Mass Balance Model of Mercury for the St. Lawrence River, Cornwall, Ontario

Charlotte Lessard

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ABSTRACT

We have developed a regional mass balance model for the St. Lawrence River near Cornwall, Ontario that describes the fate and transport of mercury in three forms, elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg), in a five compartment environment (air, water, sediments, periphyton, and benthos). Our first objective was to construct a steady-state mass balance model to determine the dominant sources and sinks of mercury in this environment. Our second objective was to construct a dynamic mass balance model to predict and hindcast mercury concentrations in this environment. We compiled mercury concentrations, fluxes, and transformation rates from previous studies completed in this section of the river to develop the model in STELLA®. The inflow of mercury was the major source to this system, accounting for 0.42 mol $month^{-1}$, or 95.5% of all mercury inputs, whereas outflow was 0.28 mol $month^{-1}$, or 63.6% of all losses, and sediment deposition was 0.12 mol $month^{-1}$, or 27.3% of all losses. The dynamic mass balance model provides estimated results that are consistent with measured data and predicts historical local industrial emissions to be approximately 400 kg $year^{-1}$. Uncertainty estimates were greatest for advective fluxes in surface water, porewater, periphyton, and benthic invertebrates. This model is useful for predicting and hindcasting mercury concentrations in other aquatic environments because it contains the three main environmental compartments, all forms of mercury, and compartments (e.g. periphyton) not included in previous mercury multi-media models.

RÉSUMÉ

Nous avons développé un bilan de masse ainsi qu'un modèle dynamique pour le mercure au niveau régional pour le fleuve Saint Laurent près de Cornwall, en Ontario. Ce travail décrit le devenir et le transport du mercure sous trois formes; mercure élémentaire (Hg^0), mercure divalent (Hg^{2+}), et méthylmercure (MeHg), dans un environnement ayant cinq compartiments (air, eau, sédiments, périphyton, et benthos). Notre premier objectif était de construire un modèle à l'état stationnaire afin de déterminer les sources et les puits dominants de mercure dans cet environnement. Notre deuxième objectif était de construire un modèle dynamique afin de prévoir et de reconstruire, à posteriori, les concentrations de mercure dans cet environnement. Nous avons compilé les concentrations de mercure, les flux et les taux de transformation à partir d'études antérieures complétées dans cette section du fleuve à l'aide du logiciel de modèlisation STELLA®. Les entrées de mercure par advection était la principale source dans le système, représentant 0.42 mol $mois^{-1}$, ou 95.5% de tous les apports de mercure, tandis que la sortie était 0.28 mol $mois^{-1}$, ou 63.6% de toutes les pertes, et le dépôt sous forme de sédimentation était 0.12 mol $mois^{-1}$, ou 27.3% de toutes les pertes. Le bilan de masse dynamique fournit des estimations qui sont compatibles avec les données mesurées et prédit des émissions historiques d'environ 400 kg $année^{-1}$. Les estimations d'incertitude les plus grande pour les flux étaient par rapport à l'advection dans les eaux de surface, l'eau interstitielle, le périphyton, et les invertébrés benthiques. Ce modèle est utile pour la prédiction et la reconstruction à posteriori des concentrations de mercure dans d'autres milieux aquatiques parce qu'il contient les trois principaux compartiments de l'environnement, toutes les formes de mercure, et des compartiments (par exemple périphyton) pas inclus dans les modèles multimédia de mercure existants.

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LIST OF ABBREVIATIONS

AOC	Area of Concern
BCF	Bioconcentration Factor
DGM	Dissolved Gaseous Mercury
DOC	Dissolved Organic Carbon
GEM	Gaseous Elemental Mercury
Hg^0	Elemental Mercury
Hg^{2+}	Divalent Mercury
Hg	Mercury
IJC	International Joint Commission
MeHg	Methyl Mercury
MOE	Ministry of the Environment
NADP	National Atmospheric Deposition Program
PM	Particulate Mercury
RAP	Remedial Action Plan
RGM	Reactive Gaseous Mercury
TF	Tank Farm
TGM	Total Gaseous Mercury
THg	Total Mercury
UV	Ultra-violet
WPCP	Water Pollution Control Plant
WPPI	Windmill Point to Pilon Island

Chapter 1

Introduction

1.1 Introduction

Mercury (Hg) or "liquid silver" has been widely studied throughout the world because of its dynamic behaviour and ubiquitous nature (Fitzgerald et al. 1991). The most toxic form, methyl mercury (MeHg), is bioaccumulative because MeHg has a high affinity for protein and is a health concern to humans and wildlife (D'Itri, 1991). At higher trophic levels in a food chain, concentrations of MeHg increase, posing a greater risk to these organisms and those who consume them. MeHg accumulation in predatory fish and consumption by humans is the primary route of human exposure today (Renzoni et al. 1998). The effects of consuming methylmercury contaminated fish and seafood were first observed in the town of Minamata, Japan where local fish, birds, cats, and citizens experienced neurological disorders which was later called Minamata Disease (D'Irti, 1991; Harada 1995). Symptoms such as brain damage, numbness of extremeties, paralysis, and loss of hearing, speech, and sight were reported. Once the disease and its cause, mercury emissions from the nearby Chisso facility, had been identified, similar environmental disasters due to mercury poisoning occurred in Canada, New Mexico, Iraq, Pakistan, and Guatemala (Bakir et al. 1973; Harada 1976; Takeuchi, 1977). Global awareness of the severity of Hg contamination in the aquatic environment and effects on the food web and humans has resulted in decades of research to understand the origin, fate, and transport of mercury.

1.1.1. Sources and Fate of Mercury in the Environment

Mercury is present in the environment as elemental mercury (Hg^0), ionic mercury (monomeric Hg^+ (rare), and divalent Hg^{2+}), and methyl mercury (MeHg). The fate and transport of mercury is dependent on its chemical form. Hg^0 is a volatile compound that is emitted to the atmosphere by evasion and has a relatively long residence time (0.5 – 2 years) (Poissant and

Casimir 1998; Schroeder and Munthe 1998). Once Hg^0 has been released into the atmosphere, speciation into gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and particulate mercury (PM) can occur due to photochemical processes and chemical and/or physical interactions (Poissant et al. 2004). Loss of mercury from the atmosphere may proceed by gas exchange (Poissant and Casimir 1998), or wet and dry deposition of Hg^{2+} if adsorption to aerosols and scavenging by rain or snow (Poissant and Pilote 1998). Hg^0 in surface waters may derive from the reduction of Hg^{2+} by abiotic (Amyot et al. 1994, 1997, 2000, 2004) or biotic processes (Mason et al. 1995), decomposition of organic Hg (Poissant et al. 2007), and from anthropogenic sources such as chlor-alkali plants (Ullrich et al. 2001). Also, Hg^0 may be oxidized to Hg^{2+} in freshwater and the ocean (Amyot et al. 1994, 1997; Lalonde et al. 2001, 2004). Supersaturation of Hg^0 in surface water compared to the atmosphere is common, especially in the summer (Vandal et al. 1991).

Hg^{2+} is the most abundant form of inorganic mercury in water and binds with inorganic ligands (e.g. Cl^-, OH^-), dissolved organic carbon (DOC), or particulate matter (Lindqvist et al. 1991; Ullrich et al. 2001). These complexes can be reduced microbially or abiotically to Hg^0 (Mason et al. 1995) or methylated by bacteria. Most of the inorganic mercury in the water column is deposited to the sediment bottom where it can accumulate or be resuspended. In anoxic sediments the chemistry of Hg is mainly controlled by its formation with sulfide, organic matter and inorganic particles (Lindberg and Harris, 1974; Mason and Lawrence, 1999). Mercuric sulfide (HgS) is insoluble and mercuric oxide (HgO) is somewhat soluble, which are commonly found in contaminated sediments (Sakamoto et al. 1995). The formation and transport of these mercury compounds are dependent on environmental conditions such as redox and pH (Ullrich et al. 2001). Atmospheric deposition is the main source of Hg^{2+} to many lakes but is not

a significant source of MeHg (Mason and Fitzgerald, 1993). Precipitation and surface run-off may be important external sources of MeHg to freshwater ecosystems besides internal methylation (Rudd, 1995).

Prior to the industrial revolution, natural sources of Hg were the majority of Hg emissions to the environment (Schroeder and Munthe, 1998). Natural sources include outgassing of the earth's mantle, evasion from soils, water, and vegetation, wild fires, volcanoes, and geothermal sources (Schroeder and Munthe, 1998). Prior to the 1970s, chlor-alkali plants were the largest emitters of Hg to the environment in many industrialized countries (Schroeder and Munthe, 1998). Other anthropogenic sources included mining activities, coal combustion, waste incineration, medical waste, sewage sludge, and metal smelters (Dommergue et al. 2010; Schroeder and Munthe, 1998). Since then, regulations and guidelines on emissions and switches in energy sources have reduced atmospheric concentrations (Dommergue et al. 2010; Iverfeldt et al. 1995; Schuster et al. 2002) but they remain approximately three times higher than preindustrial levels (Mason et al. 1994). Despite the decrease in atmospheric mercury concentrations, there still remain systems where high Hg concentrations in biota are still evident (Driscoll et al. 2007; Meili et al. 2003; Rigét et al. 2011). For this reason, Hg remains a global issue and health concern.

1.1.2. Mercury Contamination of the St. Lawrence River near Cornwall

Over the past century, Cornwall has been an important industrial area on the St. Lawrence River (Richman and Drier, 2001). The St. Lawrence River is 1400 km long and connects the Great Lakes to the Atlantic Ocean (St. Lawrence River RAP Team, 1990). In 1985, the International Joint Commission (IJC) designated this section of the river as a Great Lakes

"Area of Concern (AOC)" based on degradation of the environment (Richman and Drier 2001; Ridal et al. 2010). A Remedial Action Plan (RAP) was developed to remediate and manage the stressors within the AOC and to assess progress by research and monitoring programs (Richman and Drier 2001; St. Lawrence River RAP Team, 1997). The northern shore of this ecosystem has been affected by the construction of the St. Lawrence Seaway (est. 1959), the Moses-Saunders Dam (est. 1958), and mercury contaminated sediments from local industrial discharges (Richman and Drier, 2001). Local point sources include Domtar Fine Papers Ltd. (pulp and paper mill) which closed in 2006, the city of Cornwall's Water Pollution Control Plant (WPCP), Courtalds Fibres (a rayon manufacturer) which closed in 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 ceased operation in 1995 (Delongchamp et al. 2010). Despite the implementation of new government regulations in 1970 limiting the amount of allowable Hg discharged as effluent and the closure of the main industrial sources of Hg to the river, Hg concentrations still remain high in sediments and fish species such as yellow perch and walleye (Choy et al. 2008; Delongchamp et al. 2009; Environment Canada, 1981; Fowlie et al. 2008).

1.1.3 Study Objectives

Constructing an overall picture of how physical, chemical, and biological processes influence the fate and transport of chemicals in an ecosystem is important in understanding and preventing contamination of lakes, rivers, and their associated food webs. Several mass balance model projects have been used to establish the connection between the loading of specific chemicals and resulting concentrations in water, sediments, and biota (Mackay et al. 1994). The level of complexity, spatial resolution, and temporal resolution differs among these models,

which are used by environmental scientists and managers for policy development or research purposes (Mackay et al. 1994). This project aims to develop a mass balance model for the fate and transport of mercury in the St. Lawrence River near Cornwall, Ontario. The model will focus on total mercury (THg), elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg) in the environmental compartments of air, water, porewater, sediment, periphyton, and benthic invertebrates. A compilation of Hg concentrations, fluxes, and transformation rates from previous studies completed in this section of the river are used to develop the model. The steady-state and dynamic mass balance models for mercury were developed using the software STELLA®.

The primary objectives of this project are: (1) to develop a steady-state mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario to estimate the dominant sources and sinks; (2) to construct a dynamic mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario based on the framework and results of the steady-state mass balance model; (3) to use the dynamic mass balance model to estimate emissions from local industries based on mercury residues deposited in sediments prior to 1970. It is hypothesized that a mass balance model of mercury for the St. Lawrence River can predict the distribution of mercury in air, water, sediments and biota. The main prediction is that sediments are a net sink of mercury due to the presence of sediment depositional areas (Delongchamp et al. 2010).

1.2. Study Site

The Area of Concern (AOC) in the St. Lawrence River near Cornwall is approximately 80 km long, and falls under the jurisdiction of Ontario and Quebec, the State of New York

(U.S.A.), the federal governments of both Canada and the U.S.A., and the Mohawk territory of Akwesasne. The AOC spans from the Moses-Saunders power dam to the eastern outlet of Lake St. Francois in Quebec (Delongchamp et al., 2010). Cornwall Island divides the river into the North Channel with mercury contaminated sediments and the South Channel which contains high PCB levels in the sediments (St. Lawrence River RAP, 1992). The Ministry of the Environment Eastern Region previously "delineated" three sediment zones where higher mercury concentrations in sediments were measured. Several sediment studies have been conducted to determine the extent of Hg contamination along the Cornwall waterfront (Anderson, 1990; Delongchamp et al. 2009, 2010; Grapentine et al. 2003; MOE 1992; OMEE 1994; Richman 1999), long-term sediment stability (Rukavina 2000), and factors that may influence Hg distribution and concentration such as hydrology (Nettleton 2004). Mercury contaminated sediments extend from the Boat Launch to Pilon Island and are defined as three deposits consisting primarily of mud and muddy sands (Rukavina 2000). These depositional areas are known as Zones 1, 2, and 3 or Boat Launch, Windmill Point to Pilon Island (WPPI), and Tank Farm, respectively (Figure 1-1).

The geology of the study area consists of recent deposits generally less than 60 cm thick overlying clayey glacial sediments and till (Lepage, 2000). Comparison among and between sites showed high spatial heterogeneity in sediment type and composition suggesting that depositional conditions have been relatively uniform (Rukavina 2000). No significant differences occur in THg concentrations among and between sites (Delongchamp et al. 2009). Nettleton (2004) used a "Surface Water Modelling System" to estimate 2-dimensional, dynamic river hydrodynamics for the North and South Channels of the St. Lawrence River and showed that Zones 1, 2, and 3 had similar water depths and river velocities, even with changing flow-rates (minimum, average,

and maximum flow rates). Low bed shear stress in each zone was low, which is typical of sediment deposition areas. Since 1956, reduction of the range of water level was required by the Moses-Saunders Power Dam to maintain consistent river flows, adequate navigation depths, and protect downstream habitat (International St. Lawrence River Board of Control, 2009).

The present study will focus on the three zones located along the Cornwall waterfront of the North Channel. Zone 1, the westernmost location of the study site, is located closest to a pulp and paper mill (Domtar) and a chlor-alkali plant (ICI). Zone 2, the easternmost location, is located closest to a textile mill (Courtalds) and Zone 3 is located in the middle of the study area and the other two zones. Small rivers with a water velocity of approximately 200 $m^3 s^{-1}$ or less are preferentially treated as being homogeneous or well mixed horizontally (from shore to shore) (Milford 2002). For larger rivers a multi-segment model is more appropriate because of the changing depth, flow, and biotic conditions (Milford 2002). This model focuses on the near shore segment of the Cornwall waterfront where Zones 1, 2, and 3 are located. A multi-segment model was not constructed because of the spatial heterogeneity in sediment composition and type, Hg concentrations, and hydrology described earlier.

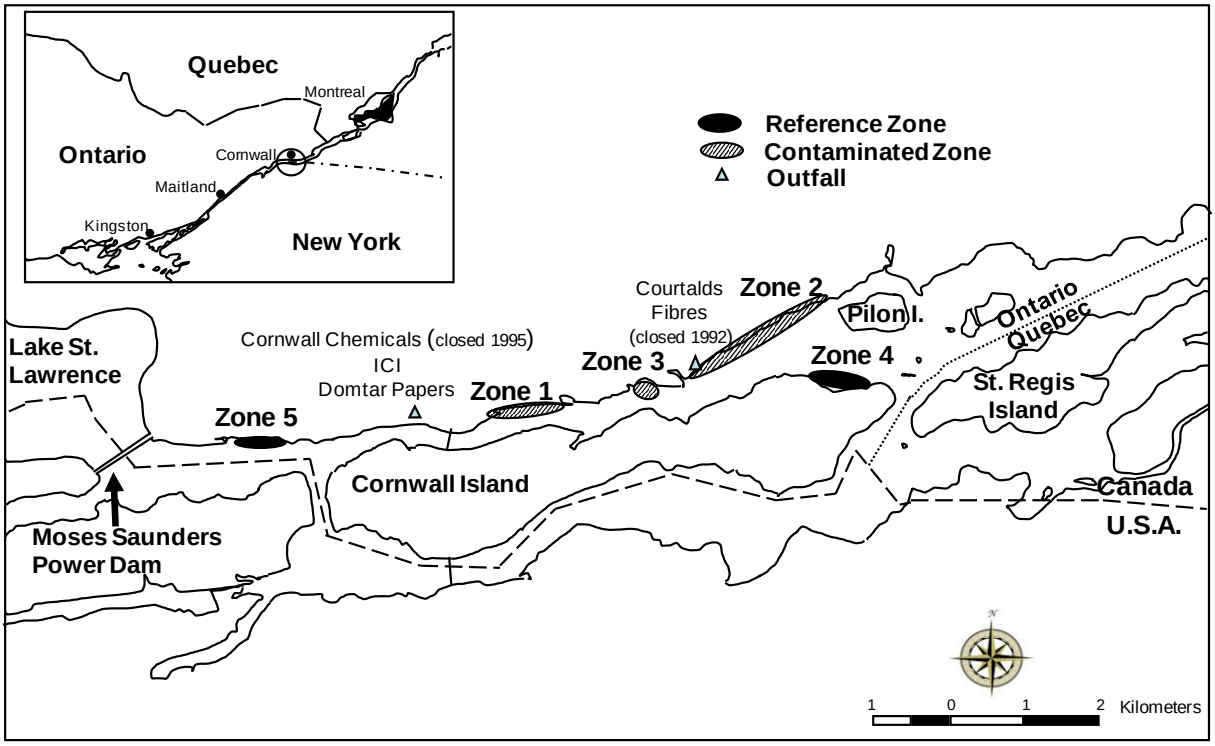

Figure 1-1: Map of study area in the St. Lawrence River near Cornwall, Ontario (modified from Ridal et al., 2010). Model contains the mercury contaminated zones 1, 2 and 3. Also shown are reference zones and outfalls in the vicinity to zones 1 and 2.

1.3 Literature Review

1.3.1. Mass Balance Models

The effect of water quality on aquatic biota has been studied worldwide in many different types of aquatic ecosystems. These studies are primarily done on large lakes and water bodies because of their importance for the economy. Rivers that connect or flow directly into or out of them omit a potential source or sink of contamination. Rivers are affected by contaminants as well but due to their spatial and temporal complexity they have not been well modeled compared to lakes. For these systems, mass balance models can be valuable tools in order to gain a better understanding of the key processes involved in assessing chemical fate when calibrated using

existing data (Cossa et al. 1998). Site-specific mass balance models can be used to forecast future conditions or reconstruct historical conditions (hind casting) and be used to assist with focusing sampling efforts or long-term monitoring.

Several mercury mass balance models have been developed for aquatic ecosystems but only a small portion of them focus on river ecosystems. Mercury models have been developed for the River Yare in Norfolk, United Kingdom (Braga et al. 2010a, 2010b), the Soča River in Slovenia (Žagar et al. 2006), and the Paraiba do Sul River in Brazil (Molisani et al. 2007). In North America, Hope (2006) created a dynamic model (using STELLA®) for the Willamette River in Oregon to identify the dominant sources of natural and anthropogenic mercury, their relative contribution, and impact on mercury levels in surface water, sediment and fish tissue. Of these mercury mass balance models, only two are multi-species mercury models (Hope 2006; Zagar et al. 2006). Diamond (1999) developed a fugacity-based multispecies "aquivalence" model of mercury dynamics for lakes. Cahill et al. (2003) presented a multimedia, multispecies, fugacity-based model to predict the fate of several speciating organic chemicals. Toose and Mackay (2004) used the fugacity-based approach for speciating chemicals with constant concentration ratios. Regional multispecies models that describe the fate and transport of mercury have been constructed for the remote lake Big Dam West, Nova Scotia, Canada (Ethier et al. 2008) and the San Francisco Bay Estuary, California, U.S.A. (MacLeod et al. 2005).

1.3.2. Mercury in the Aquatic Environment

1.3.2.1. Water

Mercury is naturally present in water at very low levels (Ullrich et al. 2001). "Uncontaminated" freshwaters generally contain <5 ng L^{-1} of THg and can be in the ug L^{-1} range for contaminated waters (Bloom, 1989; Craig 1986; Ullrich et al. 2001). The proportion MeHg to THg in the water column is usually higher than in sediments (Barringer et al. 2010; Kudo et al. 1982). In anoxic water, concentrations of THg and MeHg are frequently elevated (Ullrich et al. 2001). Typical MeHg concentrations in natural surface waters range from 0.02 to 0.1 ng L^{-1} but are found up to 4 ng L^{-1} in stratified remote lakes (Bloom, 1989; Roy et al. 2009). In the water column a large proportion of Hg is attached to suspended particles (Gobeil and Cossa 1993). Suspended matter plays an important role in the transport of Hg, especially in freshwater environments, because the settling of particulate matter is considered a major source of Hg to the sediment-water interface where methylation occurs (Hurley et al. 1991, 1994). Particulate Hg mainly consists of Hg bound to inorganic particles, organic matter, and biotic material such as bacteria, algae, and phytoplankton (Morel et al. 1998). Dissolved Hg is present in many forms: Hg^0, Hg^{2+}, and MeHg. Concentrations of Hg^0 are usually higher near the air-water interface whereas levels of THg and MeHg are higher near the sediments (Morel et al. 1998; Poulain et al. 2004).

1.3.2.2. Sediment

Sediments are the main reservoir of Hg in freshwater systems because of its high affinity for the particulate phase ($\log K_d = 5 – 6$) (Benoit et al. 1998; Coquery et al. 1997; Wang et al. 1998). Affinity for the dissolved and particulate phases is measured by the distribution

coefficient: $K_d = [Hg]_{particulate} / [Hg]_{dissolved}$, expressed in L kg^{-1}. Over 90% of the Hg that enters the aquatic environment is eventually accumulated within sediments (Kroenke et al. 2003). In oxic sediments, mercury adsorbs to organic matter and iron/manganese oxides and may be remobilized into the porewater if microbial reduction occurs (Gagnon et al. 1997; Gobeil and Cossa, 1993). In anoxic sediments, mercury adsorbs to sulfide minerals and is very susceptible to oxidation but sulfides are more of a sink for Hg than pyrite (Gagnon et al. 1997). Background concentrations reported in the literature for Hg in freshwater sediments range from 10 – 100 ug kg^{-1} (Kroenke et al. 2003). Hg concentrations in contaminated sediments can be in the ug g^{-1} range (Benoit et al. 1998; Gobeil and Cossa 1993).

At the sediment-water interface sediments consist of 95% water and 5% particles (Mackay, 2001). At greater depths the water content decreases to approximately 50% (Mackay, 2001). Hg concentrations in porewater experience a gradient where levels are generally higher at the sediment-water interface (Covelli et al. 1999; Gill et al. 1999). Seasonal trends show that porewater Hg concentrations are highest during autumn and winter because of higher oxygen levels, cooler temperatures, and decreased microbial activity (Covelli et al. 1999; Gill et al. 1999). Hg concentrations in sediment porewater are usually greater than in the overlying water column (Covelli et al. 1999).

MeHg concentrations in sediments reflect net methylation rather than actual production rates of methyl mercury because degradation or demethylation of MeHg occur simultaneously (Avramescu et al. 2011). MeHg levels in sediments rarely exceed 1 – 1.5% of THg because methylation and demethylation processes are very fast and the net formation of MeHg may be near zero (Avramescu et al. 2011). Biotic methylation of Hg occurs mainly in anoxic conditions in surface sediments and is primarily done by sulfate reducing bacteria (SRB) (Avramescu et al.

2011; Compeau and Bartha, 1985; Gilmour and Henry, 1991; Merritt and Amirbahman, 2009). Methylation rates are influenced by bioavailable Hg concentrations in sediments (Benoit et al. 2003), microbial activity (Avramescu et al. 2011), and the availability of sulfate and organic carbon (King et al. 2000; Lambertsson and Nilsson, 2006). Concentrations of MeHg in sediments have been positively correlated to organic matter (Hammerschmidt and Fitzgerald, 2004; He et al. 2007).

1.3.2.3. Periphyton

Periphyton is a mixture of algae, cyanobacteria, heterotrophic microbes, and detritus attached to surfaces (e.g. macrophytes, sediments, suspended particulate matter) in aquatic ecosystems (Cheng et al. 2008; Hintelmann et al. 1993). Periphyton is an important food source for invertebrates and some species of fish (Cremona et al. 2009; Hecky and Hesslein, 1995; McIntyre et al. 2006). It can also adsorb and remobilize contaminants such as mercury in the water column influencing the behaviour, distribution, transport and fate of mercury in the environment (Cheng et al. 2008; Headley et al. 1998; Hintelmann et al. 1993; Wang et al. 2002). It has been shown in previous studies that biofilm can reduce Hg^{2+} to Hg^{0}, the volatile form of mercury that is released into the atmosphere (Hamelin et al. 2011). The reduction of Hg^{2+} by biofilm is favoured by a neutral pH, light, and an aerobic surrounding and the reduction capacity of periphyton is lower than “free bacteria” (Wang et al. 2002). Hg methylation in periphyton is evident as well and is mainly carried out by anaerobic bacteria such as sulphate-reducing bacteria (SRB) (Cleckner et al. 1999; Desrosiers et al. 2006; Hamelin et al. 2011; Mauro et al. 2002). In some environments methylation rates were higher in periphyton than sediments because of the higher microbial biomass (Cleckner et al. 1999; Guimarães et al. 2000). High methylation rates and MeHg concentrations in periphyton may lead to high MeHg concentrations in fish and

macroinvertebrates because periphyton is a more direct food source than sediment microbes for benthic invertebrates (Cremona et al. 2009; Hamelin et al. 2011; Hecky and Hesslein, 1995; McIntyre et al. 2006).

1.3.2.4. Benthic invertebrates

In river ecosystems, the most biologically productive habitats are the shallow littoral zones where macrophyte and macroinvertebrate densities are greatest (Cremona et al. 2008; Filion and Morin, 2000). Near shore areas in the St. Lawrence River near Cornwall have elevated concentrations of mercury in sediments. Bioaccumulation of Hg^{2+} and MeHg by benthic invertebrates such as amphipods is possible through exposure to water, suspended particulate matter, sediment, and porewater. Amphipods provide a link between contaminant loads in the surrounding environment and their introduction into the food web. Amphipods were chosen in this study because they inhabit the sediment-water interface, feed on suspended particulate matter, sediment, periphyton and detritus, are a major component of the food web, and are sensitive to contaminated sediments (Cremona et al. 2009; Lawrence and Mason, 2001). Amphipods sensitivity to sediment-bound contaminants has made them a commonly used toxicity test species for metals (DeWitt et al. 1992). These organisms tend to be resistant to the toxic effects of many contaminants and accumulate them over time, making them good biomonitors of contaminants and their potential effects on the food web (Neumann et al. 1999). The highest non-toxic tissue dose of Hg accumulation by *Hyella azteca* was 56 μg Hg g^{-1} d.w. (Borgmann et al. 1993).

1.4. Thesis Objective

This thesis develops a steady-state and dynamic mass balance model for the St. Lawrence River near Cornwall, Ontario. This model is intended to provide information on the dominant sources and sinks of Hg and to predict and hindcast Hg concentrations in air, water, sediment, porewater, periphyton, and benthic invertebrates. The fate and transport of Hg in this system will aid in focusing sampling efforts and long-term monitoring.

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Chapter 2

Steady-state mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario, Canada.

Abstract

We have developed a regional mass balance model for the St. Lawrence River near Cornwall, Ontario that describes the fate and transport of mercury in three forms, elemental, divalent, and methylated, in a five compartment environment (air, water, sediments, periphyton, and benthos). Our objective was to construct a steady-state mass balance model to determine the dominant sources and sinks of mercury in this environment. We compiled mercury concentrations, fluxes, and transformation rates from previous studies completed in this section of the river to develop the model. The inflow of mercury was the major source to this system, accounting for 0.42 mol $month^{-1}$, or 95.5% of all mercury inputs, whereas outflow was 0.28 mol $month^{-1}$, or 63.6% of all losses, and sediment deposition was 0.12 mol $month^{-1}$, or 27.3% of all losses. Uncertainty estimates were greatest for advective fluxes in surface water, porewater, periphyton, and benthic invertebrates. This model is useful for predicting mercury concentrations in other aquatic environments because it contains the three main environmental compartments (air, water and sediment), all forms of mercury, and compartments (e.g. periphyton) not included in previous mercury multi-media models.

Keywords: mass balance model, contaminants, mercury, St. Lawrence River, Cornwall

2.1. Introduction

Mercury contamination in aquatic systems is a global issue because of its threat to environmental, biological, and human health (Scherbatskoy et al. 1998). Increased environmental contamination from anthropogenic sources has reached every corner of the world (Krabbenhoft and Schuster, 2002; Ullrich et al. 2001). Mercury is a neurotoxicant that can be chemically transformed by abiotic and biotic processes and is bioaccumulated primarily in its organic methylmercury form, MeHg (Chang, 1977; Ullrich et al., 2001). Mercury contamination has become the principal cause for fish-consumption advisories throughout the world (Brigham et al., 2009; Renzoni et al., 1998).

Regional mass balance models provide a quantitative understanding of the transport and fate of a contaminant in the environment. Most regional mass balance models are developed for nonionizing organic chemicals and non-speciating metals (Brandes et al. 1996; Mackay et al. 1996; McKone, 1993). These models describe the fate and transport of a chemical but do not show chemical transformation of different species. For some environmental contaminants (e.g. mercury) this can be problematic because it is a chemically and biologically reactive metal with a significant atmospheric component, and its speciation controls its distribution and mobility in the environment (MacLeod et al. 2005).

Mass balance models of the fate and transport of multi-species chemicals in aquatic systems have been developed in the past (Cahill et al. 2003; Diamond 1999; Diamond et al. 2000; Fenner et al. 2000; Hines, 2004; Toose and Mackay, 2004). Toose and Mackay (2004) have proposed a general framework where mass balance calculations for multi-species chemicals have been derived from single-species model calculations. This approach has been utilized by other researchers to develop regional mass balance models for mercury where limited data were

available (Ethier et al. 2008; MacLeod et al. 2005). The regional mass balance model in this paper uses multi-species mass balance calculations but does not incorporate the fugacity concept because sufficient data were available on mercury dynamics in this region and therefore the 'rigorous approach' was possible (Toose and Mackay, 2004). A rigorous multispecies model requires known rate constants for all species interconversions. Hines and Brezonik (2007) and the model presented in this study are the only multispecies mercury models to use the rigorous approach because all the rate constants for hydrolysis, photolytic reactions, and bacterial processes were determined for the site in question.

The objective of this study was to construct a steady-state mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario. This area of the river is contaminated by mercury from historical local emissions and mercury contamination of fish has been a problem for decades (Ridal et al. 2010). Using the steady-state mass balance model, the dominant sources and sinks may be identified and better understood for the purpose of management and future research. The mass balance model describes total mercury (THg), elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg) in the atmosphere, water, sediment, and biota of the St. Lawrence River at Cornwall, Ontario.

2.2. Model

The steady-state model describes long-term average mercury dynamics in a generic regional environment. It consists of five compartments (air, water, sediment, periphyton, and benthos) connected by transfers and pathways for each of the three forms of mercury (Figure 2-1). Mercury transport rates and advection were determined using media concentrations and transport parameters (Table 2-1 and 2-2). The key assumption was that media concentrations of

each mercury species are uniform (well-mixed) in all compartments. This assumption remains valid when interconversions (i.e. changes between elemental, divalent, and methylated forms of mercury) are fast relative to the rate of transport in and out of a compartment and between compartments. Steady-state and dynamic mass balance models were developed using the software STELLA® (v. 9.1.4), focusing on steady-state conditions under current mercury loadings to the St. Lawrence River at Cornwall. Using the measured and estimated mercury transport rates and concentrations, rate constants were calculated and used in STELLA® to determine steady state conditions assuming first order kinetics.

An air compartment in the steady-state model was included because of the air-water interaction of mercury by the processes of air-water gas exchange and deposition. The troposphere's temperature, density, and pressure decline with increasing height. To simplify for calculating volume of this compartment, we assume uniform density at a pressure of one atmosphere reducing the height to approximately 6 km (Mackay, 2001).

The river water was assumed to be a well-mixed compartment for simplicity. Processes included in the water compartment are air-water gas exchange, advection, sediment deposition, diffusion, and resuspension, adsorption and desorption by periphyton, and uptake and efflux by benthos. The closure of local industries that historically emitted mercury into the river allowed us to assume that local industries are not a source of mercury.

Similarly, the surface sediment was assumed to be a single well-mixed layer of defined depth (1 cm). A defined depth of 1 cm was used because sediment Hg concentrations and diffusion fluxes were reported for only the sediment-water interface (Delongchamp et al. 2010). The river near Cornwall is characterized by a high spatial heterogeneity in sediment type,

composition, and mercury concentrations (Biberhofer and Rukavina, 2002; Delongchamp et al. 2010). Processes influencing surface sediment concentrations considered here are sediment deposition, resuspension, diffusion, ebullition, and sediment burial. Additional fluxes of bioturbation and bioirrigation that may affect the extent of exchange across the sediment-water interface were not included in the model (Aller and Aller, 1998; Lopez 2004).

Mercury partitioning and dynamics in periphyton and benthos were included as two compartments in the regional mass balance model. Recent research shows evidence of mercury adsorption to the surface of periphyton and the potential availability of MeHg to aquatic biota (Cheng et al., 2008). This area of the St. Lawrence River contains sediment mercury concentrations from historical point source discharges (Delongchamp et al., 2009). Periphyton associated to sediment or macrophytes may experience high exposure in mercury contaminated areas because they have the ability to adsorb inorganic and organic mercury (Hintelmann et al. 1993). Once mercury has been adsorbed by periphyton, it may be demethylated / reduced or desorbed (Hintelmann et al., 1993).

Elevated mercury concentrations have been found in fish species such as yellow perch in the AOC (Fowlie et al., 2008). Yellow perch sustain important recreational and commercial fisheries and their high mercury contamination poses a risk to fish consumers (Ion et al. 1997). Mercury concentrations in amphipods were found to correlate to mercury in yellow perch in the St. Lawrence River at Cornwall (Zone 1 and 2) (Fowlie et al., 2008). Potential mercury exposure pathways to amphipods include sediments, overlying water, porewater, and other particles and provide a link between environmental media and the food web (Lawrence and Mason 2001; Williams et al., 2010).

2.3. Materials and Methods

2.3.1. *Site description*

The St. Lawrence River at Cornwall Ontario was designated an Area of Concern (AOC) in 1987 by the International Joint Commission (IJC) because of several environmental concerns including mercury contamination (Delongchamp et al., 2009). The St. Lawrence River (Cornwall) AOC is approximately 80km long and spans from the Moses-Saunders power dam to the eastern outlet of Lake St. Francois in Quebec (Delongchamp et al., 2010). This study is focused on the Cornwall waterfront of the North Channel where three zones of high mercury contamination occur due to industrial emissions (Figure 2-2). Zone 1, the westernmost location of the study site, is located closest to a pulp and paper mill (Domtar) (closed in 2006) and a chloro-alkali plant (ICI) (closed in 1995). Zone 2, the easternmost location, is located closest to a textile mill (Courtalds) (closed in 1992) and Zone 3 is located in the middle of the study area and the other two zones. Mean surface sediment concentrations of THg for Zones 1, 2, and 3 are 625 ng g^{-1}, 566 ng g^{-1}, and 811 ng g^{-1} respectively, and are not significantly different among sites (Delongchamp *et al*., 2010). Prior to the closure of the local industries, sediments recorded much higher THg concentrations, with maximum concentrations ranging between 16,000 and 34,000 ng g^{-1} (Delongchamp et al. 2009). This shallow section of the river (mean depth of 8 m) is characterized by an average but constant water discharge flow of 93,294,000 m^3 $month^{-1}$, pH range of 8.4 to 8.6, and an average dissolved organic carbon concentration of 2.5 mg/L (Table 2-1 and 2-3).

Comparison among and between sites showed that depositional conditions have been relatively uniform among the three sites (Rukavina 2000). No significant differences occur in

THg concentrations among sites (Delongchamp et al. 2009). Nettleton (2004) used a "Surface Water Modelling System" to estimate dynamic river hydrodynamics for the North and South Channels of the St. Lawrence River and showed that Zones 1, 2, and 3 had similar water depths and river velocities, even with changing flow-rates (minimum, average, and maximum flow rates). Bed shear stress in each zone was low (<1 N m^{-2}), which is typical of sediment deposition areas. Since 1956, reduction of the range of water level was required by the Moses-Saunders Power Dam to maintain consistent river flows, adequate navigation depths, and protect downstream habitat (International St. Lawrence River Board of Control, 2009). Due to the similarity in sediment composition, type, Hg distributions, and hydrology, the three zones were combined as a regional box model.

A region-specific model was selected to optimize complexity and reliability. The available information from previous studies on mercury loadings and the current understanding of mercury kinetics in the St. Lawrence River near Cornwall favoured a single-region model. This regional model served also to expand our background information on intermedia transport, advective fluxes and environmental conditions within the system. Previous research on interspecies conversions (e.g. bacterial methylation / demethylation) allowed the model to incorporate these critical processes to the mercury cycle. We also performed uncertainty and sensitivity analyses to determine the most variable and/or uncertain parameters. As more research is conducted, the initial model can be refined to improve accuracy and precision of Hg concentration and flux estimates. Furthermore, this steady-state model is useful for future research and monitoring projects.

2.3.2. *Mass balance fluxes*

Air-water gas exchange – Poissant et al. (2000) estimated mercury flux in the St. Lawrence River across the water surface using a two-layer model (Liss and Slater, 1974). Flux (F_m) is calculated by:

$$F_m = K_{ol}(C_w - C_a RT/H)$$

where H is the Henry's Law constant (Pa•m^3 mol^{-1}), C_a (ng m^{-3}) is the Hg^0 in air concentration (TGM), C_w (ng m^{-3}) is the Hg^0 concentration in water (DGM), and K_{ol} is the overall mass transfer coefficient adjusted for wind-speed (m month^{-1}) (Table 2-1 and 2-2). Poissant et al. (2000) measured TGM concentrations, DGM concentrations, and K_{ol} (expressed as K_w) values near Cornwall and found median values of 1.76 ng m^{-3} (1.51 – 1.99 ng m^{-3}), 31 pg L^{-1}, and 9.21 cm h^{-1} (0.02 – 9.28 cm h^{-1}), respectively. R is the ideal gas law constant (Pa•m^3 mol•K^{-1}), and T is the temperature of the surface water (K) (Table 2-1). Henry's Law constant was temperature-corrected with

$$H' = 0.0074\ T' + 0.1551$$

(dimensionless unit) (Sanemasa, 1975) which was converted to H

$$H = H'\ RT$$

Atmospheric deposition – Wet deposition of mercury has been monitored by the National Atmospheric Deposition Program (NADP) (2007) in St. Anicet (25 km northeast from the study area) since 1998. A summer average deposition rate was calculated from the year 2007 (Table 2-2). Poissant et al. (2004) measured dry deposition of mercury in the Baie St. François, downstream of the study site, which was used in this model (Table 2-2). MeHg wet deposition has not been monitored in St. Anicet but at site MN16 (closest to study area) for the year of 2003 (Table 2) (Hines and Brezonik, 2007). The dry deposition of MeHg was assumed to be zero

based on two studies which measured net throughfall of MeHg (Lee et al. 2000; St. Louis et al. 2001).

Atmospheric advection in and out – Using a long-term average wind speed of 1.1 m s^{-1} multiplied by atmospheric height and region width, the estimated inflow (m^3 $month^{-1}$) into the study area was determined. The inflow of air was multiplied by the median (mean not available) mercury concentration measured by Poissant et al. (2000) at Station 66 (Cornwall waterfront) aboard the Canadian Coast Guard Ship CCGS Limnos. Although only total gaseous mercury (TGM) in air has been measured at the Cornwall waterfront, Poissant et al. (2004) looked at atmospheric mercury speciation in the Bay St. François wetlands (located downstream of the study region) and found that of the TGM concentration measured, >98% was gaseous elemental mercury (Hg^0) and <1% was particulate mercury and reactive gaseous mercury. This allowed derivation of atmospheric mercury advection flux values for each species of mercury in the model.

Water advection in and out – River inflow (advection in) and outflow (advection out) were determined using the estimated inflow into Zone 1 (m^3 $month^{-1}$) multiplied by the average mercury concentration (ng m^{-3}) for Zone 1 (inflow) or Zone 1, 2, and 3 (outflow), respectively (Table 2-2 and 2-3). Although the estimated inflow for each zone is different, the inflow equals the outflow in the model to maintain steady-state conditions and decrease uncertainty for this parameter. Furthermore, a constant river flow was used because, since 1956, reduction of the range of water level was required by the Moses-Saunders Power Dam to maintain consistent river flows, adequate navigation depths and protect downstream habitat (International St. Lawrence River Board of Control, 2009). Environment Canada has measured water levels close

to the Moses-Saunders Power Dam daily since 1985 and constant water levels were apparent throughout the summer months in all years.

Sediment deposition – Ridal et al. (2010) measured mercury concentrations in surface water in Zones 1, 2, and 3 and found that 80% and 20% of THg were dissolved and particulate mercury, respectively. Delongchamp et al. (2010) measured sediment mercury concentrations (Table 3) and sedimentation rates in the depositional areas of Zones 1-3. The sediment deposition rate was calculated by multiplying the particulate mercury concentration in water (ng L^{-1}) (Table 2-2) and the sedimentation rate (mol m^{-2} $month^{-1}$). For Zones 1, 2 and 3 the depositional areas only consisted of 13.4%, 17.3%, and 3.3% of the total area, respectively (Biberhofer and Rukavina, 2002). The sediment deposition rate and other sediment fluxes (diffusion, resuspension, and burial) were adjusted to encompass only the sediment depositional areas to prevent overestimation.

Sediment diffusion – Delongchamp et al. (2010) also estimated mercury diffusion rates from sediments in the depositional areas of each zone using the following equation from Fick's first law:

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

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. We used a D_w value for inorganic mercury in water of 9.5×10^{-6} cm^2 s^{-1}, and D_w for MeHg in water was 1.3×10^{-5} cm^2 s^{-1} based on Gill et al. (1999). Tortuosity was calculated using the empirical relationship of Boudreau (1996)

$$\theta = 1 - \ln(\Phi^2)$$

and porosity was determined by

$$\Phi = 1 - (\text{bulk density} / \text{particle density})$$

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

Ebullition – The bubbling of elemental mercury at the sediment-water interface was measured by Poissant et al. (2007) using cone-shaped gas collectors suspended in the water column in Zones 1 and 2 for 7 days. The flux of total gaseous mercury (TGM) from sediments was calculated as follows:

$$F(x) = (x \bullet V) / (t \bullet S)$$

where x is the trace gas concentration (ng m^{-3} for TGM) (Table 2-2), V is the total volume of the gas collected (m^3), t is the time interval between deployment of the gas collector (h) and S is the surface of the gas collector (m^2).

Sediment resuspension – The resuspension flux was estimated by multiplying the average mercury concentration in surface sediments (0 – 1 cm) (mol m^{-3}) and the resuspension rate (m^3 $month^{-1}$) (Table 2-1 and 2-2).

Sediment burial – Once sediment particles have been deposited they may be resuspended back into the water column or become buried in the sediment layer. The burial flux was determined by multiplying the surface sediment concentration by the sedimentation rate. Delongchamp et al. (2009) measured accumulation rates from ^{210}Pb dating of 9 sediment cores sampled from Zones 1, 2, and 3.

Photochemical – Amyot et al. (2000) measured oxidation of Hg^0 in the water column of St. Lawrence River and found that Hg^0 levels decreased via oxidation at a first-order rate constant of 0.09 h^{-1}. Photooxidation is only significant in the presence of halogens which are

more concentrated in the lower portion and Gulf of the St. Lawrence River. Photoreduction was also evident in the field experiments but the production of Hg^0 is limited by the amount of photoreducible mercury. Laboratory studies showed that unfiltered river water samples spiked with Hg^{2+} and exposed to UV radiation gave a first-order rate constant for photoreduction ranging from 1.7 to 1.9 h^{-1} (Amyot et al. 2000). Photooxidation and photoreduction are assumed to only occur in the photic zone, although the water was not subdivided to incorporate this compartment. The purpose of defining the photic zone was to determine the volume of water where photochemical processes would occur. Accordingly, a photic zone of 1 m was used for the St. Lawrence River, representing the depth of 90% attenuation of UV-A radiation (O'Driscoll et al. 2007). The low attenuation rate of UV-A radiation in the St. Lawrence River are likely because of low concentrations of dissolved organic carbon and total suspended solids (see Table 2-3) which are the principal attenuators of solar radiation in most freshwaters (O'Driscoll et al. 2007). These first-order rate constants and the concentrations of inorganic and elemental mercury in the water column corrected for photic zone volume (Table 2-1 and 2-2) were multiplied to calculate net photoreduction.

Abiotic mercury methylation – Abiotic mercury methylation was assumed to be negligible and not included in the mass balance model (Celo *et al*. 2006).

Methylation and demethylation – Methylation and demethylation by bacteria was assumed to occur in the water column during the summer months because of the changing redox conditions at the sediment-water interface (Eckley and Hintelmann, 2006). A "sharp" redox boundary does exist at the sediment-water interface during the summertime providing anoxic conditions for bacteria in the sediments and water column (Avramescu *et al*., 2010).

Furthermore, it was assumed that the available form of mercury to methylation/demethylation is in continual supply because the system is advection dominated.

Potential methylation (K_m = 0.015 d^{-1}) and demethylation (K_d = 1.4 d^{-1}) rate constants have been measured for sediments sampled in the St. Lawrence River near Cornwall (Zone 1) (Avramescu et al. 2010). Microcosms not spiked with mercury isotopes ($^{200}Hg^{2+}$ and $MM^{199}Hg^{+}$) had no detectable levels of methylation or demethylation and therefore Hg spiked control treatment (T1; no inhibitors added) values were used. To determine the rate of methylation and demethylation, K_m or K_d was multiplied by the concentration of inorganic mercury or methyl mercury in the water (Table 2-2), respectively.

Sediment reduction – To explain the production and concentration of Hg^0 in the sediments, sediment reduction of Hg^{2+} was added. Since no rate constant or flux value was available from the literature, a rough estimate of the rate constant was estimated based on the concentration of Hg^0 and Hg^{2+} in sediments at steady-state.

Periphyton adsorption and desorption – To estimate mercury adsorption for periphyton it was assumed that mercury in periphyton and water are at steady-state, thus $C_{biofilm} / C_{water} = K_{adsorption} / K_{desorption}$. Assuming an adsorption half-life of ten minutes, we estimated an adsorption rate constant (k_1) of 3066 $month^{-1}$ (Quigg et al. 2006). From the calculated partition coefficient (Table 2-4) and adsorption rate constant, a desorption rate constant (k_2) was estimated to be 5.94 x 10^{-3} $month^{-1}$ for THg, 4.48 x 10^{-3} $month^{-1}$ for Hg^{2+}, and 0.019 $month^{-1}$ for MeHg. Periphyton adsorption rates were calculated by:

$$\text{adsorption rate} = C_w * V_b * k_1$$

where C_w is the mercury concentration in surface water (mol m^{-3}) (Table 2-2) and V_b is the volume of periphyton (m^3). Periphyton desorption rates were determined by:

$$\text{desorption rate} = C_b * V_b * k_2$$

where C_b is the mercury concentration in periphyton (mol m^{-3}) (Table 2-2).

To calculate the volume of periphyton located on macrophytes we first calculated macrophyte density where the mean weight of a plant is 0.2 g and the abundance is 760 plants m^{-2} (Duarte and Kalff, 1990). Secondly, it was found that the average macrophyte biomass was 0.06 m^2 g^{-1} (Armstrong et al. 2003). From these we calculated the area of macrophytes (m^2) per area of sediment (m^2) to be 9.12. Ridal et al. (2007) found that only 32% of the sediment bottom area (*SA*) was covered by macrophytes and it was assumed that the depth of periphyton was 1 mm (Bakke and Olsson, 1986). Therefore, volume of periphyton was calculated as follows:

$$V_b = 9.12 \text{ m}^2 \text{ macrophyte m}^{-2} \text{ sediment} * 0.32 * SA * 1 \text{ mm}$$

Amphipod uptake and efflux – It was assumed that mercury in amphipods and water are at steady-state, thus $C_{amphipod} / C_{water} = K_u / K_{ew}$. Assuming an adsorption half-life of ten minutes, we estimated an uptake rate constant (k_u) of 3066 $month^{-1}$ (Blust et al. 1987). From the calculated bioconcentration factor (BCF) and adsorption rate constant, a desorption rate constant (k_{ew}) was estimated to be 3.23 $month^{-1}$ for THg, 3.48 $month^{-1}$ for Hg^{2+}, and 0.55 $month^{-1}$ for MeHg.. Aqueous uptake rate was determined by:

$$\text{aqueous uptake rate} = C_w * V_a * K_u$$

where C_w is the concentration of mercury in water (ng m^{-3}) (Table 2-2), V_a is the volume of amphipods (Table 1). Amphipod aqueous efflux rate was determined by:

$$\text{amphipod efflux} = C_{amp} * V_a * K_{ew}$$

where C_{amp} is the mercury concentration in amphipods (Table 2). The V_a was estimated for this section of the river by first multiplying the mean weight of an amphipod (4×10^{-3} g) (Amyot et al. 1996) and the abundance (240 amphipods m^{-2}) (Razavi 2008). Secondly, it was found that the average amphipod biomass was 1.07 m^2 g^{-1} (Wang and Zauke 2002). From these we calculated the area of amphipods (m^2) per area of sediment (m^2) to be 1.03. It was assumed that the depth of amphipods was 12 mm (Amyot et al. 1996). Therefore, volume of amphipods was calculated as follows:

$$Va = 1.03 \text{ m}^2 \text{ amphipods m}^{-2} \text{ sediment} * SA * 0.012 \text{ m}$$

2.3.3. *Partition coefficients for mercury species*

Dimensionless partition coefficients (K_d) were calculated primarily from data collected in the study site (Table 2-4). When regional data were unavailable, values were obtained from the literature. No regional data were available for the Hg^0 K_d for suspended solids / water, sediment solids / water, biofilm / water, and amphipod / water so these values were obtained from Mackay (2001). Therefore, the model closely represents partitioning and speciation of mercury in this system.

2.3.4. *Model uncertainty and sensitivity analyses*

Model uncertainty analysis was conducted by the propagation of error analysis proposed by Hoff (1994). Error terms were calculated for each flux ($\varepsilon_x = \sigma/\langle x \rangle$, where σ is the standard

deviation of variable x and $\langle x \rangle$ is the mean value of x) and used in the mass balance calculations to derive uncertainties for loading and loss terms. Uncertainty analyses can provide information of variability on current parameter values and guide future research.

Sensitivity analysis was determined for the mass balance by one standard deviation increase and decrease of inputs (±SD) (Hamby, 1995). The sensitivity analysis is useful for showing which parameters are the most influential on model results and which parameters require more research (Hamby, 1995). The type of sensitivity analysis used in this study takes into account the parameter's variability and associated influence on the model output (Hamby, 1995).

2.4. Results

2.4.1. *Species-specific mass balances for mercury*

The steady-state mass balance model for Hg^0 shows that the dominant loading is river inflow (87.5%) and the dominant loss is evasion (70.2%) (Figure 2-3). The mass balance indicates that Hg^{2+} is being reduced to Hg^0 through photochemical (Amyot et al. 1994) or biological processes (Mason et al. 1995), which are more active in the summer (Amyot et al. 2000). Photoreduction was estimated at 0.015 mol $month^{-1}$ and photooxidation at 0.011 mol $month^{-1}$. Evasion of Hg^0 to the atmosphere is occurring due to high overall mass transfer coefficient and supersaturation of Hg^0 the water column relative to its partial pressure in air (Poissant et al., 2000).

Similarly to Hg^0, the dominant source of Hg^{2+} to the St. Lawrence River AOC is river inflow (90.8%) (Figure 2-3). Once inorganic mercury enters the study area, losses are primarily

by advection out (65.9%) and secondarily by sediment deposition (28.2%). The low flow conditions of these shallow embayments result in depositional zones for sediments (Biberhofer and Rukavina, 2002; Delongchamp et al. 2009; Nettleton, 2004; Ridal et al. 2010). Sediment resuspension and diffusion fluxes are low when compared to deposition to sediments, resulting in low amounts of mercury being released from sediment to the water. Atmospheric deposition of Hg^{2+} is a very small portion of the total loadings to the AOC compared to others regions (e.g. Brigham et al. 2009; Rood et al. 1995; Sorensen et al. 1990). Sediment contains the bulk of the regional inventory of Hg^{2+}.

MeHg is of concern in aquatic ecosystems because of the tendency to bioaccumulate in the food web. The AOC mass balance model indicates that a small net production of MeHg occurs in sediments (Figure 2-3). MeHg production in sediments is typically mediated by microbes and mostly occurs under anoxic conditions; microbial key players involved in mercury methylation in sediments are sulphate reducing bacteria and methanogenic archaea (Benoit et al. 1999; Delongchamp et al. 2009; Ranchou-Peyruse et al. 2009). Both aerobic and anaerobic environments can support methylmercury demethylation which can occur via oxidative or reductive pathways, as determined by the nature of the final carbon product of the demethylation reaction (*i.e.,* CO_2 or CH_4) (MacLeod et al. 2005). The methylation rate in sediment calculated by Avramescu et al. (2011) was valued at 1.46×10^{-4} mol $month^{-1}$. But the demethylation rate (1.46×10^{-4} mol $month^{-1}$) was similar to the methylation rate, supporting a role for both oxidative and reductive demethylation pathways in this system. Both methylation and demethylation rates are very fast but the net production of MeHg generally occurs at a constant level that rarely exceeds 1 to 1.5% of THg in sediments (Avramescu et al. 2011; Eckley et al. 2005; Eckley and Hintelmann, 2006; Hintelmann et al. 2000; Hintelmann and Ogrinc, 2003). Amphipods contain a

larger portion of MeHg inventory from aqueous uptake pathways. High mercury uptake from sources such as biofilm could partially explain amphipod body burden and future addition of this uptake pathway to the model is recommended.

The dominant source and sink for THg is advection in and out in the water column. THg from advection in is not balanced by advection out of THg because sediment accumulation is another dominant sink of THg mercury. Sediment resuspension and diffusion fluxes are low, meaning that sediments are a net sink for total mercury. The mass balance for THg is determined mostly by the dynamics of Hg^{2+}, the most prevalent form of mercury in all compartments except the air.

2.4.2. *Uncertainty and sensitivity analyses*

Error terms were calculated for each flux ($\varepsilon_x = \sigma/\langle x \rangle$, where σ is the standard deviation of variable x and $\langle x \rangle$ is the mean value of x) (Table 2-5). These ε values were greatest for advection in air, diffusion, periphyton desorption, and amphipod efflux because these fluxes are dependent on sensitive parameters (e.g. mercury concentrations in surface water, porewater, periphyton, and amphipods) (Table 2-5). This system was clearly advection dominated, with water flows being the primary transfers of mercury into and out of the system. The sediments are a net sink for Hg and contribution to sediment variance does occur from fluxes such as diffusion and accumulation. Future research may reduce uncertainty in sensitive parameters by producing more precise flux values. In the model, all compartments and major fluxes have been well defined in the steady-state model.

2.5. Discussion

This steady-state mass balance model provides an overall description of the sources and sinks of mercury in the St. Lawrence River near Cornwall. The model identified the dominant loadings and losses of mercury in this system and a better understanding of the dynamics of mercury was achieved. Error estimates were higher for advection parameters but continued monitoring of Hg concentrations in water would reduce these high uncertainties. The ability of the model to provide information on driving parameters and fluxes in the study area is important for management purposes. The quality and quantity of data available for the St. Lawrence River AOC was useful for model development and insight into future opportunities of research to improve the model. For example, this may involve reducing uncertainty on parameters (e.g. concentrations in various media) that could result in more accurate loadings.

The development of the steady-state model benefited greatly from a large and spatially extensive data set on environmental conditions and mercury loadings, concentrations, and transformations. With this information the study area was well defined, reducing variability in model results. Studies on sediment, water, and atmospheric dynamics spanned all mercury contaminated zones of the Cornwall waterfront providing more accurate estimates of air-water gas exchange, advection, sediment deposition, sediment diffusion, sediment resuspension, and sediment burial. Furthermore, the heterogeneous conditions of this section of the St. Lawrence River simplified modelling of an otherwise complex and dynamic system.

The hydraulic conditions of the river resulted in a relatively low water retention time indicating the importance of advective flows in removing mercury from the system. Upstream and *in-situ* production of mercury species assessed is the most likely source in this environment

because of lower value sources from atmospheric deposition, sediment resuspension, and sediment diffusion. Another potential source of mercury that was not included in the mass balance model was outflow from the former Cornwall canal system to the system and episodic inputs from combined sewer and storm sewer outflows which have been found to contain elevated concentrations of THg (Ridal et al. 2010). Samples taken from these outflows were twice as high as upstream canal samples indicating that the canal is a potential source of mercury to the contaminated zones (Ridal et al. 2010). Stable mercury isotope research and a better characterization of fractionation of Hg stable isotopes could provide additional insight into determining whether these outflows are a source of mercury to the AOC. Similar to previous studies, mercury isotopes could be used to confirm historical sources of contamination and current loadings to the study area (Feng et al. 2010; Foucher and Hintelmann, 2006; Foucher et al. 2009; Gehrke et al. 2009; Jackson and Muir, 2004; Jackson et al. 2008). Losses of mercury in the system are mainly advection out, sediment accumulation, and volatilization to the atmosphere. Reductions in mercury sources to the water column from upstream, photochemical processes, and biological processes may alleviate further contamination and exposure to biota in the AOC.

2.6. Conclusions

The fate of THg in the Cornwall AOC is dominated by Hg^{2+} which comprises most of the mercury in this system. Although the transport of mercury is advection dominated, sediments retain a large portion (27%) through burial. Reduction of Hg^{2+} to Hg^{0}, which volatilizes, is an important loss of mercury to the atmosphere, having an equivalent effect of reducing THg concentrations in water by approximately 0.12 ng L^{-1}. Sediment resuspension and diffusion fluxes were low compared to Hg accumulation rates in sediments, so sediments were a net sink

for mercury. Exposure of mercury to biota in the ecosystem is driven by trophic positioning in the St. Lawrence (Choy et al. 2008; Fowlie et al. 2008); Hg^{2+} and MeHg accumulation by biofilm and other autochtonous pathways provides an important entry point for Hg to the foodweb (Avramescu et al. 2011; Delongchamp et al. 2010).

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2.8. Figures

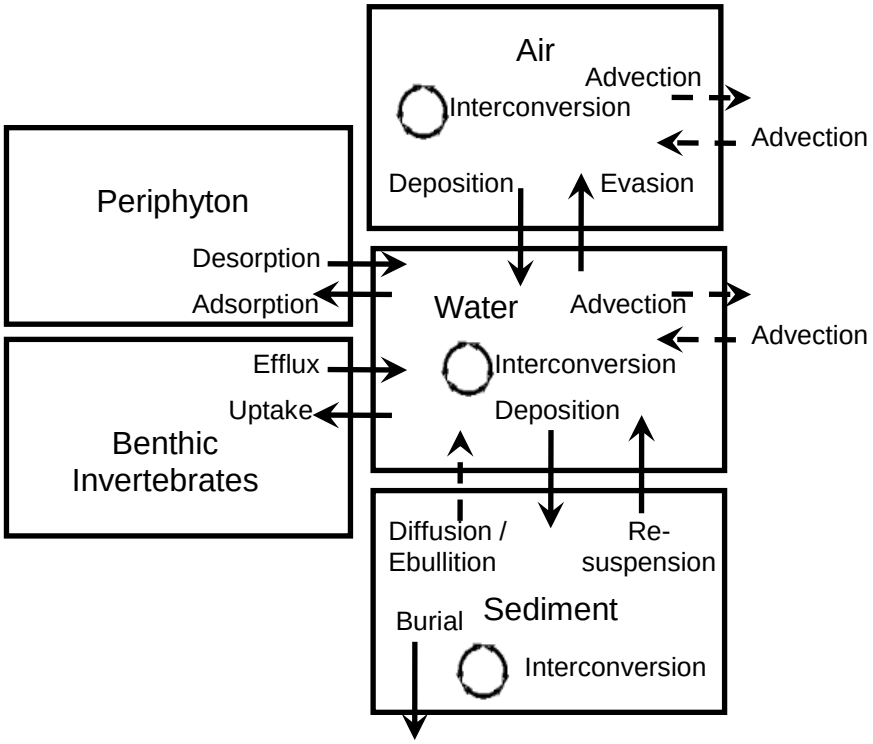

Figure 2-1. Generic multimedia model environment for the different mercury species groups. Arrows represent transfer and transformation processes described in the model.

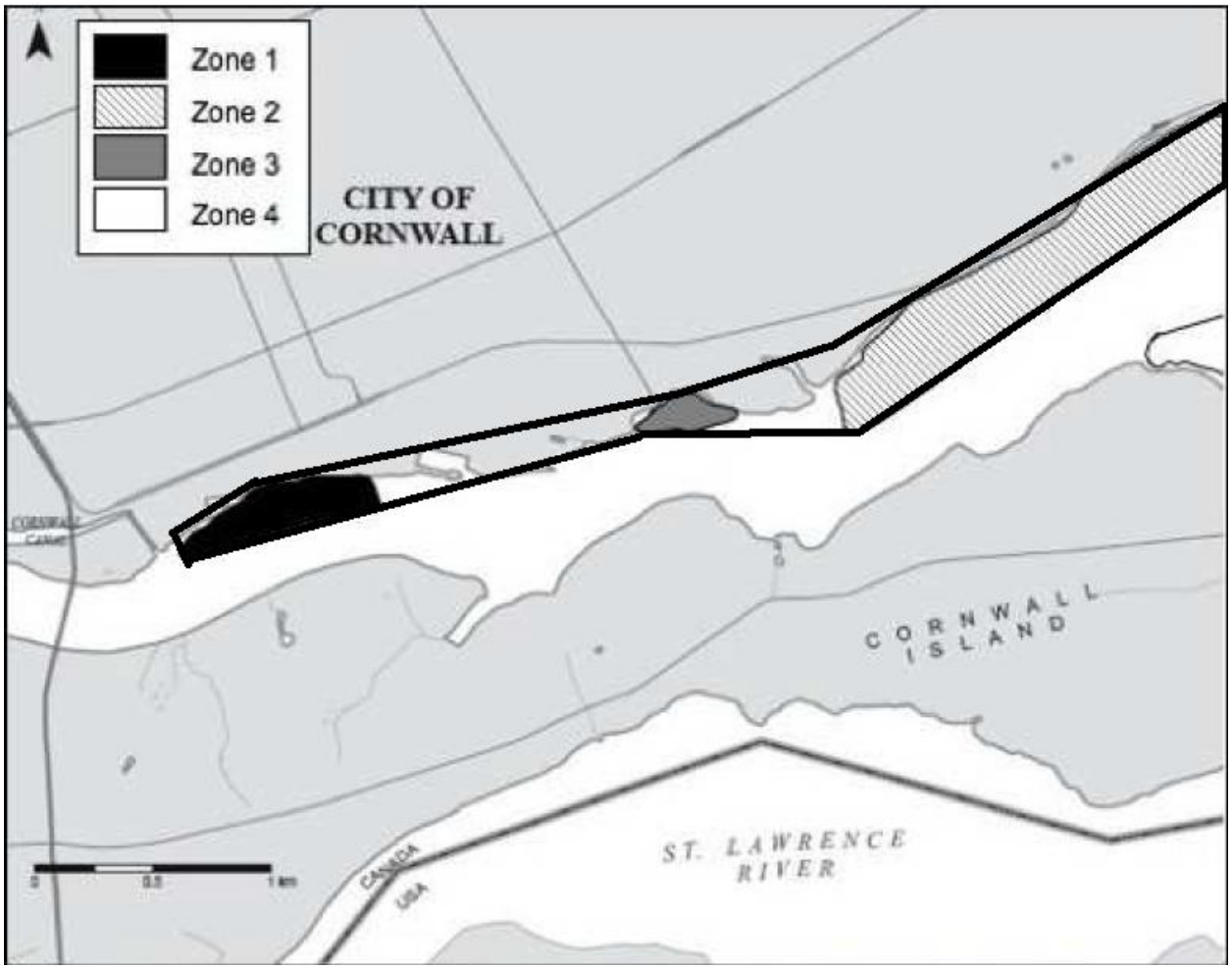

Figure 2-2. Map of regional model area (solid black line) in the St. Lawrence River, Cornwall Area of Concern (AOC) (modified from Razavi 2008).

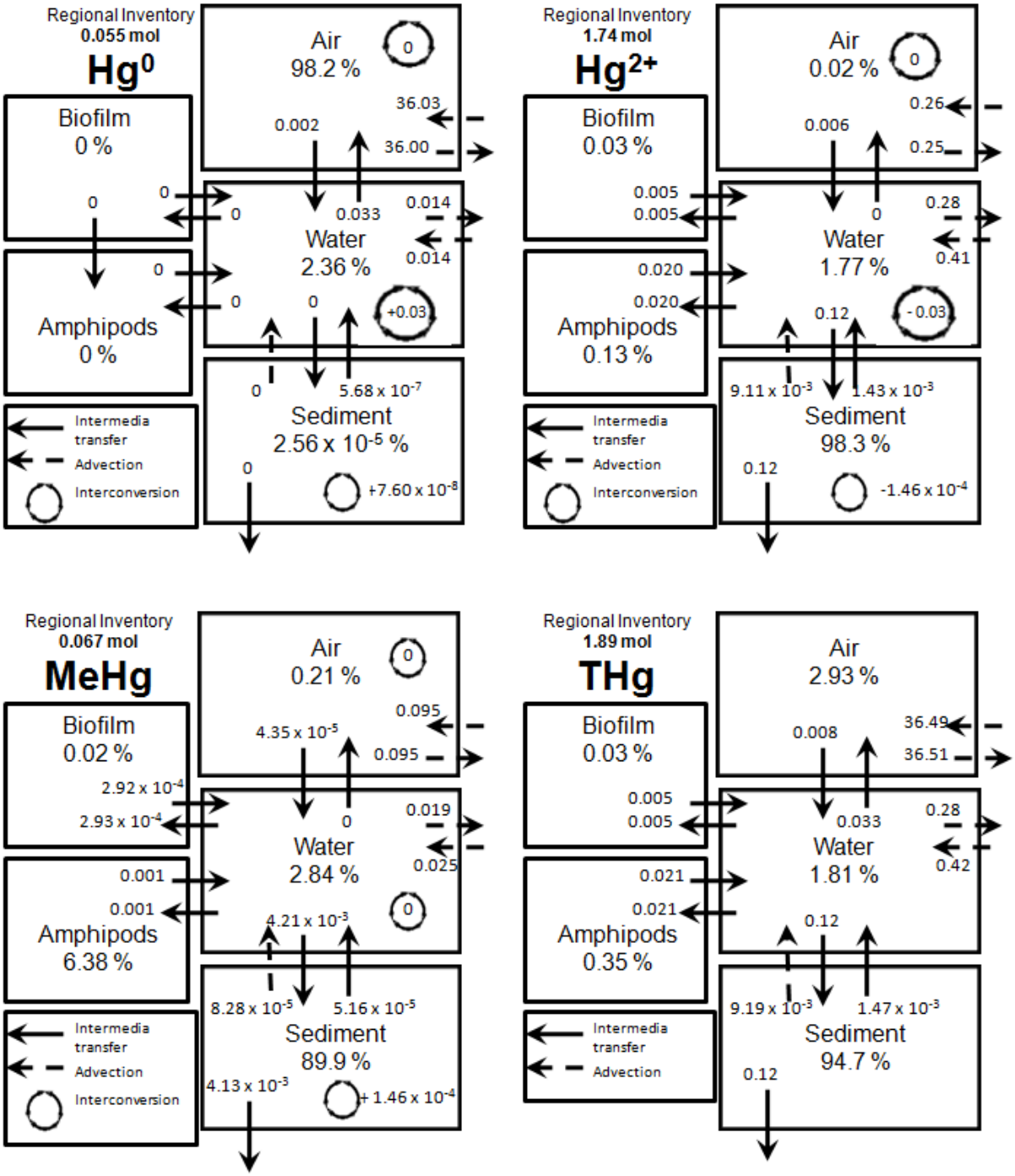

Figure 2-3. Fluxes (mol month^{-1}) of elemental mercury (Hg^0), divalent mercury species (Hg^{2+}), methyl mercury species (MeHg) and total mercury (THg) in the St. Lawrence River AOC. Percentages are the quantity of mercury in each media in proportion to the total quantity for each mercury species.

2.9. Tables

Table 2-2. Regional environmental properties (standard deviation) for the St. Lawrence River at Cornwall.

parameter name	mean value	ref
Dimensions		
region area (m^2)	1045537	Biberhofer and Rukavina 2002
air compartment height (m)	6000	Mackay 2001
water depth (m)	8.03 (1.7)	Ridal et al. 2010
sediment depth (m)	0.01	Delongchamp et al. 2010
biofilm depth (m)	0.001	Bakke and Olsson, 1986
amphipod depth (m)	0.012	Amyot et al. 1996
Volume Fractions for Subcompartments		
biofilm in water	409	Duarte and Kalff 1990; Armstrong et al. 2003; Ridal et al. 2007
amphipods in water and sediment	1731	Razavi 2008; Amyot et al. 1996; Wang and Zauke 2002
Temperature Conditions		
water temperature (^0C)	20.7 (2.9)	Ontario Power Generation 2011
Residence Times (months)		
air	0.002	*a*
water	0.09	Biberhofer and Rukavina 2002; Ridal et al. 2010; Nettleton, 2004
Discharge (m^3/month)		
river inflow	93294000	Nettleton, 2004
Transport Parameters (m/month)		
air-water MTC	67.2	Poissant et al. 2000
rain rate	0.0002	Environment Canada 2009
aerosol deposition	55188	Poissant et al. 2004
sediment resuspension	8.33×10^{-4}	Mackay 2001

[a] Estimated based on an assumed 1.1 m/s long-term average wind speed (Poissant et al. 2004).

Table 2-2. Reported mercury concentrations ± SD (if n>2) (minimum and maximum) and fluxes in the St. Lawrence River, Cornwall, ON. Median values provided in bold since mean values were unavailable. n=number of samples.

Media	n	Total Hg	n	Hg^0	n	Hg^{2+}	n	MeHg	ref
air (ng/m^3)	323	**1.76 (1.51 - 1.99)**		**1.74**[a]		**0.013**[a]		**0.005**[a]	O'Driscoll et al. 2007; Poissant et al. 2000
water (ng/L)	101	0.813 ± 0.496 (0.16 - 3.07)	633	**0.031 ± 0.001**	101	0.736 ± 0.514 (0.108 - 2.98)	101	0.047 ± 0.035 (0.007 - 0.173)	Ridal et al. 2010; O'Driscoll et al. 2007; Poissant et al. 2000
sediment (ng/g)	16	640 ± 248.1 (405.7 - 1217.1)	2	0.002 [b]	16	618 ± 250 (390.6 - 1207.5)	12	22.2 ± 13.6 (9.41 - 45.5)	Fathi, 2009; Delongchamp et al. 2010; Poissant et al. 2007
porewater (ng/L)	47	80.5 ± 73.6 (7.03 - 198.5)			20	64.2 ± 76.7 (2.83 - 191)	24	12.0 ± 15.4 (2.54 - 52.2)	Delongchamp et al. 2010; Razavi, 2008
biofilm (ng/g)	20	419.9 ± 312.9 (137.6 - 1165.8)			20	412.4 ± 312.0 (125.3 - 1158.6)	20	7.63 ± 4.02 (3.83 - 16.5)	Eveno 2010
amphipods (ng/g)	40	192.4 ± 144.8 (60.2 - 596.1)			25	161.99 ± 155.3 (21.1 - 492.1)	25	65.4 ± 27.0 (27.6 - 146.9)	Razavi 2008
wet depositional flux to water (µg/m^2/month)	28	0.70					1	0.008	NADP 2007; Hines and Brezonik, 2007
dry depositional flux to water (µg/m^2/month)	194	0.29						0	Poissant et al. 2004; Lee et al. 2000; St. Louis et al. 2001

[a]Hg^0 represents >98% of THg and Hg^{2+} and MeHg contribute <1% of THg in air (Poissant et al. 2004).

[b]Concentration in ng/m^3.

Table 2-3. St. Lawrence River water chemistry conditions at Cornwall Area of Concern, adapted from Razavi (2008).

Parameter	Value	ref
pH	8.4 - 8.6	1
Biological oxygen demand (mg O^2/L)	<2	1
Specific conductivity (µS/cm)	293 - 296	1
Dissolved oxygen (mg O^2/L)	8.5 - 9.7	1
Alkalinity (mg/L)	87.1 - 89.5	2
Total Kjeldahl nitrogen (mg/L)	0.187 - 0.265	3
Total phosphorus (mg/L)	0.012 - 0.0618	3
Total suspended solids (mg/L)	0.73	1
Suspended particulate matter (mg/L)	1.0 ± 0.6	4
Dissolved organic carbon (mg/L)	2.5 ± 0.5	4
Particulate organic carbon (mg/g)	295 ± 262	4
Dissolved iron (µM)	0.07 ± 0.04	4
Particulate iron (mmmol/g)	0.64 ± 0.09	4
Dissolved manganese (nM)	28 ± 12	4
Particulate manganese (µmol/g)	18.9 ± 7.5	4

1 Pers.comm J. Ridal, St. Lawrence River Institute of Environmental Sciences; sampling mid summer 2005.
2 (Grapentine et al., 2003); sampling October 2001.
3 (vanHerpen, 2006); sampling mid summer 2005.
4 (Quemarais et al., 1998); sampling in Spring and October 1995-96.

Table 2-4. Dimensionless partition coefficients (K) for mercury in the St. Lawrence River, Cornwall.

property	Hg^0	Hg^{2+}	MeHg
molecular weight (g/mol)	200.59	200.59	200.59
K air/water	0.32[a]	0	0
K suspended solids/water	30000[b]	1229160[c]	
K sediment solids/water	20000[b]	806555[c,d]	473908[c,d]
K sediment solids/pore water		59867[d]	7701[d]
K biofilm/water	1[b]	538191[c,e]	163008[c,e]
K amphipod/water	1[b]	165866[c,f]	1397265[c,f]

[a] Poissant *et al*., 2000. [b] Mackay *et al*., 1995. [c] Ridal *et al*. 2010. [d] Delongchamp *et al*. 2010. [e] Eveno 2010. [f] Razavi 2008.

Table 2-5. Fluxes and uncertainty and sensitivity analyses for mercury in the St. Lawrence River near Cornwall. Positive flux values represent inputs, and negative flux values represent losses.

Source	Loading (mol/month)	Error ε	Sensitivity (+1 SD)	Sensitivity (-1 SD)
THg				
Air inflow	36.49	0.73	63.04	9.94
Air outflow	36.51	0.73	63.08	9.94
River inflow	0.42	0.69	0.72	0.13
River outflow	-0.28	0.48	0.36	0.13
Gas absorption	0.002	N/A	N/A	N/A
Wet deposition	0.004	0.70	0.006	8.08×10^{-4}
Dry deposition	0.002	0.56	0.003	8.12×10^{-4}
Sediment diffusion	0.009	1.20	0.020	-0.002
Ebullition	7.60×10^{-8}	0.26	9.55×10^{-8}	5.65×10^{-8}
Resuspension	0.001	0.20	0.002	0.001
Biofilm desorption	3.55×10^{-6}	0.74	6.17×10^{-6}	9.23×10^{-7}
Amphipod efflux	0.021	0.75	0.038	0.005
Evasion	-0.033	0.03	0.034	0.032
Sedimentation	-0.12	0.39	0.17	0.073
Burial	-0.11	0.42	0.16	0.064
Biofilm adsorption	-0.005	0.61	0.008	0.002
Amphipod uptake	-0.021	0.61	0.035	0.008
Total Inputs	36.95	0.72	63.83	10.08
Total Outputs	-37.08	0.72	63.81	10.22
Hg^0				
Air inflow	36.00	0.73	62.25	9.75
Air outflow	36.03	0.73	63.08	9.94
River inflow	0.014	0.03	0.014	0.014
River outflow	-0.014	0.03	0.014	0.014
Gas absorption	0.002	N/A	N/A	N/A
Ebullition	7.60×10^{-8}	0.26	9.55×10^{-8}	5.65×10^{-8}
Evasion	-0.033	0.03	0.034	0.032
Total Inputs	36.04	0.73	62.28	9.79
Total Outputs	-36.56	0.73	63.13	9.99
Hg^{2+}				
Air inflow	0.26	0.73	0.45	0.069
Air outflow	0.25	0.72	0.43	0.070
River inflow	0.41	0.76	0.73	0.10
River outflow	-0.28	0.49	0.36	0.13
Wet deposition	0.004	0.70	0.006	0.001
Dry deposition	0.002	0.56	0.003	8.08×10^{-4}
Sediment diffusion	0.009	1.21	-0.002	0.020
Resuspension	0.001	0.19	0.002	0.001
Biofilm desorption	2.62×10^{-6}	0.76	4.60×10^{-6}	6.41×10^{-7}
Amphipod efflux	0.019	0.96	0.038	7.38×10^{-4}
Sedimentation	-0.12	0.17	0.14	0.10
Burial	-0.11	0.19	0.13	0.086
Biofilm adsorption	-0.005	0.69	0.010	0.001
Amphipod uptake	-0.019	0.69	0.033	0.006
Total Inputs	0.71	0.52	1.23	0.19
Total Outputs	-0.78	0.28	1.09	0.38
MeHg				
Air inflow	0.095	0.73	0.16	0.026
Air outflow	0.095	0.73	0.16	0.026
River inflow	0.025	0.85	0.046	0.004

River outflow	-0.019	0.64	0.031	0.007
Wet deposition	4.35×10^{-5}	N/A	N/A	N/A
Sediment diffusion	8.28×10^{-5}	0.88	0.019	-0.002
Resuspension	5.16×10^{-5}	0.60	8.36×10^{-5}	1.95×10^{-5}
Biofilm desorption	2.05×10^{-7}	0.53	3.13×10^{-7}	9.71×10^{-8}
Amphipod efflux	0.001	0.41	0.002	7.25×10^{-4}
Sedimentation	-0.004	0.27	0.005	0.003
Burial	-0.004	0.27	0.005	0.003
Biofilm adsorption	-2.92×10^{-4}	0.75	5.10×10^{-4}	7.40×10^{-5}
Amphipod uptake	-0.001	0.75	0.002	3.13×10^{-4}
Total Inputs	0.12	0.60	0.23	0.029
Total Outputs	-0.12	0.57	0.21	0.039

Chapter 3

Dynamic mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario, Canada.

Abstract

A dynamic mass balance model was developed for the St. Lawrence River near Cornwall, Ontario that predicts and hindcasts mercury concentrations and fluxes in three forms, elemental Hg (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg), in a six compartment environment (air, water, porewater, sediment, periphyton, and benthic invertebrates). Our objective was to construct a dynamic mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario based on the framework and results of a steady-state mass balance model developed previously for this site. The second objective was to estimate industrial mercury emissions based on mercury residues deposited in sediments prior to 1970, the year when regulations were implemented to reduce mercury pollution in the environment. We compiled mercury concentrations, fluxes, and transformation rates from previous studies completed in this section of the river to develop the model. Estimated mercury concentrations in all media were similar to measured data, with only minor exceptions, providing a satisfactory overall description of the mercury loadings. Alterations in water mercury concentrations and retention times produce the largest error and changes in all media concentrations. The estimated historical emissions prior to 1970 from local industries along the Cornwall waterfront were approximately 400 kg $year^{-1}$. The model is based on actual observations made in this stretch of the St. Lawrence River resulting in a minimal number of assumptions, unlike most other models.

3.1. Introduction

Since the industrial revolution, anthropogenic sources have increased mercury levels in aquatic ecosystems making mercury contamination a global issue (Mason et al. 1994; Hudson et al. 1995; Jackson, 1997; Schuster et al. 2002). Mercury is transported to remote regions by long-range atmospheric transport and geological weathering (Jackson, 1997). Industrial activities contribute a large portion of the mercury flux through the environment (Breteler et al. 1984). Local contamination of mercury from these activities has resulted in areas (e.g. the lower Great Lakes of Northern America) plagued with mercury investigations to understand the dynamics and effects of mercury in the ecosystem (Gill and Bruland 1990; Ridal et al 2010). Mercury continuously transforms among different chemical and physical forms in media and this affects its mobility and bioavailability (Gehrke et al. 2009; Ridal et al. 2010). Mercury accumulates in sediments because it associates strongly to suspended particles (Gehrke et al. 2009). The production and bioaccumulation of organic mercury (methylmercury) in the food is a concern due to its neurotoxic effects (Lindqvist et al. 1991; Chang, 1977).

Rivers are complex physical, chemical, and biological systems that are exposed to environmental problems such as hydroelectric development and the contamination of trace metals such as mercury. Models may be used to understand the dynamics of mercury in complex river systems and determine if mercury contaminated sediments are a potential source of mercury to the food web. A model that incorporates not only total mercury, but elemental mercury and methylmercury, has the ability to assess the risk of bioaccumulation in biota and humans due to mercury contamination in sediments. Focusing a model on a specific region reduces complexity and improves our understanding of the dynamics of mercury by decreasing

spatial and temporal uncertainty in the variables and biogeochemical factors that affect mercury mobility and bioavailability.

The St. Lawrence River is a major river in the world, and drains the most industrialized region of North America (Carignan and Lorrain, 2000; Milliman and Meade 1983). The St. Lawrence River near Cornwall, Ontario has elevated mercury concentrations in sediments and fish resulting in habitat degradation and other impacts (Delongchamp et al. 2009; Ridal et al. 2010). Industrial activities are considered the main sources of mercury pollution to the region because of the large quantities of contaminants discharged in the past (Lepage et al. 2000; St. Lawrence River RAP, 1992). Because the discharges were located in embayments, a large portion of the mercury accumulated in sediment deposits (Delongchamp et al. 2009). Since the closure of the local industries in the early 1990's, mercury concentrations in sediments have decreased but it may still take a long time before preindustrial levels are observed (Delongchamp et al. 2009).

The objective of this study was to construct a dynamic mass balance model for mercury in the St. Lawrence near Cornwall, Ontario. A steady-state mass balance model (Chapter 2) identified the dominant sources and sinks of mercury in the region and provided the framework for the development of the dynamic mass balance model. The dynamic mass balance was used to predict and hindcast total mercury (THg), elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg) concentrations in the environment and biota of the St. Lawrence River at Cornwall, Ontario. The second objective of this study was to estimate emissions from local industries prior to 1970 when regulations were implemented to reduce mercury pollution in the environment. This area of the St. Lawrence River was historically contaminated by mercury

from local emissions and mercury levels in the food web have been of concern for decades (Ridal et al. 2010).

3.2. Model

The dynamic mass balance model was developed using the software STELLA (v. 9.1.4) because it is an accessible approach to formulate conceptual models using a series of linked compartments and to solve the resulting differential equations that define the flows between compartments. Variable inputs and outputs to/from compartments can be defined by the user over a specified time scale and a series of mass-balance differential equations are derived. The dynamic mass balance model consists of six compartments (air, water, porewater, sediment, periphyton, and benthos) connected by transfer processes and pathways for each of the three forms of mercury (Figure 3-1). Mass flows (thicker arrows) are determined by media concentrations (boxes; stocks) of mercury (Table 3-1) and parameters (circles and small arrows) (Table 3-2). Initial concentration and parameter values are input and the model can be used to predict or hindcast distribution in this environment.

In the model, material remains in stocks for a brief moment before flowing out again (high-turnover) due to fast processes. This high-turnover produces “ringing behaviour” and to eliminate this behaviour, optimization of the time step (DT) was required (Ford, 2010). A default DT value is typically 0.25 year, which is a good selection for most models (Ford, 2010). A DT value of 0.0625 month (1/16; software developers recommend DT in powers of 1/2) was selected because ringing behaviour was no longer evident and the model maintained its accuracy (Ford, 2010). A first-order Euler Integration was used because higher-order integration methods did not produce faster or more accurate simulations.

The description and assumptions for the air, water, sediment, periphyton (biofilm), and benthic invertebrates (amphipods) compartments can be found in Chapter 2. THg and MeHg in the sediment compartment were further divided into dissolved and particulate compartments to better describe the dynamics of mercury during processes such as sediment accumulation, resuspension and diffusion. Sediment cores taken in the contaminated zones of the AOC found that the water content consisted of 69% of the sediment and thus it was assumed that 69% of the sediment volume was the volume of porewater in the study area (Delongchamp et al. 2009). This is especially useful for hindcasting mercury emissions prior to the closure of local industries along the Cornwall waterfront.

3.3. Materials and Methods

3.3.1. *Site description*

The Area of Concern (AOC) in the St. Lawrence River near Cornwall is approximately 80km long and spans from the Moses-Saunders power dam to the eastern outlet of Lake St. Francois in Quebec (Delongchamp et al., 2010). Cornwall Island divides the river into the North Channel with mercury contaminated sediments and the South Channel which contains high PCB levels in the sediments (St. Lawrence River RAP, 1992). This study is focused on the Cornwall waterfront of the North Channel where three zones of high mercury contamination occur due to industrial emissions (Figure 3-2). Zone 1, the westernmost location of the study site, is located closest to a pulp and paper mill (Domtar) (closed in 2006) and a chloro-alkali plant (ICI) (closed in 1995). Zone 2, the easternmost location, is located closest to a textile mill (Courtalds) (closed in 1992) and Zone 3 is located in the middle of the study area and the other two zones. The

maximum historical sediment concentrations of THg for Zones 1, 2, and 3 are 34000 ng g^{-1}, 16000 ng g^{-1}, and 28000 ng g^{-1} respectively (Delongchamp *et al*., 2009).

Comparison among sites showed that depositional conditions have been relatively uniform among the three sites (Rukavina 2000). No significant differences occur in THg concentrations among and between sites (Delongchamp et al. 2009). Nettleton (2004) used a "Surface Water Modelling System" to estimate dynamic river hydrodynamics for the North and South Channels of the St. Lawrence River and showed that Zones 1, 2, and 3 had similar water depths and river velocities, even with changing flow-rates (minimum, average, and maximum flow rates). Bed shear stress in each zone was low (<1 N m^{-2}), which is typical of sediment deposition areas. Since 1956, reduction of the range of water level was required by the Moses-Saunders Power Dam to maintain consistent river flows, adequate navigation depths, and protect downstream habitat (International St. Lawrence River Board of Control, 2009). Due to the similarity in sediment composition, type, Hg concentrations, and hydrology the three zones were combined as a regional box model.

3.3.2. *Mass balance fluxes*

All mass balance fluxes determined in the steady-state mass balance model were used in the dynamic mass balance model as well (Chapter 2). Since the sediment compartment was further separated into dissolved and particulate phases, the dynamic mass balance model requires adsorption and desorption rates of mercury onto particles. To estimate mercury adsorption for sediment particles it was assumed that mercury in the dissolved and particulate phases are at steady-state, thus $C_{particle} / C_{water} = K_{adsorption} / K_{desorption}$. Assuming a desorption half-life of 11 years for THg and 2.1 years for MeHg, we estimated desorption rate constants (k_2) of 5.25 x 10^{-3}

month^{-1} and 0.028 month^{-1}, respectively (Fagerstrom and Jernelov, 1971; Hintelmann et al. 2000; Kudo et al. 1975). From the calculated partition coefficient (Table 3-3) and desorption rate constant, an adsorption rate constant (k_1) was estimated to be 16.7 month^{-1} for THg sediments and 17.09 month^{-1} for MeHg sediments. Particle adsorption rates were calculated by:

$$\text{adsorption rate} = Cporewater * Vporewater * Vs * k_1$$

where *Cporewater* is the porewater mercury concentration (mol m^{-3}) (Table 3-1), *Vporewater* is the volume of porewater (m^3) (Table 3-2), and *Vs* is the volume of sediments (m^3) (Table 3-2). Sediment desorption rates were determined by:

$$\text{desorption rate} = Cs * Vs * k_2$$

where *Cs* is the mercury concentration of sediments (mol m^{-3}) (Table 2).

3.3.3. *Partition coefficients for mercury species*

Dimensionless partition coefficients (K_d) were calculated primarily from data collected in the study site (Table 3-3). When regional data were unavailable, values were obtained from the literature. No regional data were available for the Hg^0 K_d for suspended solids / water, sediment solids / water, biofilm / water, and amphipod / water. Therefore, the model closely represents partitioning and speciation of mercury in this system.

3.3.4. *Model sensitivity analyses*

Model results are sensitive to variations in input parameters because of the unequal uncertainties and variability of model input parameters and associated outputs. A sensitivity analysis called the sensitivity index was used to calculate the output percent difference when one

parameter was varied from a mean value (median value where mean not available) to a maximum value or minimum value (Hoffman and Gardner, 1983). These sensitivity analyses are useful for showing which parameters are the most influential on model results and which parameters require more research (Hamby, 1995).

3.4. Results and Discussion

3.4.1. *Mercury concentrations in the environment and biota*

The dynamic model was useful for examining the temporal changes in mercury concentrations and fluxes. In the atmosphere, Hg^0 was the dominant form of mercury (99%) and particulate and reactive gaseous mercury were <1% of the THg. In the water column, THg and MeHg concentrations were stable over time but Hg^0 showed a diurnal fluctuation because of changes in the rate of evasion. THg concentrations in sediment showed a slight decreasing trend whereas MeHg exhibited increasing concentrations as the summer progressed. Although these modelled trends were only conducted over the summer, these trends have been observed in sediment cores taken in the study area (Delongchamp et al. 2009). Periphyton and benthic invertebrates accumulated mercury from the water column to levels measured by Eveno (2010) and Razavi (2008) and Hg concentrations reach steady-state conditions.

3.4.2. *Model Evaluation*

We compared modeled and measured results for the concentrations of THg and MeHg in the St. Lawrence River near Cornwall (Figures 3-3 and 3-4). The diagonal line in Figures 3-3 and 3-4 indicates a 1:1 relationship between modeled and observed concentrations of mercury. Both figures indicate that the model is providing a satisfactory overall description of mercury loadings, fate and transport in the region that is consistent with observations. Future addition of

other compartments such as vegetation and fish may provide sources of Hg to these media and potential risks to the ecosystem. Macrophytes accumulate mercury from sediment and water compartments and may transfer mercury to the food web during decomposition or secretion (Thompson-Roberts et al. 1999). In the St. Lawrence River, macrophyte mercury concentrations are not correlated to water and sediment concentrations (Thompson-Roberts et al. 1999) but they may still be a source of methylmercury from bacterial methylation (Guimarães et al. 1998). Benthic invertebrates are a major food source for yellow perch and elevated mercury concentrations have been measured in this species (Fowlie et al. 2008).

3.4.3. *Model output for THg and MeHg*

The average mass (moles) of THg, MeHg, and Hg^0 in each medium was entered into the model as an initial value and then the model was simulated over a time scale of months. Mass fluxes were either varied by month, were allowed to remain constant, or were calculated by the model (Tables 3-4 and 3-5). The model was simulated over 3 months (summer). Inflow accounts for 93.3% of the total inputs of THg, and other external inputs (wet and dry deposition) account for an additional 1.22%. Outputs of THg are dominated by outflow (69.6%) and sediment deposition (21.7%); evasion accounted for 4.78% of the total outputs. The dynamics of mercury in this section of the river were advection dominated which supports the results of the steady-state mass balance model.

For MeHg, inflow was 92.6% of the total MeHg input and other external inputs (wet deposition) provided an additional 0.16%. Thus, internal cycling and production of MeHg are important processes because they account for 8.41% of the inputs. Using methylation and

demethylation rate constants measured by Avramescu et al. (2011) resulted in a calculated methylation rate of 1.46 x 10^{-4} mol $month^{-1}$ and demethylation rate of 3.02 x 10^{-3} mol $month^{-1}$. Estimated methylation and demethylation rates predicted by the model were 1.78 x 10^{-4} mol $month^{-1}$ and 9.34 x 10^{-4} $month^{-1}$, respectively which corresponds to a net methylmercury concentration in sediment of 21.9 ng g^{-1} (initial $[MeHg]_{sediment}$ = 22.2 ng g^{-1}). Sulfate reducing bacteria and methanogens are believed to be the most important methylators and demethylators respectively in this study area (Avramescu et al. 2011). Due to the high demethylation rates observed we cannot ignore the importance of detoxification by bacteria where MeHg is degraded to CH_4 and Hg^0 (Avramescu et al. 2011). Outflow was the largest output of MeHg at 77.8% and sediment deposition was the second largest output of MeHg at 15.1%.

3.4.4. *Estimate of historical emissions*

To estimate historical emissions in the study area prior to 1970, the Hg sedimentation rate was changed based on ^{210}Pb dating of sediment cores collected by Delongchamp et al. (2009) and an emission flux was added to the THg water column. To obtain a surface sediment THg concentration of 24285.27 ng g^{-1}, the emission rate was estimated by the model to be approximately 400 kg $year^{-1}$. Hg emissions in water effluent from ICI Forest Products prior to 1970 were >150 kg $year^{-1}$ (St. Lawrence River RAP Team, 1997). Based on Ontario Ministry of the Environment reports (1992), Courtalds discharged the highest loading per year of mercury to the river but exact amounts are unknown. THg sediment profiles from Zones 1, 2 and 3 showed higher mercury concentrations prior to 1970 when regulations were implemented to reduce mercury pollution in the environment (Delongchamp et al. 2009). A similar historical pattern for mercury deposition in sediments was observed in Lake St. Francis, 10-40 km downstream of this study area (Pelletier and Lepage, 2003). Since mercury dynamics in the St. Lawrence River are

advection dominated, a portion of mercury emissions from industries near Cornwall would continue downstream to areas like Lake St. Francis. The San Francisco Bay Area sediments are historically contaminated with mercury from hydraulic mining operations and wastewater discharges contribute 19 kg $year^{-1}$ (MacLeod et al. 2005). The Detroit River sediments were also highly contaminated with mercury from industrial emissions valued at 96,000 kg $year^{-1}$ (Hamby and Post, 1985).

3.4.5. *Sensitivity analyses*

Changes to the model were evaluated for certain parameters to determine the overall effect on mercury concentrations and fluxes. Using the minimum overall mass transfer coefficient (K_{ol} = 0.73 mol $month^{-1}$; Poissant et al. 2000), Hg^0 in the water increased by 0.17%. A maximum overall mass transfer coefficient (K_{ol} = 240.9 mol $month^{-1}$; Poissant et al. 2000) resulted in a decrease in Hg^0 concentrations in water by 0.10% and 1.0%. A maximum THg concentration (see Table 2-1) for river inflow increased THg in water, porewater, sediment, periphyton, and benthic invertebrates by 6.64%, 0.48%, 62.0%, 0.34%, and 1.34%, respectively. A maximum MeHg concentration in water increased MeHg in water, sediment, periphyton and benthic invertebrates by 0.42%, 2.3%, 0.45%, and 0.38%, respectively. To demonstrate that the dynamics of mercury in the St. Lawrence River near Cornwall are advection dominated, the flow of river was increased by 50% (discharge = 186,588,000 m^3 $month^{-1}$). This increase in discharge increased THg in water, sediment, periphyton, and benthic invertebrates by 2.84%, 26.0%, 0.40%, and 0.54%, respectively. Therefore, changing the flow rate of Hg in the river has little to no effect because there is no effect on the Hg accumulation to the system. This suggests that the St. Lawrence River near Cornwall is advection dominated. But it is important for the Moses Saunders Dam to maintain constant river flows and water levels because it is still unknown

whether changing the river discharge would have effects on Hg in other environmental and biotic components not accounted for in this model.

3.4.6. *Conclusions*

The dynamic mass balance model developed for the St. Lawrence River near Cornwall predicts and hindcasts THg and species-specific concentrations in air, water, porewater, sediment, periphyton, and benthic invertebrates. Model estimates were similar to measured data. Modeled and measured results were compared for THg and MeHg concentrations and results indicated that the model is providing a satisfactory overall description of mercury loadings in the region. Estimated mercury concentrations in all media were similar to observed concentrations. The dynamic mass balance model showed that the system is advection dominated due to low water retention times, high deposition and burial rates, relatively low diffusion and resuspension rates, and loss of Hg^0 by evasion. Variable water mercury concentrations contribute the largest error for advective fluxes and changes in these concentrations affect mercury in all media. Changes in parameter values such as the mass-transfer coefficient, Hg concentrations derived from upstream, and discharge showed no large effect on mercury concentrations in each media. An estimate of historical local emissions prior to 1970 by the model was valued at approximately 400 kg $year^{-1}$.

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3.6. Figures

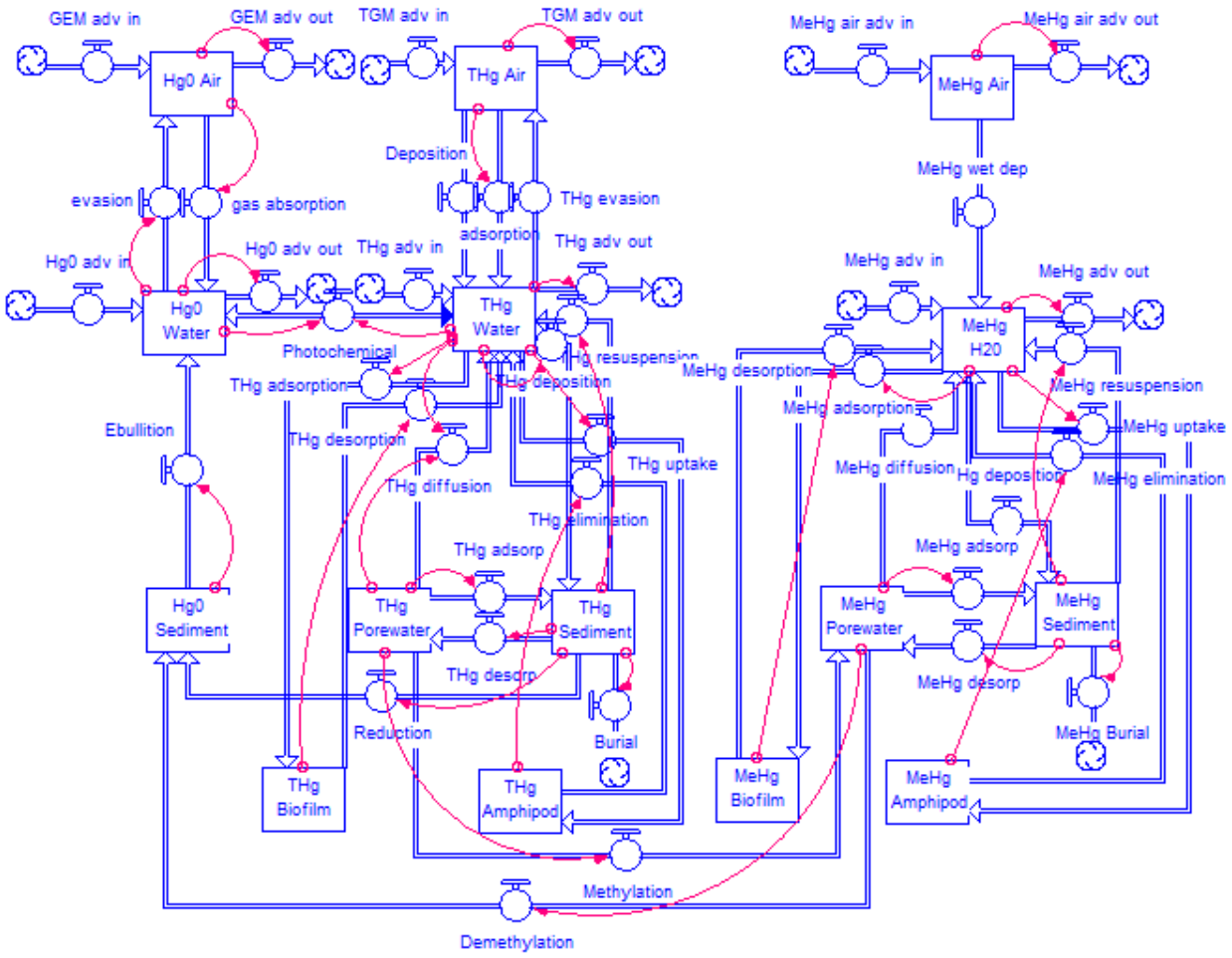

Figure 3-1. Visual representation of the dynamic mass balance model for THg, Hg^0, and MeHg in the St. Lawrence River near Cornwall, Ontario using Stella®. Boxes are masses of mercury (moles); thicker arrows are mass flows (mol $month^{-1}$); circles and small arrows are converters or variables defined in the mass flow.

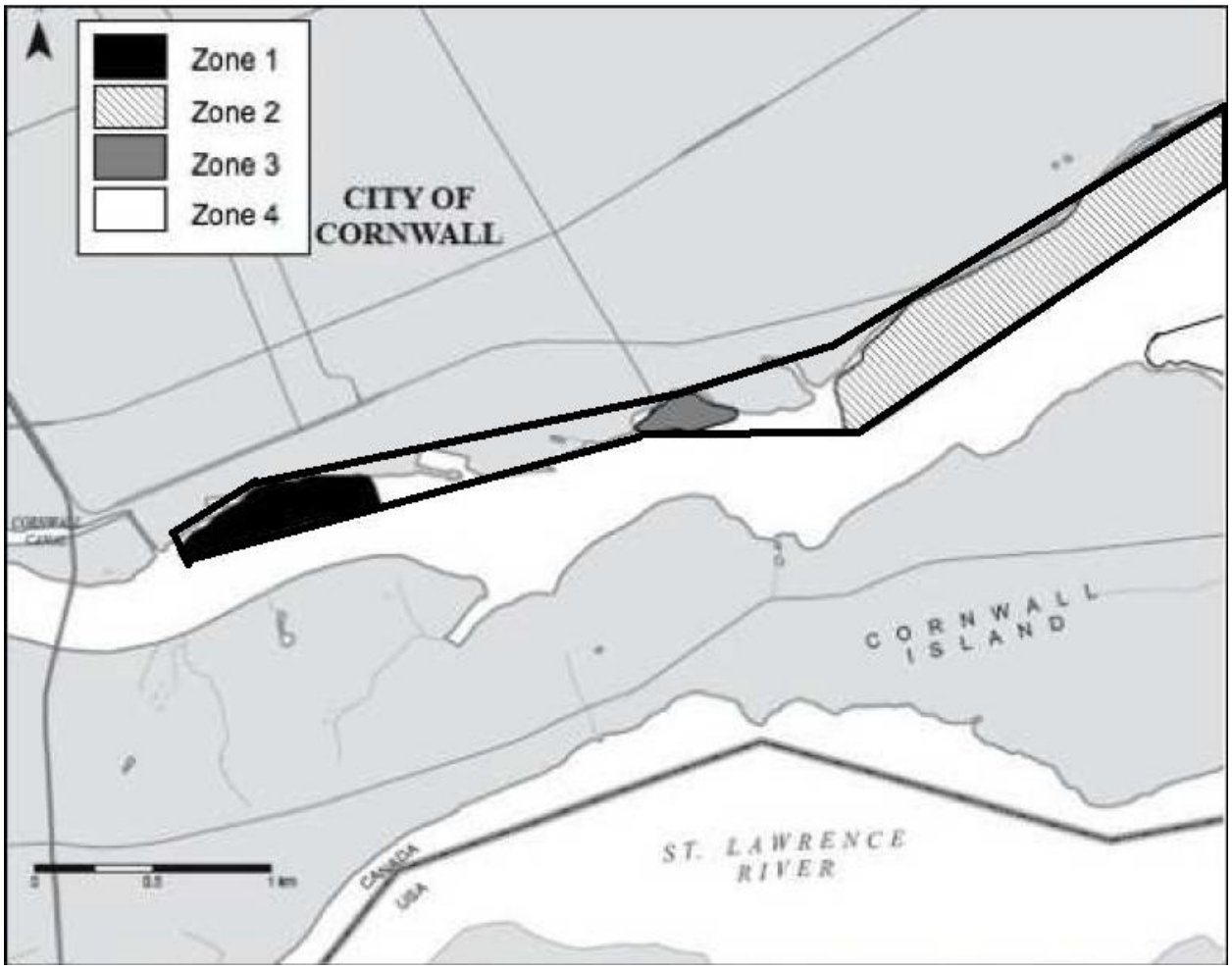

Figure 3-2: Map of regional model area (solid black line) in the St. Lawrence River, Cornwall Area of Concern (AOC) (modified from Razavi 2008).

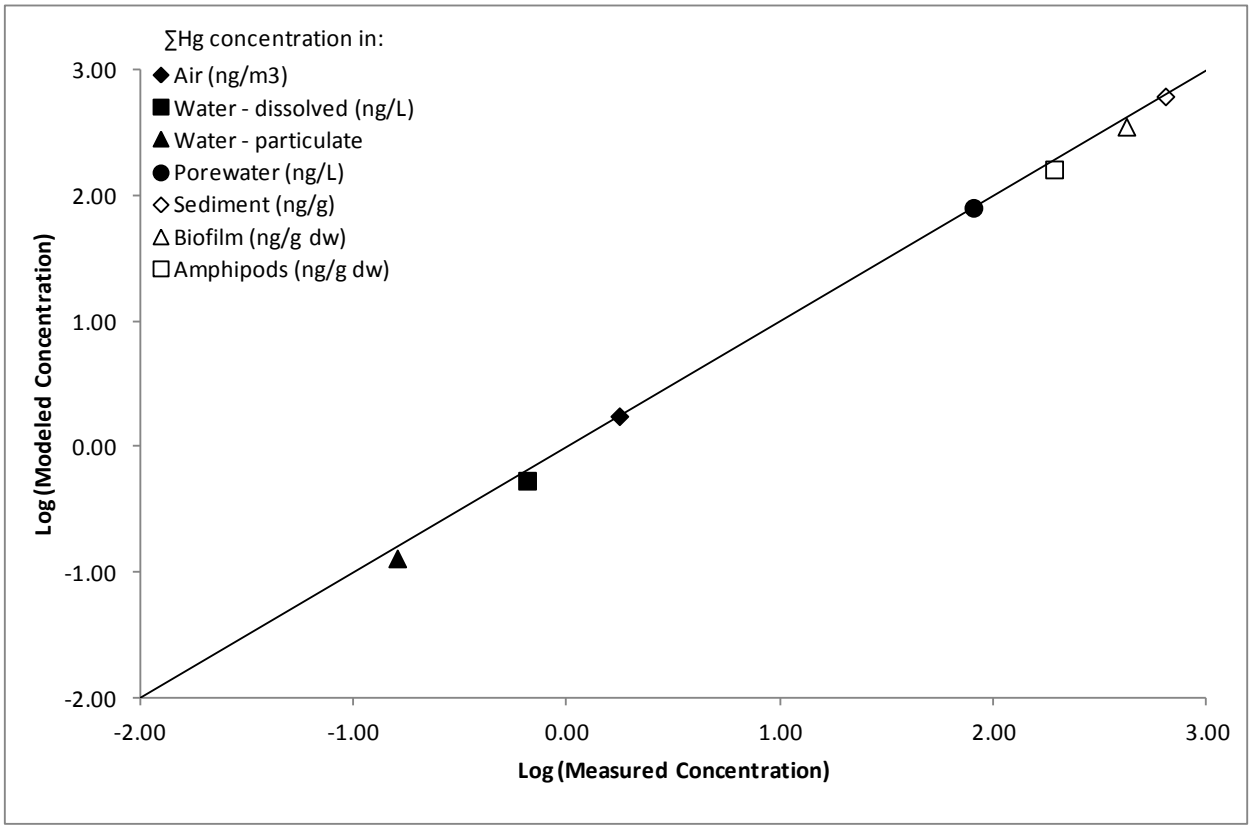

Figure 3-3. Comparison of modeled and observed concentrations of total mercury in the St. Lawrence River near Cornwall, Ontario.

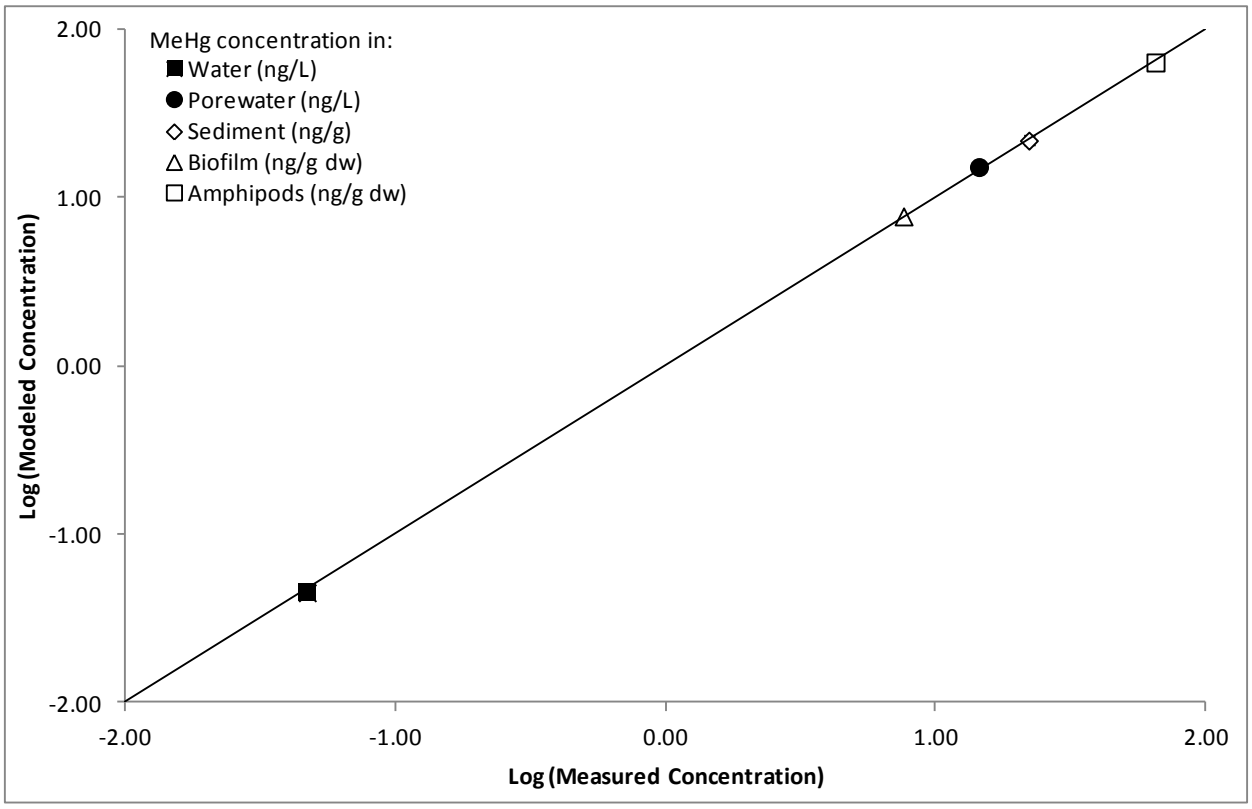

Figure 3-4. Comparison of modeled and observed concentrations of methyl mercury in the St. Lawrence River near Cornwall, Ontario.

3.7. Tables

Table 3-1. Reported mercury concentrations ± SD (if n>2) (minimum and maximum) and fluxes in the St. Lawrence River, Cornwall, ON. Median values provided in bold since mean values were unavailable. n=number of samples.

Media	n	Total Hg	n	Hg^0	n	Hg^{2+}	n	MeHg	ref
air (ng/m^3)	323	**1.76 (1.51 - 1.99)**		**1.74**[a]		**0.013**[a]		**0.005**[a]	O'Driscoll et al. 2007; Poissant et al. 2000
dissolved in water (ng/L)	101	0.650 ± 0.397 (0.128 - 2.45)	633	**0.031 ± 0.001**	101	0.736 ± 0.514 (0.108 - 2.98)	101	0.047 ± 0.035 (0.007 - 0.173)	Ridal et al. 2010; Poissant et al. 2000; O'Driscoll et al. 2007
particulate in water (ng/L)	101	0.162 ± 0.099 (0.032 - 0.614)							Ridal et al. 2010
sediment (ng/g)	16	640 ± 248.1 (405.7 - 1217.1)	2	0.002 [b]	16	618 ± 250 (390.6 - 1207.5)	12	22.2 ± 13.6 (9.41 - 45.5)	Delongchamp et al. 2010; Poissant et al. 2007
porewater (ng/L)	47	80.5 ± 73.6 (7.03 - 198.5)			20	64.2 ± 76.7 (2.83 - 191)	24	12.0 ± 15.4 (2.54 - 52.2)	Delongchamp et al. 2010
biofilm (ng/g)	20	419.9 ± 312.9 (137.6 - 1165.8)			20	412.4 ± 312.0 (125.3 - 1158.6)	20	7.63 ± 4.02 (3.83 - 16.5)	Eveno 2010
amphipods (ng/g)	40	192.4 ± 144.8 (60.2 - 596.1)			25	161.99 ± 155.3 (21.1 - 492.1)	25	65.4 ± 27.0 (27.6 - 146.9)	Razavi 2008
wet depositional flux to water (µg/m^2/month)	28	0.70					1	0.008	NADP 2007; Hines and Brezonik, 2007
dry depositional flux to water (µg/m^2/month)	194	0.29						0	Poissant et al. 2004; Lee et al. 2000; St. Louis et al. 2001

[a] Hg^0 represents >98% of THg and Hg^{2+} and MeHg contribute <1% of THg in air (Poissant et al. 2004).

[b] Concentration in ng/m^3.

Table 3-2. Regional environmental properties (standard deviation) for the St. Lawrence River at Cornwall.

parameter name	mean value	ref
Dimensions		
region area (m^2)	1045537	Biberhofer and Rukavina 2002
air compartment height (m)	6000	Mackay 2001
water depth (m)	8.03 (1.7)	Ridal et al. 2010
sediment depth (m)	0.01	Delongchamp et al. 2010
biofilm depth (m)	0.001	Bakke and Olsson, 1986
amphipod depth (m)	8.04	Ridal et al. 2010; Delongchamp et al. 2010
Volume Fractions for Subcompartments		
sediment porewater	966	Delongchamp et al. 2010
biofilm in water	409	Duarte and Kalff 1990; Armstrong et al. 2003; Ridal et al. 2007
amphipods in water and sediment	1731	Razavi 2008; Amyot et al. 1996; Wang and Zauke 2002
Temperature Conditions		
water temperature (^0C)	20.7 (2.9)	Ontario Power Generation 2011
Residence Times (months)		
air	0.002	*a*
water	0.09	Biberhofer and Rukavina 2002; Ridal et al. 2010; Nettleton, 2004
Discharge (m^3/month)		
river inflow	93294000	Nettleton, 2004
Transport Parameters (m/month)		
air-water MTC	67.2	Poissant et al. 2000
rain rate	0.0002	Environment Canada 2009
aerosol deposition	55188	Poissant et al. 2004
sediment resuspension	8.33×10^{-4}	Mackay 2001

[a] Estimated based on an assumed 1.1 m/s long-term average wind speed (Poissant et al. 2004).

Table 3-3. Dimensionless partition coefficients (K) for mercury in the St. Lawrence River, Cornwall.

property	Hg^0	Hg^{2+}	MeHg
molecular weight (g/mol)	200.59	200.59	200.59
K air/water	0.32[a]	0	0
K suspended solids/water	30000[b]	1229160[c]	
K sediment solids/water	20000[b]	806555[c,d]	473908[c,d]
K sediment solids/pore water		59867[d]	7701[d]
K biofilm/water	1[b]	538191[c,e]	163008[c,e]
K amphipod/water	1[b]	165866[c,f]	1397265[c,f]

[a] Poissant *et al*., 2000. [b] Mackay *et al*., 1995. [c] Ridal *et al*. 2010. [d] Delongchamp *et al*. 2010. [e] Eveno 2010. [f] Razavi 2008.

Table 3-4. Inputs, outputs, and masses of THg at the St. Lawrence River, Cornwall, Ontario, June to August.

	THg (mol)	% of total inputs or output	Variable, constant, or modeled parameter
Inputs, 0.45 mol total			
Inflow	0.42	93.3	constant
Wet deposition	3.66×10^{-3}	0.81	monthly
Dry deposition	1.85×10^{-3}	0.41	constant
Gas absorption	1.96×10^{-3}	0.44	modeled
Ebullition	7.42×10^{-8}	1.65×10^{-5}	modeled
Sediment diffusion	3.09×10^{-3}	0.69	modeled
Resuspension	1.43×10^{-3}	0.32	modeled
Biofilm desorption	4.27×10^{-3}	0.95	modeled
Amphipod efflux	0.018	4.00	modeled
Outputs, 0.46 mol total			
Outflow	0.32	69.6	modeled
Evasion	0.022	4.78	modeled
Sediment deposition	0.10	21.7	modeled
Biofilm adsorption	4.25×10^{-3}	0.92	modeled
Amphipod uptake	0.018	3.91	modeled

Table 3-5. Inputs, outputs, and masses of MeHg at the St. Lawrence River, Cornwall, Ontario, June to August.

	MeHg (mol)	% of total inputs or output	Variable, constant, or modeled parameter
Inputs, 0.027 mol total			
Inflow	0.025	92.6	constant
Wet deposition	4.35×10^{-5}	0.16	constant
Dry deposition	0	0	constant
Sediment diffusion	7.13×10^{-4}	2.70	modeled
Resuspension	5.08×10^{-5}	0.19	modeled
Methylation	1.78×10^{-4}	0.66	modeled
Biofilm desorption	3.03×10^{-4}	1.12	modeled
Amphipod efflux	1.22×10^{-3}	4.52	modeled
Outputs, 0.027 mol total			
Outflow	0.021	77.8	modeled
Sediment deposition	4.07×10^{-3}	15.1	modeled
Demethylation	9.34×10^{-4}	3.46	modeled
Biofilm adsorption	2.82×10^{-4}	1.04	modeled
Amphipod uptake	1.20×10^{-3}	4.44	modeled

Appendix A

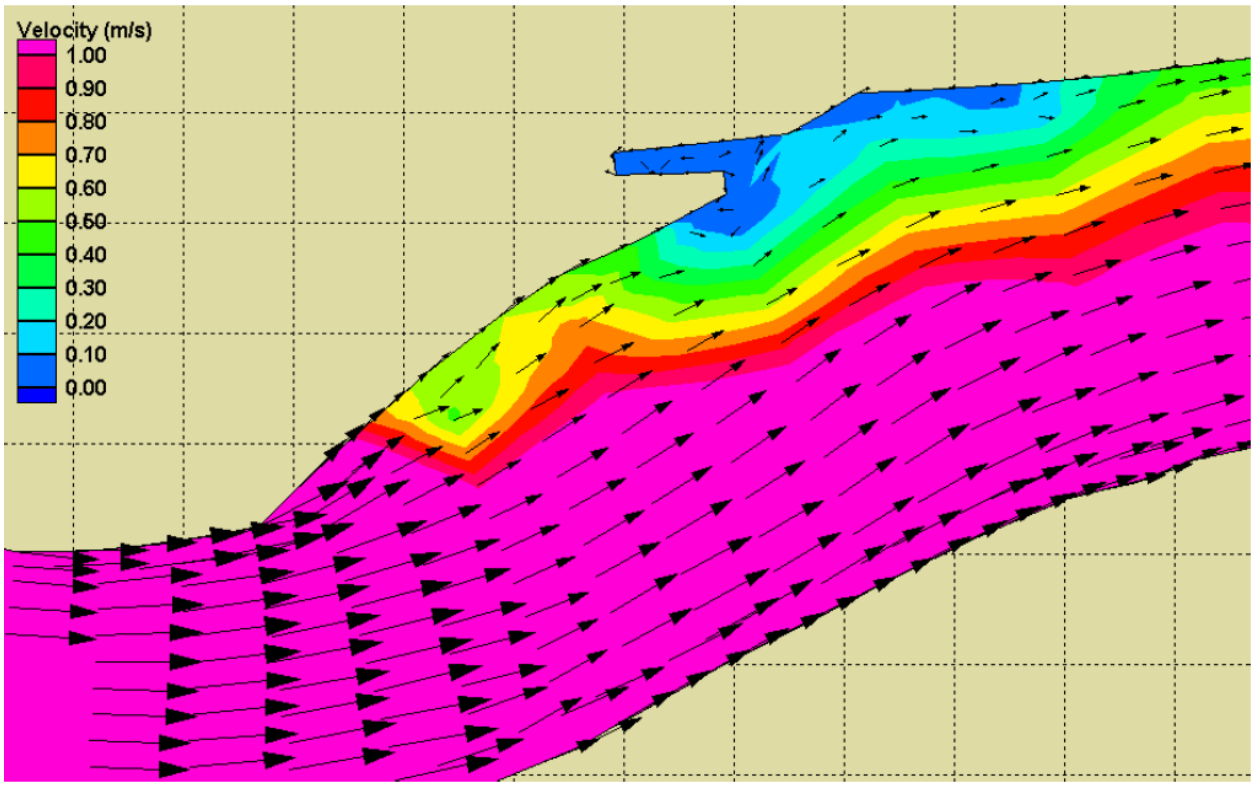

Figure 1: Depth average river velocity in the vicinity of Zone 1 (Nettleton 2004).

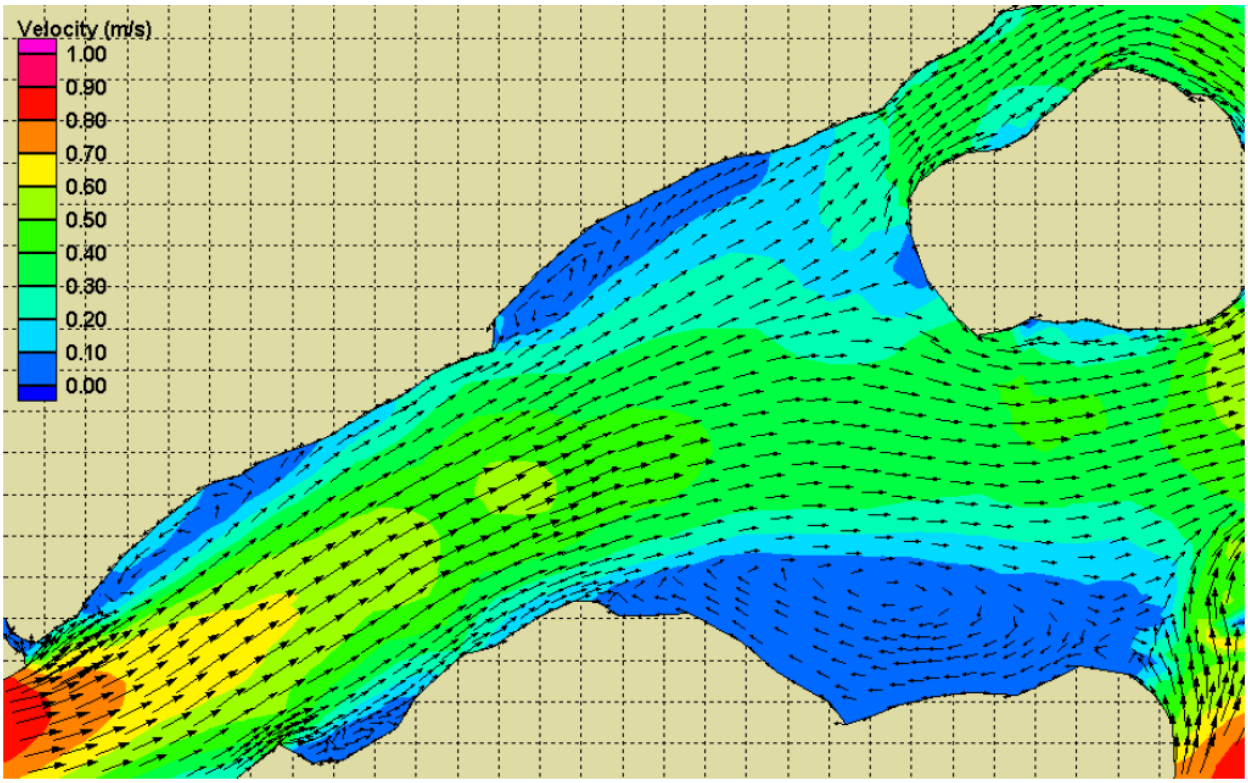

Figure 2: Depth average river velocity in the vicinity of Zone 2 (Nettleton 2004).

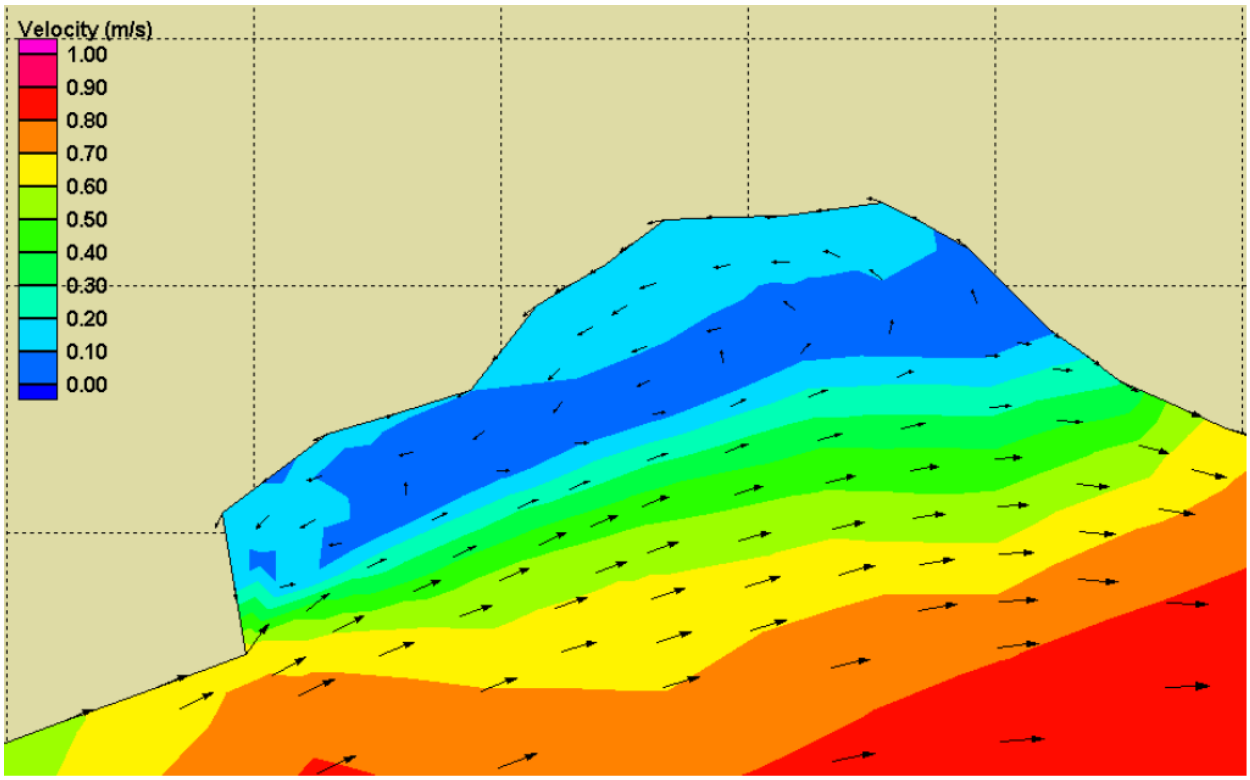

Figure 3: Depth average river velocity in the vicinity of Zone 3 (Nettleton 2004).

Appendix B

Table 1: Wet deposition of THg to the St. Lawrence River. Data from Mercury Deposition Network (http://nadp.sws.uiuc.edu.mdn/).

	THg 2006 (mol month^{-1})	THg 1998-2007 average (mol month^{-1})
January	4.63×10^{-3}	1.59×10^{-3}
February	3.20×10^{-3}	1.32×10^{-3}
March	5.55×10^{-3}	2.60×10^{-3}
April	1.81×10^{-3}	3.49×10^{-3}
May	4.80×10^{-3}	3.49×10^{-3}
June	1.76×10^{-3}	4.08×10^{-3}
July	5.72×10^{-3}	3.94×10^{-3}
August	1.75×10^{-3}	3.46×10^{-3}
September	2.03×10^{-3}	3.89×10^{-3}
October	3.66×10^{-3}	3.69×10^{-3}
November	3.54×10^{-3}	2.29×10^{-3}
December	2.60×10^{-3}	1.77×10^{-3}

Appendix C

Formulation of differential equations by Stella®. Boxes are masses (moles), arrows are mass flows (mol $month^{-1}$), and circles are mathematical converters.

Hg0_Air(t) = Hg0_Air(t - dt) + (GEM_adv_in - GEM_adv_out) * dt
INIT Hg0_Air = 0.054
INFLOWS:
GEM_adv_in = CaGEM/Vair*Air_flow
OUTFLOWS:
GEM_adv_out = Hg0_Air/Vair*Air_flow

Hg0__Sediment(t) = Hg0__Sediment(t - dt) + (Reduction - Ebullition) * dt
INIT Hg0__Sediment = 1.41E-8
INFLOWS:
Reduction = THg_Sediment*Kreduction
OUTFLOWS:
Ebullition = ((Hg0__Sediment/Volume_Sediment)*Vgas)/(Time_interval*SA_gas_collector)*depositional_area

Hg0__Water(t) = Hg0__Water(t - dt) + (Ebullition + Hg0_adv_in + gas_absorption + Photochemical - Hg0_adv_out - evasion) * dt
INIT Hg0__Water = 1.30E-3
INFLOWS:
Ebullition = ((Hg0__Sediment/Volume_Sediment)*Vgas)/(Time_interval*SA_gas_collector)*depositional_area
Hg0_adv_in = DGM*River_Discharge
gas_absorption = kol_x_SA*(Hg0_Air/Vair/H')
Photochemical = THg__Water*0.90*Kred-Hg0__Water*Koxid
OUTFLOWS:
Hg0_adv_out = Hg0__Water/Volume_Water*River_Discharge
evasion = kol_x_SA*(Hg0__Water/Volume_Water/H')

MeHg_Air(t) = MeHg_Air(t - dt) + (MeHg_air_adv_in - MeHg_air_adv_out) * dt
INIT MeHg_Air = 1.43E-4
INFLOWS:
MeHg_air_adv_in = CaMeHg/Vair*Air_flow
OUTFLOWS:
MeHg_air_adv_out = MeHg_Air/Vair*Air_flow

MeHg_Sediment(t) = MeHg_Sediment(t - dt) + (MeHg_adsorp + MeHg_deposition - MeHg_desorp - MeHg_resuspension - MeHg_Burial) * dt
INIT MeHg_Sediment = 0.062
INFLOWS:
MeHg_adsorp = MeHg__Porewater/Porewater_Volume*Volume_Sediment*Ka_3
MeHg_deposition = MeHg__H20*K23_MeHg
OUTFLOWS:
MeHg_desorp = MeHg_Sediment/Volume_Sediment*Porewater_Volume*Kd_3
MeHg_resuspension = MeHg_Sediment*Kresuspension
MeHg_Burial = MeHg_Sediment*K3_MeHg

MeHg__Biofilm(t) = MeHg__Biofilm(t - dt) + (MeHg_adsorption - MeHg_desorption) * dt
INIT MeHg__Biofilm = 1.08E-5
INFLOWS:
MeHg_adsorption = MeHg__H20/Volume_Water*Vb*Biofilm_Ka
OUTFLOWS:
MeHg_desorption = MeHg__Biofilm*Biofilm_Kd_MeHg

MeHg__H20(t) = MeHg__H20(t - dt) + (MeHg_wet_dep + MeHg_resuspension + MeHg_efflux + MeHg_diffusion + MeHg_desorption + MeHg_adv_in - MeHg_deposition - MeHg_uptake - MeHg_adsorption - MeHg_adv_out) * dt
INIT MeHg__H20 = 1.96E-3
INFLOWS:
MeHg_wet_dep = 4.35E-5
MeHg_resuspension = MeHg_Sediment*Kresuspension
MeHg_efflux = MeHg___Amphipod*MeHg_Kew
MeHg_diffusion = ABS((Porosity*MeHg_DwxSA/Tortuosity)*((MeHg__H20/Volume_Water-MeHg__Porewater/Porewater_Volume)/Sediment__Depth))
MeHg_desorption = MeHg__Biofilm*Biofilm_Kd_MeHg
MeHg_adv_in = Cw_MeHg*River_Discharge
OUTFLOWS:
MeHg_deposition = MeHg__H20*K23_MeHg
MeHg_uptake = MeHg__H20/Volume_Water*Va*MeHg_Ku
MeHg_adsorption = MeHg__H20/Volume_Water*Vb*Biofilm_Ka
MeHg_adv_out = MeHg__H20/Volume_Water*River_Discharge

MeHg__Porewater(t) = MeHg__Porewater(t - dt) + (MeHg_desorp + methylation - MeHg_adsorp - MeHg_diffusion - demethylation) * dt
INIT MeHg__Porewater = 7.08E-5
INFLOWS:
MeHg_desorp = MeHg_Sediment/Volume_Sediment*Porewater_Volume*Kd_3
methylation = THg_Porewater*km
OUTFLOWS:
MeHg_adsorp = MeHg__Porewater/Porewater_Volume*Volume_Sediment*Ka_3
MeHg_diffusion = ABS((Porosity*MeHg_DwxSA/Tortuosity)*((MeHg__H20/Volume_Water-MeHg__Porewater/Porewater_Volume)/Sediment__Depth))
demethylation = MeHg__Porewater*Kdemethylation

MeHg___Amphipod(t) = MeHg___Amphipod(t - dt) + (MeHg_uptake - MeHg_efflux) * dt
INIT MeHg___Amphipod = 2.25E-3
INFLOWS:
MeHg_uptake = MeHg__H20/Volume_Water*Va*MeHg_Ku
OUTFLOWS:
MeHg_efflux = MeHg___Amphipod*MeHg_Kew

THg_Air(t) = THg_Air(t - dt) + (TGM_adv_in + THg_evasion - TGM_adv_out) * dt
INIT THg_Air = 0.055

INFLOWS:
- TGM_adv_in = CaTGM/Vair*Air_flow
- THg_evasion = 0.033

OUTFLOWS:
- TGM_adv_out = THg_Air/Vair*Air_flow

THg_Porewater(t) = THg_Porewater(t - dt) + (THg_desorp - THg_adsorp - THg_diffusion) * dt
INIT THg_Porewater = 3.87E-4

INFLOWS:
- THg_desorp = THg_Sediment/Volume_Sediment*Porewater_Volume*Kd_2

OUTFLOWS:
- THg_adsorp = THg_Porewater/Porewater_Volume*Volume_Sediment*Ka_2
- THg_diffusion = ABS((Porosity*Dw_x_SA/Tortuosity)*((THg__Water/Volume_Water-THg_Porewater/Porewater_Volume)/Sediment__Depth))

THg_Sediment(t) = THg_Sediment(t - dt) + (THg_deposition + THg_adsorp - Reduction - THg_resuspension - THg_desorp - Burial) * dt
INIT THg_Sediment = 1.78

INFLOWS:
- THg_deposition = THg__Water*0.20*K23
- THg_adsorp = THg_Porewater/Porewater_Volume*Volume_Sediment*Ka_2

OUTFLOWS:
- Reduction = THg_Sediment*Kreduction
- THg_resuspension = THg_Sediment*Kresuspension
- THg_desorp = THg_Sediment/Volume_Sediment*Porewater_Volume*Kd_2
- Burial = THg_Sediment*K3

THg__Amphipod(t) = THg__Amphipod(t - dt) + (THg_uptake - THg_elimination) * dt
INIT THg__Amphipod = 6.65E-3

INFLOWS:
- THg_uptake = THg__Water/Volume_Water*Va*Ku

OUTFLOWS:
- THg_elimination = THg__Amphipod*Kew

THg__Biofilm(t) = THg__Biofilm(t - dt) + (THg_adsorption - THg_desorption) * dt
INIT THg__Biofilm = 5.97E-4

INFLOWS:
- THg_adsorption = THg__Water/Volume_Water*Vb*Biofilm_Ka

OUTFLOWS:
- THg_desorption = THg__Biofilm*Biofilm_Kd

THg__Water(t) = THg__Water(t - dt) + (wet_deposition + THg_adv_in + THg_desorption + THg_elimination + dry_deposition + gas + THg_resuspension + THg_diffusion - THg_adv_out - THg_adsorption - THg_uptake - THg_deposition - Photochemical - THg_evasion) * dt
INIT THg__Water = 0.034

INFLOWS:
- wet_deposition = 3.66E-3
- THg_adv_in = CwTHg*River_Discharge

- THg_desorption = THg__Biofilm*Biofilm_Kd
- THg_elimination = THg__Amphipod*Kew
- dry_deposition = 1.85E-3
- gas = kol_x_SA*(THg_Air/Vair/H')*0.98
- THg_resuspension = THg_Sediment*Kresuspension
- THg_diffusion = ABS((Porosity*Dw_x_SA/Tortuosity)*((THg__Water/Volume_Water-THg_Porewater/Porewater_Volume)/Sediment__Depth))

OUTFLOWS:

- THg_adv_out = THg__Water/Volume_Water*River_Discharge
- THg_adsorption = THg__Water/Volume_Water*Vb*Biofilm_Ka
- THg_uptake = THg__Water/Volume_Water*Va*Ku
- THg_deposition = THg__Water*0.20*K23
- Photochemical = THg__Water*0.90*Kred-Hg0__Water*Koxid
- THg_evasion = 0.033

- Air_flow = 4.162752E12
- Biofilm_Ka = 3066
- Biofilm_Kd = 8.51
- Biofilm_Kd_MeHg = 27.06
- CaGEM = 0.054
- CaMeHg = 1.43E-4
- CaTGM = 0.055
- CwTHg = 4.55E-9
- Cw_MeHg = 2.67E-10
- depositional_area = 140042
- Deposition__Velocity = 55188
- Dep_Vel_x_SA = Deposition__Velocity*Surface_Area
- DGM = 1.55E-10
- Dw = 2.49E-3
- Dw_x_SA = Dw*depositional_area
- H' = 0.0074*Water_temp+0.1551
- K23 = 17.62
- K23_MeHg = 2.15
- K3 = 0.067
- K3_MeHg = 0.067
- Ka_2 = 16.67
- Ka_3 = 17.09
- Kdemethylation = 67.2
- Kd_2 = 5.25E-3
- Kd_3 = 0.028
- Kew = 3.23
- km = 0.46
- kol = 67.2
- kol_x_SA = kol*Surface_Area

- Koxid = 65.7
- Kred = 1606
- Kreduction = 4.30E-8
- Kresuspension = 8.33E-4
- Ku = 3066
- MeHg_Dw = 3.35E-3
- MeHg_DwxSA = MeHg_Dw*depositional_area
- MeHg_Kew = 0.55
- MeHg_Ku = 3066
- Porewater_Volume = 966
- Porosity = 0.88
- River_Discharge = 93294000
- SA_gas_collector = 0.27
- Sedimentation_Rate = 1.33
- Sediment_Wet_Weight = 0.195
- Sediment__Depth = 0.01
- Surface_Area = 1045537
- Time_interval = 0.062
- Tortuosity = 1.66
- Va = 1731
- Vair = 6273222000
- Vb = 409
- Vgas = 0.0009
- Volume_Sediment = 1400
- Volume_Water = 8395662
- Water_temp = 20.7