trends in mercury deposition in the St. Lawrence River may aid in the evaluation of the impact of efforts to reduce mercury inputs to the river. Most importantly, this study will provide data essential to the evaluation of the risk mercury poses to this ecosystem and the human population that uses it.

CHAPTER 2

MERCURY TRANSPORT IN SEDIMENTS OF THE ST. LAWRENCE RIVER NEAR CORNWALL, ONTARIO

2.1 Introduction

The St. Lawrence River (Canada, U.S.A) drains the most industrialized region of North America (Carignan and Lorrain 2000). The rapid industrialization of populated areas over the past century has resulted in localized degradation of water quality and bottom sediments (Reavie *et al.* 1998). This has been the case near Cornwall, Ontario, where local industrial activity (e.g. chlor-alkali, pulp and paper, textiles) has resulted in PCB and mercury (Hg) contamination. The International Joint Commission (IJC) identified the St. Lawrence River near Cornwall as one of 42 'problem areas' for the aquatic environment, and it was designated an Area of Concern (AOC) in 1985, primarily because of Hg contamination. Hg concentrations in these sediments exceed background levels, and exceed Ministry of the Environment (MOE) sediment criteria for the protection of aquatic life (Golder Associates 2004). Previous studies in the area indicate that levels of Hg in surface layers of the sediments have decreased since the 1970s, and that cleaner sediments are covering the more contaminated historical discharges (St. Lawrence River RAP 1997). However, contaminated sediments remain a potential source of Hg to the system, posing a risk to fish, wildlife and humans through biomagnification in the food web.

Mercury concentrations in certain fish from the Cornwall waterfront exceed Ontario guidelines for consumption by humans (Grapentine *et al.* 2003). Research in other aquatic environments suggest that the methyl mercury (MeHg) in fish originates primarily from anoxic sediments (Benoit *et al.* 1998B; Krabbenhoft *et al.* 1998; Covelli *et al.* 1999; Gill *et al.* 1999). This situation raises concerns that elevated Hg in sediments from the Cornwall AOC are contributing to the high Hg concentrations in top predators. Biological uptake at the base of the food chain likely exerts the primary control on the amount of MeHg reaching larger fish (Mason *et al.* 2000). Benthic invertebrates are likely to be exposed to sediment contaminants, both through ingestion of sediment or other contaminated food sources, and through exposure to contaminants in pore waters. Therefore, it is important to investigate not only particle-bound Hg concentrations, but also dissolved Hg concentrations in the sediment column.

In the Cornwall AOC, where sediment Hg concentrations increase with depth (Dreier 2001), there is potential for Hg to diffuse from deeper sediments to less contaminated surface sediments, where it may be taken up by benthic organisms. Pore waters mediate the fluxes of Hg at the sediment-water interface, and are potentially important sources of Hg to the water column, and to biota living in the sediments. The cycling of gases in sediments can also enhance the mobility of Hg within the sediment column (Huttunen *et al.* 2001). Ebullition may entrain some contaminants such as MeHg to overlying waters. This mode of transport typically occurs in organic-rich, anoxic freshwater sediments, where anaerobic decomposition is the source of substantial methane production. Hence, detailed sediment and pore water profiles are needed to estimate the importance of sediment-water transport in the cycling of Hg in the sediment and at the sediment-water interface.

We measured profiles of methyl MeHg and THg in sediments, pore water, and the overlying water of the St. Lawrence River AOC during the summer of 2004 and 2005. The objectives of this study were: (1) to compare concentrations of dissolved and particulate Hg in surface sediments of three different zones within the AOC that are affected by different industrial activities; (2) to quantify deposition rates of THg and MeHg to the sediments; and (3) to determine whether sediments contribute significant THg and MeHg to the river via pore water diffusion.

2.2 Materials and Methods

2.2.1 Study Site

The Cornwall AOC includes a stretch of the St. Lawrence River approximately 80 km long, from the Moses-Saunders power dam to the eastern outlet of Lake St. François in Quebec. This stretch of the river impacts many jurisdictions, including the provinces of Ontario and Quebec, the state of New York, as well as the Mohawks of Akwesasne. Within these boundaries, the river is divided into two branches by Cornwall Island; the South Channel, which contains high levels of PCBs, and the North Channel, with Hg contaminated sediments (St. Lawrence River RAP 1992). Research was conducted in three zones located along the Cornwall waterfront of the North Channel (see Figure 1-2, Chapter 1). Lamoureux Park (LP) is the westernmost sampling location, and is closest to an industrial complex formerly comprised of a pulp and paper mill (Domtar) and a chlor-alkali plant (ICI). Windmill Point to Pilon Island (WPPI) is the largest and easternmost zone, stretching from the former site of a textile mill (Courtaulds) to the eastern edge of Pilon Island. The Tank Farm (TF) is the smallest sampling zone and is situated between the LP and WPPI sites. A reference site (RF) was selected upstream and outside of areas exposed to past industrial effluents.

2.2.2 Sample Collection

Sediment cores were collected from three sites along the Cornwall waterfront of the St. Lawrence River (see Figure 1-2, Chapter 1) from May to August, 2004 and 2005 (LP-1, 45°00'40.2" N, 74°43'55.4" W; LP-2, 45°00'40.2" N, 74°43'54.5" W; LP-3, 45°00'40.2" N, 74°43'54.1" W; TF-1, 45°00'57.6" N, 74°42'23.0" W; TF-2, 45°00'57.6" N, 74°42'23.9" W; WPPI-1, 45°01'13.2" N, 74°41'25.4" W; WPPI-2, 45°01'33.5" N, 74°40'50.4" W; WPPI-3, 45°01'33.7" N, 74°40'50.8" W) . Sediments were collected using corers designed specifically for high-resolution paleolimnological work (Glew 1989). Using acoustic data and maps of the river bed, cores were collected from depositional areas at depths ranging from 7 to 12 m. Redox potential was measured throughout the cores within one hour of collection. Cores were extruded on site at 1 cm intervals, under a nitrogen atmosphere to minimize changes in redox potential. The sediment slices were placed in air-tight centrifuge tubes, and were transported on ice to the laboratory for pore water separation. Grab samples were collected from a reference site using an Eckman dredge, and frozen until further analysis.

Pore water profiles were obtained from duplicate sediment cores taken on each sampling occasion. In the lab, pore water was separated from sediment samples by centrifugation at 4000-rpm for 30 minutes followed by filtration using 0.45 μm syringe filters (with HT Tuffryn membrane), also done under a nitrogen atmosphere. Pore water samples were acidified and refrigerated in the dark for THg (1 % BrCl), MeHg (0.5 % HCl), and metals (0.5 % HNO_3) analysis. Sediment subsamples were freeze-dried for dating and THg analysis, and wet sediments were frozen for future MeHg analysis. Gas bubbles released at the sediment surface were collected using a stainless steel cone covering an area of 2685 cm^2.

The gases were collected by water displacement, into a 0.5 L Teflon sample bottle fitted to the top of the steel cone. The sample bottle was removed by a diver, and was stored in the dark at 4°C until analysis (Chau *et al.* 1977).

2.2.3 Analytical Methods

Methyl mercury in sediments was extracted and analyzed by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai *et al.* (1997). Sediment THg analysis was conducted on homogenized freeze dried sediment using an automatic Mercury Analyzer based on thermal decomposition, dual-step gold amalgamation, and detection via Cold-Vapor Atomic Absorption using an SP-3D mercury analyzer (Nippon Instruments Corp). The method detection limit (MDL) was 0.01 ng per sample. Precision, as indicated by the relative percent difference (RPD) of duplicate samples, was found to average 5.5 % for THg in sediments (n = 62 pairs), and 8.2 % for MeHg in sediments (n = 79 pairs). The accuracy of our determinations of THg and MeHg in sediments was estimated by analyses of analytical procedural blanks, and spiked samples. The mean recovery of spiked samples was 102 ± 0 % for THg (n = 5), and 107 ± 8 % for MeHg (n = 7).

To retrieve an adequate volume of pore water for analysis, 1 cm interval samples from duplicate cores were pooled. Methyl mercury concentrations were determined in pore water by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai *et al.* (1996). The MDL was estimated as 0.02ng L^{-1}. Water samples were analyzed for THg using pre-oxidation by BrCl, and $SnCl_2$ reduction with pre-concentration by two-stage gold amalgamation, followed with detection using cold vapour atomic fluorescence spectroscopy (CV-AFS). The analysis was conducted using a Tekran

2600 system following the modified US EPA Method 1631 guideline for mercury analysis (US EPA 2001). The MDL was estimated as 0.2 ng L^{-1}. Analysis of procedural blanks consisting of de-ionized water revealed no mercury contamination during THg analysis, or during MeHg extraction and analysis. The mean recovery of spiked samples was 105 ± 11% for THg (n = 10), and 103 ± 2 % for MeHg (n = 4).

Iron (Fe) and manganese (Mn) were analyzed by Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) by the University of Ottawa's geology department (MDL = 0.1 mg L^{-1}). CH_4 and CO_2 concentrations in gas were measured by flame ionization detection (FID) using a chromatographic RGA5 system (Trace Analytical, Maryland). Sediment subsamples were dried to determine water content and analyzed for loss on ignition (550°C for organic carbon content, 950°C for carbonate content).

2.2.4 ^{210}Pb dating

Analysis of ^{210}Pb was performed on each core at selected depths to determine age and sediment accumulation rates. ^{210}Pb and ^{226}Ra activity were measured by gamma spectrometry, using a digital high purity germanium well detector (DSPec, Ortec), following methods described by Appleby (2001). Supported ^{210}Pb, as determined by ^{226}Ra activity, was subtracted from total ^{210}Pb activity to determine the unsupported ^{210}Pb fraction, which is used for the calculation of sediment dates, and sedimentation rates. The mean sedimentation rate for each core is calculated from the slope of unsupported ^{210}Pb activity versus cumulative dry mass (Figure 2-2), based on the Constant Flux/Constant Sedimentation (CF/CS) model, which assumes a constant sedimentation rate. Using Spearman's correlation, these sedimentation rates were compared to sedimentation rates calculated using the

Constant Rate of Supply (CRS) model, which accounts for variable sediment accumulation rates. Both models (Appleby and Oldfield 1978) estimated similar (R^2 = 0.761, SE_{est} = 0.08 g cm^{-2} yr^{-1}) sedimentation rates (Figure 2-1). Overall, nine cores were dated, and for those that did not reach background ^{210}Pb concentrations, we inferred supported ^{210}Pb from the ^{226}Ra concentrations by taking the average of the ^{226}Ra found in the core (Appleby 2001).

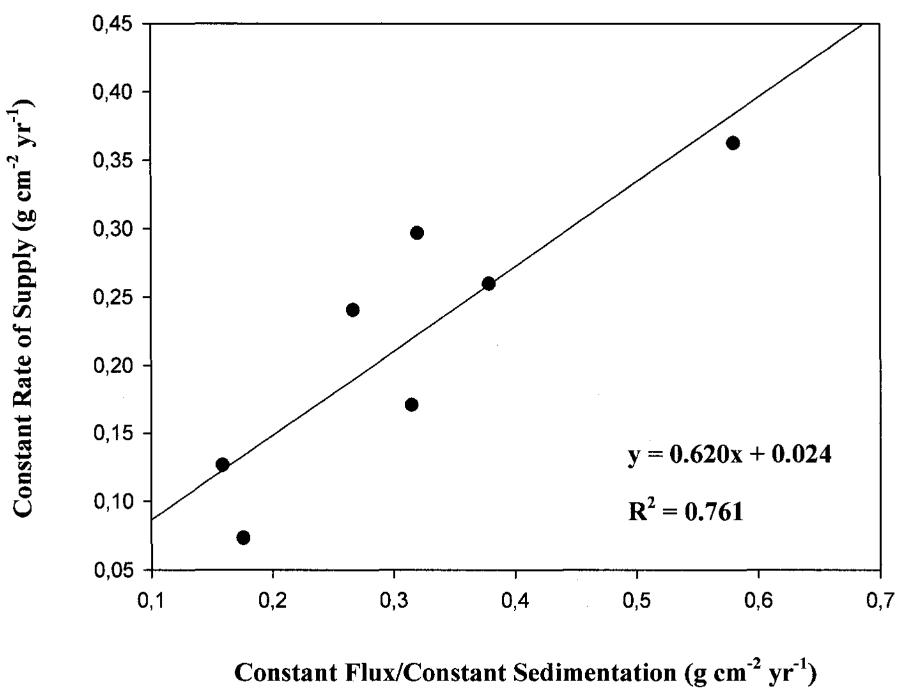

FIGURE 2-1 Comparison of sedimentation rates (g cm^{-2} yr^{-1}) calculated using the Constant Flux/Constant Supply model (CF/CS) and the Constant Rate of Supply model (CRS).

2.2.5 Hg Flux Calculations

Mercury diffusion from sediments was determined based on the Hg concentration gradient in the top 1 cm of interstitial fluid and the overlying water column Hg concentration. For diffusion of Hg across the sediment-water interface, in the absence of bioturbation and bioirrigation, a generally accepted form of Fick's first law is:

$$\text{diffusive flux (F)} = - (\varphi D_w / \theta^2) (\delta C / \delta x) \quad (1)$$

where F is the flux of a solute with concentration C at depth x, θ is the tortuosity (dimensionless), φ is the sediment porosity, and D_W is the diffusion coefficient of the solute of interest in water without the presence of the sediment matrix. In accordance with Gill *et al.* (1999), we adopted a D_W value for inorganic Hg in water of 9.5×10^{-6} cm^2 s^{-1}, and for MeHg in water of 1.3×10^{-5} cm^2 s^{-1}.

Tortuosity is not readily measured, but has been shown to be related to porosity. For all flux calculations, tortuosity was calculated using the following empirical relationship (Boudreau 1996)

$$\theta = 1 - \ln (\varphi^2) \quad (2)$$

Porosity (φ) was calculated by measuring the weight loss of sediments freeze-dried over 48 hours to constant weight and calculating

$$\varphi = 1 - (\text{bulk density} / \text{particle density}) \quad (3)$$

where a particle density of 2.65 g cm^{-3} was used (Brady and Weil 2002).

2.3 Results and Discussion

2.3.1 ^{210}Pb Inventories and Sedimentation Rates

Activity of unsupported ^{210}Pb decreases with depth in all cores, with the exception of cores TF-1 and TF-2. In other cores, irregularities were observed only in surface layers. In most cases, the natural log of unsupported ^{210}Pb activity decreased almost linearly with cumulative dry mass (Figure 2-2). Decay curves could be fitted with R^2 values > 0.59 indicating a uniform accumulation of sediments for all cores. Carignan and Lorrain (2000) measured sedimentation rates of 0.11 to 1.78 g cm^{-2} yr^{-1} in the St. Lawrence River. Here, sedimentation rates for the Cornwall AOC were found to vary within this range, with values from 0.18 g cm^{-2} yr^{-1} for site LP-3 to 0.58 g cm^{-2} yr^{-1} for site WPPI-4 (Table 2-2). A sedimentation rate for the TF site was not calculated because ^{210}Pb activity showed no decline with depth (Figure 2-2).

2.3.2 Description of Cores

The cores consisted of a uniform, brown-black clayey mud with a brownish surface coloration in the top 1 – 2 cm. Small pores, pieces of wood or shell were noted during sampling. Although small pieces of shell were rarely seen, small pores and pockets of gas were present throughout the length of many cores, especially those from the Lamoureux Park site. Layers of wood chips were observed at various depths in cores WPPI-1 (12 – 18 cm and 24 – 28 cm), and LP-2 (2 – 10 cm and 12 – 18 cm). Traces of oil were present in all cores, and were especially prevalent in sediments from the Tank Farm site. Benthic organisms were rarely seen in the cores that were collected from the Cornwall waterfront.

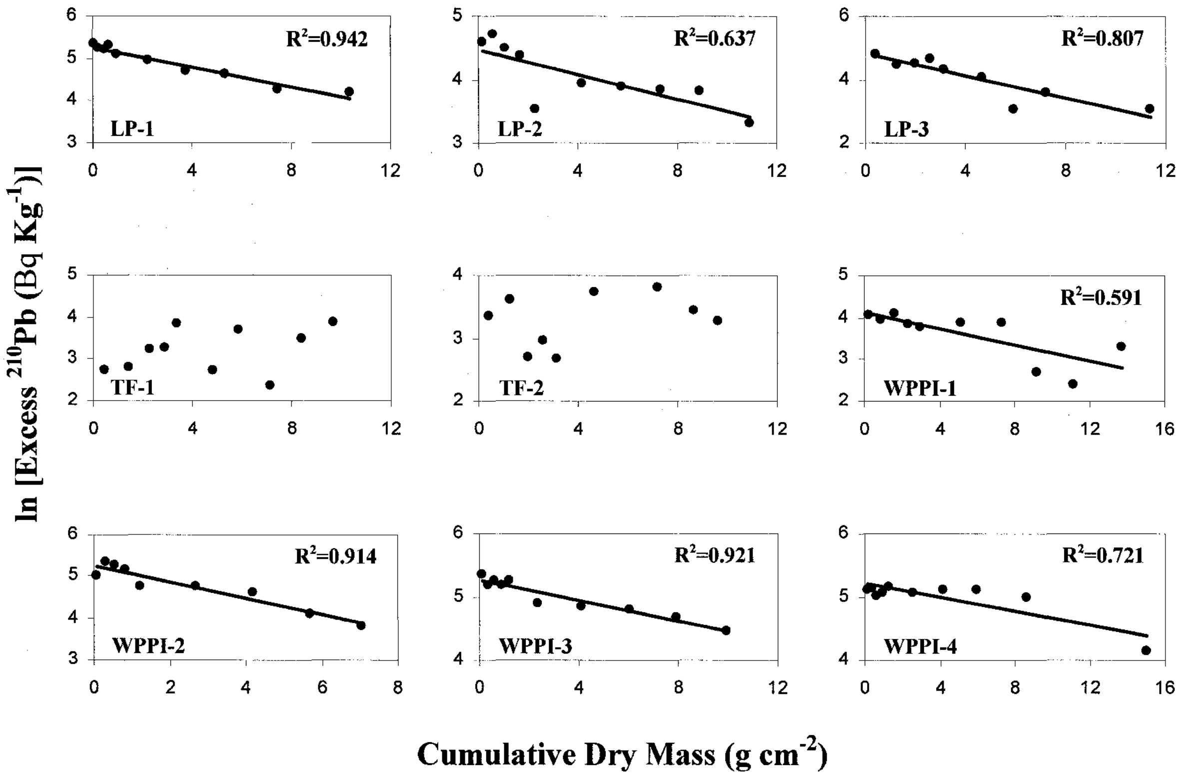

FIGURE 2-2 Profiles of the natural log of excess ^{210}Pb activity is plotted against cumulative dry mass. Mean sedimentation rate (g cm^{-2} yr^{-1}) was calculated by dividing λ by the slope, where λ is the ^{210}Pb radioactive decay constant (0.03114 yr^{-1}). Sedimentation rates can be found in Table 2-2.

2.3.3 Mercury in Surface Sediments

Concentrations of THg (640 ± 248 ng g^{-1} d.w.) and MeHg (22.2 ± 13.8 ng g^{-1} d.w.) in surface sediments from all three zones are substantially greater than THg (15.9 ± 2.88 ng g^{-1} d.w.) and MeHg (0.24 ± 0.09 ng g^{-1} d.w.) concentrations in sediment from a reference site (RF) (see Table C-1, Appendix C), located upstream of the area exposed to past industrial effluents. This difference was found to be significant (one-way ANOVA, $P < 0.05$). These results support the evidence for a local, as opposed to regional, source of Hg to the AOC, which is consistent with other assessments (Filion and Morin 2000; Richman and Dreier 2001; Grapentine *et al.* 2003).

TABLE 2-1 Concentrations of THg and MeHg in Sediment[a] and Pore water[b]

site	sediment THg (ng g^{-1})	sediment MeHg (ng g^{-1})	% MeHg/THg in sediment	pore water THg[c] (ng L^{-1})	pore water MeHg (ng L^{-1})	% MeHg/THg in pore water
LP-1	556.6	45.47	8		11.1	
LP-2	591.6	34.49	6	7.03	4.20	60
LP-3	727.1	39.28	5	34.62	6.57	19
TF-1	1217.1	9.60	1		254	
TF-2	405.7	15.08	4	91.78	11.1	12
WPPI-1	780.0	18.58	2		8.40	
WPPI-2	442.5	15.02	3		4.15	
WPPI-3	508.0	12.63	2	198.48	7.50	4
WPPI-4	532.7	9.41	2	70.62	52.2	74

[a]Sediment concentrations are for the top 1 cm sediment layer of one core. [b]Pore water concentrations are for the top 1 cm sediment layer obtained from 2 separate cores. Concentrations for site WPPI-4 are for the top 2 cm sediment layer. [c]THg analysis was only done on samples collected in 2005, not on samples collected in 2004 due to inadequate sample volume.

Surface sediment (0 – 1 cm) THg concentrations across all zones ranged from 406 to 1220 ng g^{-1} dry weight (Table 2-1). Even the lowest THg levels exceed the Sediment Quality Guideline (SQG) for the lowest effect level of 170 ng g^{-1} and most exceed the probable effect level (PEL) of 486 ng g^{-1} established by the Canadian Council of Ministers of the Environment (1997). Sediment contaminant concentrations reported in other studies of the St. Lawrence River exhibit THg concentrations similar to those found here. Previous sediment surveys performed by the MOE along the Cornwall waterfront reported THg concentrations above 200 ng g^{-1} (Persaud *et al.* 1993) at all three sites, and above 2000 ng g^{-1} at the WPPI site (Richman 1994; Richman 1996; Richman 1999; Richman 2000) and the TF site (Grapentine *et al.* 2003). In the present study, the lowest and highest THg levels were found in sediments from the TF site. This variation is an indication of the heterogeneity of the river bed. The difference in THg concentrations between sites was found to be not significant (one-way ANOVA, $P > 0.05$), due to the broad range of Hg concentrations within each site (Table 2-1).

Surface sediment MeHg levels ranged from 9.41 to 45.5 ng g^{-1} dry weight (Table 2-1). The mean MeHg concentration between sites was significantly different (one-way ANOVA, $P < 0.001$). Whereas the TF and WPPI sites had similar concentrations of 12 – 14 ng g^{-1}, the reference site (RF) had the lowest MeHg concentration of 0.24 ng g^{-1} ($P < 0.001$), and the LP site had the highest MeHg concentration of 40 ng g^{-1} ($P < 0.01$) (Figure 2-3). The LP site also had the highest fraction of MeHg relative to THg, ranging from 5 to 8 % (Table 2-1). These results differ from those found by Grapentine *et al.* (2003), where the highest MeHg concentrations and the highest MeHg to THg ratios were found in the WPPI site. In a field survey of wetlands the proportion of MeHg in sediments ranged between 0.3 and 5.7 % of the THg (Holmes and Lean 2006). An even higher percent MeHg of THg in sediment, ranging from 0.1 to 16.3 %, was detected in sediments of the Quabbin Reservoir, Massachussetts (Gilmour *et al.* 1992). Regression analysis showed no relationship between MeHg and THg in the surface sediment layer of the St. Lawrence River, suggesting that methylation is not controlled by total mercury concentration.

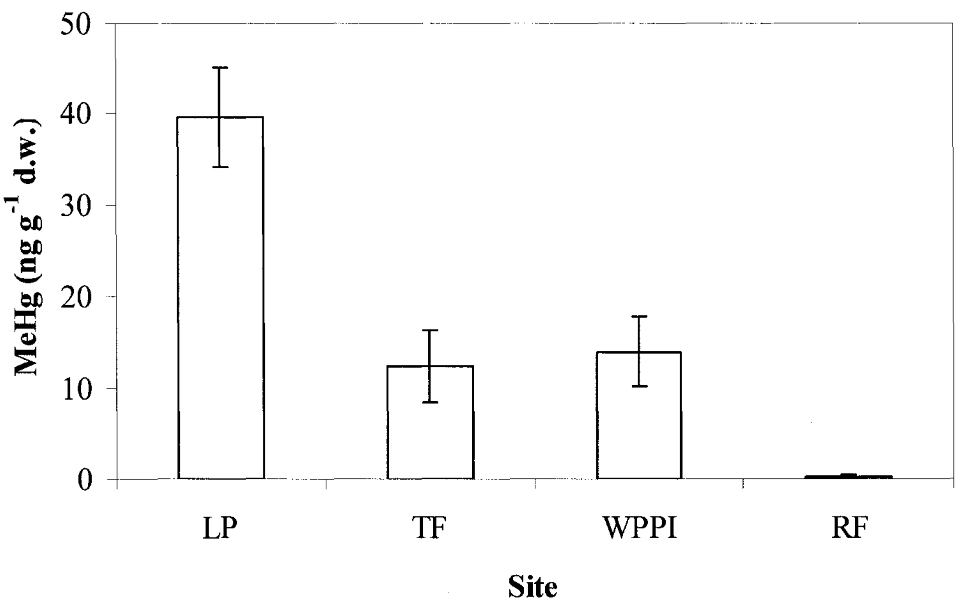

FIGURE 2-3 Mean concentration of methyl mercury (MeHg) in surface sediments (0-1 cm) of three study sites and a reference site from the St. Lawrence River (Cornwall) Area of Concern. Error bars represent the standard deviation.

2.3.4 Pore Water Profiles

Mercury may be released to the sediment pore waters by degradation of organic matter, the dissolution of Fe-Mn oxides, as well as the oxidation of Hg-laden iron sulfides. Once in solution, dissolved mercury in anoxic sediments may diffuse to the sediment-water interface along a concentration gradient. Several methods have been used to measure sediment pore water profiles of mercury, including centrifugation, sediment filtration (by gravity or vacuum), whole-core squeezing, and *in situ* dialysis. A critical review of these techniques was conducted by Mason *et al.* (1998), who showed that the method used here was a reliable method for quantifying mercury.

Profiles of dissolved THg ranged from 7.5 to 947.0 ng L^{-1} (Figure 2-4), and represent less than 0.05 % of the solid-phase THg. The profiles are characterized by a subsurface peak followed by decreasing concentrations with depth below 10 cm. In the LP site, solid-phase and pore water THg are correlated (R^2 = 0.762), suggesting that dissolved Hg is controlled by an exchange equilibrium between these two phases. This is not the case in the WPPI site, where dissolved Hg concentrations may be controlled by other factors. The increased concentrations of dissolved THg just below the sediment-water interface could be related to the solubility changes of Fe and Mn (hydr)oxides associated to anoxic conditions. It is well known that these compounds, insoluble in oxidizing conditions, are efficient scavengers for many soluble heavy metals such as Hg (Lockwodd and Chen 1973). However, in low-redox conditions such as the Cornwall sediments (-87.7 to -259.5 mV) (see Figure B-1, Appendix B), these oxides are used in microbial degradation of organic matter and are solubilized (Froelich *et al.* 1979). The decrease in Hg with depth may be a consequence of precipitation as insoluble mercury sulfide. Hg may also be removed from solution through co-precipitation with iron sulfides (Gobeil and Cossa 1993) however this is not consistent with the dissolved Fe (Fe^{2+}) profile in core LP-3 (Figure 2-4), because an increase of this species is observed in the deepest layers. This increase in dissolved iron is consistent with the low sulfide concentrations (see Table B-2, Appendix B) and highly suboxic conditions of the sediments (see Figure B-1, Appendix B). Profiles of dissolved MeHg ranged from 1.7 to 254 ng L^{-1}

(Figure 2-5). There is no apparent trend in the dissolved MeHg profiles, either with depth or between sites. The highest levels were observed in core TF-1 (99 – 254 ng L^{-1}), in contrast to the relatively low levels of core TF-2 (6 – 11 ng L^{-1}). The percentage of MeHg to THg in pore water ranged from 2 to 97 % (see Figure C-1, Appendix C).

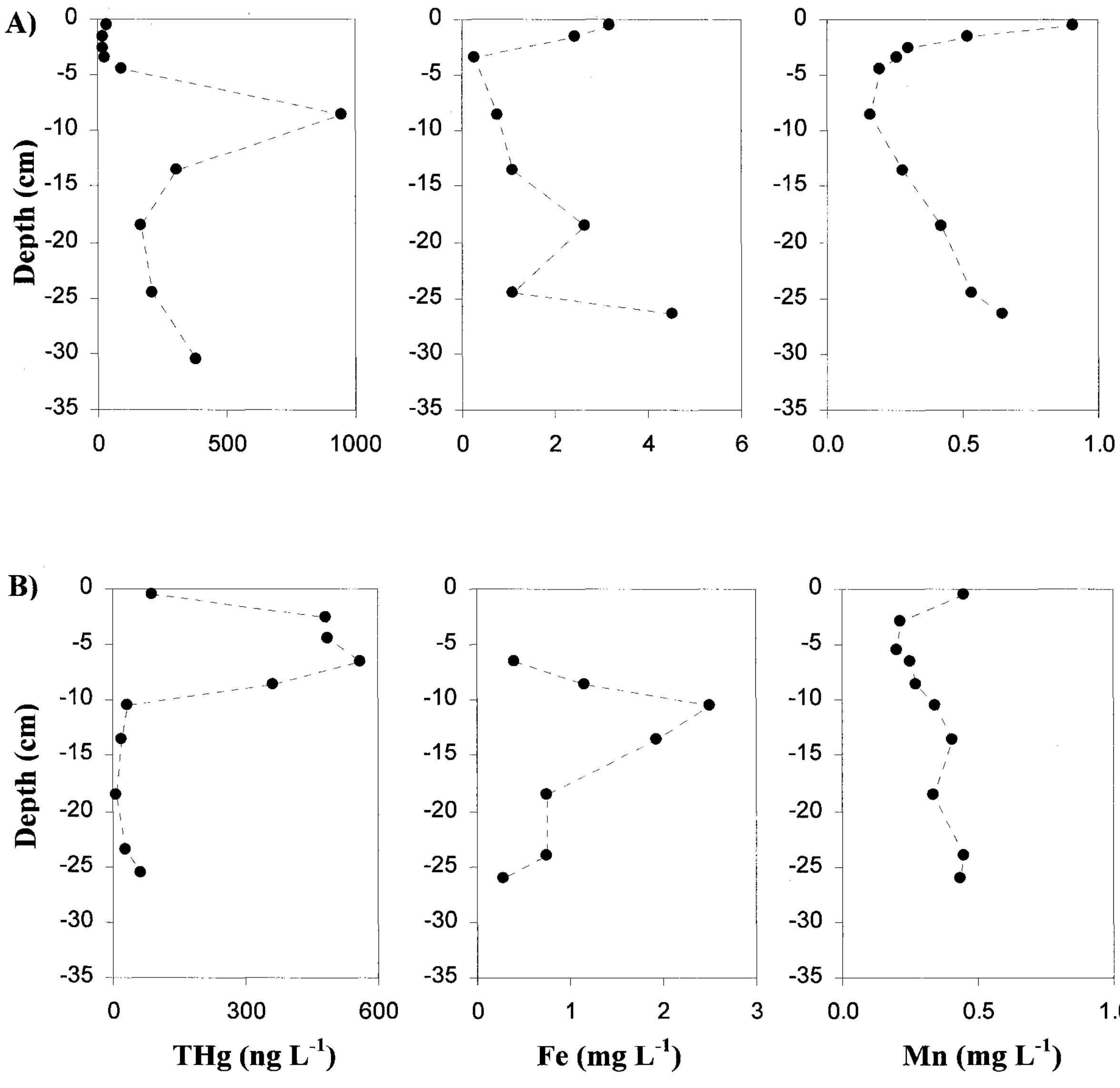

FIGURE 2-4 Pore water profiles of total mercury (THg), iron (Fe), and manganese (Mn) in cores from the **a)** Lamoureux Park (LP-3), and **b)** Tank Farm (TF-2) sites along the Cornwall waterfront.

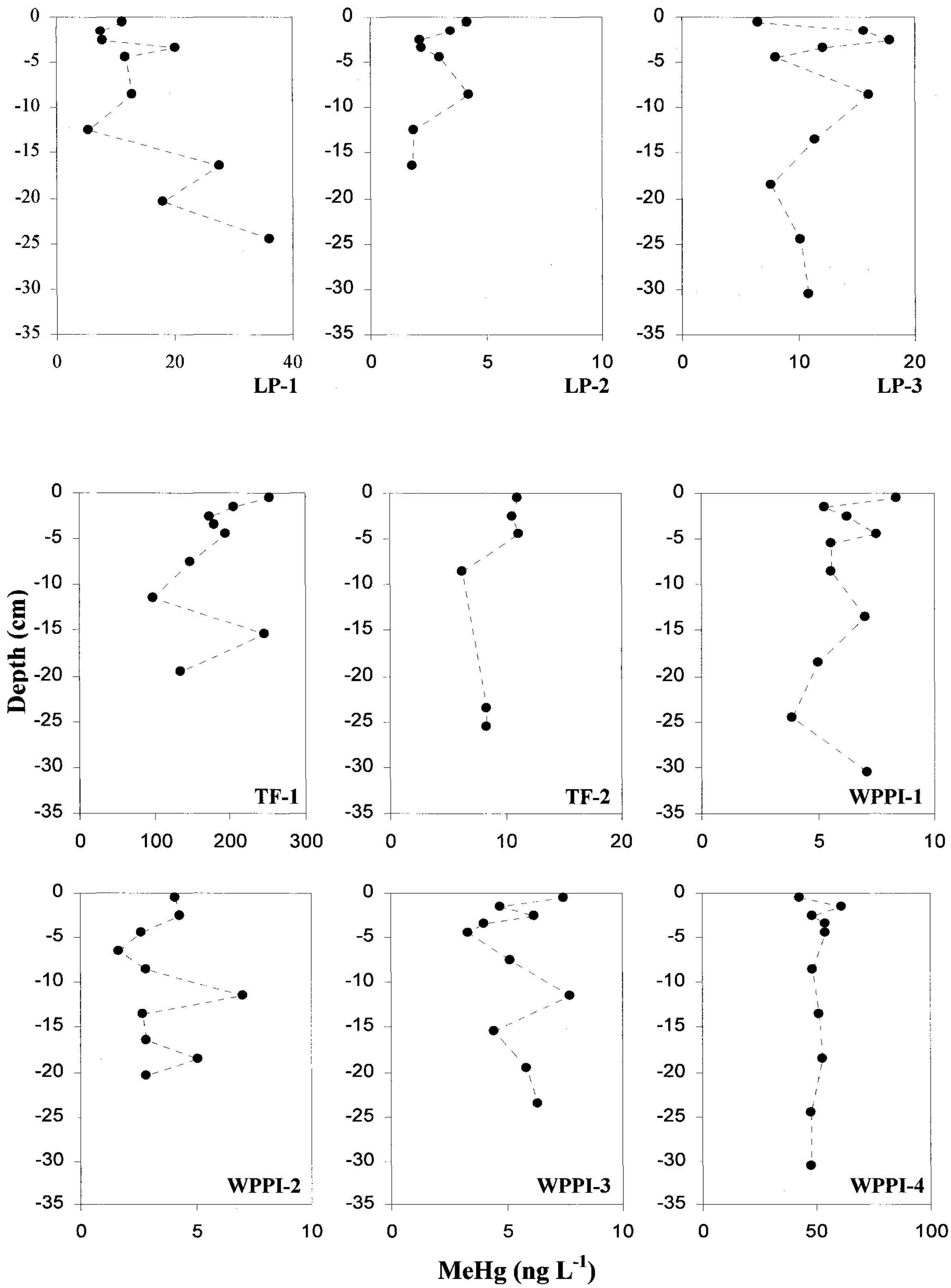

FIGURE 2-5 Vertical profiles of dissolved methyl mercury (MeHg) in pore waters for nine sediment cores from the St. Lawrence River (Cornwall) Area of Concern.

2.3.5 Mercury Deposition and Diffusion

The fine scale assessment of mercury in pore water allowed us to calculate the THg, and MeHg diffusive fluxes at the sediment-water interface (Table 2-2). Sediment-water diffusional fluxes were determined based on the concentration gradient between the Hg concentration in the top 1 cm of interstitial fluid and the overlying water column. Pore water concentrations in surface sediments ranged from 7.03 to 198 ng L^{-1} for THg, and from 4.15 to 254 ng L^{-1} for MeHg (Table 2-1). Interstitial concentrations at the sediment surface were from 7 to 340 times higher than the concentrations in overlying water for THg (0.58 – 1.02 ng L^{-1}), and from 220 to 8200 times higher than the concentrations in overlying water (0.02 – 0.03 ng L^{-1}) for MeHg. Gobeil and Cossa (1993) did not observe such high enrichments (up to 14 times) of THg in sediments of the Laurentian Trough, however, Gagnon *et al.* (1997) measured enrichments ranging from 12 to over 100 times in the Laurentian Trough.

The calculated diffusive flux of THg from pore water gradients for the 3 study sites along the Cornwall waterfront ranged from 1.2 to 48.2 ng cm^{-2} yr^{-1}, while MeHg flux had a smaller range from 1.2 to 14.6 ng cm^{-2} yr^{-1} (Table 2-2) THg diffusive fluxes were within the range of fluxes measured in heavily contaminated sediments of the Gulf of Trieste in the northern Adriatic Sea, which ranged from 0.99 to 236 ng cm^{-2} yr^{-1} (Covelli *et al.* 1999), and of those measured in the Saguenay Fjord in Canada, which ranged from 3.8 to 36.0 ng cm^{-2} yr^{-1} (Gagnon *et al.* 1997). MeHg fluxes measured in the Cornwall AOC were higher than MeHg fluxes (0.006 ng cm^{-2} yr^{-1}) measured in Spring Lake in northern Minnesota (Hines *et al.* 2004). MeHg diffusive fluxes ranged from 0.01 to 54.7 ng cm^{-2} yr^{-1} in Lavaca Bay, Texas (Gill *et al.* 1999), from -3.83 to 86.5 ng cm^{-2} yr^{-1} in the Gulf of Trieste (Covelli *et al.* 1999),

TABLE 2-2 Sedimentation Rates, Accumulation Rates, and Sediment-Water Diffusive Fluxes[a] of THg and MeHg

	sedimentation rate	THg accumulation	diffusion (ng cm^{-2} yr^{-1})		% remobilisation	
site	(g cm^{-2} yr^{-1})	(ng cm^{-2} yr^{-1})	THg	MeHg	THg	MeHg
LP-1	0.27	148		4.0		2.7
LP-2	0.32	186	1.2	1.2	0.6	0.6
LP-3	0.18	128	6.8	1.8	5.4	1.4
TF-1				14.6		
TF-2			9.1	1.5		
WPPI-1	0.32	249		1.8		0.7
WPPI-2	0.16	70		1.5		2.1
WPPI-3	0.38	192	48.2	2.5	25.1	1.3
WPPI-4	0.58	309	13.7	14.0	4.4	4.4

[a]Flux determinations based on average pore water Hg concentration in the top 1 cm sediment layer obtained from 2 separate cores. A positive value indicates the flux is from the sediment to the overlying water.

and from 1.14 to 16.1 ng cm^{-2} yr^{-1} in Barn Island Salt Marsh (Langer *et al.* 2001).

The lowest sediment to water flux of THg and MeHg was observed at site LP-2. Site WPPI-3 had the highest THg flux, reflecting the abundance of THg in the interstitial water at this site. The highest MeHg flux was seen at site TF-1, which also had the highest pore water MeHg concentration. Note that the above fluxes are diffusive fluxes only. Additional fluxes caused by bioturbation, bioirrigation, and resuspension of sediments can also affect the extent of exchange across the sediment-water interface (Aller and Aller 1998; López 2004). Rutgers van der Loeff *et al.* (1984) found that bioturbation increased fluxes of organic and inorganic complexes at the sediment-water interface up to 2 – 10 times more than those calculated from molecular diffusion. Also, there is evidence that sediments of the Cornwall AOC are conducive to the production and release of methane gas, and calculations do not account for losses of mercury with bubbles of gas (Bothner *et al.* 1980).

Methanogenesis is a terminal sink for electrons generated during the anaerobic degradation of organic matter and is important in the diagenesis of recently deposited sediments. Methanogenic bacteria proliferate below the surface layer in organic-rich sediments in which oxygen penetration is limited. Both elevated CH_4 and CO_2 concentrations and high sediment-water fluxes characterize the most anaerobic zones. As indicated in Table 2-3, the LP zone was the richer in terms of CH_4 concentration whereas the WPPI zone was richer in terms of CO_2 concentration. CH_4 and CO_2 concentrations in the gas collector were typical and similar to those of other hypereutrophic lakes (e.g. Huttunen *et al.* 2001). Furthermore, CH_4 flux in the LP zone was 1.36 times that of the WPPI zone, whereas CO_2 flux in the WPPI zone was 2-5 times that of the LP zone (Table 2-3). CH_4 / CO_2 ratios indicate that methanogenesis predominates in the LP zone, a process that may result in increased losses of Hg from the sediments via gas evasion.

TABLE 2-3 Concentration of CH_4 and CO_2 Evolved From Sediment

zone	$[CH_4]$ ppmv (%)	CH_4 flux (ppmv cm^{-2} h^{-1})	$[CO_2]$ ppmv (%)	CO_2 flux (ppmv $cm^{-2}h^{-1}$)	ratio CH_4/CO_2
LP (Aug5-05)	307 848 (30.8)	0.68	5 713 (0.57)	0.013	53.9
WPPI (Jul29-05)	227 164 (22.7)	0.50	14 858 (1.5)	0.033	15.2

The mercury accumulation rate for the surface stratum of a sediment core (Table 2-2) is calculated as the product of particle deposition rates calculated from ^{210}Pb (in g cm^{-2} yr^{-1}) and Hg and MeHg concentrations on those particles (in ng g^{-1}) (Hermanson 1998; Heyvaert *et al.* 2000). The potential importance of the diffusive flux on the cycling of mercury is calculated by comparing the upward diffusion of mercury with particulate fluxes of mercury to the sediment. The ratio between diffusive and particle bound flux indicates the fraction of deposited heavy metals that is remobilized in the sediment. In general, for those sites where data are available, flux estimates show that less than 5 % of THg settling down to the river-bottom is recycled at the sediment-water interface and the rest is buried in the sediment (Table 2-2). Site LP-3 is an exception, with 25 % of THg being remobilized at the sediment surface. Also, less than 5 % of THg deposited to the sediments is returned to bottom waters through MeHg diffusion. It is interesting to note that at site WPPI-4, 100 % of the THg released at the sediment-water interface, corresponding to 4.5 % of deposited THg, occurs in methylated form. In these calculations it was assumed that the whole amount of MeHg associated with the sediments, pore waters and related fluxes is produced *in situ*. The fate of Hg at the sediment-water interface can be determined from the Hg budget. A tentative annual benthic Hg budget for the Lamoureux Park (LP), and the Windmill Point to Pilon Island (WPPI) sampling points was constructed, assuming steady-state conditions (Figure 2-6).

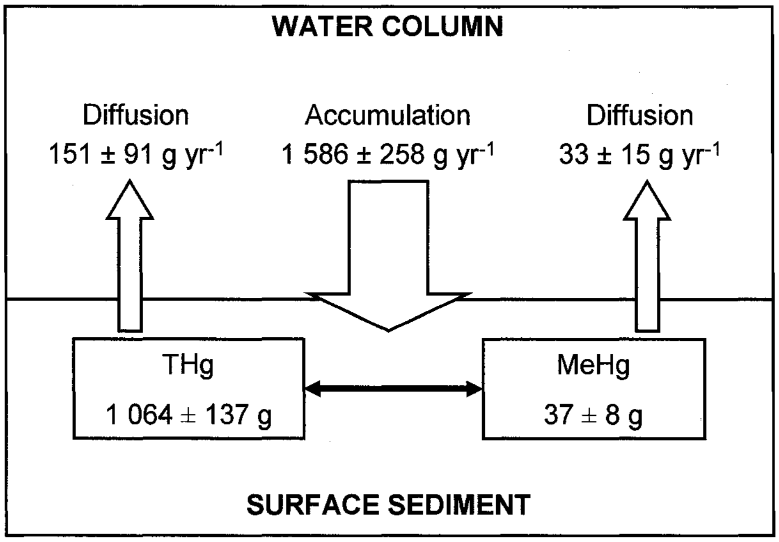

FIGURE 2-6 Reservoirs and fluxes of mercury in surface sediments (0-1 cm) and at the sediment-water interface over the entire area of the Lamoureux Park and the Windmill Point to Pilon Island (WPPI) sites of the St. Lawrence River near Cornwall. The combined sediment surface area of the LP and WPPI sites is 0.87 km^2.

2.4 Conclusion

Results of this study show that the diffusive flux of mercury to the overlying water is small compared to the flux of particulate bound mercury depositing to the sediments, suggesting that sediments from the St. Lawrence River near Cornwall are a net sink for mercury. Despite this, the anoxic surface sediments appear to provide conditions which are conducive to Hg methylation, and these experiments suggest that the flux of dissolved methyl mercury from sediments is a source to the river. Exposure of benthic organisms to this bioavailable form of Hg may result in uptake of, and adverse biological effects associated with, this trace metal. At present, the contaminated sediments are a potential source of methyl mercury to the biota and the river system.

Recent evidence indicates that fish from Lamoureux Park have higher Hg levels than fish collected from other sites along the Cornwall waterfront. This disparity could not be explained by differences in either sediment THg concentrations, or Hg diffusive fluxes between sites. However, our observations suggest that the LP site has unique characteristics which could be the cause of high Hg concentrations in fish from this site. These characteristics include: (1) the highest levels of solid-phase MeHg; (2) the highest proportions of MeHg to THg in both surface sediments, and pore waters; and, (3) the presence of sub-surface layers of wood chips and high releases of methane bubbles from the sediments. It is possible that lower levels of the food chain, such as benthic invertebrates, are exposed to higher levels of MeHg at the LP site, translating to higher levels of MeHg in top predators.

CHAPTER 3

HISTORICAL MERCURY TRENDS IN SEDIMENTS OF THE CORNWALL AREA OF THE ST. LAWRENCE RIVER

3.1 Introduction

Mercury profiles in sediments have often been used as archives of historical mercury contamination in freshwater environments (Gobeil and Cossa 1993; Engstrom and Swain 1997; Fitzgerald *et al.* 1998; Lockhart *et al.* 2000; Johannessen *et al.* 2005; Lindberg *et al.* 2006). Accurate interpretation of sediment records assumes that diagenetic redistribution does not alter the mercury profile, however, diagenetic processes have the potential to reshape elemental profiles in sediments. In a critical review of the subject, Rasmussen (1994) discusses post-depositional movement resulting in imprecise vertical profiles in aquatic environments leading to the incorrect interpretation of mercury trends. Countering Rasmussen's arguments, Fitzgerald *et al.* (1998) provided evidence that sediment cores faithfully record historical changes in mercury delivery to sediments. In view of these opposing arguments, sedimentary records of mercury should only be interpreted after a careful evaluation of the importance of diagenesis.

In a section of the St. Lawrence River near Cornwall, Ontario, mercury concentrations in sediments exceed most of the national and provincial sediment criteria for the protection of aquatic life (Anderson 1990; OMEE 1994; Grapentine *et al.* 2003) (see Chapter 1, section *1.3.1.4* for SQGs). Industrial activities were the main sources of mercury pollution to this stretch of the river during a large part of the twentieth century (St. Lawrence River RAP 1992). The important dischargers to the area included ICI Forest Products (formerly CIL), a chlor-alkali plant; Cornwall Chemicals; Domtar Fine Papers, a pulp and paper mill; Courtaulds, a textile mill; and the Cornwall Water Pollution Control Plant (WPCP).

The chlor-alkali plant at ICI Forest Products opened in 1935. ICI used a mercury cell process to convert salt to sodium hydroxide and chlorine by electrolysis. Losses of about 410 g day^{-1} of mercury in liquid effluent were reported in 1970 and losses were likely at least equal to or greater than that amount during the previous decades of operation. Prior to 1960, Ontario's industrial plants and municipalities did little to control their liquid waste discharges to the environment. Federal regulations passed in 1972 set the maximum allowable amount of mercury to be discharged in chlor-alkali plant waste water at 2.5 g $tonne^{-1}$ of chlorine production. Until the 1995 closure of its chlor-alkali plant, ICI Forest Products released 85 g day^{-1} of mercury in its liquid effluent (Ryan and Edmonds 1992), and 195 g day^{-1} through air emissions (ICI Forest Products fact sheet, November 1992). In 1995, two months after the plant closed, total mercury emissions (air and water) had dropped from 150 g day^{-1} to 20 g day^{-1} (St. Lawrence River RAP 1997).

Cornwall Chemicals, producers of sodium hydrosulfide, hydrochloric acid, carbon tetrachloride, and carbon disulfide, discharged approximately 3 g day^{-1} of mercury in 1989-1990 (Tuszynski 1992). Mercury came from contaminated caustic used to neutralize effluent, and ICI brine used to regenerate water softener for the boilers. Cornwall Chemicals closed in 1995.

Because Domtar Fine Papers pulp and paper mill released its effluent in a common diffuser with effluent from Cornwall Chemicals and ICI Forest Products, mercury loadings to the river were often described as coming from Domtar/ICI/Cornwall Chemicals, even though the bulk of the mercury was from ICI, with a much smaller proportion from Cornwall Chemicals and Domtar (St. Lawrence River RAP 1997). In the past, pulp and paper mills used mercury as a slimicide to kill moulds growing on wood fibers. This practice was halted in 1970 at

Domtar Fine Papers, and since then the mill has been a minor discharger of mercury to the St. Lawrence River. After 1970, the mercury discharged by the mill came primarily from naturally occurring mercury in tree bark and from low level contamination of process chemicals. Average daily discharges were 2 g day^{-1} in 1990 (MISA Monitoring 1990) and 0.003 – 0.03 g day^{-1} in 1996 (St. Lawrence River RAP 1997). Domtar Fine Papers closed in March, 2006.

Courtaulds has been making rayon since 1925. Prior to 1978, the waste water from the company discharged into a natural bay of the St. Lawrence River through a near-shore diffuser (St. Lawrence River RAP 1997). Based on Ontario Ministry of the Environment data (1992), Courtaulds discharged the highest loading per year of mercury to the river. Since Windmill Point deflects the main flow of the river around this bay, contamination of the waters and sediment of the bay resulted. Even though the diffusers installed in late 1977 discharged the wastewater into the main current to achieve proper dispersion, much of the contaminated sediment remains. Courtaulds Fibers, which closed in 1992, discharged an average of 74 g day^{-1} of mercury to the river in 1990 (Tuszynski 1992).

These industrial facilities historically discharged significant quantities of mercury to the St. Lawrence River (Lepage *et al.* 2000). Although some of the contaminated effluent would have been transported downstream from Cornwall, because the dischargers were located in embayments along the waterfront, much of the effluent settled to the bottom sediments. High concentrations of mercury have been observed in sediment depositional areas along the Cornwall waterfront. Studies from 1970 to 1997 found sediment concentrations as high as 44 $\mu g\ g^{-1}$ in 1975 (Richman and Dreier 2001). Since the closure of ICI Forest Products /

Cornwall Chemicals and Courtaulds in the early 1990s, contaminated sediments have been buried by a layer of 'cleaner' sediment (see Table 1-1, Chapter 1).

This paper examines the history of local Hg contamination along the Cornwall waterfront using dated sediment cores and investigates factors that influence methyl mercury concentrations in the sediment column. Also, pore water measurements are used to quantify diffusion of total and methyl mercury to the overlying water relative to burial rates in order to validate the assumption that diagenetic remobilization does not alter the mercury profile in sediments from the St. Lawrence River.

3.2 Materials and Methods

3.2.1 Study Site

The St. Lawrence River near Cornwall was designated an Area of Concern (AOC) by the International Joint Commission (IJC) in 1985. Mercury contamination was one of the major concerns. The Cornwall AOC includes a stretch of the St. Lawrence River approximately 80 km long, from the Moses-Saunders power dam to the eastern outlet of Lake St. François in Quebec. This stretch of the river impacts many jurisdictions, including the provinces of Ontario and Quebec, the state of New York, as well as the Mohawks of Akwesasne. The present study focuses on three zones located along the Cornwall waterfront of the North Channel (Figure 1-2). Lamoureux Park (LP) was the westernmost sampling location, and closest to the Domtar pulp and paper mill. Windmill Point to Pilon Island (WPPI) was the largest and easternmost zone, stretching from the old Courtaulds textile mill to the eastern edge of Pilon Island. The Tank Farm (TF) was the smallest sampling zone, situated between the LP and WPPI sites. A reference site (RF) was selected upstream and outside of areas exposed to past industrial effluents.

3.2.2 Sediment Coring and Processing

Sediment cores were collected from three sites along the Cornwall waterfront of the St. Lawrence River (Figure 1-2) from May to August, 2004 and 2005 (see Chapter 2, section 2.2.2 for sampling coordinates), using a modified gravity corer (Glew 1989), or a percussion corer. Using acoustic data and maps of the river bed, cores were collected from depositional areas at water depths ranging from 7 to 12 m. Cores were extruded on site at 1 cm intervals, with acid-rinsed plastic utensils, under a nitrogen atmosphere to minimize changes in redox potential and prevent the oxidation of sulfides, and placed directly into pre-labeled, air-tight centrifuge tubes. Samples were stored on ice for transportation to the laboratory. Samples were centrifuged and the supernatant was removed for pore water analysis, which is described in the previous study (see section 2.2.2 of Chapter 2). Grab samples were collected from a reference site using an Eckman dredge, and frozen until further analysis.

Each sediment interval was manually homogenized in its centrifuge tube until uniform. An aliquot of wet sediment from each interval was frozen for MeHg analysis. The rest of the sediment was freeze-dried and homogenized using a mortar and pestle. Percent water was calculated using the weight lost on freeze-drying and the weight of pore water removed after centrifugation. Sediments from each interval were heated to 550°C for organic carbon content and 950°C for carbonate content.

3.2.3 Analytical Methods

Methyl mercury in sediments was extracted and analyzed by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai *et al.* (1997). Sediment THg analysis was conducted on homogenized freeze dried sediment using an automatic Mercury Analyzer based on thermal decomposition, dual-step gold amalgamation, and detection via Cold-Vapor Atomic Absorption using an SP-3D mercury analyzer (Nippon Instruments Corp). The method detection limit (MDL) was 0.01ng. Precision, as indicated by the relative percent difference (RPD) of duplicate samples, was found to average 5.5 % for THg in sediments (n = 62 pairs), and 8.2 % for MeHg in sediments (n = 79 pairs). The accuracy of our determinations of THg and MeHg in sediments was estimated by analyses of analytical procedural blanks, and spiked samples. The mean recovery of spiked samples was 102 ± 0 % for THg (n = 5), and 107 ± 8 % for MeHg (n = 7).

In order to retrieve an adequate volume of pore water for analysis, 1 cm interval samples from duplicate cores were pooled. Methyl mercury concentrations were determined in pore water by capillary gas chromatography coupled with atomic fluorescence spectrometry (GC-AFS) as described by Cai *et al.* (1996). The MDL was estimated as 0.02ng L^{-1}. Water samples were analyzed for THg using pre-oxidation by BrCl, and $SnCl_2$ reduction with pre-concentration by two-stage gold amalgamation, followed with detection using cold vapour atomic fluorescence spectroscopy (CV-AFS). The analysis was conducted using a Tekran 2600 system following the modified US EPA Method 1631 guideline for mercury analysis (US EPA 2001). The MDL was estimated as 0.2 ng L^{-1}. Analysis of procedural blanks consisting of de-ionized water revealed no mercury contamination during THg analysis, or during MeHg extraction and analysis. The mean recovery of spiked samples was 105 ± 11% for THg (n = 10), and 103 ± 2 % for MeHg (n = 4).

Redox potential (Eh) was measured throughout the cores within one hour of collection, using a VWR Scientific Model 2100 meter and Corning redox combo probe. The probe was calibrated using Zobell's solution standardized at approximately 300 mV and 234 mV. Iron (Fe) and manganese (Mn) in pore water were analyzed by Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) by the University of Ottawa's geology department (MDL = 0.1 mg L^{-1}). Sulfides in pore water were determined colorimetrically, using a modified form of the method described by Cline (1969). The absorbance of samples at 670 nm was read using a UV-visible spectrophotometer within 48 hours of sample collection (MDL = 0.006 μM).

3.2.4 Radiometric Dating

Analysis of ^{210}Pb was performed on each core at selected depths to determine age and sediment accumulation rates. ^{210}Pb and ^{226}Ra activity were measured by gamma spectrometry, using a digital high purity germanium well detector (DSPec, Ortec), following method described by Appleby (2001). Supported ^{210}Pb was subtracted from total activity to determine the unsupported fraction, which is used for the calculation of sediment dates, and sedimentation rates. Calculation of dates for all cores was based on the Constant Rate of Supply (CRS) model of Appleby and Oldfield (1978).

3.2.5 Statistical Analysis

Mean contaminant concentrations in sediment and water were compared among stations using a one way ANOVA. The Tukey's Studentized Range Test was applied to test station differences and to determine if contaminant concentrations in sediment and water at each station were significantly different between stations. Higher contaminant concentrations in sediment and water in one site when compared to another would suggest local contaminant sources.

3.3 Results and Discussion

3.3.1 Total mercury in sediments

The vertical distribution of THg in sediment cores from the LP, WPPI, and TF sites are presented in Figures 3-1, 3-2, and 3-3 respectively. THg concentrations range between 326 and 43600 ng g^{-1}, all of which are above concentrations of 15.98 ± 2.88 ng g^{-1} measured at the reference site (RF). The majority of sediments sampled are also above typical background concentrations for uncontaminated sediments. Across Canada, Rasmussen (1994) found that background concentrations in freshwater sediments fall between 20 and 175 ng g^{-1} dry weight (Rasmussen 1994). In the Strait of Georgia historical background concentrations of 60 ng g^{-1} were measured (Johannessen *et al.* 2005).

In general, the shape of the THg profiles from each study site shows an increase in concentration to one or more subsurface peaks as depth increases. The highest concentrations were found at depths below 5 cm in cores LP-2, LP-3, WPPI-1, TF-1, and TF-2. Although

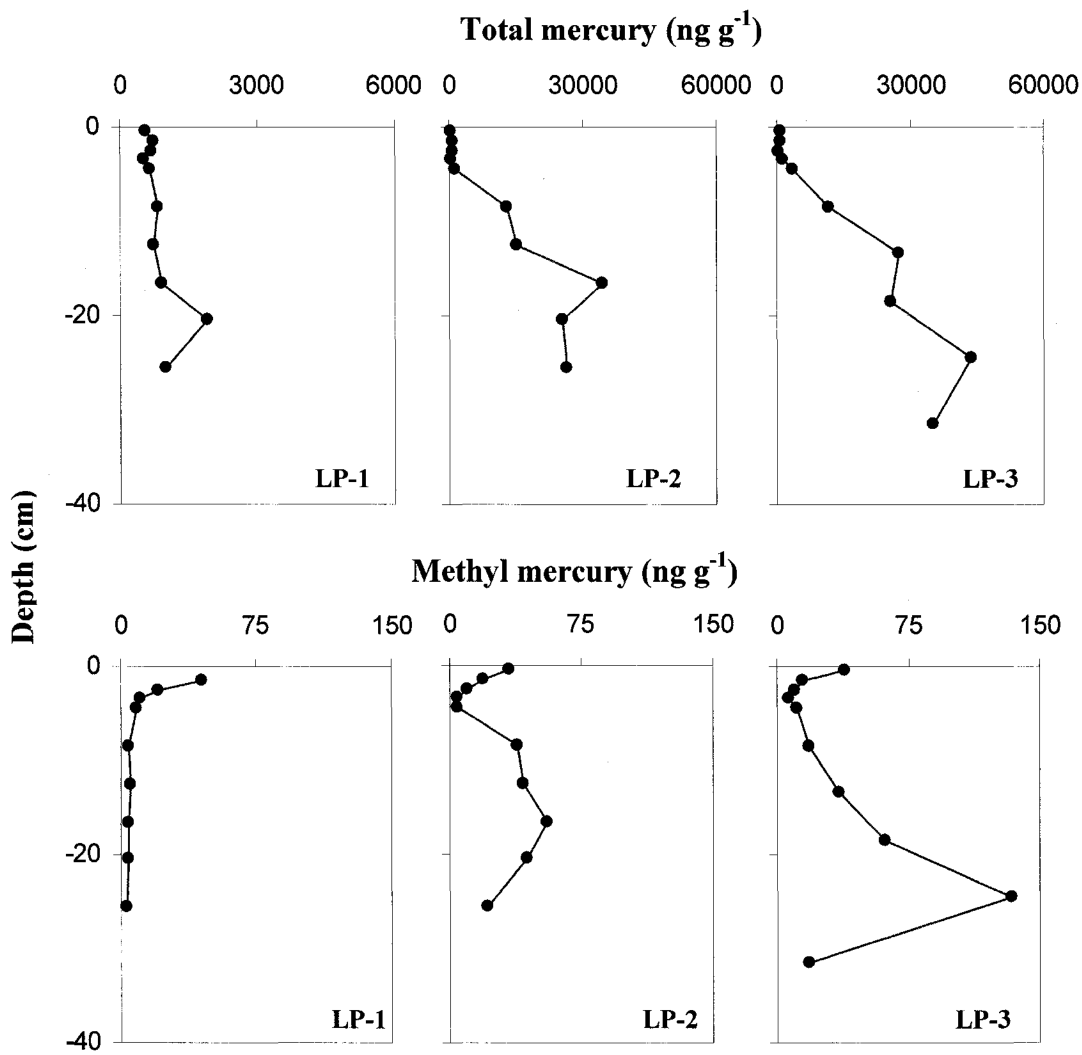

FIGURE 3-1 Depth profiles of total mercury (THg) and methyl mercury (MeHg) in three sediment cores from the Lamoureux Park (LP) site. Note the difference in scale along the THg axis for the different cores.

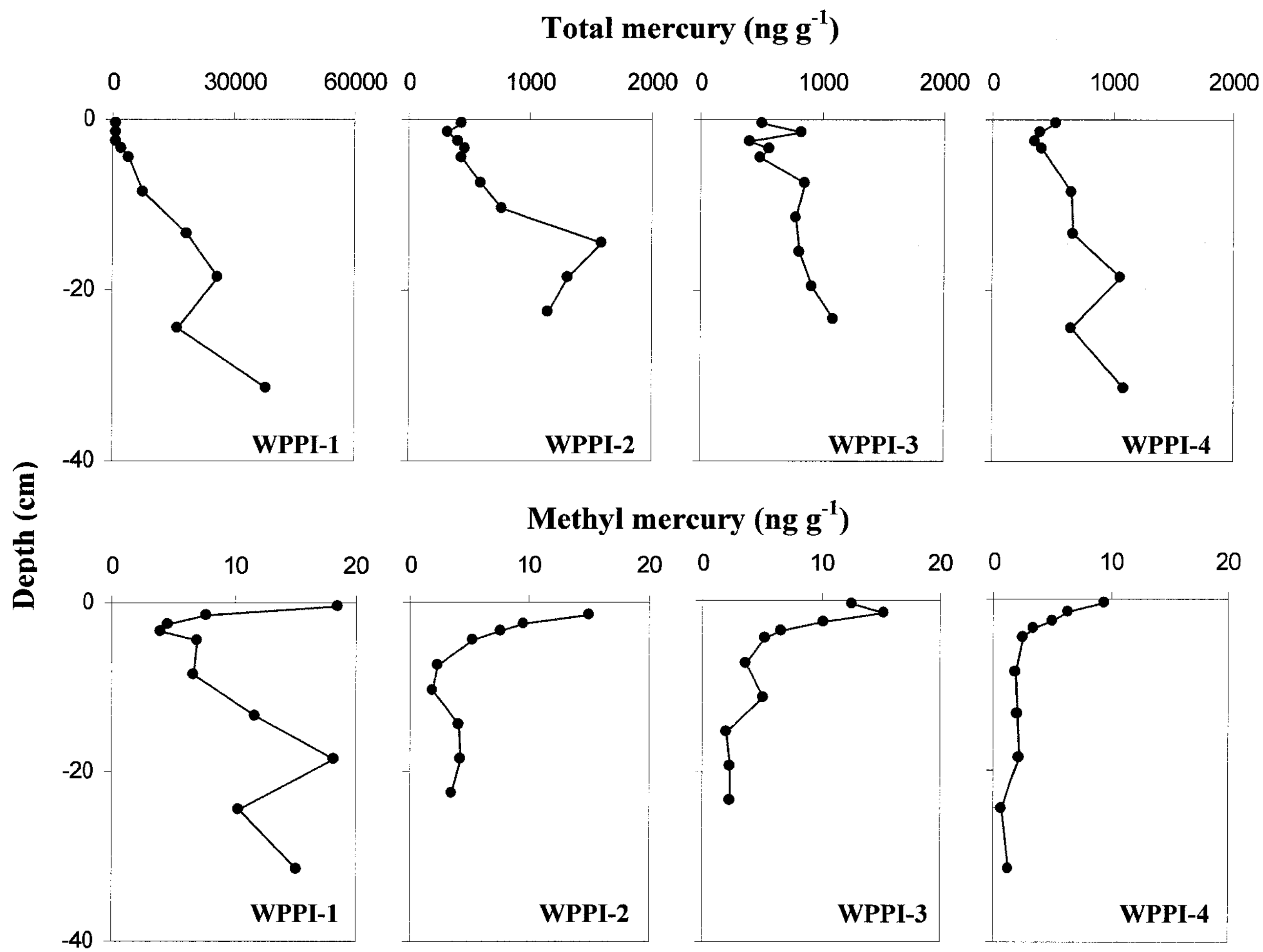

FIGURE 3-2 Depth profiles of total mercury (THg) and methyl mercury (MeHg) concentrations in four sediment cores from the Windmill Point to Pilon Island (WPPI) site. Note the difference in scale along the THg axis for the different cores.

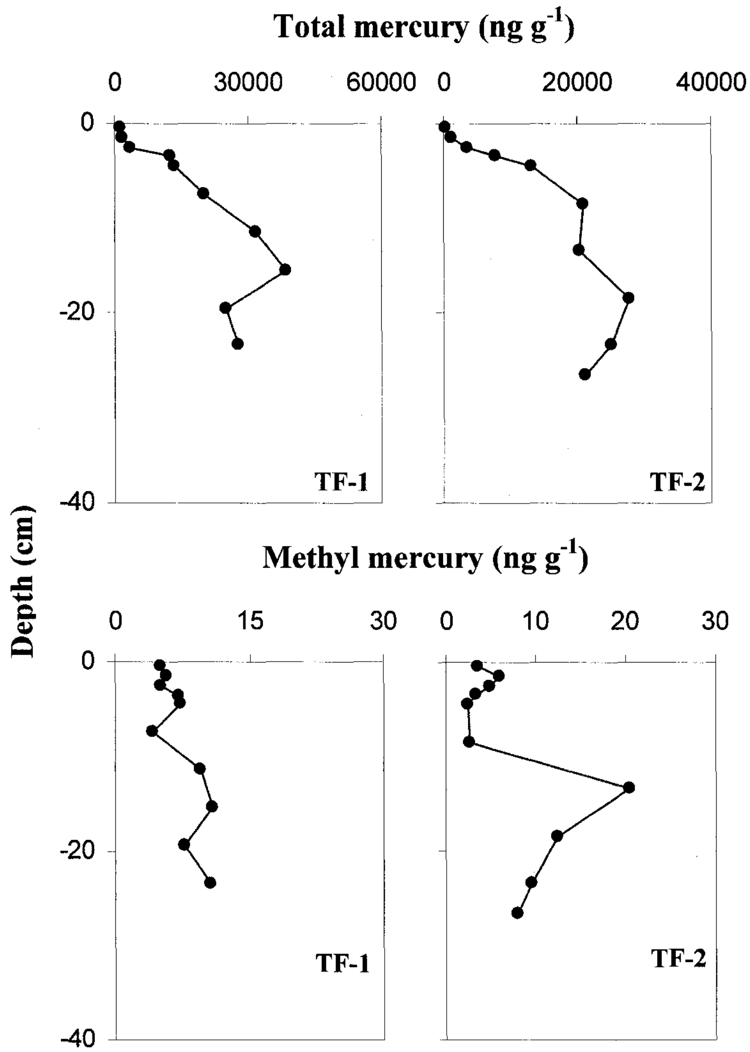

FIGURE 3-3 Depth profiles of total mercury (THg) and methyl mercury (MeHg) in two sediment cores from the Tank Farm (TF) site. Note the difference in scale along the THg axis for the different cores.

surface sediments in all the cores appear to have much lower Hg concentrations than deeper sediments, they still exceed the national interim Sediment Quality Guideline of 170 ng g^{-1}, and most exceed the Probable Effect Level (PEL) of 486 ng g^{-1} for Hg in sediments (CCME 2005). Both whole core and surface sediment Hg concentrations were compared between sites. Results of this test show that there is no significant difference in THg concentration between sites ($P > 0.05$) due to the high variability of concentrations within each zone.

The water content in sediments varied between 28 and 88 % (see Appendix B, Table B-3), with no significant difference between the three zones. Average organic carbon content (see Table B-1, Appendix B) of the LP site (17 %) and the TF site (21 %) was significantly higher ($P < 0.001$) than that of the WPPI site (9 %). It is thought that the carbon content can influence the Hg concentrations of sediments (Lindberg *et al.* 2006). This relationship was investigated, and a correlation was found between the organic carbon content and THg in zones LP ($n = 70$, $r = 0.69$, $P < 0.01$) and TF ($n = 20$, $r = 0.82$, $P < 0.01$), but not in zone WPPI ($n = 73$). Normalization of THg for organic carbon content does not change the observed variations in the THg profiles.

A study done by the Ontario Ministry of Environment and Energy (OMEE 1994) in the Cornwall area showed that THg concentrations were not correlated to particle size. The lack of correlation between mercury and particle size is an indication that mercury was enriched beyond the typical particle size/contaminant concentration relationship since fine suspended matter is known to have the greatest capacity to adsorb dissolved mercury (D'Itri 1990).

3.3.2 Factors Affecting Sediment MeHg Depth Profiles

MeHg concentrations at all sites vary considerably with depth below the sediment surface ranging between ~0.8 and 134 ng g^{-1} (Figure 3-1, 3-2, and 3-3). All MeHg profiles show trends similar to THg profiles, with the exception of concentrations in surface sediments where percent MeHg generally increases toward the sediment-water interface, to levels as high as 6 % at the LP site (Figure 3-4). MeHg concentrations decrease with depth away from the surface and remain low, except in cores LP-2, LP-3, WPPI-1, TF-1, and TF-2, where there is a second peak between 10 and 30 cm, corresponding to a peak in THg, where MeHg concentrations are equal to or greater than surface concentrations. Despite these high concentrations, % MeHg at these depths is below 1 %, driven by the high concentrations of solid-phase THg.

Typical profiles of relatively unmixed sediments show that % MeHg is generally low in the oxic surface sediments and at depth, and that MeHg production occurs in a relatively narrow subsurface zone within the sediments (e.g. Gagnon *et al.* 1996; Benoit *et al.* 1998A; Bloom *et al.* 1999). In St. Lawrence River sediments there is a peak in MeHg concentration, and in % MeHg (Figure 3-4) at the sediment surface, indicating the absence of a well defined oxic layer. Past studies have found that percent methyl mercury in sediments is strongly correlated with potential methylation rates, thus % MeHg can be used as an approximation of the relative rates of Hg methylation in sediments (Benoit *et al.* 2003; Sunderland *et al.* 2004). The ambient MeHg (Figures 3-1, 3-2, and 3-3) and % MeHg (Figure 3-4) profiles suggest that methylation is either taking place throughout the sediment column, with the highest rates being at the sediment surface or is diffusing to the surface more rapidly than THg.

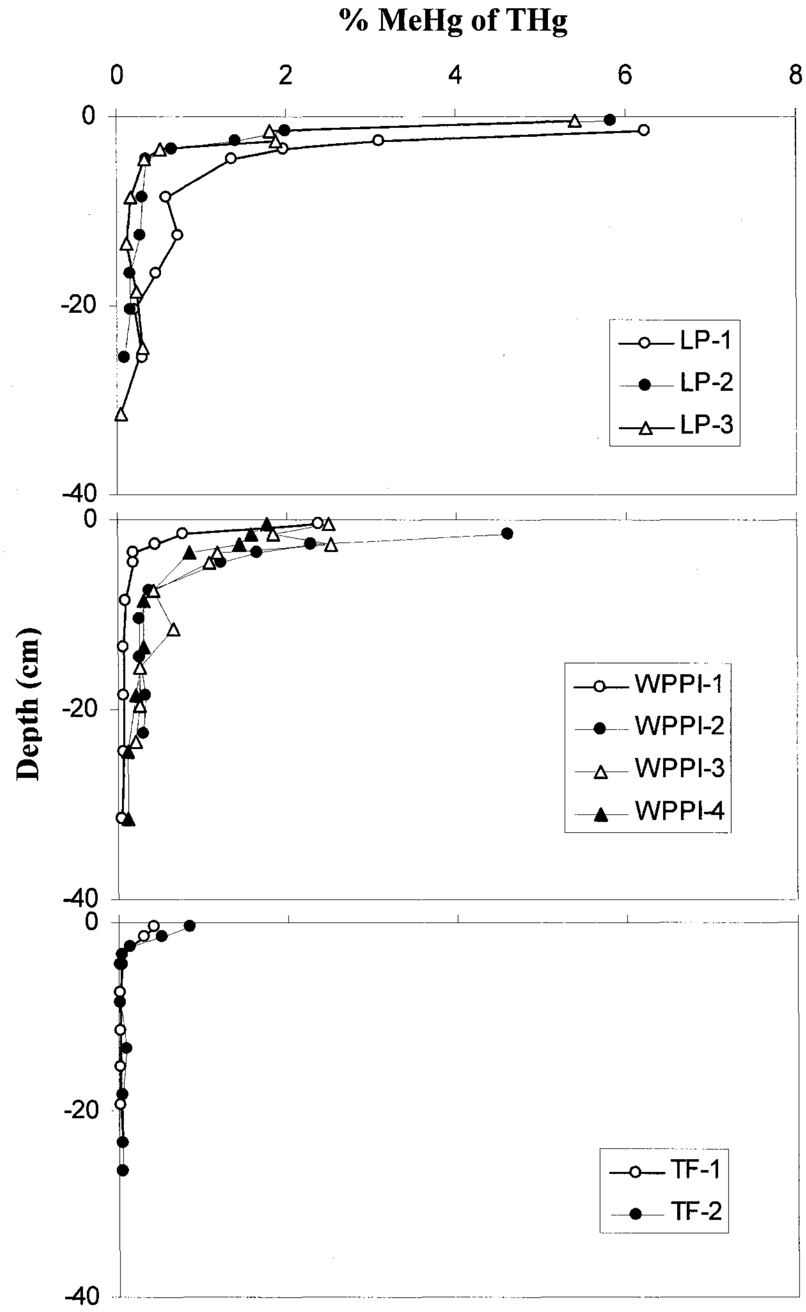

FIGURE 3-4 Depth distribution of percent methyl mercury (MeHg) to total mercury (THg) in sediment cores from the Lamoureux Park (LP), Windmill Point to Pilon Island (WPPI), and Tank Farm (TF) sites of the Cornwall Area of Concern.

The abundance of MeHg in aquatic systems is controlled by two competing microbiological processes: mercury methylation (Jensen and Jernelöv 1969) and methyl mercury demethylation (Spangler *et al.* 1973). In aquatic sediments, Hg methylation activity is thought to be due to sulfate reducing bacteria (SRB) (Compeau and Bartha 1973; Choi and Bartha 1993; Devereux *et al.* 1996; King *et al.* 1999; King *et al.* 2000), but abiotic formation is possible (Weber 1993). Hg availability is a fundamental prerequisite for Hg methylation (Benoit *et al.* 2003). However a weak correlation between THg and MeHg is often observed when factors affecting SRB activities become important (Hines *et al.* 2000; Conaway *et al.* 2003; Hammerschmidt and Fitzgerald 2004; Sunderland *et al.* 2004), such as the availability of sulfide (King *et al.* 2000) and organic carbon (Lambertsson and Nilsson 2006). According to Benoit *et al.* (1999), low levels of sulfide in sediments promote Hg methylation through the formation of neutral Hg-S, the form that penetrates bacterial (SRB) cell membranes diffusively rather than by way of a dedicated Hg^{2+} cellular transport mechanism. Since the sulfide concentrations were low (see Appendix B, Table B-2) and relatively constant at all sites along the Cornwall waterfront (< 1.7 μM) the environment for Hg methylation was favorable. High organic carbon content creates ideal conditions for Hg methylation by promoting microbial activity, lowering redox potential close to the sediment surface, and providing electron donors for sulfate reducing bacteria. Organic carbon also affects the partitioning of MeHg between the solid and dissolved phases, high levels typically favoring retention by the solid-phase (Hammerschmidt and Fitzgerald 2004). Although surface sediments of the LP site had significantly higher concentrations than WPPI and TF sites of both MeHg and organic carbon, the correlation between the two factors was not significant.

Various studies have found that microbial activity and sulfate reduction, as well as mercury methylation rates, are highest in the upper few centimeters of the sediment column (Korthals and Winfrey 1987; Gilmour *et al.* 1992; Devereux *et al.* 1996; King *et al.* 1999; Ravenschlag *et al.* 2000). The relationship between THg and MeHg in surface sediments and at depth was examined. There is no correlation between THg and MeHg in surface sediments (0 – 5 cm), but below 10 cm, there is a significant correlation (R^2 = 0.63, $P < 0.01$) (Figure 3-5). It appears that at depth, methylation is controlled by the availability of THg, whereas at the sediment surface, other factors are contributing to much higher methylation rates.

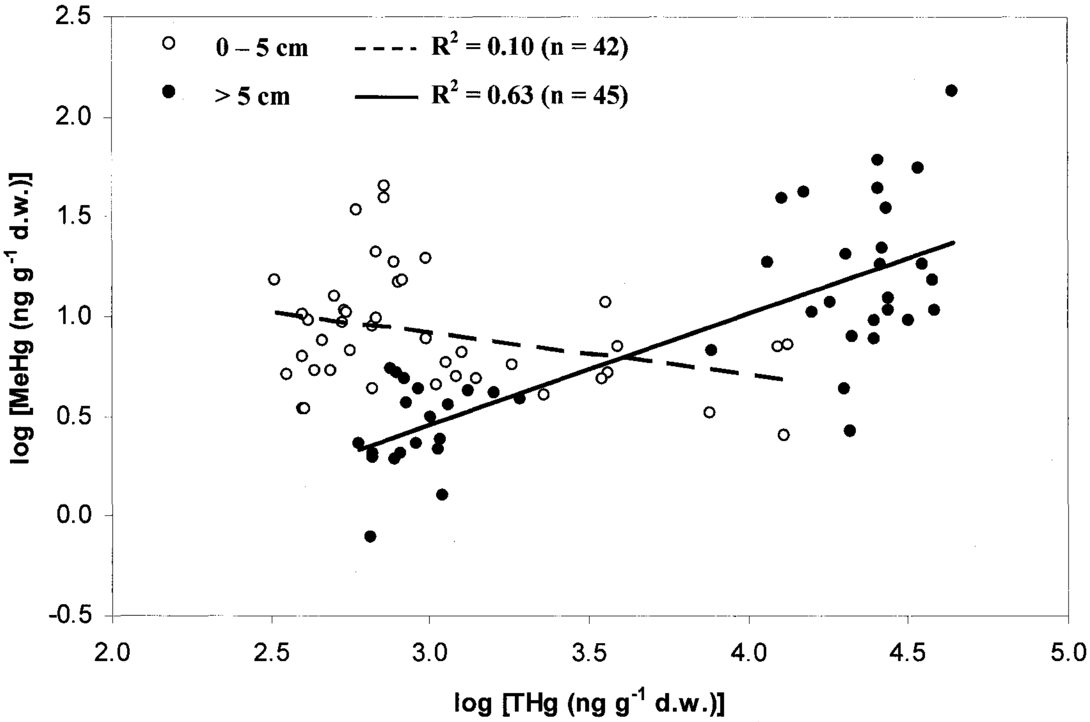

FIGURE 3-5 Relationship between total mercury (THg) and methyl mercury (MeHg) in all cores collected from the Cornwall Area of Concern. The correlation between THg and MeHg in surface sediments (0 – 5 cm) is represented by a dotted line and in sediments below 5 cm by a solid line.

3.3.3 Hg Diagenesis

Accurate interpretation of sediment records assumes that diagenetic processes do not alter sediment mercury profiles. Any processes that affect the mobility of Hg will complicate interpretation of sediment cores as a proxy for the emission record. Gobeil *et al.* (1999) reported that remobilization and diffusion of Hg within sediments can occur under conditions of very low sedimentation rates and/or oxidation. Mercury diffusion and burial rates were determined for the study site (see Table 2-2, Chapter 2), and results show that the upward diffusion of Hg is much slower than the downward flux because of sedimentation. Sedimentation rates along the Cornwall waterfront, ranging from 0.2 to 1.7 cm yr^{-1}, are high enough to swamp upward, diffusion. The proportion of total mercury present in the pore water phase and available for upward diffusion is less than 0.05 % of the solid-phase Hg. The proportion of methyl mercury present in pore waters is even lower, at less than 0.009 %. Also, upward diffusion of THg in the sediment column could lead to a peak in solid-phase Hg near the sediment surface, where Eh levels increase. This was not found in any of the cores (Figures 3-1, 3-2, and 3-3). In addition, pore water profiles of THg and MeHg concentrations (see Figures 2-4 and 2-5, Chapter 2) show that there is no major gradient driving upward mercury diffusion. Finally, this provides evidence that mercury profiles in sediments from the St. Lawrence River are not altered by diagenetic redistribution and can be used to reconstruct historical mercury loading to the system.

3.3.4 ^{210}Pb Inventories

Activity of unsupported ^{210}Pb decreases with depth in all cores, with the exception of cores TF-1 and TF-2 (see Figure 2-2, Chapter 2). Based on the CRS model the deepest sediment layers at 55 cm in the LP zone, and at 32 cm in the WPPI zone, are about 85 and 48 years old respectively. Only the two sediment cores from the TF zone could not be dated because ^{210}Pb activity showed no decline with depth.

3.3.5 Industrial History

Mercury emissions and deposition to sediments of the study site peaked in the 1960s, mainly due to discharges from ICI Forest Products and Courtaulds. In the 1970s, federal regulations and plant modifications limited the amount of Hg released by the chlor-alkali industry, the pulp and paper mill, and Courtaulds. Consequently, the direct discharge to the study sites was reduced. Emissions were then drastically reduced in the early 1990s, when Courtaulds, ICI Forest Products, and Cornwall Chemicals closed. According to plume tracking models, the downstream WPPI site was influenced by the effluent from all of the above mentioned industries, whereas the LP and TF sites were only impacted by effluent from the Domtar/ICI/Cornwall Chemicals combined discharger (Nettleton 1994).

3.3.6 Sediment Records

The mercury accumulation rates in the St. Lawrence River for the past half century are shown in Figure 3-6. Hg concentrations peaked during the sediment interval spanning the beginning of the first operation (early 1900's to 1970), the highest rates of 11900 ng cm^{-2} yr^{-1} being measured closest to the Courtaulds diffuser (WPPI-1) around 1970. Hg accumulation declined from 1970 to the early 1990s, in response to regulations and modifications implemented around 1970 to meet discharge limits. Hg accumulation rates at all sites have decreased, in some cases up to 60 fold, from pre-1970 accumulation rates, which ranged from 181 to 9340 ng cm^{-2} yr^{-1}. Current accumulation rates are from 80 to 263 ng cm^{-2} yr^{-1}, with maximum rates measured in the downstream sites. The historical record is not as clear in the WPPI-2, WPPI-3, and WPPI-4 cores, where Hg accumulation rates are not consistently low in recent sediments. This is likely due to their location within the WPPI zone, downstream from the former Courtaulds diffuser and the most contaminated sediments of the WPPI-1 area. The downstream sites may be receiving resuspended sediments from the more contaminated WPPI-1.

The Hg accumulation records in sediment cores collected from the Cornwall waterfront reflect source histories. Pronounced sub-surface peaks in Hg concentration in the cores correspond to historic mercury discharges from the described industrial facilities that operated along the river in the mid-1990s. A Kruskall-Wallis One Way Analysis of Variance on Ranks was used to test the hypothesis that average 1905–1970 Hg concentrations are higher than average 1970–1992 concentrations, and that average 1970–1992 concentrations are higher than average 1992–2005 concentrations. Temporally, the overall mercury concentrations decreased significantly after 1970 ($P < 0.05$), and again after 1992 ($P < 0.05$) (Figure 3-7).

Although Hg concentrations of newly deposited sediment are much lower, there is no evidence of a return to naturally occurring levels, despite the closure of Courtaulds, ICI Forest Products, and Cornwall Chemicals around 1995. From 1995 to 2006, Domtar Fine Papers and the Cornwall Water Pollution Control Plant were the only local industrial dischargers to the Cornwall Area of Concern, and they are considered minor sources of mercury. Domtar Fine Papers closed in early 2006, at the end of this study. In future studies, mercury concentrations in newly deposited sediments should reflect the closure of Domtar Fine Papers in early 2006. There is also a possibility that the currently high concentrations of Hg in surface sediments are caused by the deposition of Hg-rich particles originating from the resuspension of contaminated sediments from within the study sites.

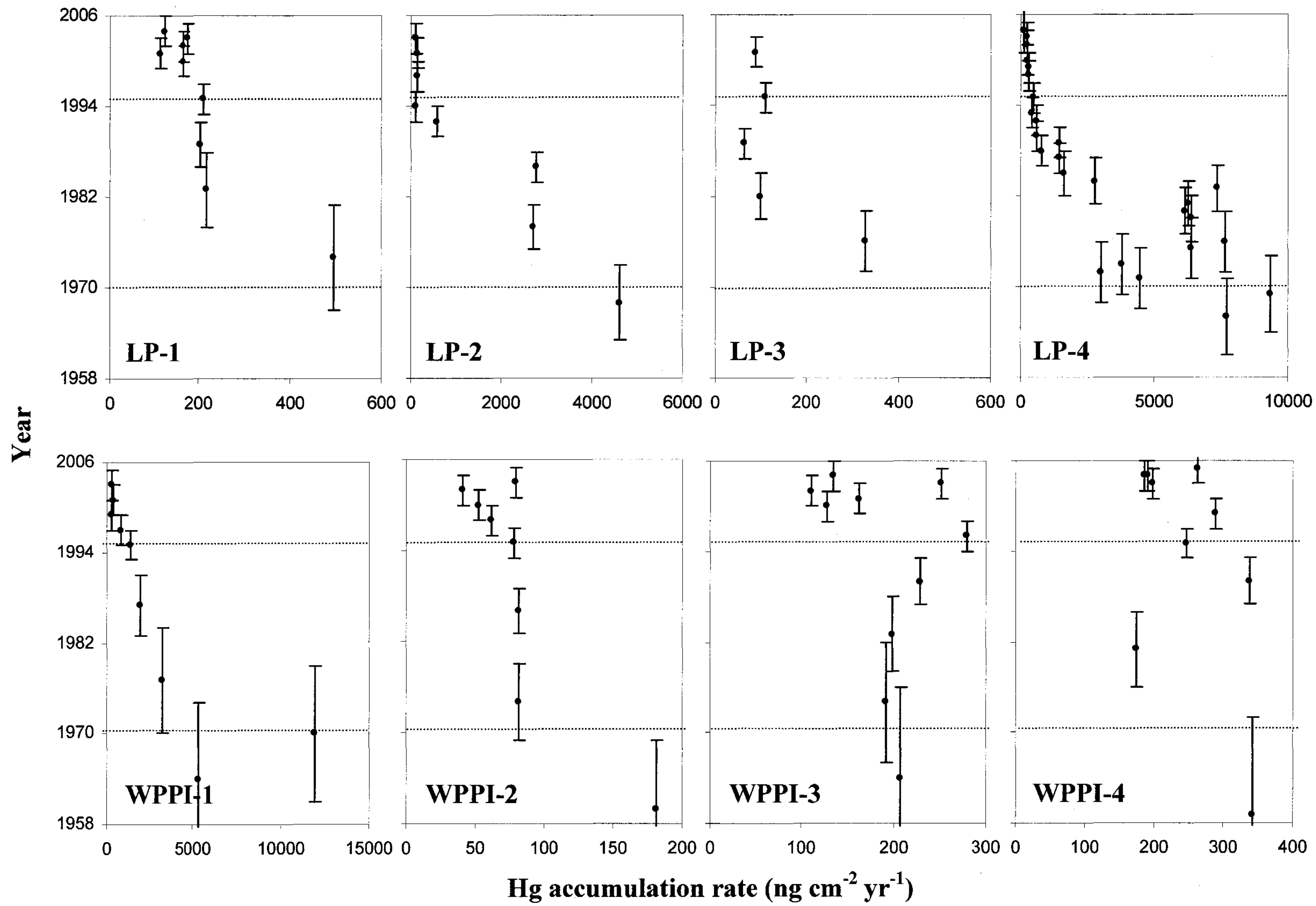

FIGURE 3-6 Mercury accumulation rates are plotted over time for 8 cores from Lamoureux Park (LP) and Windmill Point to Pilon Island (WPPI). Dotted lines indicate the period in which plant regulations/modifications were introduced to reduce mercury emissions in 1970, and the final year in which ICI, Courtaulds, and Cornwall Chemicals closed in 1995. The uncertainty of the Constant Rate of Supply (CRS) dates is indicated by standard deviation bars.

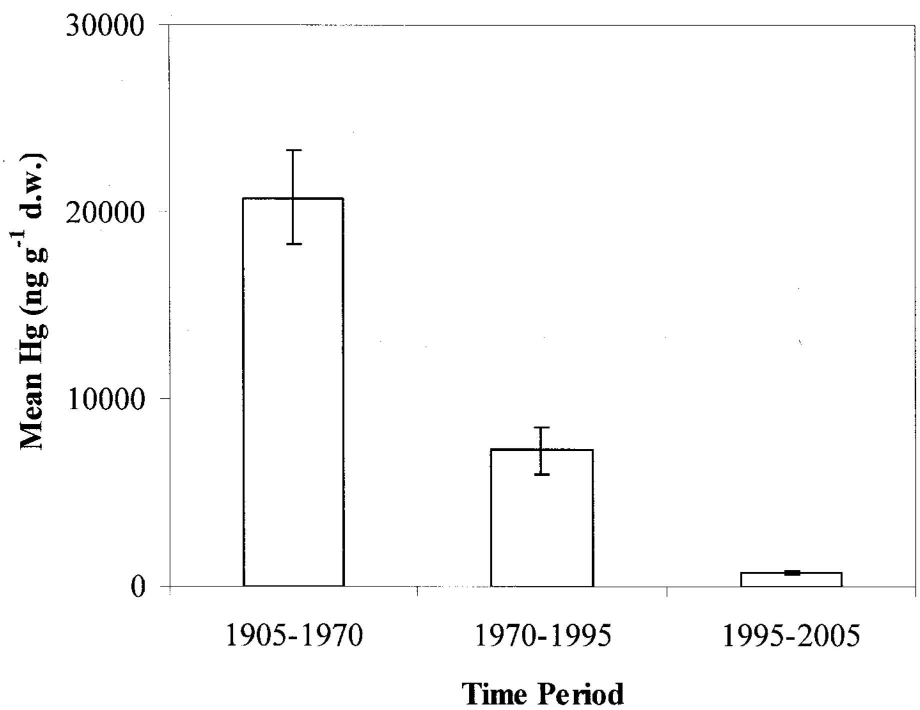

FIGURE 3-7 Comparison of mean total mercury (THg) concentrations of sediments from three different time periods; 1905 – 1970 (n = 26), 1970 – 1995 (n = 35), and 1995 – 2005 (n = 42). Sediments are from LP and WPPI sites. Error bars represent the standard error.

3.4 Conclusion

Direct pore water measurements allowed us to establish that upward diffusion is small (<5%) compared to sediment burial. Therefore, Hg trends in our cores are not altered by diagenetic redistribution, and the sediment mercury profiles correspond well to the source histories in most instances in spite of greater than an order of magnitude difference in concentrations between sites. These case histories present compelling evidence that sediments accumulating in the two sites (LP and WPPI) of the St. Lawrence River provide a faithful record of mercury inputs for a period of at least half a century. The histories of mercury contamination in the cores is consistent with the known histories of Courtaulds, ICI, Domtar and Cornwall

Chemicals, and the presence of low levels of mercury in the top slices infers that these industries were the source. The current distribution of mercury within and between sampling sites is heterogeneous, and a weak influence of an anthropogenic source is still visible. The persistence of high mercury concentrations in surficial sediments may also be explained by resuspension of contaminated sediments as well as by bioirrigation and bioturbation, constituting a continual source of mercury to the system. In the Cornwall AOC, the highest Hg methylation rates occur at the sediment-water interface, potentially providing a vector for MeHg entry into the water column and resulting in the exposure of organisms feeding at the sediment surface.

CHAPTER 4

CONCLUSION

4.1 Conclusions

Freshwater sediments often serve as a repository for anthropogenic mercury. The potential for sediments to act as sources of mercury, especially in highly contaminated areas, has been critical in developing remediation strategies. If sediment conditions are conducive to methyl mercury production and subsequent upward diffusion, they may be contributing to contamination of the food web and remedial action should be considered. This research project was aimed at investigating (1) the spatial distribution of THg and MeHg concentrations in sediments of the Cornwall Area of Concern, (2) the importance of accumulation and diffusion at the sediment surface on the fate and transport of THg and MeHg, and (3) the temporal trends in Hg concentration and accumulation in response to reductions in anthropogenic mercury emissions. The results presented in this thesis have led to a better understanding of the fate and transport of mercury in sediments and at the sediment-water interface. Most importantly, this study will provide data essential to the evaluation of the risk that mercury contaminated sediments pose to river systems and the human populations that use them.

The annual mercury benthic budget described in Chapter 2 for two contaminated sites along the Cornwall waterfront, is unique as it is based on original data collected during this study. The budget shows that Hg and MeHg diffusion from sediments to the overlying water is equivalent to < 5 % of mercury deposited to bottom sediments for Lamoureux Park, and $<16\%$ for Windmill Point to Pilon Island. This demonstrates that at present, mercury accumulation is the significant process determining the fate of mercury in the study sites of the Cornwall area of the St. Lawrence River.

Results from Chapter 2 also help to elucidate why concentrations of mercury in fish from the Lamoureux Park site are higher than concentrations in fish from other areas along the Cornwall waterfront. It was first suspected that Hg diffusion from sediments to the overlying water was driving the high levels of MeHg in top predators, however, this does not appear to be the case. Mercury contamination in these fish is likely a result of the unique conditions at the Lamoureux Park site, including high MeHg concentrations and methylation rates in surface sediments, and the highest releases of methane gas, which can potentially entrain Hg from deep contaminated sediment layers to the sediment surface. These conditions are critical in the bioaccumulation of Hg by benthic organisms, which are potentially exposed to THg and MeHg from both the pore water and the sediment, and often serve as an essential link in the transfer of MeHg to higher trophic levels.

In Chapter 3, pore water measurements of Hg, Fe, and Mn have been used to discount Hg diagenesis as a significant process in sediments from the Cornwall area. Therefore, dated sediment cores from the site could be used to reconstruct temporal changes in mercury accumulation and concentration over the past half century. Depth profiles of Hg concentration in sediments were found to correspond well to the source histories in most instances. Mercury concentrations in sediments of Lamoureux Park and Windmill Point to Pilon Island decreased considerably after 1970 when emission controls were implemented, and again after the mid-1990s when the major dischargers closed down. In most cores, surface sediments are much 'cleaner' than deeper sediments, yet they still exceed national Sediment Quality Guidelines. Also, it appears that resuspension of sediments from upstream sites may act as a continual source of mercury to sediments at the downstream end of the Cornwall Area of Concern.

Chapter 3 further examined factors controlling MeHg concentrations. The results showed that *in situ* MeHg production was positively related to THg concentration in the lower sediment layers however this relationship was not significant in the top sediment layers. This suggests that Hg methylation is an important process in surface sediments, while in deeper layers methylation and demethylation have reached equilibrium.

Overall, the results of this study demonstrate that sediments of the St. Lawrence River near Cornwall are a net mercury sink. Over time contaminated sediments have been buried, however they are not truly removed from further interaction with the overlying system, as *in situ* methylation continues to act as a source of methyl mercury to biota and the surrounding environment. This research also has important implications for studies that interpret mercury profiles in sediments for historical purposes, because it shows that mercury deposition to sediments is very rapid relative to post-depositional migration and transformation in sediments.

4.2 Significance of Findings

The conclusions outlined in the previous section are significant for research dealing with the fate of mercury in freshwater systems in several ways. This research is the first to measure mercury concentrations in both sediment and pore water phases in the Cornwall area of the St. Lawrence River and draw linkages to bioaccumulation of mercury in the food web. To our knowledge, this is the first study to quantify both deposition and return flux at the sediment-water interface for this site. Overall, the research presented in the rest of the thesis shows that sediments are a net sink, not a source of Hg. Finally, it is anticipated that results of this work, along with data collected by a multidisciplinary research team, will be used to construct a mass balance model for the cycling of THg and MeHg in the St. Lawrence River Area of Concern. In the future, this information may be used in predictive models of the cycling and bioaccumulation of mercury in other large river systems.

4.3 Recommendations for Future Research

Beyond the results of this study, there remain several areas in which further research is needed to better understand the cycling and fate of mercury in sediments of the St. Lawrence River near Cornwall.

Based on diffusion and accumulation calculations, the annual benthic budget illustrated in Chapter 2 implies that the major flux of Hg is from the overlying water to the sediment. However, diffusion is not the only mechanism for transferring Hg and MeHg from sediments to the water column. The budget does not account for losses of mercury via the release of methane gas at the sediment surface. Additionally, effects of bioturbation, bioirrigation, and sediment resuspension need to be included as there is evidence these processes can increase the release of Hg from sediments (Rutgers van der Loeff 1984; Aller and Aller 1998; López 2004). The determination of Hg fluxes at the sediment-water interface using benthic chambers is recommended for comparison with calculated diffusional fluxes.

In addition, other points were not considered in this project, but merit investigation. Acid-volatile sulfides (AVS) were not evaluated in this study. The accumulation of mercury in AVS, which is highly reactive and rapidly degrades in the presence of oxygen (Rickard *et al.* 1995), presents a threat, and may provide considerable insight to the stability of Hg in sediments, and therefore to the overall fate of mercury within the river system. Similarly, the characterization of nutrient levels in sediments of the St. Lawrence system, and their effects on rates of methylation in this environment requires further assessment. Finally, during the preparation of this manuscript, the local pulp and paper mill ceased operation. This may provide an opportunity to evaluate the effect that this closure has on mercury accumulation and methylation rates at impacted sites. In the Cornwall Area of Concern, continued observation of biota and surficial sediments in the future will be necessary in order to monitor the gradual progress of natural decontamination.

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APPENDIX A

QA / QC Data

TABLE A-1 Replicate Samples for Sediment Total Mercury Analysis

sample ID	core	depth (cm)	analysis 1 Hg (ng g^{-1})	analysis 2 Hg (ng g^{-1})	average (ng g^{-1})	% RPD
CW4 3-4	WPPI-2	3-4	469	461	465	1.27
CW6 1-2	LP-1	1-2	698	758	728	5.77
CW6 2-3	LP-1	2-3	567	796	681	23.80
CW7 0-1	LP-2	0-1	576	608	592	3.84
CW7 16-17	LP-2	16-17	38038	30593	34316	15.34
CW7 20-21	LP-2	20-21	26367	24992	25679	3.79
CW10 0-1	WPPI-1	0-1	780	781	780	0.08
CW10 24-25	WPPI-1	24-25	15132	16813	15972	7.44
CW12 19-20	WPPI-3	19-20	978	848	913	10.04
CW14 7-8	TF-1	7-8	27646	12455	20051	53.57
CW14 19-20	TF-1	19-20	23381	26823	25102	9.70
CW15 0-1	WPPI-4	0-1	509	556	533	6.25
CW15 1-2	WPPI-4	1-2	380	422	401	7.44
CW15 3-4	WPPI-4	3-4	366	343	355	4.63
CW15 4-5	WPPI-4	4-5	393	411	402	3.12
CW15 8-9	WPPI-4	8-9	669	655	662	1.45
CW15 13-14	WPPI-4	13-14	649	680	664	3.27
CW15 18-19	WPPI-4	18-19	1133	1002	1068	8.68
CW15 24-25	WPPI-4	24-25	679	622	651	6.21
CW15 31-32	WPPI-4	31-32	1117	1079	1098	2.44
CW18 0-1	LP-3	0-1	774	680	727	9.13
CW18 1-2	LP-3	1-2	842	769	806	6.45
CW18 2-3	LP-3	2-3	535	571	553	4.56
CW18 3-4	LP-3	3-4	1266	1291	1278	1.39
CW18 4-5	LP-3	4-5	3728	3495	3611	4.56
CW18 8-9	LP-3	8-9	11683	11587	11635	0.58
CW18 13-14	LP-3	13-14	29170	25687	27428	8.98
CW18 18-19	LP-3	18-19	25843	25918	25881	0.20
CW18 24-25	LP-3	24-25	42509	44682	43596	3.52
CW18 31-32	LP-3	31-32	34099	36252	35176	4.33
CW19 0-1	TF-2	0-1	416	395	406	3.71
CW19 1-2	TF-2	1-2	1144	1139	1141	0.28
CW19 2-3	TF-2	2-3	3485	3540	3512	1.11
CW19 3-4	TF-2	3-4	7595	7633	7614	0.35
CW19 4-5	TF-2	4-5	14065	11915	12990	11.70
CW19 8-9	TF-2	8-9	21527	20363	20945	3.93
CW19 13-14	TF-2	13-14	19626	20910	20268	4.48
CW19 18-19	TF-2	18-19	27972	27568	27770	1.03
CW19 23-24	TF-2	23-24	25627	24502	25064	3.17
CW19 26-27	TF-2	26-27	22474	20113	21293	7.84
F01	RF	surface grab	12	13	12	2.67
F02	RF	surface grab	16	15	16	5.09
F03	RF	surface grab	18	18	18	0.31
F04	RF	surface grab	14	14	14	2.94
F05	RF	surface grab	20	19	19	2.36
CW21 0-1	LP-4	0-1	528	538	533	1.37
CW21 2-3	LP-4	2-3	831	814	822	1.43
CW21 60-62	LP-4	60-62	22679	24407	23543	5.19

TABLE A-2 Replicate Samples for Sediment Methyl Mercury Analysis

sample ID	Core	depth (cm)	analysis 1 MeHg(ng g^{-1})	analysis 2 MeHg(ng g^{-1})	average (ng g^{-1})	% RPD
CW10 0-1	WPPI-1	0-1	16.45	20.71	18.58	16.23
CW10 13-14	WPPI-1	13-14	12.77	10.65	11.71	12.79
CW10 18-19	WPPI-1	18-19	16.17	20.41	18.29	16.41
CW10 2-3	WPPI-1	2-3	4.55	4.61	4.58	1.01
CW10 24-25	WPPI-1	24-25	10.11	10.64	10.37	3.63
CW10 31-32	WPPI-1	31-32	15.18	15.04	15.11	0.66
CW10 3-4	WPPI-1	3-4	4.30	3.85	4.07	7.91
CW10 4-5	WPPI-1	4-5	7.45	6.56	7.01	8.99
CW10 8-9	WPPI-1	8-9	6.31	7.04	6.67	7.77
CW12 11-12	WPPI-3	11-12	5.07	5.42	5.24	4.69
CW12 1-2	WPPI-3	1-2	15.17	15.29	15.23	0.56
CW12 15-16	WPPI-3	15-16	2.23	1.91	2.07	10.92
CW12 19-20	WPPI-3	19-20	2.02	2.59	2.31	17.58
CW12 2-3	WPPI-3	2-3	9.71	10.60	10.15	6.18
CW12 23-24	WPPI-3	23-24	2.29	2.53	2.41	7.23
CW12 3-4	WPPI-3	3-4	7.13	6.29	6.71	8.90
CW12 4-5	WPPI-3	4-5	5.43	5.16	5.29	3.62
CW12 7-8	WPPI-3	7-8	3.45	3.99	3.72	10.21
CW14 0-1	TF-1	0-1	8.37	10.84	9.60	18.17
CW14 11-12	TF-1	11-12	32.16	34.18	33.17	4.31
CW14 1-2	TF-1	1-2	10.62	8.81	9.72	13.13
CW14 15-16	TF-1	15-16	31.11	27.66	29.38	8.30
CW14 19-20	TF-1	19-20	43.51	33.22	38.36	18.98
CW14 2-3	TF-1	2-3	12.60	12.28	12.44	1.86
CW14 23-24	TF-1	23-24	24.97	24.49	24.73	1.36
CW14 4-5	TF-1	4-5	25.17	21.42	23.29	11.39
CW14 7-8	TF-1	7-8	36.32	31.05	33.69	11.06
CW19 18-19	TF-2	18-19	41.06	37.85	39.46	5.75
CW19 23-24	TF-2	23-24	28.47	28.97	28.72	1.23
CW19 25-26	TF-2	25-26	30.58	23.46	27.02	18.64
CW19 3-4	TF-2	3-4	10.14	9.21	9.68	6.75
CW19 4-5	TF-2	4-5	8.58	8.50	8.54	0.63
CW19 8-9	TF-2	8-9	15.21	15.83	15.52	2.83
CW4 10-11	WPPI-2	10-11	2.16	1.71	1.94	16.20
CW4 1-2	WPPI-2	1-2	16.57	13.48	15.02	14.54
CW4 18-19	WPPI-2	18-19	4.05	4.44	4.24	6.45
CW4 22-23	WPPI-2	22-23	4.03	3.13	3.58	17.60
CW4 2-3	WPPI-2	2-3	9.48	9.52	9.50	0.26
CW4 3-4	WPPI-2	3-4	7.10	8.15	7.63	9.80
CW4 7-8	WPPI-2	7-8	1.99	2.65	2.32	20.10
CW6 12-13	LP-1	12-13	5.25	5.73	5.49	6.20
CW6 16-17	LP-1	16-17	4.13	4.64	4.38	8.22
CW6 20-21	LP-1	20-21	3.34	4.45	3.90	20.20
CW6 2-3	LP-1	2-3	21.83	20.44	21.14	4.64
CW6 24-25	LP-1	24-25	3.23	3.11	3.17	2.64
CW6 3-4	LP-1	3-4	10.50	11.06	10.78	3.69
CW6 4-5	LP-1	4-5	9.20	8.77	8.98	3.39
CW6 8-9	LP-1	8-9	5.19	4.57	4.88	9.02
CW7 0-1	LP-2	0-1	32.24	36.74	34.49	9.22
CW7 1-2	LP-2	1-2	21.10	18.49	19.79	9.33
CW7 20-21	LP-2	20-21	49.41	39.51	44.46	15.74
CW7 2-3	LP-2	2-3	9.96	9.56	9.76	2.91
CW7 25-26	LP-2	25-26	20.58	23.27	21.93	8.68
CW7 3-4	LP-2	3-4	4.57	4.02	4.30	9.12
CW7 4-5	LP-2	4-5	4.72	4.93	4.82	3.12
F1	RF	F1	0.29	0.30	0.30	1.46
F2	RF	F2	1.04	1.04	1.04	0.25
F3	RF	F3	0.45	0.47	0.46	3.01
F5	RF	F5	0.85	0.79	0.82	5.06

APPENDIX B

LOI, Sulfide, Redox, and Water Content Data

TABLE B-1. Sediment Organic Carbon and Carbonate Content

sample ID	core	depth (cm)	% organic carbon	% carbonate
CW4 0-1	WPPI-2	0-1	10.0523	3.6607
CW4 1-2	WPPI-2	1-2	12.4041	3.7084
CW4 2-3	WPPI-2	2-3	12.2246	3.8604
CW4 3-4	WPPI-2	3-4	11.1302	3.7355
CW4 4-5	WPPI-2	4-5	11.4943	3.8440
CW4 7-8	WPPI-2	7-8	8.3366	4.1390
CW4 10-11	WPPI-2	10-11	9.1206	4.6083
CW4 14-15	WPPI-2	14-15	8.7151	4.7554
CW4 18-19	WPPI-2	18-19	8.3791	5.5799
CW4 22-23	WPPI-2	22-23	6.7194	5.6653
CW6 0-1	LP-1	0-1	15.1492	3.4071
CW6 1-2	LP-1	1-2	15.0467	3.3084
CW6 2-3	LP-1	2-3	15.9931	3.2140
CW6 3-4	LP-1	3-4	15.3232	3.1749
CW6 4-5	LP-1	4-5	16.0436	3.0179
CW6 8-9	LP-1	8-9	13.9965	2.9111
CW6 12-13	LP-1	12-13	19.2456	2.5207
CW6 16-17	LP-1	16-17	16.6253	2.7104
CW6 20-21	LP-1	20-21	9.9963	4.0243
CW6 25-26	LP-1	25-26	16.9895	3.2158
CW7 0-1	LP-2	0-1	12.0538	3.2768
CW7 1-2	LP-2	1-2	12.7451	2.9902
CW7 2-3	LP-2	2-3	10.3072	2.8328
CW7 3-4	LP-2	3-4	13.7615	2.5229
CW7 4-5	LP-2	4-5	30.5599	1.9440
CW7 8-9	LP-2	8-9	23.8004	8.7812
CW7 12-13	LP-2	12-13	20.3524	10.0243
CW7 16-17	LP-2	16-17	16.4732	15.3123
CW7 20-21	LP-2	20-21	28.6209	14.0219
CW7 25-26	LP-2	25-26	22.0532	14.1318
CW10 0-1	WPPI-1	0-1	5.5101	4.1472
CW10 1-2	WPPI-1	1-2	5.9526	4.1033
CW10 4-5	WPPI-1	4-5	9.0196	5.1765
CW10 8-9	WPPI-1	8-9	11.8123	8.5782
CW10 13-14	WPPI-1	13-14	12.5024	10.4446
CW10 18-19	WPPI-1	18-19	27.9461	9.4391
CW10 24-25	WPPI-1	24-25	20.7668	10.2180
CW10 31-32	WPPI-1	31-32	16.0447	11.4037
CW12 0-1	WPPI-3	0-1	14.5261	3.2529
CW12 1-2	WPPI-3	1-2	15.3009	3.0372
CW12 2-3	WPPI-3	2-3	13.2456	3.0702
CW12 3-4	WPPI-3	3-4	14.1104	2.9448
CW12 4-5	WPPI-3	4-5	12.4764	3.0155
CW12 7-8	WPPI-3	7-8	20.0000	2.9773
CW12 11-12	WPPI-3	11-12	39.7467	1.9903
CW12 15-16	WPPI-3	15-16	18.0621	3.4229
CW12 19-20	WPPI-3	19-20	14.4814	3.1963
CW12 23-24	WPPI-3	23-24	14.6341	3.6585
CW14 0-1	TF-1	0-1	13.9476	2.1889
CW14 1-2	TF-1	1-2	15.5200	2.4000
CW14 2-3	TF-1	2-3	17.5676	2.7413
CW14 3-4	TF-1	3-4	25.8974	5.0000
CW14 4-5	TF-1	4-5	27.6615	6.8597
CW14 7-8	TF-1	7-8	21.6495	12.0848
CW14 11-12	TF-1	11-12	20.4507	9.3963
CW14 15-16	TF-1	15-16	22.8395	7.7160
CW14 19-20	TF-1	19-20	25.2569	9.2482
CW14 23-24	TF-1	23-24	41.2234	5.7447
CW15 0-1	WPPI-4	0-1	12.1444	5.5063
CW15 1-2	WPPI-4	1-2	12.9356	5.1093
CW15 2-3	WPPI-4	2-3	12.0907	5.2393
CW15 3-4	WPPI-4	3-4	11.5658	5.1799

TABLE B-1. Continued

CW15 4-5	WPPI-4	4-5	11.9540	4.9808
CW15 8-9	WPPI-4	8-9	12.0593	6.1645
CW15 13-14	WPPI-4	13-14	12.0943	5.7767
CW15 18-19	WPPI-4	18-19	12.9969	5.7339
CW15 24-25	WPPI-4	24-25	9.9633	5.9085
CW15 31-32	WPPI-4	31-32	7.5895	5.6534
CW18 0-1	LP-3	0-1	10.2727	3.5088
CW18 1-2	LP-3	1-2	8.5339	3.5357
CW18 2-3	LP-3	2-3	9.1400	3.4252
CW18 3-4	LP-3	3-4	8.6965	3.4902
CW18 4-5	LP-3	4-5	14.2248	4.4139
CW18 8-9	LP-3	8-9	15.4518	6.6939
CW18 13-14	LP-3	13-14	17.7843	11.4431
CW18 18-19	LP-3	18-19	15.3460	15.5199
CW18 24-25	LP-3	24-25	14.7963	26.1530
CW18 31-32	LP-3	31-32	21.8182	16.4773
CW19 0-1	TF-2	0-1	3.7199	3.4542
CW19 1-2	TF-2	1-2	4.2017	3.4686
CW19 2-3	TF-2	2-3	8.6229	3.7507
CW19 3-4	TF-2	3-4	11.1379	4.5775
CW19 4-5	TF-2	4-5	17.7794	6.1930
CW19 8-9	TF-2	8-9	25.0440	9.9015
CW19 13-14	TF-2	13-14	55.4306	6.0318
CW19 18-19	TF-2	18-19	28.6923	7.3754
CW19 23-24	TF-2	23-24	19.8848	8.5478
CW19 26-27	TF-2	26-27	22.3377	9.8330
CW21 0-1	LP-4	0-1	9.7751	3.0271
CW21 1-2	LP-4	1-2	7.9991	2.8709
CW21 2-3	LP-4	2-3	11.2772	2.6912
CW21 3-4	LP-4	3-4	9.0161	2.7309
CW21 4-5	LP-4	4-5	9.0941	2.5784
CW21 6-7	LP-4	6-7	8.1151	2.8201
CW21 7-8	LP-4	7-8	8.4731	3.6559
CW21 8-9	LP-4	8-9	10.8363	3.0800
CW21 9-10	LP-4	9-10	10.6133	2.7176
CW21 10-11	LP-4	10-11	25.5543	2.6172
CW21 11-12	LP-4	11-12	23.3059	3.3883
CW21 12-13	LP-4	12-13	16.9400	4.8669
CW21 13-14	LP-4	13-14	18.0874	5.0143
CW21 15-16	LP-4	15-16	23.8522	6.3128
CW21 17-18	LP-4	17-18	29.7209	13.4975
CW21 20-21	LP-4	20-21	17.4021	7.7838
CW21 21-22	LP-4	21-22	20.6952	8.3899
CW21 22-23	LP-4	22-23	15.6509	10.0888
CW21 25-26	LP-4	25-26	24.9292	14.0834
CW21 26-27	LP-4	26-27	20.7226	10.7558
CW21 27-28	LP-4	27-28	14.6515	9.0469
CW21 28-29	LP-4	28-29	14.4928	9.8430
CW21 29-30	LP-4	29-30	19.4041	10.0076
CW21 30-32	LP-4	30-32	18.4776	15.6418
CW21 34-36	LP-4	34-36	17.0029	20.8803
CW21 36-38	LP-4	36-38	19.9827	21.2775
CW21 38-40	LP-4	38-40	20.1235	16.2874
CW21 40-42	LP-4	40-42	19.9623	17.4603
CW21 42-44	LP-4	42-44	26.3228	16.9963
CW21 44-46	LP-4	44-46	17.7353	16.2892
CW21 48-50	LP-4	48-50	34.1605	15.3115
CW21 50-52	LP-4	50-52	37.0423	15.2847
CW21 52-54	LP-4	52-54	36.6736	13.4091
CW21 54-56	LP-4	54-56	40.0411	11.8891
CW21 56-58	LP-4	56-58	42.1310	12.3493
CW21 58-60	LP-4	58-60	43.8390	13.1982
CW21 60-62	LP-4	60-62	47.3776	11.4460
CW21 62-64	LP-4	62-64	36.3344	17.6264
CW21 64-66	LP-4	64-66	28.2119	24.2003

TABLE B-2. Pore Water Sulfide Concentrations

sample ID	core	depth (cm)	sulfide (µM)
PWC CW4 0-1	WPPI-2	0-1	0.132
PWC CW4 1-2	WPPI-2	1-2	0.000
PWC CW4 2-3	WPPI-2	2-3	0.247
PWC CW4 3-4	WPPI-2	3-4	0.000
PWC CW4 4-5	WPPI-2	4-5	0.000
PWC CW4 5-6	WPPI-2	5-6	0.397
PWC CW4 6-7	WPPI-2	6-7	0.220
PWC CW4 7-8	WPPI-2	7-8	0.000
PWC CW4 8-9	WPPI-2	8-9	0.000
PWC CW4 9-10	WPPI-2	9-10	0.123
PWC CW4 10-11	WPPI-2	10-11	0.158
PWC CW4 11-12	WPPI-2	11-12	0.000
PWC CW4 12-13	WPPI-2	12-13	0.096
PWC CW4 13-14	WPPI-2	13-14	0.000
PWC CW4 14-15	WPPI-2	14-15	0.088
PWC CW4 15-16	WPPI-2	15-16	0.000
PWC CW4 16-17	WPPI-2	16-17	0.008
PWC CW4 17-18	WPPI-2	17-18	0.000
PWC CW4 18-19	WPPI-2	18-19	0.088
PWC CW4 19-20	WPPI-2	19-20	0.052
PWC CW4 20-21	WPPI-2	20-21	0.132
PWC CW4 21-22	WPPI-2	21-22	0.273
PWC CW4 22-23	WPPI-2	22-23	0.000
PWC CW4 23-24	WPPI-2	23-24	0.220
PWC CW5/6 0-1	LP-1	0-1	0.017
PWC CW5/6 1-2	LP-1	1-2	0.000
PWC CW5/6 2-3	LP-1	2-3	0.000
PWC CW5/6 3-4	LP-1	3-4	0.176
PWC CW5/6 4-5	LP-1	4-5	0.026
PWC CW5/6 5-6	LP-1	5-6	0.026
PWC CW5/6 6-7	LP-1	6-7	0.247
PWC CW5/6 7-8	LP-1	7-8	0.070
PWC CW5/6 8-9	LP-1	8-9	0.751
PWC CW5/6 9-10	LP-1	9-10	0.052
PWC CW5/6 10-11	LP-1	10-11	0.202
PWC CW5/6 11-12	LP-1	11-12	0.061
PWC CW5/6 12-13	LP-1	12-13	0.512
PWC CW5/6 13-14	LP-1	13-14	0.034
PWC CW5/6 14-15	LP-1	14-15	0.043
PWC CW5/6 15-16	LP-1	15-16	0.000
PWC CW5/6 16-17	LP-1	16-17	0.000
PWC CW5/6 17-18	LP-1	17-18	0.000
PWC CW5/6 18-19	LP-1	18-19	0.698
PWC CW5/6 19-20	LP-1	19-20	0.000
PWC CW5/6 20-21	LP-1	20-21	0.000
PWC CW5/6 21-22	LP-1	21-22	0.000
PWC CW5/6 22-23	LP-1	22-23	0.105
PWC CW5/6 23-24	LP-1	23-24	4.261
PWC CW5/6 24-25	LP-1	24-25	0.000
PWC CW5/6 25-26	LP-1	25-26	0.114
PWC CW7 0-1	LP-2	0-1	0.000
PWC CW7 1-2	LP-2	1-2	0.000
PWC CW7 2-3	LP-2	2-3	0.000
PWC CW7 3-4	LP-2	3-4	0.000
PWC CW7 4-5	LP-2	4-5	0.000
PWC CW7 5-6	LP-2	5-6	0.000
PWC CW7 6-7	LP-2	6-7	0.000
PWC CW7 7-8	LP-2	7-8	0.468
PWC CW7 8-9	LP-2	8-9	0.406
PWC CW7 9-10	LP-2	9-10	0.000
PWC CW7 10-11	LP-2	10-11	0.000
PWC CW7 11-12	LP-2	11-12	0.353
PWC CW7 12-13	LP-2	12-13	0.317

TALBE B-2. Continued

PWC CW7 13-14	LP-2	13-14	0.000
PWC CW7 14-15	LP-2	14-15	0.000
PWC CW7 15-16	LP-2	15-16	0.026
PWC CW7 16-17	LP-2	16-17	0.000
PWC CW7 17-18	LP-2	17-18	0.000
PWC CW7 18-19	LP-2	18-19	0.000
PWC CW7 19-20	LP-2	19-20	0.008
PWC CW7 20-21	LP-2	20-21	0.424
PWC CW7 21-22	LP-2	21-22	0.114
PWC CW7 22-23	LP-2	22-23	0.105
PWC CW7 23-24	LP-2	23-24	0.432
PWC CW7 24-25	LP-2	24-25	0.043
PWC CW7 25-26	LP-2	25-26	0.326
PWC CW8 0-1	LP-2	0-1	0.000
PWC CW8 1-2	LP-2	1-2	0.000
PWC CW8 2-3	LP-2	2-3	0.000
PWC CW8 3-4	LP-2	3-4	0.000
PWC CW8 4-5	LP-2	4-5	0.000
PWC CW8 5-6	LP-2	5-6	0.000
PWC CW8 6-7	LP-2	6-7	0.000
PWC CW8 7-8	LP-2	7-8	0.000
PWC CW8 8-9	LP-2	8-9	0.000
PWC CW8 9-10	LP-2	9-10	0.000
PWC CW8 10-11	LP-2	10-11	0.000
PWC CW8 11-12	LP-2	11-12	0.079
PWC CW8 12-13	LP-2	12-13	0.114
PWC CW8 13-14	LP-2	13-14	0.008
PWC CW8 14-15	LP-2	14-15	0.141
PWC CW8 15-16	LP-2	15-16	0.158
PWC CW8 16-17	LP-2	16-17	0.000
PWC CW8 17-18	LP-2	17-18	0.061
PWC CW8 18-19	LP-2	18-19	0.070
PWC CW9/10 0-1	WPPI-1	0-1	0.034
PWC CW9/10 1-2	WPPI-1	1-2	0.503
PWC CW9/10 2-3	WPPI-1	2-3	0.317
PWC CW9/10 3-4	WPPI-1	3-4	0.017
PWC CW9/10 4-5	WPPI-1	4-5	0.008
PWC CW9/10 5-6	WPPI-1	5-6	0.344
PWC CW9/10 6-7	WPPI-1	6-7	0.981
PWC CW9/10 7-8	WPPI-1	7-8	0.901
PWC CW9/10 8-9	WPPI-1	8-9	0.388
PWC CW9/10 9-10	WPPI-1	9-10	0.220
PWC CW9/10 10-11	WPPI-1	10-11	0.239
PWC CW9/10 11-12	WPPI-1	11-12	0.595
PWC CW9/10 12-13	WPPI-1	12-13	0.793
PWC CW9/10 13-14	WPPI-1	13-14	0.273
PWC CW9/10 14-15	WPPI-1	14-15	0.238
PWC CW9/1015-16	WPPI-1	15-16	0.220
PWC CW9/10 16-17	WPPI-1	16-17	0.247
PWC CW9/10 17-18	WPPI-1	17-18	0.105
PWC CW9/10 18-19	WPPI-1	18-19	0.026
PWC CW9/10 19-20	WPPI-1	19-20	0.202
PWC CW9/10 20-21	WPPI-1	20-21	0.105
PWC CW9/10 21-22	WPPI-1	21-22	0.070
PWC CW9/10 22-23	WPPI-1	22-23	0.269
PWC CW9/10 23-24	WPPI-1	23-24	0.576
PWC CW9/10 24-25	WPPI-1	24-25	0.052
PWC CW9/10 25-26	WPPI-1	25-26	0.714
PWC CW9/10 31-32	WPPI-1	31-32	0.521
PWC CW11/12 0-1	WPPI-3	0-1	0.150
PWC CW11/12 1-2	WPPI-3	1-2	0.131
PWC CW11/12 2-3	WPPI-3	2-3	0.239
PWC CW11/12 3-4	WPPI-3	3-4	0.328
PWC CW11/12 4-5	WPPI-3	4-5	0.091
PWC CW11/12 5-6	WPPI-3	5-6	0.131
PWC CW11/12 6-7	WPPI-3	6-7	0.269

TABLE B-2. Continued

PWC CW11/12 7-8	WPPI-3	7-8	0.229
PWC CW11/12 8-9	WPPI-3	8-9	0.309
PWC CW11/12 9-10	WPPI-3	9-10	0.338
PWC CW11/12 10-11	WPPI-3	10-11	0.249
PWC CW11/12 11-12	WPPI-3	11-12	0.388
PWC CW11/12 12-13	WPPI-3	12-13	0.299
PWC CW11/12 13-14	WPPI-3	13-14	0.378
PWC CW11/12 14-15	WPPI-3	14-15	0.239
PWC CW11/12 15-16	WPPI-3	15-16	0.427
PWC CW11/12 16-17	WPPI-3	16-17	0.506
PWC CW11/12 17-18	WPPI-3	17-18	0.566
PWC CW11/12 18-19	WPPI-3	18-19	0.398
PWC CW11/12 19-20	WPPI-3	19-20	0.368
PWC CW11/12 20-21	WPPI-3	20-21	0.467
PWC CW11/12 21-22	WPPI-3	21-22	0.239
PWC CW11/12 22-23	WPPI-3	22-23	0.299
PWC CW11/12 23-24	WPPI-3	23-24	0.437
PWC CW13/14 0-1	TF-1	0-1	0.286
PWC CW13/14 1-2	TF-1	1-2	0.301
PWC CW13/14 2-3	TF-1	2-3	0.494
PWC CW13/14 3-4	TF-1	3-4	0.516
PWC CW13/14 4-5	TF-1	4-5	0.472
PWC CW13/14 5-6	TF-1	5-6	0.353
PWC CW13/14 6-7	TF-1	6-7	1.681
PWC CW13/14 7-8	TF-1	7-8	0.279
PWC CW13/14 8-9	TF-1	8-9	0.294
PWC CW13/14 9-10	TF-1	9-10	0.309
PWC CW13/14 10-11	TF-1	10-11	0.361
PWC CW13/14 11-12	TF-1	11-12	0.227
PWC CW13/14 12-13	TF-1	12-13	0.227
PWC CW13/14 15-16	TF-1	15-16	0.056
PWC CW13/14 16-17	TF-1	16-17	0.138
PWC CW13/14 17-18	TF-1	17-18	0.197
PWC CW13/14 18-19	TF-1	18-19	0.205
PWC CW13/14 19-20	TF-1	19-20	0.249
PWC CW13/14 20-21	TF-1	20-21	0.331
PWC CW13/14 21-22	TF-1	21-22	0.257
PWC CW13/14 22-23	TF-1	22-23	0.197
PWC CW13/14 23-24	TF-1	23-24	0.242

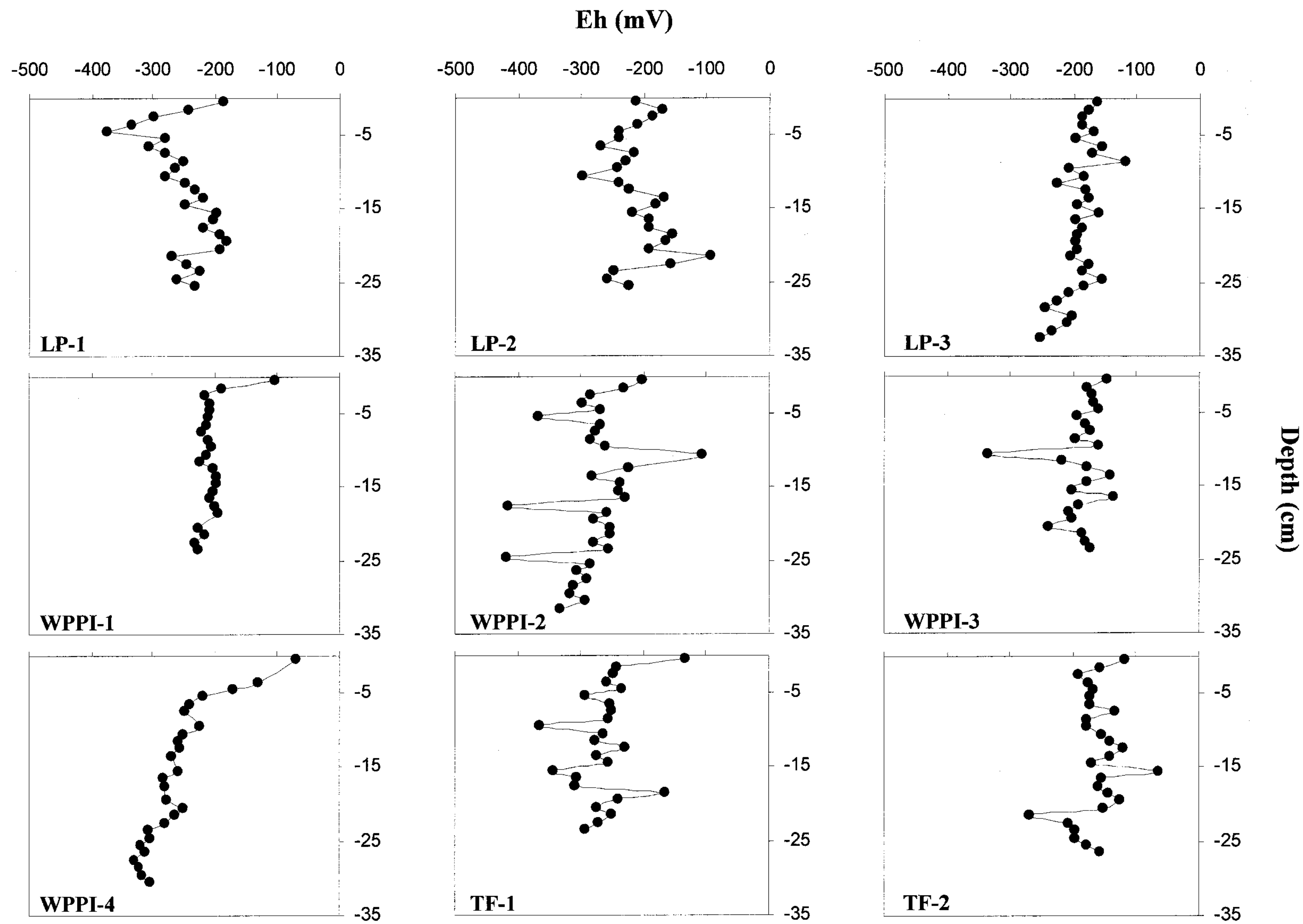

FIGURE B-1. Sediment profiles of redox potential.

TABLE B-3. Sediment Weight and Water Content

sample ID	core	depth (cm)	interval wet weight (g)	% water
CW4 0-1	WPPI-2	0-1	16.9905	82
CW4 1-2	WPPI-2	1-2	46.2806	80
CW4 2-3	WPPI-2	2-3	43.9873	76
CW4 3-4	WPPI-2	3-4	55.0930	73
CW4 4-5	WPPI-2	4-5	52.2925	65
CW4 7-8	WPPI-2	7-8	56.8462	58
CW4 10-11	WPPI-2	10-11	53.5494	65
CW4 14-15	WPPI-2	14-15	59.6736	73
CW4 18-19	WPPI-2	18-19	63.7496	70
CW4 22-23	WPPI-2	22-23	61.5296	66
CW5 0-1	LP-1	0-1	19.2379	81
CW5 1-2	LP-1	1-2	46.9781	75
CW5 2-3	LP-1	2-3	48.1786	73
CW5 3-4	LP-1	3-4	56.6350	73
CW5 4-5	LP-1	4-5	55.9747	73
CW5 8-9	LP-1	8-9	53.7493	73
CW5 12-13	LP-1	12-13	60.0911	69
CW5 16-17	LP-1	16-17	66.5439	60
CW5 20-21	LP-1	20-21	60.4578	70
CW5 24-25	LP-1	24-25	68.2772	58
CW6 0-1	LP-1	0-1	21.4695	86
CW6 1-2	LP-1	1-2	44.0905	81
CW6 2-3	LP-1	2-3	51.8260	80
CW6 3-4	LP-1	3-4	55.9392	79
CW6 4-5	LP-1	4-5	55.8965	76
CW6 8-9	LP-1	8-9	54.2698	70
CW6 12-13	LP-1	12-13	59.3092	67
CW6 16-17	LP-1	16-17	66.0726	69
CW6 20-21	LP-1	20-21	51.3938	52
CW6 25-26	LP-1	25-26	60.4741	62
CW7 0-1	LP-2	0-1	33.0923	70
CW7 1-2	LP-2	1-2	57.4938	63
CW7 2-3	LP-2	2-3	66.9312	59
CW7 3-4	LP-2	3-4	67.0118	53
CW7 4-5	LP-2	4-5	67.3899	59
CW7 8-9	LP-2	8-9	56.5666	68
CW7 12-13	LP-2	12-13	56.6572	67
CW7 16-17	LP-2	16-17	54.0868	67
CW7 20-21	LP-2	20-21	57.7407	68
CW7 25-26	LP-2	25-26	40.1508	67
CW10 0-1	WPPI-1	0-1	40.8109	59
CW10 1-2	WPPI-1	1-2	49.7436	51
CW10 2-3	WPPI-1	2-3	64.6995	50
CW10 3-4	WPPI-1	3-4	60.8783	49
CW10 4-5	WPPI-1	4-5	56.7561	51
CW10 8-9	WPPI-1	8-9	49.1317	68
CW10 13-14	WPPI-1	13-14	47.5560	64
CW10 18-19	WPPI-1	18-19	39.0918	74
CW10 24-25	WPPI-1	24-25	43.5033	71
CW10 31-32	WPPI-1	31-32	45.4531	68
CW12 0-1	WPPI-3	0-1	27.2427	81
CW12 1-2	WPPI-3	1-2	50.3741	77
CW12 2-3	WPPI-3	2-3	47.0245	75
CW12 3-4	WPPI-3	3-4	53.6709	73
CW12 4-5	WPPI-3	4-5	52.3212	72
CW12 7-8	WPPI-3	7-8	53.3518	66
CW12 11-12	WPPI-3	11-12	49.9426	62
CW12 15-16	WPPI-3	15-16	50.8789	62
CW12 19-20	WPPI-3	19-20	55.1875	63
CW12 23-24	WPPI-3	23-24	61.4079	61
CW14 0-1	TF-1	0-1	78.6168	37
CW14 1-2	TF-1	1-2	60.0988	42
CW14 2-3	TF-1	2-3	61.4380	48

TABLE B-3. Continued

CW14 3-4	TF-1	3-4	51.0360	59
CW14 4-5	TF-1	4-5	51.2501	68
CW14 7-8	TF-1	7-8	49.4807	71
CW14 11-12	TF-1	11-12	47.5729	71
CW14 15-16	TF-1	15-16	39.3114	74
CW14 19-20	TF-1	19-20	48.4889	72
CW14 23-24	TF-1	23-24	44.5942	73
CW15 0-1	WPPI-4	0-1	48.3425	78
CW15 1-2	WPPI-4	1-2	40.6165	77
CW15 2-3	WPPI-4	2-3	36.7089	75
CW15 3-4	WPPI-4	3-4	41.2044	73
CW15 4-5	WPPI-4	4-5	42.6910	73
CW15 8-9	WPPI-4	8-9	55.1645	72
CW15 13-14	WPPI-4	13-14	46.2906	72
CW15 18-19	WPPI-4	18-19	39.4234	69
CW15 24-25	WPPI-4	24-25	47.5639	60
CW15 31-32	WPPI-4	31-32	44.2807	27
CW18 0-1	LP-3	0-1	37.8495	74
CW18 1-2	LP-3	1-2	55.5291	62
CW18 2-3	LP-3	2-3	51.0230	59
CW18 3-4	LP-3	3-4	46.3107	58
CW18 4-5	LP-3	4-5	50.5883	64
CW18 8-9	LP-3	8-9	45.5018	70
CW18 13-14	LP-3	13-14	42.2379	66
CW18 18-19	LP-3	18-19	38.1975	67
CW18 24-25	LP-3	24-25	42.0132	64
CW18 32-33	LP-3	32-33	49.4017	70
CW19 0-1	TF-2	0-1	47.8989	42
CW19 1-2	TF-2	1-2	63.1081	45
CW19 2-3	TF-2	2-3	54.9122	55
CW19 3-4	TF-2	3-4	66.0419	57
CW19 4-5	TF-2	4-5	56.4390	64
CW19 8-9	TF-2	8-9	46.5984	74
CW19 13-14	TF-2	13-14	37.7557	80
CW19 18-19	TF-2	18-19	41.9769	76
CW19 23-24	TF-2	23-24	50.5731	73
CW19 26-27	TF-2	26-27	49.5858	72
CW21 0-1	LP-4	0-1	34.8255	67
CW21 1-2	LP-4	1-2	39.0908	59
CW21 2-3	LP-4	2-3	36.1549	57
CW21 3-4	LP-4	3-4	36.4757	52
CW21 5-6	LP-4	5-6	47.6718	46
CW21 7-8	LP-4	7-8	42.6954	48
CW21 9-10	LP-4	9-10	40.6505	50
CW21 12-13	LP-4	12-13	29.4512	67
CW21 17-18	LP-4	17-18	31.9872	68
CW21 22-23	LP-4	22-23	32.8772	63
CW21 27-28	LP-4	27-28	31.9294	62
CW21 34-36	LP-4	34-36	67.1164	62
CW21 44-46	LP-4	44-46	64.5398	63
CW21 54-56	LP-4	54-56	59.6402	69
CW21 64-66	LP-4	64-66	55.0820	61

APPENDIX C

Mercury Data

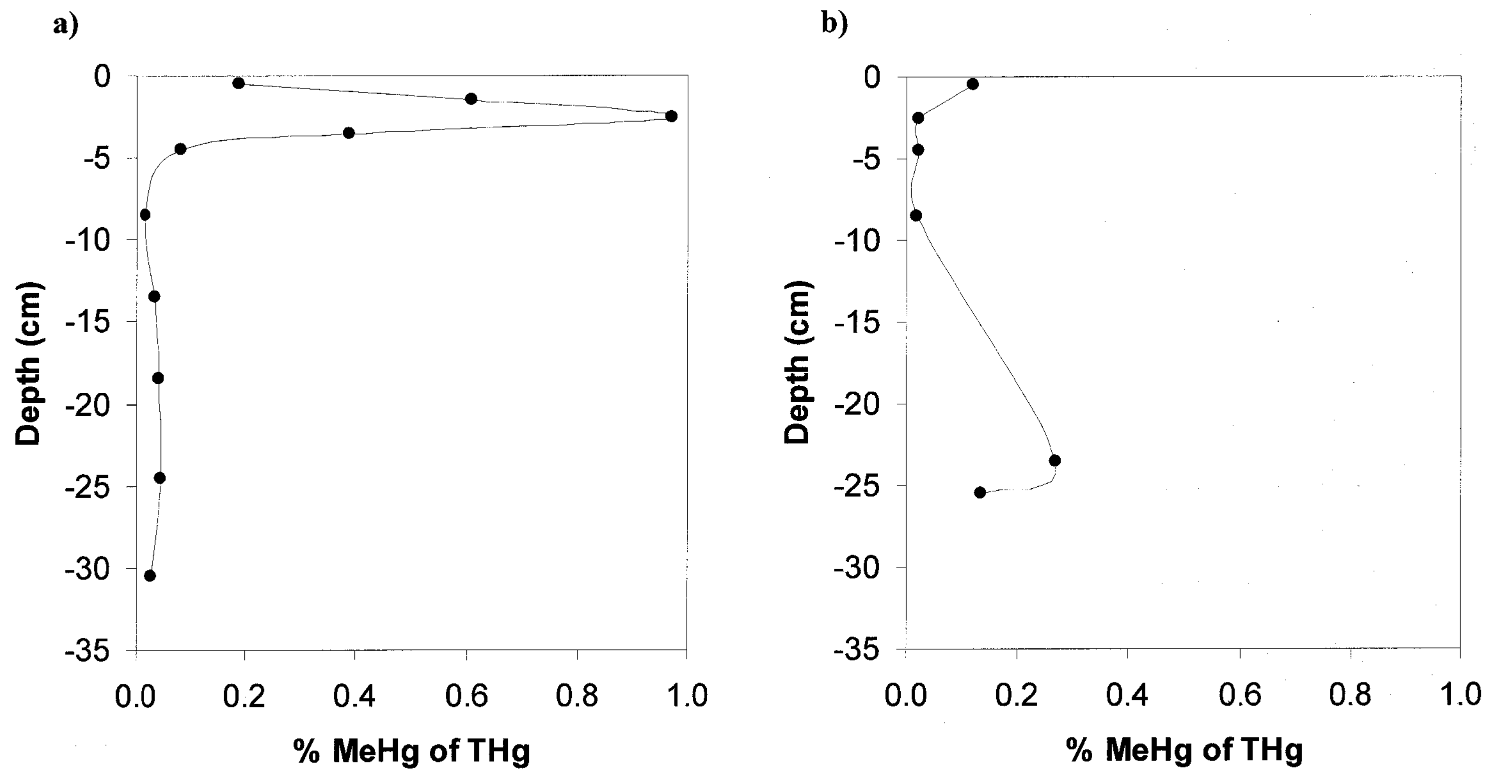

FIGURE C-1. Percent MeHg of THg in pore water from cores **a)** LP-3, and **b)** WPPI-4.

TABLE C-1. Mercury Concentrations in Surface Sediment from the Reference Site

sample ID	analysis 1 (ng g^{-1})	analysis 2 (ng g^{-1})	average THg (ng g^{-1})	SD	MeHg (ng g^{-1})
F01	12.20	12.67	12.44	0.33	0.131
F02	16.12	15.00	15.56	0.79	0.351
F03	18.22	18.30	18.26	0.06	0.184
F04	13.88	14.47	14.18	0.42	0.198
F05	19.77	19.12	19.45	0.46	0.321

APPENDIX D

Radioisotope Data

TABLE D-1. Radioisotope Data and Sedimentation Rates

sample ID	core	depth (cm)	cum. dry weight (g)	total ^{210}Pb (Bq Kg^{-1})	excess ^{210}Pb (Bq Kg^{-1})	SE	^{137}Cs (Bq Kg^{-1})	SE	sedimentation rate (g cm^{-2} yr^{-1})	% SE	CRS date	SE
CW4 0-1	WPPI-2	0-1	0.0979	176.50	150.67	10.47	17.17	1.43	0.1797	11.6	2003	2
CW4 1-2	WPPI-2	1-2	0.3058	238.90	208.97	11.38	23.64	1.60	0.1240	11.1	2002	2
CW4 2-3	WPPI-2	2-3	0.5516	223.95	194.13	12.05	24.54	1.81	0.1256	12.0	2000	2
CW4 3-4	WPPI-2	3-4	0.8451	198.62	171.97	10.07	22.78	1.44	0.1320	12.5	1998	2
CW4 4-5	WPPI-2	4-5	1.2182	142.16	118.23	8.81	19.47	1.29	0.1780	14.0	1995	2
CW4 7-8	WPPI-2	7-8	2.6884	134.63	115.52	8.51	18.70	1.21	0.1358	17.2	1986	3
CW4 10-11	WPPI-2	10-11	4.1783	126.68	101.75	8.95	32.88	1.67	0.1047	24.1	1974	5
CW4 14-15	WPPI-2	14-15	5.6998	83.67	60.45	8.59	45.59	1.88	0.1141	37.0	1960	9
CW4 18-19	WPPI-2	18-19	7.0665	64.20	44.20	8.71	53.11	2.07	0.1061	43.9	1947	14
CW6 0-1	LP-1	0-1	0.0742	233.77	208.21	12.04	18.40	1.55	0.2211	14.6	2004	2
CW6 1-2	LP-1	1-2	0.2510	213.49	185.93	11.76	18.66	1.54	0.2417	15.1	2003	2
CW6 2-3	LP-1	2-3	0.4636	211.02	181.36	11.88	20.11	1.70	0.2411	15.5	2002	2
CW6 3-4	LP-1	3-4	0.6937	229.54	204.58	12.12	19.03	1.61	0.2070	15.7	2001	2
CW6 4-5	LP-1	4-5	0.9490	191.57	165.11	11.39	19.18	1.60	0.2476	16.5	2000	2
CW6 8-9	LP-1	8-9	2.2155	162.44	138.93	10.10	17.08	1.42	0.2513	19.0	1995	2
CW6 12-13	LP-1	12-13	3.7514	124.42	108.11	9.12	14.44	1.37	0.2685	22.6	1989	3
CW6 16-17	LP-1	16-17	5.3273	119.05	102.19	9.35	18.81	1.51	0.2336	27.0	1983	5
CW6 20-21	LP-1	20-21	7.4359	90.22	71.03	8.71	26.40	1.59	0.2569	35.2	1974	7
CW6 25-26	LP-1	25-26	10.3399	83.06	67.14	8.39	27.06	1.54	0.1787	44.2	1960	12
CW7 0-1	LP-2	0-1	0.1787	119.86	98.68	10.18	14.71	1.43	0.1933	12.8	2003	2
CW7 1-2	LP-2	1-2	0.5952	127.58	110.95	10.48	10.19	1.26	0.1597	12.5	2001	2
CW7 2-3	LP-2	2-3	1.1020	106.52	89.36	8.67	12.14	1.12	0.1807	13.1	1998	2
CW7 3-4	LP-2	3-4	1.6983	93.12	79.01	8.74	12.65	1.04	0.1846	14.7	1994	2
CW7 4-5	LP-2	4-5	2.2972	48.26	34.35	6.89	18.67	1.25	0.3954	22.5	1992	2
CW7 8-9	LP-2	8-9	4.1589	77.76	51.47	9.04	80.55	2.59	0.2162	21.1	1986	2
CW7 12-13	LP-2	12-13	5.7327	67.20	48.51	8.89	73.31	2.56	0.1789	23.1	1978	3
CW7 16-17	LP-2	16-17	7.3362	64.66	46.70	9.88	84.82	2.98	0.1350	27.6	1968	5
CW7 20-21	LP-2	20-21	8.9150	63.56	45.55	10.04	76.30	2.88	0.0886	32.9	1953	7
CW7 25-26	LP-2	25-26	10.9022	45.75	27.70	9.94	93.59	3.10	0.0655	37.9	1928	15
CW10 0-1	WPPI-1	0-1	0.2739	76.51	58.12	7.61	9.78	0.99	0.3308	20.3	2003	2
CW10 1-2	WPPI-1	1-2	0.8892	72.46	51.83	6.47	12.66	0.97	0.3506	20.6	2001	2
CW10 2-3	WPPI-1	2-3	1.5849	77.68	60.43	7.91	14.13	1.13	0.2806	21.9	1999	2
CW10 3-4	WPPI-1	3-4	2.3066	62.49	46.21	6.94	15.14	1.11	0.3412	24.1	1997	2
CW10 4-5	WPPI-1	4-5	3.0218	61.61	43.50	6.92	26.19	1.42	0.3395	25.5	1995	2
CW10 8-9	WPPI-1	8-9	5.2084	72.69	48.40	13.22	159.96	3.58	0.2406	36.4	1987	4
CW10 13-14	WPPI-1	13-14	7.3395	66.56	48.39	8.99	112.53	3.11	0.1742	37.6	1977	7
CW10 18-19	WPPI-1	18-19	9.2395	35.13	14.67	13.15	142.54	4.27	0.4608	97.4	1970	9
CW10 24-25	WPPI-1	24-25	11.1768	33.87	11.09	18.23	169.70	4.41	0.3345	117.2	1964	10
CW10 31-32	WPPI-1	31-32	13.7609	51.04	27.60	10.77	188.19	4.33	0.1642	63.4	1957	13
CW12 0-1	WPPI-3	0-1	0.1039	237.89	211.42	12.16	20.58	1.73	0.2638	16.0	2004	2
CW12 1-2	WPPI-3	1-2	0.3356	204.95	179.07	10.51	19.37	1.46	0.3036	16.4	2003	2

TABLE D-1. Continued

CW12 2-3	WPPI-3	2-3	0.6065	222.13	192.34	11.19	17.71	1.50	0.2746	16.9	2002	2
CW12 3-4	WPPI-3	3-4	0.9055	204.66	179.07	11.34	21.23	1.59	0.2852	17.5	2001	2
CW12 4-5	WPPI-3	4-5	1.2249	220.30	190.99	11.69	22.55	1.61	0.2578	18.0	2000	2
CW12 7-8	WPPI-3	7-8	2.4670	156.55	133.20	10.33	18.38	1.43	0.3273	20.6	1996	2
CW12 11-12	WPPI-3	11-12	4.1438	145.22	126.87	12.00	19.74	1.61	0.2866	24.7	1990	3
CW12 15-16	WPPI-3	15-16	6.0642	141.96	119.50	9.58	26.61	1.64	0.2426	29.6	1983	5
CW12 19-20	WPPI-3	19-20	7.9682	131.58	106.47	10.35	33.61	1.84	0.2095	38.2	1974	8
CW12 23-24	WPPI-3	23-24	9.9251	110.47	86.29	10.24	44.91	2.02	0.1906	44.2	1964	12
CW14 0-1	TF-1	0-1	0.5075	26.41	15.22	6.27	3.46	0.76	0.9677	48.7	2004	2
CW14 1-2	TF-1	1-2	1.4592	29.02	16.43	6.57	14.56	1.16	0.8679	48.1	2002	2
CW14 2-3	TF-1	2-3	2.2807	38.70	25.61	6.82	18.43	1.24	0.5361	38.5	2001	2
CW14 3-4	TF-1	3-4	2.9243	40.43	26.47	8.73	48.04	2.20	0.4990	43.9	2000	2
CW14 4-5	TF-1	4-5	3.3878	63.11	46.37	13.17	84.34	3.21	0.2738	41.2	1999	2
CW14 7-8	TF-1	7-8	4.4913	37.79	15.18	12.06	135.18	3.96	0.6336	74.7	1995	3
CW14 11-12	TF-1	11-12	5.8608	62.25	39.82	11.14	185.21	4.34	0.2667	45.0	1993	4
CW14 15-16	TF-1	15-16	7.1585	38.80	10.65	13.32	209.00	5.09	0.4838	51.8	1990	5
CW14 19-20	TF-1	19-20	8.4187	52.44	32.38	10.92	149.08	4.06	0.2767	53.1	1988	6
CW14 23-24	TF-1	23-24	9.7027	65.68	48.63	12.92	191.39	5.05	0.1514	44.0	1981	9
CW15 0-1	WPPI-4	0-1	0.1242	195.64	165.92	11.99	22.51	1.70	0.4934	14.3	2005	2
CW15 1-2	WPPI-4	1-2	0.3821	196.04	168.78	12.70	21.33	1.62	0.4770	14.6	2004	2
CW15 2-3	WPPI-4	2-3	0.6600	179.04	151.64	10.28	19.82	1.55	0.5218	14.5	2004	2
CW15 3-4	WPPI-4	3-4	0.9597	183.01	158.52	10.68	18.77	1.51	0.490	14.6	2003	2
CW15 4-5	WPPI-4	4-5	1.2749	197.46	172.99	13.50	17.81	1.41	0.4397	15.4	2002	2
CW15 8-9	WPPI-4	8-9	2.5644	184.02	159.08	10.49	18.67	1.55	0.4362	15.9	1999	2
CW15 13-14	WPPI-4	13-14	4.2144	190.92	164.90	14.58	24.28	1.71	0.3704	18.6	1995	2
CW15 18-19	WPPI-4	18-19	6.0004	193.08	164.06	12.39	26.44	1.94	0.3165	20.7	1990	3
CW15 24-25	WPPI-4	24-25	8.6831	170.49	145.71	10.26	30.78	1.73	0.2677	26.3	1981	5
CW15 31-32	WPPI-4	31-32	15.0422	82.73	62.82	11.60	32.71	1.75	0.3103	36.9	1959	13
CW18 0-1	LP-3	0-1	0.4454	139.39	121.34	10.73	11.45	1.25	0.1209	11.8	2001	2
CW18 1-2	LP-3	1-2	1.3015	107.83	88.37	9.29	13.23	1.31	0.1346	14.0	1995	2
CW18 2-3	LP-3	2-3	2.0148	107.11	89.76	9.20	12.18	1.22	0.1105	15.0	1989	2
CW18 3-4	LP-3	3-4	2.6064	127.30	107.16	10.22	22.55	1.51	0.0757	16.3	1982	3
CW18 4-5	LP-3	4-5	3.1251	94.82	73.77	9.26	42.29	1.90	0.0904	20.0	1976	4
CW18 8-9	LP-3	8-9	4.6447	82.51	58.89	14.31	92.55	2.87	0.0601	33.7	1956	6
CW18 13-14	LP-3	13-14	5.9616	41.58	20.88	10.94	57.85	2.47	0.0976	61.8	1938	10
CW18 18-19	LP-3	18-19	7.2107	58.73	36.38	9.97	65.89	2.65	0.0261	62.2	1914	18
CW18 24-25	LP-3	24-25	8.6807	0.00	-18.86	2.18	32.32	2.10	0.1096	82.8	1897	31
CW18 32-33	LP-3	32-33	9.6594	32.85	20.83	10.82	77.24	3.02	0.030	73.0	1885	18
CW19 0-1	TF-2	0-1	0.4454	39.51	28.37	5.91	3.52	0.69	0.2659	24.8	2003	2
CW19 1-2	TF-2	1-2	1.3015	45.20	37.49	6.57	5.26	0.80	0.1779	23.2	1999	2
CW19 2-3	TF-2	2-3	2.0148	24.44	14.72	7.15	19.81	1.34	0.4164	51.2	1997	2
CW19 3-4	TF-2	3-4	2.6064	33.39	19.56	7.85	47.75	2.05	0.2973	43.5	1995	2
CW19 4-5	TF-2	4-5	3.1251	30.36	14.68	10.42	89.04	3.10	0.3775	72.7	1993	3
CW19 8-9	TF-2	8-9	4.6447	53.22	41.83	12.11	118.63	4.18	0.1031	34.0	1985	4

TABLE D-1. Continued

CW19 13-14	TF-2	13-14	5.9616	0.00	-10.60	3.28	47.31	3.41	0.2174	26.3	1979	5
CW19 18-19	TF-2	18-19	7.2107	61.39	44.79	12.54	139.38	4.33	0.0672	33.8	1974	5
CW19 23-24	TF-2	23-24	8.6807	53.42	31.31	12.07	218.28	5.06	0.0411	44.7	1946	8
CW19 26-27	TF-2	26-27	9.6594	42.51	26.64	10.72	121.03	3.85	0.0152	47.7	1909	16
CW21 0-1	LP-4	0-1	0.2914	139.15	123.47	9.94	11.74	1.30	0.2592	8.10	2004	3
CW21 1-2	LP-4	1-2	0.3961	125.88	114.09	10.15	9.49	1.21	0.2693	12.1	2003	2
CW21 2-3	LP-4	2-3	0.4198	115.34	96.71	10.26	12.49	1.35	0.3039	13.6	2002	2
CW21 3-4	LP-4	3-4	0.4873	93.41	79.40	9.90	11.50	1.28	0.3546	15.3	2000	2
CW21 5-6	LP-4	5-6	0.5818	63.19	46.16	7.71	12.84	1.22	0.5608	19.3	1998	2
CW21 7-8	LP-4	7-8	0.5720	101.95	80.69	11.13	21.15	1.58	0.2933	17.2	1995	2
CW21 9-10	LP-4	9-10	0.4922	60.07	40.22	9.24	18.57	1.47	0.5354	25.5	1992	2
CW21 12-13	LP-4	12-13	0.3092	106.88	81.63	17.37	86.10	3.57	0.2348	24.4	1988	2
CW21 17-18	LP-4	17-18	0.2928	51.51	35.13	13.19	38.45	2.75	0.4712	39.7	1983	3
CW21 22-23	LP-4	22-23	0.3464	58.06	35.93	12.68	79.99	3.14	0.4044	37.7	1979	3
CW21 27-28	LP-4	27-28	0.3652	53.47	34.45	11.05	71.45	3.13	0.3506	36.3	1973	4
CW21 34-36	LP-4	34-36	0.3606	36.58	23.98	10.78	48.84	2.70	0.3672	49.0	1963	6
CW21 44-46	LP-4	44-46	0.3408	52.24	42.47	10.97	82.07	3.28	0.1004	42.7	1940	10
CW21 54-56	LP-4	54-56	0.2832	46.76	33.16	16.30	80.88	4.08	0.0738	65.2	1922	15