

AN INTEGRATED ANALYSIS OF THE POTENTIAL EFFECTIVENESS OF MERCURY EMISSION REDUCTION STRATEGIES IN THE GREAT LAKES

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ABSTRACT

Using atmospheric transport and fate models, it has been possible to link the changes in emissions to the change in atmospheric deposition for the last thirty years for the criteria air pollutants, but it has only been in the last decade that advances have been made to allow these linkages to be developed for persistent toxic substances, including mercury. This study employs the results of the HYSPLIT model, which describes the sources and/or source regions that contribute the most mercury deposited to each of the Great Lakes. The linkages among contributions of mercury from the atmosphere, tributaries, sediments and non-point source run-off to the uptake and/or the bioaccumulation in fish is a much more difficult problem. Because of this, the potential effectiveness of mercury control strategies are often evaluated solely in terms of changes in atmospheric deposition rather than mercury concentrations in fish tissue. However, given that the primary route of human exposure to mercury is through consumption of contaminated fish, characterizing the relationship between mercury emission reductions and changes in concentrations in fish is critical for understanding the effectiveness of current management strategies.

This study investigates some of the key areas of uncertainty in the relationships between mercury emissions, deposition and concentrations in the sediments, water, and fish of aquatic systems through the application of three sub-models to Lake Ontario. The HYSPLIT atmospheric fate and transport model is integrated with coupled environmental fate and food-web bioaccumulation models for Lake Ontario that describe the abiotic partitioning of mercury and trophic dynamics. There are a number of uncertainties associated with this approach due to both missing process information and the lack of data for development and evaluation of these types of models. Hence, the model application described in this paper is best used as a screening level analysis to explore the sensitivity of the model to different parameters and data sources. Using a range of values for missing or less certain information, key uncertainties are hypothesized and provide suggestions focus future research and modeling efforts. This is demonstrated using an application of mercury emission reductions from the 1996 coal fired utilities in the US and Canada and the predicted changes in fish uptake of mercury in Lake Ontario.

INTRODUCTION

Mercury is a highly toxic element that is ubiquitous in the environment. The use and release of mercury as a by-product of human activities such as fossil fuel combustion, coal-fired power plants, base metal smelting and waste incineration has resulted in large releases of mercury to the atmosphere and disrupted natural biogeochemical cycles¹. There has been a postulated increase in the global reservoir of atmospheric mercury of at least 3-5 times the pre-industrial levels², and recent literature anticipates this enrichment may be as much as an order of magnitude greater than levels that occurred prior to human influence^{3,4}.

There are several different forms of mercury in the environment, each with distinct physical and chemical properties. Elemental mercury, Hg^0 , comprises more than 97% of the atmospheric pool of mercury⁵. The stability (long-half life) of Hg^0 in the atmosphere means that mercury emitted in this form is often transported and deposited long distances from the original source. When elemental mercury is oxidized to divalent inorganic mercury Hg(II) , it is readily scavenged from the atmosphere through wet and dry deposition. Hg(II) is the principle form of mercury in water, soils and sediments. However, the main organic form of mercury, methylmercury, is the chemical species that bioaccumulates in organisms⁶ and is the most potent toxin to humans and exposed wildlife⁷. The mediating role of atmospheric chemistry, abiotic and biotic conditions on the speciation and potential bioaccumulation of mercury in organisms means that an integrated analysis is needed to evaluate the effectiveness of mercury abatement strategies at reducing potential exposure of humans and wildlife to harmful levels of mercury in the environment.

The successful development of source receptor modeling of the loading of several persistent toxic substances from the atmosphere to the Great Lakes⁸ has been one of the most important new scientific achievements and its application by the International Joint Commission (IJC) is providing a major contributions to the US and Canadian policy-makers who will need to decide on the future strategies needed to achieve loading reductions under the Binational Strategy. The Great Lakes have a relatively small watershed, but have a very large airshed covering much of North America. Understanding how emission sources of persistent toxics within this airshed impact the Lakes is crucial to achieving water quality and ecosystem protection goals.

Toward the end of the 1980s, the Commissioners of the IJC asked one of its Boards, the International Air Quality Advisory Board (IAQAB), to take an active role in providing advice on Annex 15 of the Great Lakes Water Quality Agreement (GLWQA). This Annex 15 (on Airborne Toxic Substances) was one of the additions included in 1987 Protocol to the Great Lakes Water Quality Agreement.

The IAQAB found that the method for determining the atmospheric deposition input to the Great Lakes was very crude. It was based on lake mass balance studies using estimates of the accumulation, the loadings from the known point and non-point loadings and the outflows to come up with a calculation, by difference, of the unknown loadings, where atmospheric deposition was one of them. Therefore, one of the significant recommendation of the Board to the Commissioners in the late 1980's was to encourage the community of atmospheric modelers to develop atmospheric deposition models for the Great Lakes which could both predict loadings from any US/Canada emission inventory and attribute these

loadings back to the source regions to support decision makers on source control options. In the early 1990's, a couple of atmospheric modelers began to work on modeling the deposition a few of the persistent toxics but very little progress was made.

In the mid-1990's, the Board became aware of a research team at Queens College in New York that was using the NOAA Hysplit model (Hybrid Single-Particle Lagrangian Integrated Trajectory model, Version 4)^{9, 10}, for the deposition of dioxin/furans to the Great Lakes. It was a very ambitious effort, but if successful, it would be the scientific breakthrough that the IAQAB was looking for to use to achieve the goal of predicting loadings to the Great Lakes with attribution back to the US/Canadian source regions.

Later Dr. Cohen was engaged by the IAQAB to develop the deposition models using Hysplit for the Great Lakes. In the last several years, the deposition of dioxin/furans, cadmium, atrazine and mercury has been modeled and corroborated using monitoring data from the Great Lakes Integrated Atmospheric Deposition Network (http://www.msc-smc.ec.gc.ca/arqp/iadn_e.cfm) and the Mercury Deposition Network (<http://nadp.sws.uiuc.edu/mdn/>). In addition to identifying the most significant known source sectors, the model output typically demonstrated that the amount of mercury transported via the atmosphere from the distant sources is typically a significant portion of the total loading to the Lakes, particularly Lake Superior.

The objective of this paper is to provide a preliminary framework for using an integrated analysis of the potential effectiveness of mercury emissions reductions in terms of declines in concentrations in organisms in the Great Lakes regions. This is done by integrating the source-receptor model described above with a model of the distribution, partitioning and bioaccumulation of mercury in Lake Ontario.

Deterministic mass balance models have been developed and applied to organic substances (PCBs, dioxins, PAHs) and mercury in some of the other Great Lakes^{11, 12} to support water quality management decisions, however, such models have not combined models of the atmospheric chemistry and deposition of mercury with fate and bioaccumulation sub-models. In addition, while previous ecosystem scale studies in freshwater regions have looked at the relationship between *deposition* of mercury and accumulation in the food web, they have not included an assessment of the anthropogenic component of deposition and its significance as a source of contamination¹³⁻¹⁶. Using the approach suggested in this study, it is possible to investigate the relative significance of anthropogenic and natural mercury sources as contributors to observed mercury levels in fish, which has been the subject of vigorous scientific debate^{17,18}.

This analysis provide an example of how multimedia models can be used to derive endpoints for analyzing the effectiveness of mercury emissions controls that can be directly translated into associated declines in risk to human and ecological health. The application of an integrated source-receptor, fate, and bioaccumulation model in this study also helps to anticipate the potential lag time between changes in anthropogenic releases of mercury in Canada and the U.S. and declining concentrations in the Lake Ontario ecosystem. However, given the current uncertainties regarding the speciation of mercury in the environment and entry into the food chain, the example application presented in this paper is most valuable as a method for highlighting key areas of scientific uncertainty that presently restrict the

confidence that can be placed in this type of modeling effort, thereby providing a direction for future research.

METHODS

Three sub-models were linked to conduct the analysis presented in this paper. The first sub-model relies on the work of the IAQAB, using the HYSPLIT atmospheric transport model, and is summarized below (hereon referred to as the "Cohen model"). The other two sub-models were adapted from existing time dependent environmental fate and food web models that were parameterized using ecosystem and chemical specific data from Lake Ontario and the Great Lakes region. Each of these three sub-models is described in further detail below.

Source-Receptor Model Background (Cohen Model)

The Cohen model was developed using mercury emissions data from inventories covering 1996 sources throughout the U.S. and Canada. Accordingly, the model also uses meteorological data and ambient mercury concentration data from 1996. Data on mercury emissions from coal combustion in commercial, industrial and institutional boilers and process heaters data were obtained from the 1995-1996 U.S. EPA inventory^{19,20}. Because of the limited availability of data for coal-fired electricity generation boilers, municipal waste incinerators and medical waste incinerators, 1999 data were used to characterize emissions from these sources in the model. There have been significant reductions in mercury emissions from U.S. municipal waste incinerators and medical waste incinerators since emission inventories for 1995-1996 were compiled. Thus, the Cohen model does not necessarily reflect the most current source-receptor relationships in the Great Lakes region but does provide a good estimate of relative mercury contributions from different geographical regions and source categories.

As with all modeling work, there are uncertainties that must be noted. The current limited understanding of the chemical behavior of atmospheric mercury is the most important area of uncertainty in the Cohen model. In addition, the evaluation of model results is limited by the paucity of ambient and emissions measurements of mercury, particularly data that describe the speciation of mercury in these measurement programs. However, the model results were evaluated with the available, but limited, monitoring data. Finally, there were limitations in the information in the available emissions inventories, which had to be dealt with using the best approaches to develop a consistent emission inventory for this work.

Environmental Fate Model

The general framework for the environmental fate model used in this study was modified from Gobas et al.²¹, and the model by Mackay et al.²² developed by the participants of the Lake Ontario Mass Balance Workshop, organized by the International Joint Commission in Niagara on the Lake, from May 31 to June 2, 1991. This model framework was further adapted for mercury by Sunderland²³.

The environmental fate model used in this study describes physical and biological transport and transformation of mercury in the water column and benthic sediments based on two mass balance equations for each of the main mercury species that characterize the movement of mercury in and out of the water and sediments. The mass balance equations were solved through a Euler-type numerical integration. Individual models were developed for total

mercury (Hg-T), monomethylmercury (CH₃Hg or MMHg), elemental mercury (Hg⁰) and divalent inorganic mercury (Hg(II)). Inorganic mercury in the sediments and water is operationally defined as the difference between Hg-T and MMHg and consists of both divalent inorganic mercury species (Hg(II)) and elemental mercury (Hg⁰). In the model, the benthic sediment compartment is divided into an “active layer” and a “truly buried” inaccessible sediment layer. The active sediment layer can potentially exchange mercury with the water column and buried sediments through resuspension, diffusion and burial. Truly buried sediments act as a sink for mercury, removing it from further interaction with the sediment-water interface and benthic organisms. The active sediment layer is also where conversion of inorganic mercury to MMHg takes place, represented as a net loss of Hg(II) and a net input of MMHg in the respective models. A mass balance is assumed for the active sediment layer, meaning that the settling flux is equal to the combined fluxes associated with solids resuspension and burial at all times. Although this is a simplification of the processes occurring in the active sediment layer, it is expected to be a reasonable representation of chemical dynamics associated with the net deposition and resuspension of sediment solids²⁴.

Empirical data from Lake Ontario and the Great Lakes region were used to develop rate constants that describe the rate of reaction and transport of mercury species. Specifically, the model describes transport and reaction as a function of: (i) direct inputs of mercury (e.g., atmospheric deposition), (ii) water inflow (rivers and tides) and outflow (tides), (iii) volatilization of elemental mercury (Hg⁰) from the water column, (iv) sorption to suspended sediments, (v) deposition of suspended sediments, (vi) transfer of mercury from the sediments into the water column via diffusion and resuspension of benthic sediments, (vii) burial of sediments, and (viii) species interconversions in the sediments and water (e.g., methylation of Hg(II), demethylation of CH₃Hg (MMHg) to Hg(II), and reduction of Hg(II) to Hg⁰).

Food-Chain Bioaccumulation Model

The food chain bioaccumulation model for Lake Ontario consists of several sub-models that describe mercury accumulation in plankton, benthic invertebrates and four fish species at different trophic levels (see Figure 1). These species were chosen because they have traditionally been used as biomonitors for persistent bioaccumulative toxins in Lake Ontario and contaminant time trend data were available to test the performance of the model. The model has been adapted for mercury from the original steady-state bioaccumulation model for PCBs by Gobas²⁵. Using a series of first-order rate constants, the model considers the effects of organism weight (growth dilution), diet composition (assimilation efficiency) and excretion rates of mercury when modeling mercury dynamics among different species and different age classes.

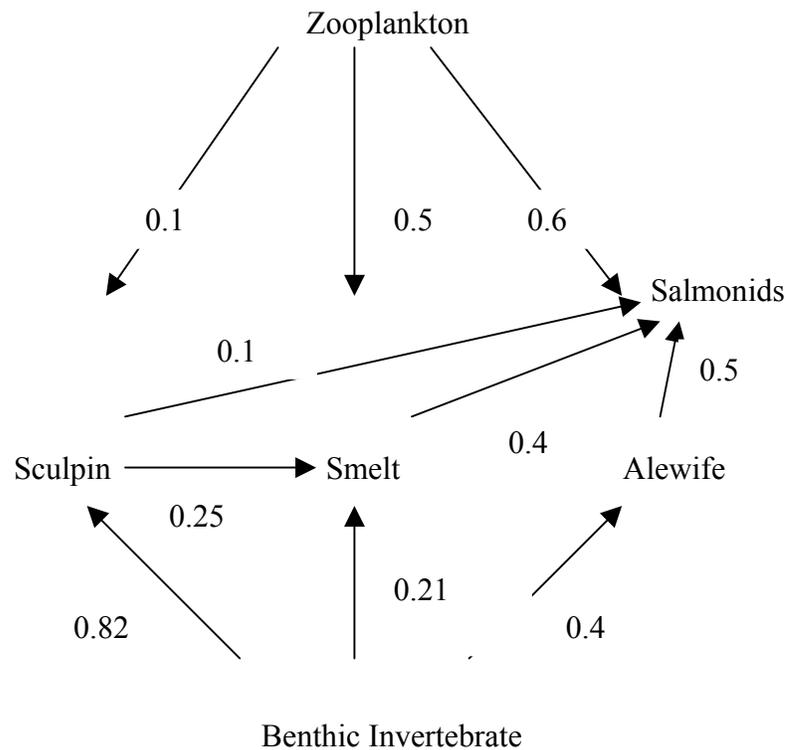


Fig. 1. Conceptual model of Lake Ontario food-web (Adapted from Gobas et al.²¹).

Integration of Three Models

The Cohen source-receptor model was used to anticipate different loading scenarios for mercury characterized in the environmental fate model. This was done by assigning "deposition factors" for each of the source categories characterized in the Cohen model to estimate kilograms of mercury deposited to Lake Ontario per tonne of mercury emitted from different source types. The environmental fate model was then used to calculate a concentration of total and methylmercury in water and sediments, given each of the different loading scenarios. The concentration of "bioavailable" mercury in the water and sediments determined using the environmental fate model drives calculations of mercury uptake and accumulation in the food web. To simplify this analysis, plankton and benthic invertebrates were assumed to be in equilibrium with the "bioavailable" fraction of mercury in the water and sediments, respectively. Fish accumulation rates were based on potential mercury exposure through dietary uptake (Figure 1), fecal elimination, growth dilution, and gill ventilation. The overall modeling approach for Lake Ontario treats water and sediments as a single homogeneous compartment to gain a whole-ecosystem understanding of mercury dynamics in the lake. This is a simplification of chemical dynamics as previous studies have found regional differences in atmospheric mercury²⁶ sediment deposition²⁷ and water-airside evasion^{28, 29}.

RESULTS AND DISCUSSION

Source-Receptor Relationships

The Cohen model results show that mercury deposition from anthropogenic sources to the Great Lakes comes from local, regional and continental sources. To achieve the goals of the Binational Strategy and the GLWQA, reductions would be necessary on US and Canadian national scales.

The emission inventory developed by Cohen for the modeling is shown in map form in Figure 2 to demonstrate the geographical distribution of the total anthropogenic mercury emissions across the U.S. and Canada in 1996.

The [annual] emissions in the two countries are broken down by source category in Figure 3. The relative importance of coal combustion in the U.S. and metallurgical processes (e.g. smelting) in Canada is apparent. It should be noted that emissions from metallurgical processes in Canada have been sharply curtailed in more recent years. The populations used to normalize the national emissions to a per capita basis were 265,000,000 for the U.S. and 30,000,000 for Canada from 1996 census estimates made in each country.

For each source category, the emissions of mercury need to be speciated into the three forms—elemental mercury, reactive gaseous mercury and particulate mercury. Unfortunately, this information is sometimes missing. The U.S. emissions inventory had estimates of the speciation, which were used to make estimates of the speciation from the corresponding source categories in Canada. The atmospheric fate of the different mercury species is quite distinct. Accordingly, source-receptor relationships are strongly dependent on the emissions profile of the individual source, and the accuracy of this modeling analyses would increase if more and better information regarding this issue becomes available.

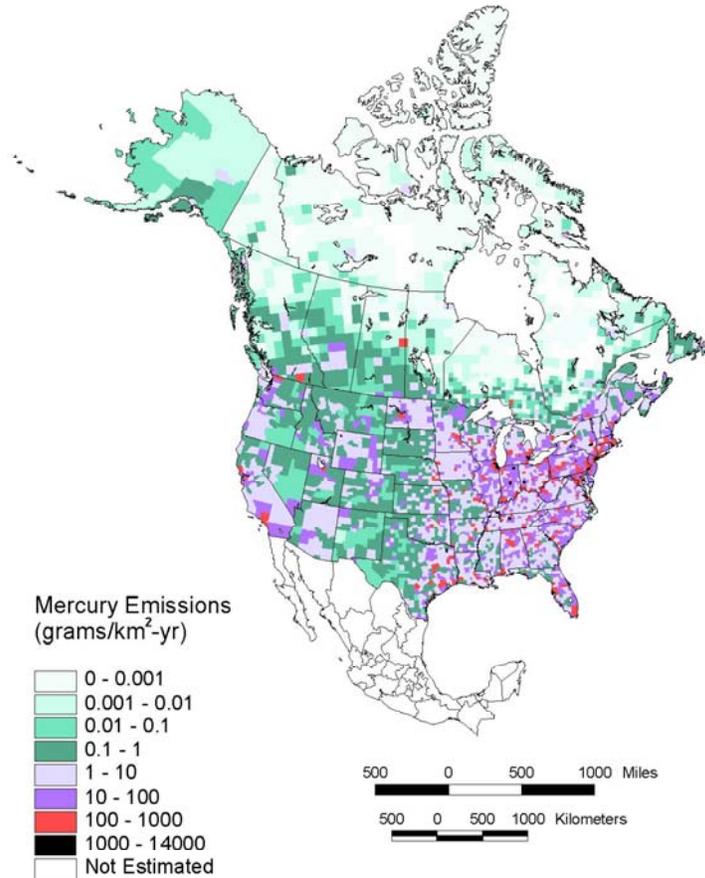


Fig. 2. Geographic distribution of total mercury emissions to the atmosphere from U.S. and Canadian anthropogenic sources (1995/1996).

Using the Hysplit model, Cohen generates a matrix that estimates the contribution, wet plus dry deposition of mercury, of each source region (based on its emissions) to each receptor of interest. Looking at Lake Ontario as the receptor of interest for this paper, Figure 4 graphically portrays in map form the appropriate part of the matrix, i.e. the geographical distributions of mercury source contributions to atmospheric deposition. Note that the source regions in the Ohio River Valley appear to be the most significant for the 1996 mercury deposition for Lake Ontario.

It is worth noting that Cohen also made preliminary estimates of the impact of different source categories on deposition to each of the Great Lakes, recognizing that the uncertainties in emission make this an imprecise exercise. Figure 5 looks at the fuel combustion, incineration, metallurgical operations, and manufacturing source categories, showing the per capita contribution to Lake Ontario. For the purpose of this paper, the mercury emissions from fuel combustion (predominately coal combustion) are worth noting since in the example that comes later will assume that reductions are made to this category to examine the change in fish uptake and the uncertainty in making such estimates.

Combined External Loading to Lake Ontario

The Cohen model estimates that total direct atmospheric loading to Lake Ontario from 1995-1996 anthropogenic sources is approximately $9 \text{ ug m}^{-2} \text{ yr}^{-1}$ (214 kg). In addition to anthropogenic sources, a "natural" background

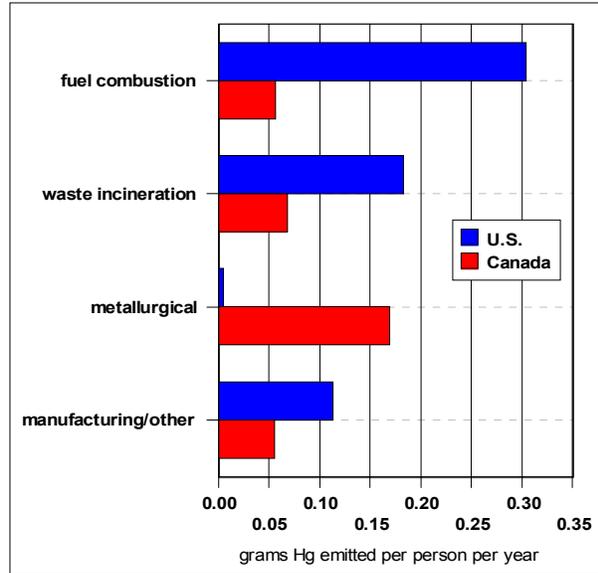


Fig. 3. Annual per-capita mercury emissions from U.S. and Canadian sources (aggregated source categories).

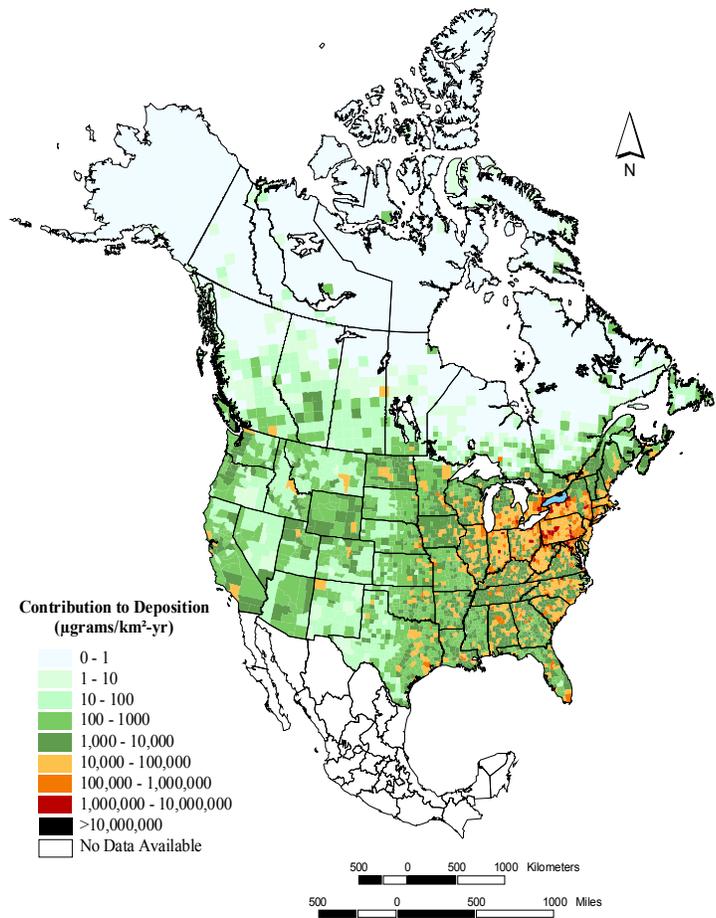


Fig. 4. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Ontario ($\text{mg km}^{-2} \text{ yr}^{-1}$).

loading rate of mercury prior to human influence must be added to generate an estimate of the total direct mercury deposition from the atmosphere. Estimates of natural (deposition prior to human influence) loading rates generally range between $2.0 \mu\text{g m}^{-2} \text{yr}^{-1}$ and $3.7 \mu\text{g m}^{-2} \text{yr}^{-1}$ in the literature^{2, 30, 31}. Assuming a natural loading rate of approximately $3 \mu\text{g m}^{-2} \text{yr}^{-1}$ and incorporating a recycled component of historical atmospheric mercury loading based on the work by Pirrone et al.^{32, 33} gives an estimate of 143 kg/yr of natural and recycled mercury that is directly deposited to Lake Ontario from the atmosphere (Figure 6). There may also be a "global background" component of deposition, however no data were available to estimate potential inputs from this source.

The total external loading rate of mercury to Lake Ontario is poorly characterized at present. In addition to atmospheric deposition, potential mercury sources include inputs from the Niagara River and smaller tributaries, runoff from the catchment area, and groundwater. Rolffhus et al.¹¹ estimated that inputs from groundwater were small in Lake Superior, hence they are not considered explicitly in this model. Total loading was approximated using the product of the concentration of mercury on suspended sediment solids in Lake Ontario³⁴, the sediment accumulation rate and bulk density. After subtracting the atmospheric component of total loading, mercury inputs from tributaries and runoff in was estimated at 702 kg yr^{-1} (Figure 7). Given the current discharge rate of water flowing into Lake Ontario²¹, this corresponds to a mean concentration of 2.17 ng L^{-1} . This concentration is reasonable for a freshwater tributary like the Niagara River, which accounts for ~70% of all water inflow into Lake Ontario. When considering the effectiveness of emissions reductions strategies, it is important to note that some of the mercury that is initially deposited in the watershed region will be flushed from the soils into the lake during storm events and in runoff. Thus, manipulations of the potential effectiveness of emissions controls strategies in terms of declines in total loading to the system require better estimates of the fraction of

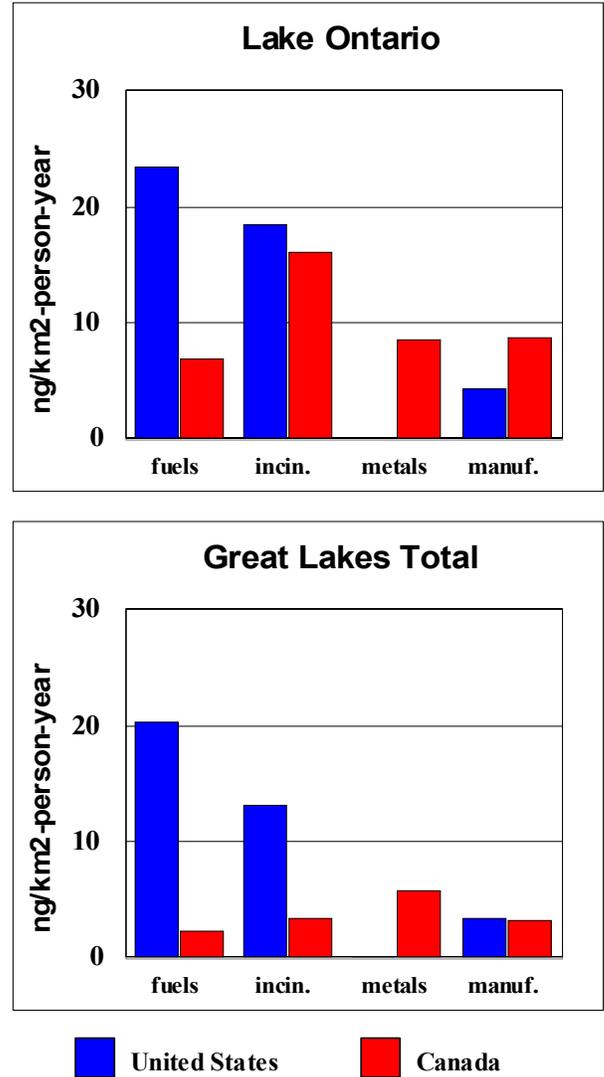


Fig. 5. Per-capita mercury contributions to Lake Ontario from U.S. and Canadian sources (ng Hg deposited per km² of lake surface per person per year); "fuels" = fuel combustion; "incin" = waste incineration; "metals" = metallurgical processes; "manuf" includes "other" source types (e.g., lamp breakage) in addition to manufacturing processes (e.g., chloralkali production).

atmospherically derived mercury deposited in the watershed that is drained into lakes and the time scale over which such processes occurs.

There are limited empirical data for MMHg concentrations and fluxes in Lake Ontario. However, if the concentration of MMHg is approximated using the mean fraction of Hg-T present in a number of other rivers³⁵, the contributions from the watershed are expected to be substantial (Figure 8). Because the amount of MMHg in the water and sediments drives the food-web bioaccumulation model, the estimated effectiveness of emissions reductions at reducing fish mercury levels is sensitive to the rate at which atmospherically derived inorganic mercury is converted to MMHg and subsequently leached from the watershed into the lake.

Model Results

Mass budgets for total mercury (Hg-T) and MMHg (Figures 7 and 8) both indicate that the majority of the mercury in Lake Ontario is contained in the sediment compartment. Accordingly, dynamic processes occurring at the sediment-water interface are an important transfer process. Sediment to water diffusion of mercury was estimated for both models (MMHg/Hg-T) using molecular diffusivity coefficients estimated by Gill et al.³⁶. In contrast to several other studies^{37,38}, this analysis suggests that diffusion is a significant mode of mercury transfer between the sediments and water, particularly for MMHg.

The mass budgets for Hg-T and MMHg show that most of the mercury entering Lake Ontario from tributaries, runoff, and atmospheric deposition is scavenged from the

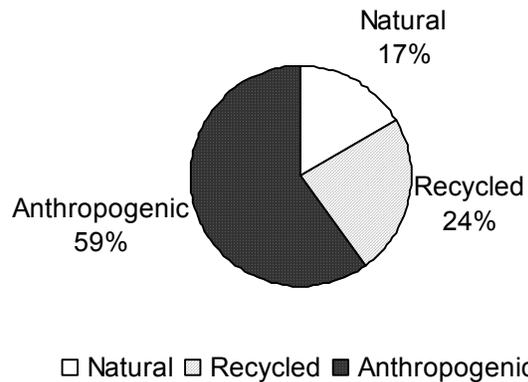


Fig. 6. In addition to mercury that originates from anthropogenic emissions (estimated from the Cohen model), total direct atmospheric mercury deposition to Lake Ontario ($\sim 360 \text{ kg yr}^{-1}$) includes both a naturally present and a recycled (continuously deposited and re-emitted mercury) component.

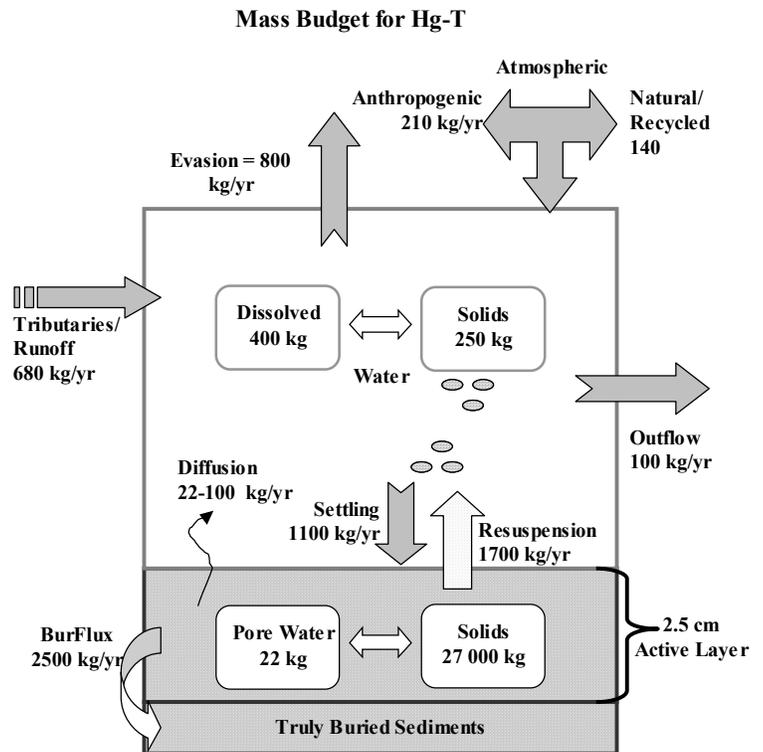


Fig. 7. Estimated mass budget for total mercury Hg-T in Lake Ontario. The majority of mercury in this system is contained in the sediment compartment, likely a reflection of historic mercury inputs from point sources in the region between the 1940s and 1970s³³.

water column and desposited to the sediments. Only a small fraction of total mercury inputs are lost in outflowing waters that enter the St. Lawrence River. This is consistent with other studies that showed Lake Ontario is predominately a depositional system³⁴ and effectively filters contaminants present in inflowing waters from the other Great Lakes and the Niagara River before it is discharged into the St. Lawrence River³⁹. This process helps to explain why Lake Ontario has the most contaminated sediments of all of the Great Lakes²⁷.

The large reservoirs of Hg-T in the active layer of the sediment compartment (27,000 kg) relative to present day fluxes (order of magnitude 10^2 to 10^3 kg yr⁻¹), means that concentrations in the sediment compartment will respond relatively slowly to changes in total loading.

In contrast, the mass budget for MMHg suggests that this pool of mercury is much more dynamic in Lake Ontario and largely depend on the rate at which key uncertain processes (photodegradation in the water column and *in situ* methylation in the sediments) occur. The persistence and accumulation of MMHg in the water and sediments drives the rate of mercury accumulation in the food web. Thus, another key uncertainty highlighted in this analysis that requires further characterization are the degradation processes affecting the stability of MMHg in the water column and factors determining the production and persistence of MMHg in the sediments.

Running the model for Hg-T in a time-dependent fashion revealed that it would take several decades for the system to reach steady state with respect to current inputs (Figure 9, Table 1). Presently the model suggests that the water column is a net source of total mercury, largely

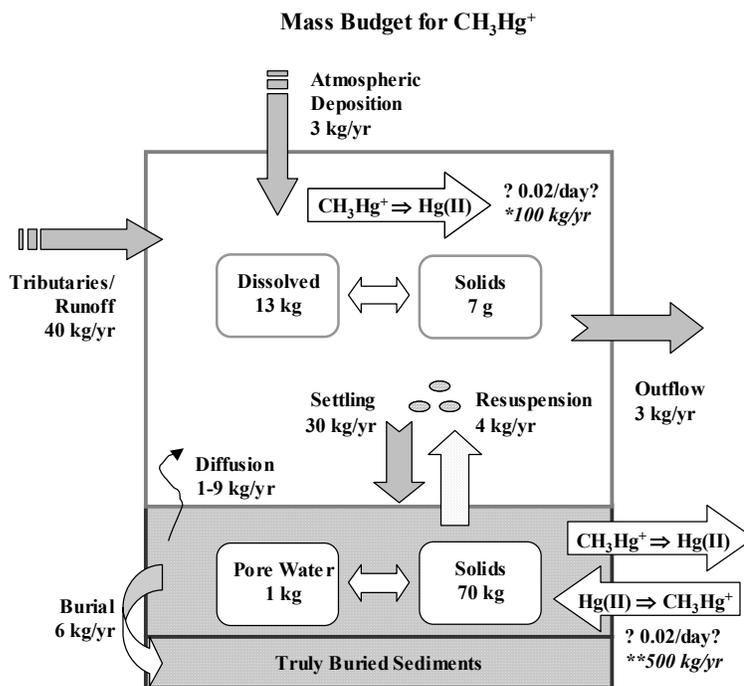


Fig. 8. Mass budget for methylmercury (MMHg) in Lake Ontario. Due to limited empirical data, these values are highly uncertain. However, the model indicates that MMHg inputs from the watershed surrounding Lake Ontario are significant. Two of the most critical uncertainties that need to be better characterized to understand MMHg dynamics are the rate of MMHg photodegradation in the water column and *in situ* methylation in the sediment compartment. *The photodegradation rate shown was measured experimentally in some high-altitude lakes and is therefore highly uncertain for Lake Ontario. **The methylation rate shown was measured using high-activity stable mercury isotopes as a tracer in the Florida Everglades³⁸ and is therefore also highly uncertain.

due to the high rate of dissolved gaseous mercury evasion from the water column. This finding concurs with the work of Mason et al.¹², who found that gas evasion (modeled results) represent around 45% of all Hg outputs from the system, whereas the remaining 55% moves to the sediment in Lake Michigan. The sediments of Lake Ontario contain a large reservoir of mercury and act as a net source of mercury to the water column through resuspension and diffusion. The disequilibrium between present day mercury inputs and sediment concentrations in Lake Ontario is consistent with the work of Pirrone et al.³³, who postulated that the system-wide averaging processes within the lake prior to final accumulation in sediments as well as *in situ* mixing of sediments are likely the primary reasons for the loss of correspondence between atmospheric Hg deposition and Hg accumulation in sediments. The authors of this study noted that although local point sources (i.e. waste waters) were dominant sources of Hg accumulated in Lake Ontario sediments from 1940 to 1970, (after this period atmospheric deposition was the major source), the system was still experiencing the residual effects of that contamination. This occurs because historically deposited Hg-T is being mixed and redistributed in the active sediment layer, as shown in Fig. 7.

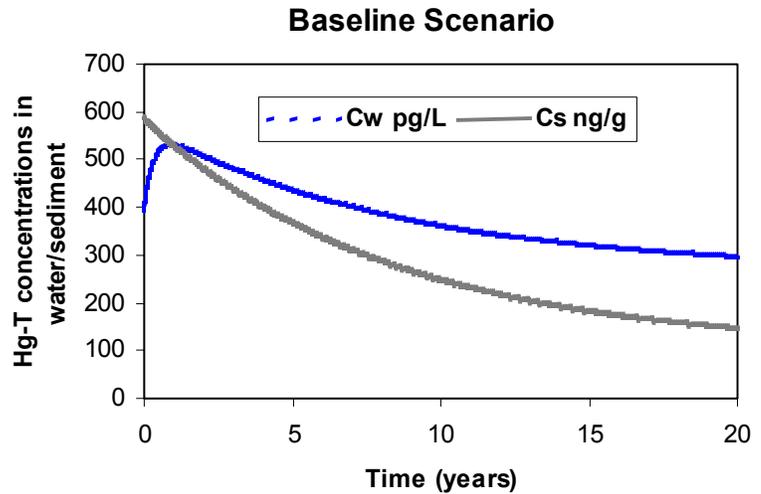


Fig. 9. Time dependent simulation of changes in mercury concentrations in Lake Ontario with no changes in estimated loading in 1995-1996. Note that the system is not at steady state and concentrations continue to decline over several decades.

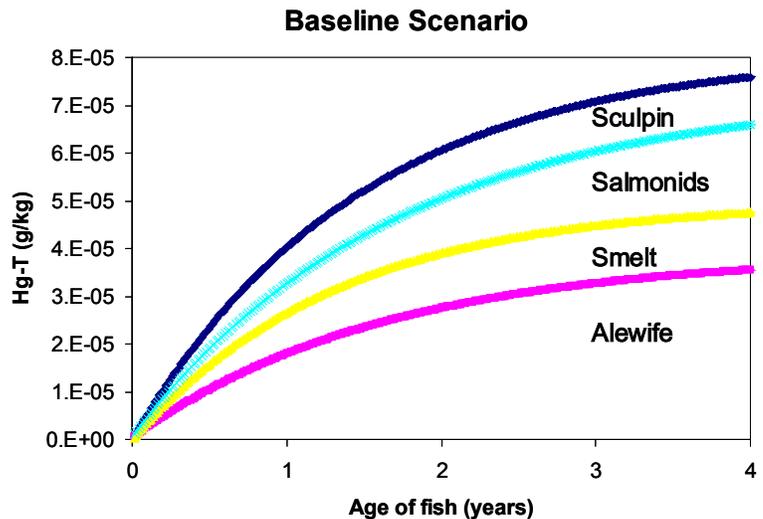


Fig. 10. Mercury concentrations in fish of different age classes in Lake Ontario, assuming no change in current emissions or loading rates. Concentrations in the food web are also not at steady state, thus it is critical to consider the age class of the species being studied to anticipate the level of mercury bioaccumulation.

The effectiveness of two scenarios for emission reductions were investigated using the model to simulate changes in mercury concentrations in Lake Ontario (Table 1). Although it was possible to investigate achieved declines in steady state concentrations of mercury in the water and sediments, the range of uncertainty related to the reactivity of different sources of inorganic mercury inputs that determine the rate of MMHg production in the sediments, the rate of degradation of MMHg in the water column, and the amount of MMHg from the watershed restricted confidence in forecasted changes in mercury concentrations in fish.

Table 1. Changes in anthropogenic mercury releases, loading to Lake Ontario and concentrations in water and sediments at steady state under different loading scenarios. Baseline scenario assumes no change in anthropogenic emissions, "70% Coal" assumes a 70% reduction in mercury emissions from coal-fired utilities, and "50% Overall" is based on a 50% reduction in anthropogenic emissions from all sources. * Reductions in total loading with different emission control scenarios are likely greater than estimates shown as values do not incorporate declines in atmospheric inputs from the catchments that drain into Lake Ontario. **These calculations assume that on a decadal time scale (necessary to achieve steady state) a 50% decline in emissions will translate into a 50% decline in loadings to Lake Ontario.

	Baseline Scenario	70% Coal	50% Overall
Emissions U.S. and Canada (All Sources/1996)	155 t yr ⁻¹	124 t yr ⁻¹	77.5 t yr ⁻¹
Direct Atmospheric Loading to Lake Ontario from Anthropogenic Sources	214 kg yr ⁻¹	162 kg yr ⁻¹ (24% reduction)	107.2 (50% reduction)
Total Estimated Loading Lake Ontario (atmosphere/tributaries/runoff)	1043 kg yr ⁻¹	*990 kg yr ⁻¹	*935 kg yr ⁻¹
Hg-T Concentration in Water at Steady State Note: Current Mean Concentration ²⁹ ~ 390 pg L ⁻¹	268 pg L ⁻¹	254 pg L ⁻¹	**134 pg L ⁻¹
Hg-T Concentration in Sediments at Steady State Note: Current Mean Concentration ²⁷ ~ 586 ng g ⁻¹	101 ng g ⁻¹	96 ng g ⁻¹	**51 ng g ⁻¹

CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

Overall, the integrated model developed in this study suggests that for total mercury in Lake Ontario there will be a decadal-scale lag time between emission reductions and declines in concentrations in sediments and water to reflect present-day inputs. However, the model suggests that it is the more dynamic and actively cycling pool of MMHg in the sediments and water that drives the temporal response of concentrations in organisms. The model indicates that the production, accumulation and persistence of MMHg in Lake Ontario determining exposure of organisms is a function of three uncertain parameters in this study: 1) *in situ* production of mercury in the sediments, 2) the magnitude of MMHg production (and by

proxy production within) the drainage basin, and 3) the rate of MMHg breakdown (via photo reduction or other processes) in the water column. Hence, to adequately model the effectiveness of different emission reduction strategies at reducing concentrations in fish, more information is needed on the reactivity of different sources of inorganic mercury in the ecosystem. Differences in reactivity among atmospherically derived mercury, mercury from the watershed and tributaries that complexes with organic molecules, and the large reservoir of historic mercury in the sediments as suggested in recent research⁴⁰ would cause different pools of mercury to be selectively converted to MMHg and are critical for quantifying the effectiveness of proposed emission reductions and the persistence of MMHg in the water and sediments.

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