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

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HIGHLIGHTS

- A dynamic model is described for mercury in the St. Lawrence River near Cornwall.
- Modeled mercury concentrations in all media were similar to measured values.
- The model was most sensitive to aqueous mercury concentrations and fluxes.
- Industrial mercury emissions to the river were ~400 kg $year^{-1}$ prior to 1970.
- This model is useful for predicting and hindcasting mercury concentrations.

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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 (area of approximately 100 km^2) to develop the model. Estimated mercury concentrations in all media were similar to measured data ($R^2 = 0.99$), with only minor exceptions, providing a satisfactory overall description of the mercury loadings and transformation rates of the different mercury species. The estimated historical emissions prior to 1970 from local industries along the Cornwall waterfront were approximately 400 kg $year^{-1}$. A storm sewer discharge of 5000 m^3/day resulted in a significant increase in mercury concentrations, particularly in sediment (617 ng g^{-1} to 624 ng g^{-1}; $p = 0.004$). Model results suggest that discharges of mercury from sources such as local industries and storm sewers have an impact on mercury in media such as sediment and water. This model should provide a basis for predicting and hindcasting mercury concentrations in other river environments as well, because it considers three distinct forms of mercury, and contains environmental media common to all rivers, including some (e.g. periphyton) not typically included in previous mercury models.

1. Introduction

Since the industrial revolution, human activity has increased mercury in aquatic ecosystems, making mercury contamination a global issue (Mason et al., 1994; Hudson et al., 1993; Jackson, 1997; Schuster et al., 2002). Mercury is transported to remote regions by long-range atmospheric transport and geological weathering (Cohen et al., 2004). Industrial activities contribute a large portion of the mercury flux through the environment (Pirrone et al., 2010). High mercury contamination has resulted in numerous studies on the environmental behavior of mercury, especially in areas of concerns such as those in the lower Laurentian Great Lakes and St. Lawrence River (e.g. Gill and Bruland, 1990; Ridal et al., 2010). Mercury continuously transforms among different chemical and physical forms, and this affects its mobility and bioavailability (Gehrke et al., 2009; Stein et al., 1996). Mercury accumulates in sediments because it associates strongly with suspended particles and organic matter (Gehrke et al., 2009; Ullrich

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et al., 2001). The production and bioaccumulation of organic mercury (methylmercury) in the food web 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 stressors, including hydroelectric development and the contamination of trace metals such as mercury. Models may be used to help understand the dynamics of mercury in complex river systems and determine if mercury contaminated sediments are a potential source of methylmercury to the food web. A model incorporating not only total mercury, but also elemental mercury and methylmercury, may provide insights on the risk of bioaccumulation in biota and humans due to mercury's ability to exchange between water, air, and sediments.

The St. Lawrence River is one of the world's major rivers, 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 mostly near embayments, a large portion of the mercury accumulated in sediment depositional areas (Delongchamp et al., 2009). Since the closure of the local industries in the early 1990s, mercury concentrations in sediments have decreased by approximately 4-fold, but they are still higher than reference sites upstream of these industries, and they still exceed sediment quality guidelines for protecting aquatic wildlife (Delongchamp et al., 2009).

The objective of this study was to construct a dynamic mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario. A steady-state mass balance model (Lessard et al., 2013) identified the dominant sources and sinks of mercury in the region and provided the framework for a dynamic mass balance model. The dynamic mass balance model was developed to estimate and hindcast total mercury (THg), elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methyl mercury (MeHg) concentrations in water, sediment, and biota of the St. Lawrence River at Cornwall, Ontario. The second objective of this study was to use this dynamic model 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 a concern for decades (Richman and Drier, 2001). The third objective of this study was to use the dynamic model to estimate the impact of storm sewer discharge on mercury fluxes and concentrations in the study area.

2. Methods

2.1. Site description

The Area of Concern (AOC) in the St. Lawrence River near Cornwall is approximately 80 km 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 in the sediments occur due to industrial emissions (Fig. 1). Zone 1, the westernmost location of the study site, is located closest to a pulp and paper mill (Domtar) (closed in 2006) and a chlor-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 34,000 ng g^{-1}, 44,000 ng g^{-1}, and 28,000 ng g^{-1} respectively (Delongchamp et al., 2009; Richman and Drier, 2001).

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 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 spatial similarity in sediment composition, type, Hg concentrations, and hydrology the three zones were combined as a local box model.

2.2. Model framework

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 (Fig. S1, Supplemental Information). Mass flows (thicker arrows) are determined by media concentrations (boxes; stocks) of mercury (Table 1) and parameters (circles and small arrows) (Table 2). Initial concentration and parameter values are inputted and the model can be used to predict or hindcast mercury distribution in this environment.

In the model, material remains in various media for a brief moment before flowing out again (high-turnover). This high-turnover produces "ringing behavior" and to eliminate this behavior, 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 (1/16; software developers recommend DT in powers of 1/2) was selected because ringing behavior 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 invertebrate (amphipods) compartments can be found in Lessard et al. (2013, Supplementary Information). 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 average water content of the sediment was 69% and thus it was assumed that 69% of the sediment volume was the volume of porewater in the study area (Delongchamp et al., 2009). The water content of sediment found in the AOC is within the range to what was observed in the literature (den Heyer and Kalff, 1998; Schallenberg and Kalff, 1993). This information is especially useful for hindcasting mercury emissions prior to the closure of local industries along the Cornwall waterfront.

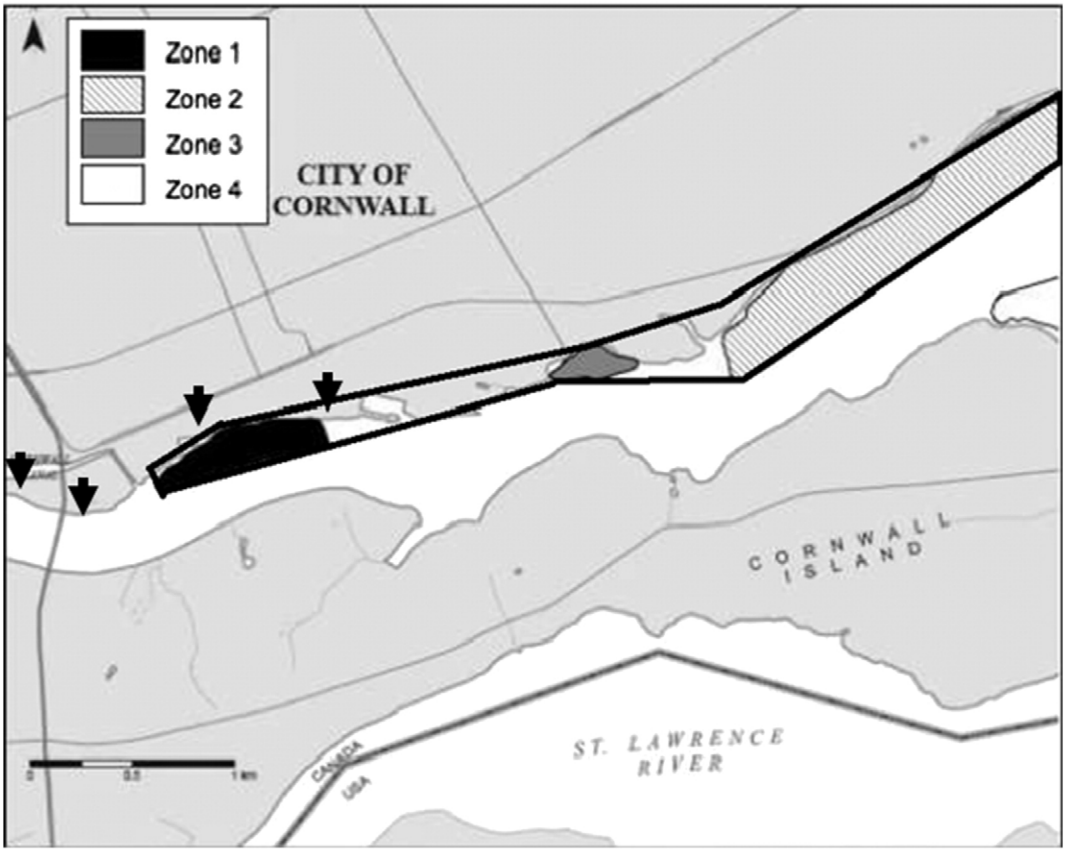

Fig. 1. Map of regional model area (solid black line) in the St. Lawrence River, Cornwall Area of Concern (AOC) (modified from Razavi, 2008). Also shown are the locations of the sewer outfalls in the vicinity of Zone 1. These outfalls include (from left to right) the storm sewer outfall for the former Domtar/ICI complex upstream of Zone 1, the Brookdale Avenue CSO, and the Pitt Street and Amelia Street storm sewers.

2.3. 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 (Lessard et al., 2013). 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 $C_{particle}/C_{water} = K_{adsorption}/K_{desorption}$. The estimated adsorption rate constant (k_1) was 3066 month^{-1} (Donald Mackay, Trent University, Personal communication). Assuming a desorption

Table 1
Reported mercury concentrations ± SD (if n > 2), range (in brackets), and atmospheric 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 2
Regional environmental properties (standard deviation) for the St. Lawrence River at Cornwall.

Parameter name	Mean value	Ref.
Dimensions		
Region area (m^2)	1,045,537	Biberhofer and Rukavina (2002)
Air compartment height (m)	2000	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		
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 (°C)	20.7 (2.9)	Environment Canada (2009)
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	93,294,000	Nettleton (2004)
Transport parameters (m/month)		
Air–water MTC	67.2	Poissant et al. (2000)
Rain rate	0.0002	Environment Canada (2009)
Aerosol deposition	55,188	Poissant et al. (2004)
Sediment deposition	210	Delongchamp et al. (2010)
Sediment resuspension	8.33×10^{-6}	Mackay (2001)

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

half-life of 11 years for THg and 2.1 years for MeHg, we estimated desorption rate constants (k_2) of 5.25×10^{-3} month^{-1} and 0.028 month^{-1}, respectively (Fagerstrom and Jernelov, 1972; Hintelmann et al., 2000; Kudo et al., 1982). From the calculated partition coefficient (Table 3) and adsorption rate constant, a desorption rate constant (k_2) 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:

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

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

Table 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	215.62
K air/water	0.32[a]	0	0
K suspended solids/water	30,000[b]	1,229,160[c]	
K sediment solids/water	20,000[b]	806,555[c,d]	473,908[c,d]
K sediment solids/pore water		59,867[d]	7701[d]
K biofilm/water	1[b]	538,191[c,e]	163,008[c,e]
K amphipod/water	1[b]	165,866[c,f]	1,397,265[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.

2.4. Partition coefficients for mercury species

Dimensionless partition coefficients (K_d) were calculated primarily from data collected in the study site (Table 3). When regional data were unavailable, values were obtained from the literature (see Table 3). No regional data were available for the Hg^0 K_d for suspended solids/water, sediment solids/water, biofilm/water, and amphipod/water. Even without regional data for Hg^0 K_d for suspended solids/water, sediment solids/water, biofilm/water, and amphipod/water, the model closely represents partitioning and speciation of mercury in this system.

2.5. 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

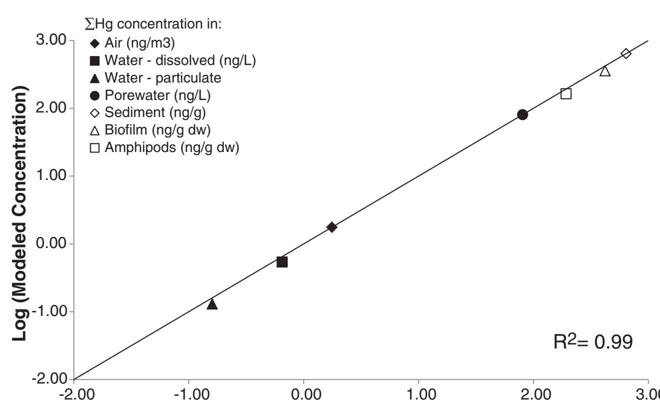

Fig. 2. Comparison of modeled and observed concentrations of total mercury in the St. Lawrence River near Cornwall, Ontario.

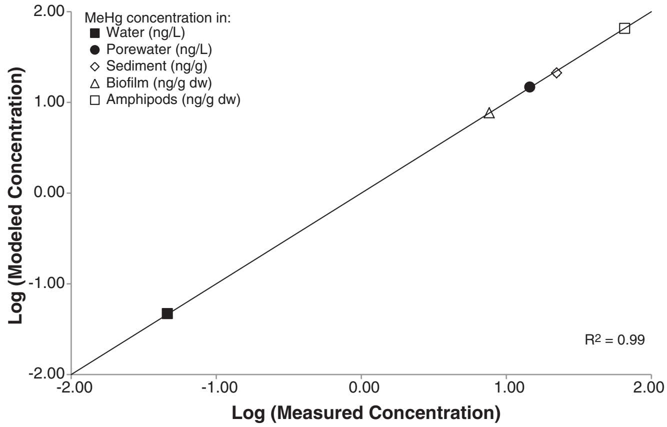

Fig. 3. Comparison of modeled and observed concentrations of methyl mercury in the St. Lawrence River near Cornwall, Ontario.

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. Results and discussion

3.1. 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 sediment MeHg exhibited increasing concentrations as the summer progressed. Although these modeled trends were only conducted over summer, the model may be used to track mercury recorded in sediment cores taken within the study area (Delongchamp et al., 2009). Model results indicate that periphyton and benthic invertebrates accumulated mercury from the water column up to levels measured by Eveno (2010) and Razavi (2008) and Hg concentrations reached steady-state conditions.

3.2. Model evaluation

We compared modeled and measured results for the concentrations of THg and MeHg in the St. Lawrence River near Cornwall (Figs. 2 and 3). The diagonal line in Figs. 2 and 3 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 aquatic organisms. Macrophytes accumulate mercury from sediment and water compartments and may transfer mercury to the food web from grazing and 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 fish species sampled along the Cornwall waterfront (Fowlie et al., 2008).

3.3. 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 calculated by the model (Tables 4 and 5). The model was simulated over a 3 month period (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 (68.1%) and sediment deposition (21.3%); evasion accounted for 6.88% 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 89.3% 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 9.76% of the inputs. Using methylation and demethylation rate constants measured by Avramescu et al. (2011) resulted in a calculated methylation rate of 2.92×10^{-8} mol month^{-1} and demethylation rate of 3.79×10^{-11} mol month^{-1}. Estimated methylation and demethylation rates predicted by the model were 2.93×10^{-9} mol month^{-1} and 3.61×10^{-11} month^{-1}, respectively which corresponds to a net methylmercury concentration in water of 0.047 ng L^{-1} (initial $[MeHg]_{water} = 0.046$ ng L^{-1}). Sulfate reducing bacteria and methanogens are believed to be the most important methylators and

Table 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	Variable, monthly
Dry deposition	1.85×10^{-3}	0.41	Constant
Gas absorption	1.96×10^{-3}	0.44	Modeled
Ebullition	7.44×10^{-8}	1.65×10^{-5}	Modeled
Sediment diffusion	3.09×10^{-3}	0.69	Modeled
Resuspension	1.44×10^{-3}	0.32	Modeled
Biofilm desorption	4.31×10^{-3}	0.96	Modeled
Amphipod efflux	0.018	4.00	Modeled
Outputs, 0.47 mol total			
Outflow	0.32	68.1	Modeled
Evasion	0.025	5.32	Modeled
Sediment deposition	0.10	21.3	Modeled
Biofilm adsorption	4.29×10^{-3}	0.91	Modeled
Amphipod uptake	0.018	3.83	Modeled

Table 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, 0.028 mol total			
Inflow	0.025	89.3	Constant
Wet deposition	4.35×10^{-5}	0.16	Constant
Dry deposition	0	0	Constant
Sediment diffusion	1.14×10^{-3}	4.07	Modeled
Resuspension	4.91×10^{-5}	0.18	Modeled
Methylation	6.58×10^{-13}	2.35×10^{-9}	Modeled
Biofilm desorption	2.94×10^{-4}	1.05	Modeled
Amphipod efflux	1.25×10^{-3}	4.46	Modeled
Outputs, 0.028 mol total			
Outflow	0.022	78.6	Modeled
Sediment deposition	4.24×10^{-3}	15.1	Modeled
Demethylation	3.61×10^{-11}	1.29×10^{-7}	Modeled
Biofilm adsorption	2.94×10^{-4}	1.05	Modeled
Amphipod uptake	1.25×10^{-3}	4.46	Modeled

demethylators respectively in this study area (Avramescu et al., 2011). Due to the 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). Sediment deposition was the second largest output of MeHg at 15.1%.

3.4. Estimate of historical emissions

To estimate historical emissions in the study area prior to 1970, the 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 24,000 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 (1992), Courtaulds 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 primarily advection dominated, a portion of mercury emissions from industries near Cornwall would continue downstream to areas like Lake St. Francis, a downstream fluvial lake. The San Francisco Bay Area sediments are historically contaminated with mercury from hydraulic mining operations and wastewater discharges that contribute 19 kg $year^{-1}$ (MacLeod et al., 2005). The Detroit River sediments were also highly contaminated with mercury from industrial emissions estimated at 96,000 kg $year^{-1}$ (Hamby and Post, 1985).

3.5. Storm sewer discharge

To estimate the impact of storm sewer discharge in the study area, a storm sewer flux was added to the THg and MeHg water columns using 2012 mercury concentration and discharge data collected by Ridal (unpublished data). To determine what storm size has a significant effect on the Hg balance in the study area, the storm sewer Hg concentration was held constant and different discharges were inputted into the dynamic mass balance model. A storm sewer discharge of 5000 m^3/day resulted in a significant increase in mercury concentrations, particularly in sediment (617 ng g^{-1} to 624 ng g^{-1}; $p = 0.004$). Mercury concentrations increased in water, sediment, periphyton, and benthic invertebrates by 28%, 6.0%, 0.52%, and 5.8%, respectively. A storm of this size occurred on June 23, 2012 and September 18, 2012, which corresponded to a total precipitation amount of 21 mm. Therefore, storm events have an impact on the balance of mercury in the study area by supplying more particulate mercury, and a projected increase in storm frequency due to climate change will have an influence on mercury dynamics.

3.6. Sensitivity analyses

Changes to the model were evaluated for all parameters (only a few parameters presented below) 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 mercury concentrations in water 0.24%. A maximum THg concentration (see Table 1) for river inflow increased THg in water, porewater, sediment, periphyton, and benthic invertebrates by 6.74%, 0.48%, 62.0%, 0.12%, and 1.34%, respectively. A maximum MeHg concentration in water increased MeHg in water, sediment, and benthic invertebrates by 0.42%, 2.3%, and 0.38%, respectively. To demonstrate the sensitivity of the system to discharge, the flow of river was increased by 50% (discharge = 186,588,000 m^3 $month^{-1}$). This increase in discharge increased THg concentration in water, sediment, periphyton, and benthic invertebrates by 2.94%, 27.0%, 0.05%, and 0.54%, respectively. The small changes observed to mercury in water, periphyton, and benthic invertebrates suggest that their accumulation is mediated by the kinetics of accumulation and elimination, not Hg supply by water.

4. Conclusions

The dynamic mass balance model developed for the St. Lawrence River near Cornwall estimates 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, primarily due to low hydraulic residence times, and high deposition and burial rates. Variable mercury concentrations in water 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 all media. An estimate of historical local emissions prior to 1970 by the model was valued at approximately

400 kg year^{-1}. A storm sewer discharge of 5000 m^3/day resulted in an increase in mercury concentrations, particularly in sediment (617 ng g^{-1} to 624 ng g^{-1}; $p = 0.004$). This model should provide a basis for mercury in other river environments.

Supplemental information includes Table 1, Table 2, and Fig. S1 that shows the dynamic model for mercury species in the St. Lawrence River AOC at Cornwall using the STELLA software. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.08.080.

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