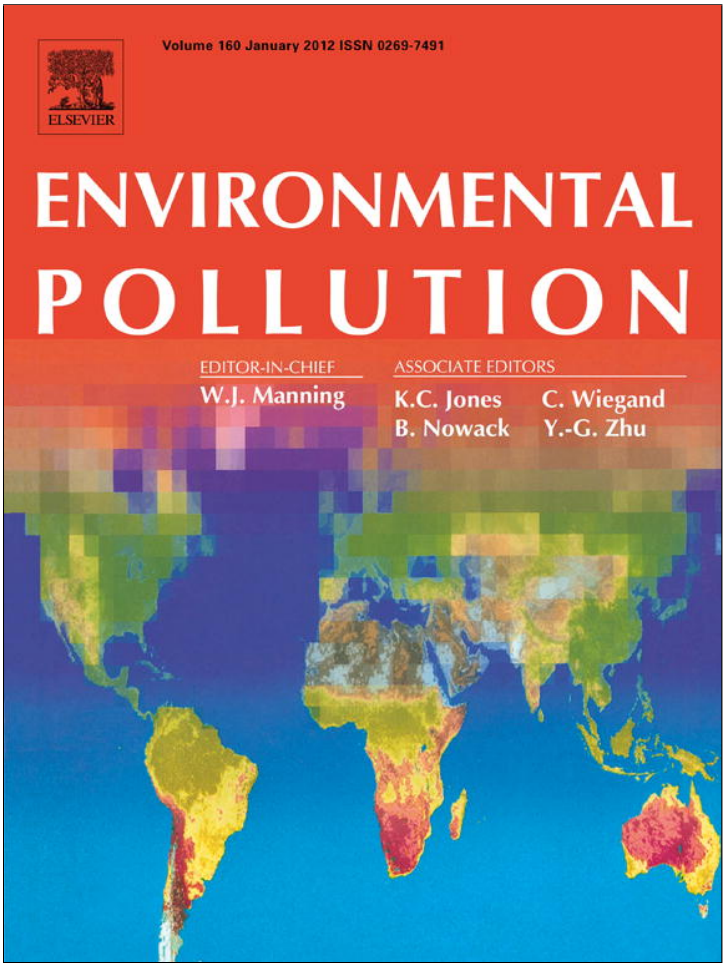
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Steady-state mass balance model for mercury in the St. Lawrence River near Cornwall, Ontario, Canada

Charlotte R. Lessard[a], Alexandre J. Poulain[a], Jeffrey J. Ridal[b], Jules M. Blais[a,*]

[a] Department of Biology, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5
[b] St. Lawrence River Institute of Environmental Sciences, Cornwall, Ontario, Canada K6H 4Z1

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ABSTRACT

We have developed a local 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.

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 methyl mercury form, MeHg (Ullrich et al., 2001). Mercury contamination has become the principal cause of fish-consumption advisories throughout the world (Brigham et al., 2009).

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 often 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 (Diamond, 1999; Diamond et al., 1992, 2000).

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; Gandhi et al., 2007; Harris et al., 1996; Hines, 2004; Hudson et al., 1993; Toose and Mackay, 2004). Toose and Mackay (2004) proposed a general framework where mass balance calculations for multi-species chemicals were derived from single-species model calculations (Diamond, 1999; Diamond et al., 1992, 2000). This approach has been utilized by other researchers to develop regional mass balance models for mercury where limited data were available (MacLeod et al., 2005; Ethier et al., 2008). The local mass balance model in this paper uses multi-species mass balance calculations and sufficient data were available on mercury dynamics in this region to allow the 'rigorous approach' (Toose and Mackay, 2004). A rigorous multispecies model requires known rate constants for species interconversions. Gandhi et al. (2007), Hines and Brezonik (2007) and the model presented in this study are among the few multispecies mercury models to use the rigorous approach thus far because rate constants for hydrolysis, photolytic reactions, and bacterial processes were previously 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

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* Corresponding author.
E-mail address: jules.blais@uottawa.ca (J.M. Blais).

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been a problem for decades (Ridal et al., 2010). The steady-state mass balance model was used to identify and better understand the dominant mercury sources and sinks 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, periphyton and benthic invertebrates of the St. Lawrence River at Cornwall, Ontario.

2. Methods

2.1. 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 80 km long and extends 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 historical local industrial emissions (Fig. 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 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 Ontario Ministry previously delineated these three zones where higher mercury concentrations in sediments were measured (Nettleton, 2004). Mean surface sediment concentrations of THg for Zones 1, 2, and 3 are 625 ng g^{-1} (±90 ng g^{-1}), 566 ng g^{-1} (±148 ng g^{-1}), and 811 ng g^{-1} (±573 ng g^{-1}) respectively, and are not significantly different between 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, slow-moving section of the river (mean depth of 8 m) is characterized by an average (summer) water discharge flow of 93,294,000 m^3 $month^{-1}$, pH range of 8.4–8.6, and an average dissolved organic carbon concentration of 2.5 mg/L (Table 1 and S1, Supplemental Information).

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 sediment 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 (Nettleton, 2004). 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, mercury distributions, and hydrology, the three zones were combined as a local box model.

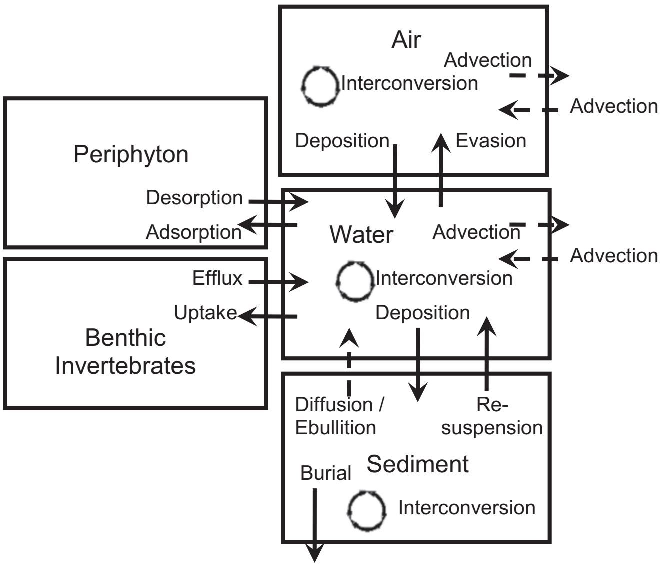

Fig. 1. Generic multimedia model environment for the different mercury species groups. Arrows represent transfer and transformation processes described in the model.

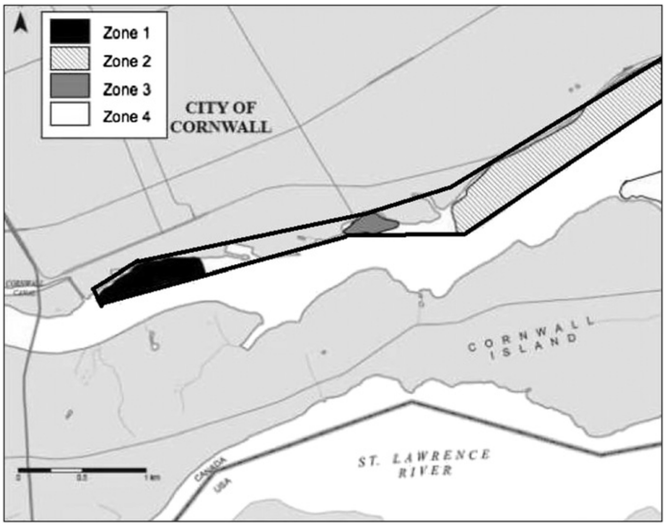

Fig. 2. Map of regional model area (solid black line) in the St. Lawrence River, Cornwall Area of Concern (AOC) (modified from Razavi, 2008).

2.2. Model framework

The steady-state model describes long-term summer average mercury dynamics in a generic local environment. A steady-state approach was considered suitable for this section of the river that has maintained a steady water level by the Moses-Saunders Power Dam since 1956 to maintain consistent river flows, navigation depths, and

Table 1
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		
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 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	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	55188	Poissant et al., 2004
Sediment deposition	210	Delongchamp et al., 2010
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).

river velocities (International St. Lawrence River Board of Control, 2012). The model consists of five compartments (air, water, sediment, periphyton, and benthos) connected by transfers and pathways for each of the three forms of mercury (Fig. 1). Mercury transport rates and advection were determined using media concentrations and transport parameters (Tables 1 and 2). The key assumption was that media concentrations of each mercury species are spatially 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), focussing 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 to account for the air–water interaction of mercury by the processes of air–water gas exchange and wet and dry deposition. The troposphere is in most contact with the surface water and extends to a height of approximately 10 km (Mackay, 2001). The troposphere's temperature, density, and pressure decline with increasing height. We assume uniform density at a pressure of 1 atm reducing the height to approximately 6 km (Mackay, 2001). The model is a localized situation and it is unlikely that the mercury would migrate higher than 2 km during the time that air resides over the study area. Therefore, an air compartment height of 2 km has been selected. The air in the 2 km compartment is well-mixed and available for exchange at the air–water interface.

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 no longer 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 mercury 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 (e.g. bubbling of gas from sediment), 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 treated as two compartments in the local mass balance model. Recent research shows evidence of mercury adsorption to the surface of periphyton and the potential availability of MeHg in periphyton to aquatic biota (Cheng et al., 2008; Hamelin et al., 2011). This area of the St. Lawrence River contains high 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). In the model, mercury partitioning in periphyton was determined by adsorption and desorption of mercury from the water column. 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 in the model were exposed to mercury through aqueous uptake and ingestion of periphyton.

A description of how each mass balance flux was calculated for each of the media is given in Supplemental Information (S1). Details on dimensionless partition coefficients are also in Supplemental Information (S2).

2.3. 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 arithmetic 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).

3. Results

3.1. Total mercury

The dominant source and sink for THg is advection in (93.3%) and out (69.6%) in the water column (Fig. 3). THg from advection in is not balanced by advection out of THg because sediment accumulation (21.7%) is another dominant sink of THg mercury. Sediment resuspension and diffusion fluxes are low (1.01%), 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.

3.2. Elemental 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%) (Fig. 3). 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). 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 calculated at 0.015 mol month^{-1} and photooxidation at 0.011 mol month^{-1}.

Table 2

Reported mercury concentrations ± SD (if $n > 2$), range (in brackets), and atmospheric deposition 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)		**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	0.8 ± 0. 5 (0.16–3.07)		**0.031 ± 0.001**	101	0.7 ± 0.5 (0.108–2.98)	101	0.047 ± 0.035 (0.007–0.173)	Ridal et al., 2010; Poissant et al., 2000
Sediment (ng/g)	9	640 ± 250 (405.7–1217.1)	2	0.002[b]	9	618 ± 250 (391–1207)	9	22 ± 14 (9.41–45.5)	Delongchamp et al., 2010; Poissant et al., 2007
Porewater (ng/L)	5	80.5 ± 73.6 (7.03–198.5)			5	60 ± 80 (2.8–191)	9	12 ± 15 (2.5–52)	Delongchamp et al., 2010
Biofilm (ng/g)	10	420 ± 313 (138–1170)			10	412 ± 312 (125.3–1158.6)	10	7.63 ± 4.02 (3.83–16.5)	Eveno, 2010
Amphipods (ng/g)	40	192 ± 145 (60.2–596)			25	162 ± 155 (21.1–492)	25	65 ± 27 (27.6–147)	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.

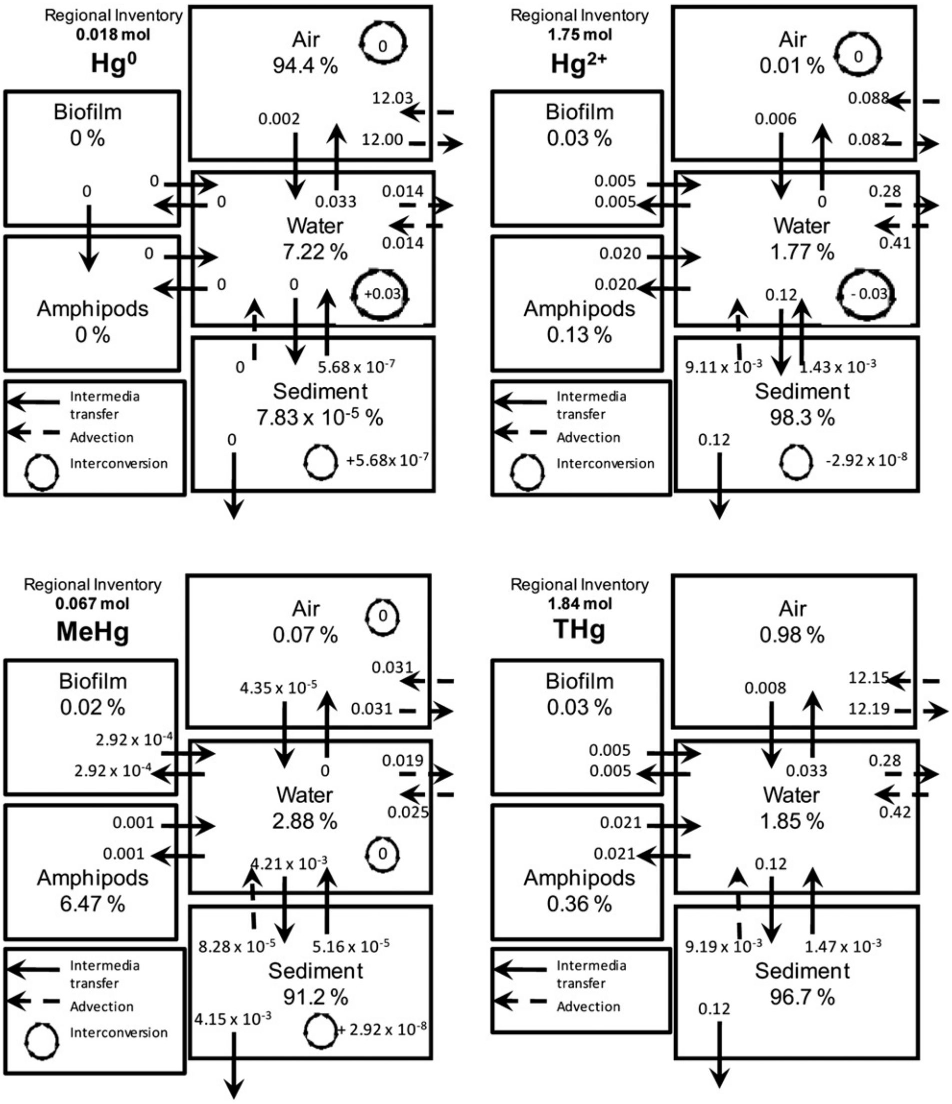

Fig. 3. Fluxes (mol $month^{-1}$) of elemental mercury (Hg^0), divalent mercury species (Hg^{2+}), methyl mercury species (MeHg) and total mercury (THg) in the St. Lawrence River AOC. Percentages are the quantity of mercury in each media in proportion to the total quantity for each mercury species.

3.3. *Inorganic mercury*

Similarly to Hg^0, the dominant source of Hg^{2+} to the St. Lawrence River AOC is river inflow (90.8%) (Fig. 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 (Ridal et al., 2010; Biberhofer and Rukavina, 2002; Nettleton, 2004; Delongchamp et al., 2009). Sediment resuspension and diffusion fluxes are low when compared to deposition to sediments, resulting in low amounts of mercury released from sediment to the water column. Atmospheric wet and dry deposition of Hg^{2+} (0.89%) is a very small portion of the total loadings to the AOC compared to some other regions (e.g. Brigham et al., 2009; Rood et al., 1995; Sorensen et al., 1990). Sediment contains the bulk of the local inventory of Hg^{2+} (98.3%).

3.4. *Methyl mercury*

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 (Fig. 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 (Delongchamp et al., 2009; Benoit et al., 1999; Ranchou-Peyruse et al., 2009). Both aerobic and anaerobic environments can support methyl mercury 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) for the area was estimated at 2.92×10^{-8} mol $month^{-1}$. The demethylation rate (3.75×10^{-11} mol $month^{-1}$) was lower than the methylation rate, and most likely supports 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 1–1.5% of THg in sediments (Hintelmann et al., 2000). Periphyton played a role in the availability of methyl mercury in the water column to other organisms locally and downstream with an uptake rate of 5.08×10^{-3} mol $month^{-1}$. Amphipods contain a larger portion of MeHg inventory from aqueous uptake pathways and accumulated mercury at a rate of 0.021 mol month^{-1}. High mercury uptake from sources such as periphyton could partially explain amphipod body burden and future addition of this uptake pathway to the model is recommended.

3.5. *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 S3, Supplemental Information). 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 S3, Supplemental Information). 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 mercury 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.

4. 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 mercury 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.

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 uncertainty 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.

The inclusion of periphyton and benthic invertebrate compartments gave some insight into potential mercury pathways to other organisms (e.g. fish). Periphyton should not be ignored in the overall mass balance of mercury because high concentrations of mercury in biofilm may be a source to fish. High mercury concentrations in biofilm were due to the uptake of Hg^{2+}, which is methylated within the periphyton and available for consumers. Fish may be indirectly exposed to elevated mercury concentrations in biofilm through the consumption of benthic invertebrates. Benthic invertebrates prefer periphyton (compared to sediment microbes) because it is a more direct food source (Cremona et al., 2009). Furthermore, a rapid turnover of periphyton biofilm biomass may result in high mercury concentrations in higher trophic position consumers in the food web (Robinson et al., 1997). Modelling efforts have shown that a small biomass of microalgae with rapid turnover can support a larger biomass of consumers with slower turnover (McIntyre et al., 2006). Also, grazers can increase the productivity of periphyton, enhancing consumer growth, development, and consequently increasing mercury concentrations.

The hydraulic conditions of the river resulted in a relatively low water residence time (0.09 months), indicating the importance of advective flows for mercury in the system. Upstream and *in-situ* production of the various 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 isotopes could provide additional insight into determining whether these outflows are a source of mercury to the AOC (Foucher et al., 2009). Losses of mercury in the system are mainly advection out (93.3%), sediment accumulation (21.7%), and volatilization (4.78%) 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.

5. Conclusion

The fate of THg in the Cornwall AOC is dominated by Hg^{2+} which comprises most of the mercury in this system (>80%). 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} over a three month period. Sediment resuspension and diffusion fluxes were low compared to mercury 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 River (Fowlie et al., 2008; Choy et al., 2008); Hg^{2+} and MeHg accumulation by biofilm and other autochthonous pathways provides an important entry point for mercury to the food web (Delongchamp et al., 2010; Avramescu et al., 2011).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2012.12.001.

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