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Reconciling models and measurements to assess trends in atmospheric mercury deposition

Elsie M. Sunderland [a,*], Mark D. Cohen [b], Noelle E. Selin [c], Gail L. Chmura [d]

[a] US Environmental Protection Agency, Office of the Science Advisor, Washington, DC, USA
[b] NOAA Air Resources Laboratory, 1315 East West Highway, SSMC3, R/ARL, Silver Spring, MD, USA
[c] Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
[d] Department of Geography and Global Environment and Climate Change Centre, McGill University, 805 Sherbrooke St. West, Montreal QC, Canada

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Mercury deposition trends are estimated from sediment data and atmospheric models.

Abstract

Changes in atmospheric mercury deposition are used to evaluate the effectiveness of regulations controlling emissions. This analysis can be complicated by seemingly incongruent data from different model runs, model types, and field measurements. Here we present a case study example that describes how to identify trends in regional scale mercury deposition using best-available information from multiple data sources. To do this, we use data from three atmospheric chemistry models (CMAQ, GEOS-Chem, HYSPLIT) and multiple sediment archives (ombrotrophic bog, headwater lake, coastal salt marsh) from the Bay of Fundy region in Canada. Combined sediment and modeling data indicate that deposition attributable to US and Canadian emissions has declined in recent years, thereby increasing the relative significance of global sources. We estimate that anthropogenic emissions in the US and Canada account for 28–33% of contemporary atmospheric deposition in this region, with the rest from natural (14–32%) and global sources (41–53%).

Keywords: Historical pollution; Mercury; Models; Pre-industrial; Sediment

1. Introduction

Recent regulatory efforts aimed at minimizing harmful health effects from methylmercury (MeHg) exposure have focused on reducing anthropogenic mercury (Hg) emissions (NEG-ECP, 2003; USEPA, 2005). Gaseous elemental mercury (Hg(0)) accounts for the majority of atmospheric Hg, has an atmospheric lifetime of approximately one year, and distributes globally (Selin et al., 2007). Reductions in atmospheric deposition achieved by federal regulations therefore depend, in part, on relative contributions from regional and global anthropogenic and natural (e.g., crustal degassing, volcanoes, soils) Hg sources. Field measurements of atmospherically deposited Hg are presently insufficient to evaluate temporal trends and source–receptor relationships because wet deposition measurements are restricted to a few monitoring locations and dry deposition measurements are not commonly made due to limited analytical technology (Lindberg et al., 2007; Miller et al., 2005). Although a variety of regional and global scale atmospheric models for Hg have been developed, results often differ as a function of the modeling domain, resolution of outputs, input meteorology, emissions information, and underlying model formulation (Ryaboshapko et al., 2007). Despite uncertainties in both modeling data and measurements, environmental managers must use best-available information to evaluate emission

* Corresponding author at: USEPA, 1 Congress Street, Mail Code CWQ, Boston, MA 02114, USA. Tel.: +1 617 918 1543; fax: +1 617 918 1505.
E-mail address: sunderland.elsie@epa.gov (E.M. Sunderland).

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reduction programs and assess future regulatory alternatives. In this study, we estimate relative contributions to Hg deposition from regional, global and natural sources in the Bay of Fundy region, Canada using data from a variety of sediment core types (bogs, lakes, tidal salt marshes), wet deposition measurements, and three different atmospheric models (CMAQ, GEOS-Chem and HYSPLIT).

When sediments from lakes, bogs, and coastal salt marshes are undisturbed they can provide valuable information on historical atmospheric Hg deposition (e.g., Bricker, 1996; Engstrom et al., 1994; Roos-Barraclough et al., 2002; Swain et al., 1992). However, processes controlling Hg mobility and redistribution must be taken into account to properly interpret these data. For example, Rasmussen (1994) pointed out that Hg enrichment in surface layers of sediment cores resulting from diagenetic remobilization is easily mistaken as a signal of anthropogenic pollution. To illustrate the importance of such processes and associated difficulties interpreting trends in historical Hg deposition, we examine evidence of post-depositional disturbance in multiple sediment archives from the Bay of Fundy region. We use this analysis to determine our relative confidence in atmospheric deposition estimates from the different sediment cores analyzed.

Whereas sediment data represent site-specific deposition estimates, models can be used to derive source–receptor relationships and aggregate results across a region of interest. Modeling results are affected by limitations in model input data (e.g., emissions inventories) and incomplete scientific understanding (e.g., atmospheric chemistry) (Lin et al., 2006), but quantitative estimates of these uncertainties are difficult to obtain. Recently, an expert panel on atmospheric mercury processes asserted that uncertainty associated with current models must be relayed to and understood by policy makers (Lindberg et al., 2007). Addressing this issue, the National Research Council Committee on Models in Environmental Regulatory Decision-Making concluded that considering results from multiple models assists in identifying scientific uncertainties that cannot be formally quantified through probabilistic simulation techniques and sensitivity analysis (NRC, 2007). Here we assemble deposition results for the Bay of Fundy from three different types of atmospheric mercury models (global, GEOS-Chem; regional Eulerian, CMAQ; regional Lagrangian, HYSPLIT). We discuss differences in the types of information that can be derived from each modeling framework and, where possible, compare modeled and measured deposition estimates.

After assessing the strengths and weaknesses of modeling outputs and empirical data, we combine results to estimate atmospheric Hg deposition trends in the Bay of Fundy region. To the best of our knowledge, this is the first regional-scale example of how multiple atmospheric models and sediment archives can be used to estimate components (US and Canada, global, natural) of atmospheric Hg deposition. This type of analysis is generally needed to determine Hg deposition reductions achievable by regulating sources in the US and Canada.

2. Evaluation of data sources

2.1. Sediment core data overview

We use sediment core data from an ombrotrophic bog, two headwater lakes, and three tidal salt marshes sampled in non-industrialized areas along the New Brunswick (NB) coastline of the Bay of Fundy (Fig. 1). We selected this region to

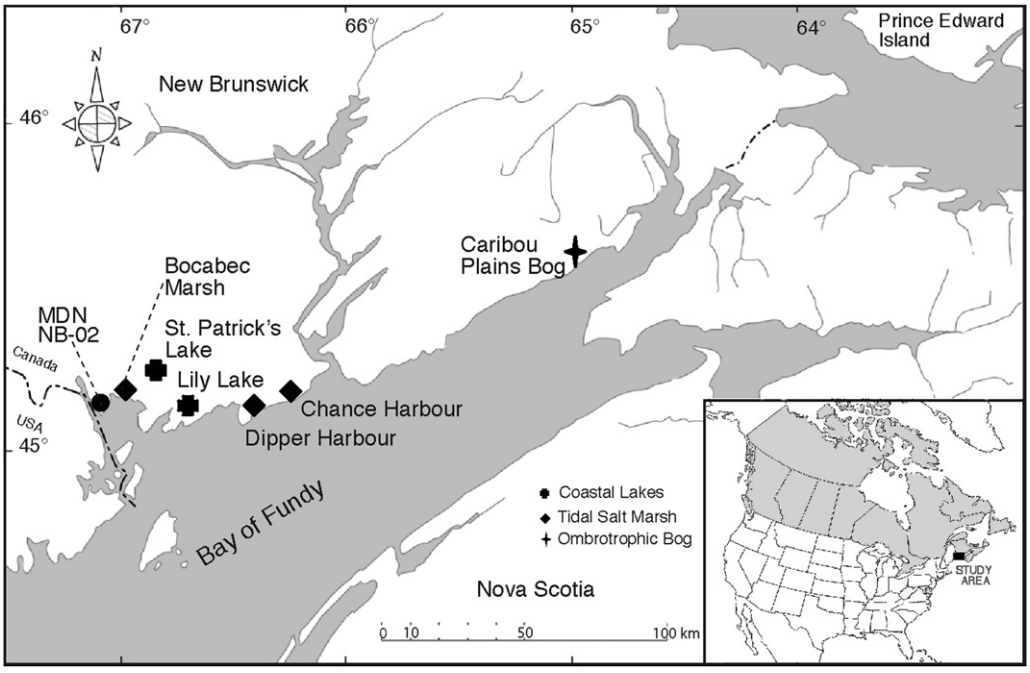

Fig. 1. Locations of sediment core sampling locations and Mercury Deposition Network (MDN) station (NB-02) in New Brunswick, Canada adapted from Chmura et al. (2001).

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maximize compatibility between modeled and measured atmospheric Hg loading estimates, wet deposition data from the Mercury Deposition Network (MDN) station in St. Andrews (NB-02), and ecosystem scale modeling in Passamaquoddy Bay, NB at the mouth of the Bay of Fundy (Sunderland et al., 2004, 2006). Atmospheric modeling in this region (described below) suggests there is limited spatial variability in deposition among sampling locations for the sediment cores included in our analysis.

Data from bog and lake cores are from previously published reports (Kainz et al., 1998; Pilgrim et al., 2000; Rutherford and Matthews, 1998). We collected salt marsh sediment data between 1994 and 1996 from high marsh areas (the high marsh zone), which is known to preserve a better signal of atmospherically deposited contaminants than lower elevation regions that are flooded diurnally (Bricker, 1996). Further details of sampling and analytical procedures used for salt marsh sediments can be found elsewhere (Chmura et al., 2001; Sunderland et al., 2004) and in the electronic supplement.

2.1.1. Reliability of sediments as historical archives

To evaluate the integrity of sediment data as historical archives of Hg deposition, we consider three common indicators of diagenetic remobilization (Fig. 2): (1) redox related controls on mobility, (2) physical and biological redistribution, and (3) coincident enrichment of Hg with organic carbon.

Iron (Fe), manganese (Mn), and direct measurements of redox potential (Eh) all provide simple indicators of redox related Hg migration in sediments. Among the cores presented here, both Bocabec salt marsh and St. Patrick's Lake show significant correlations between vertical Hg profiles and Fe,

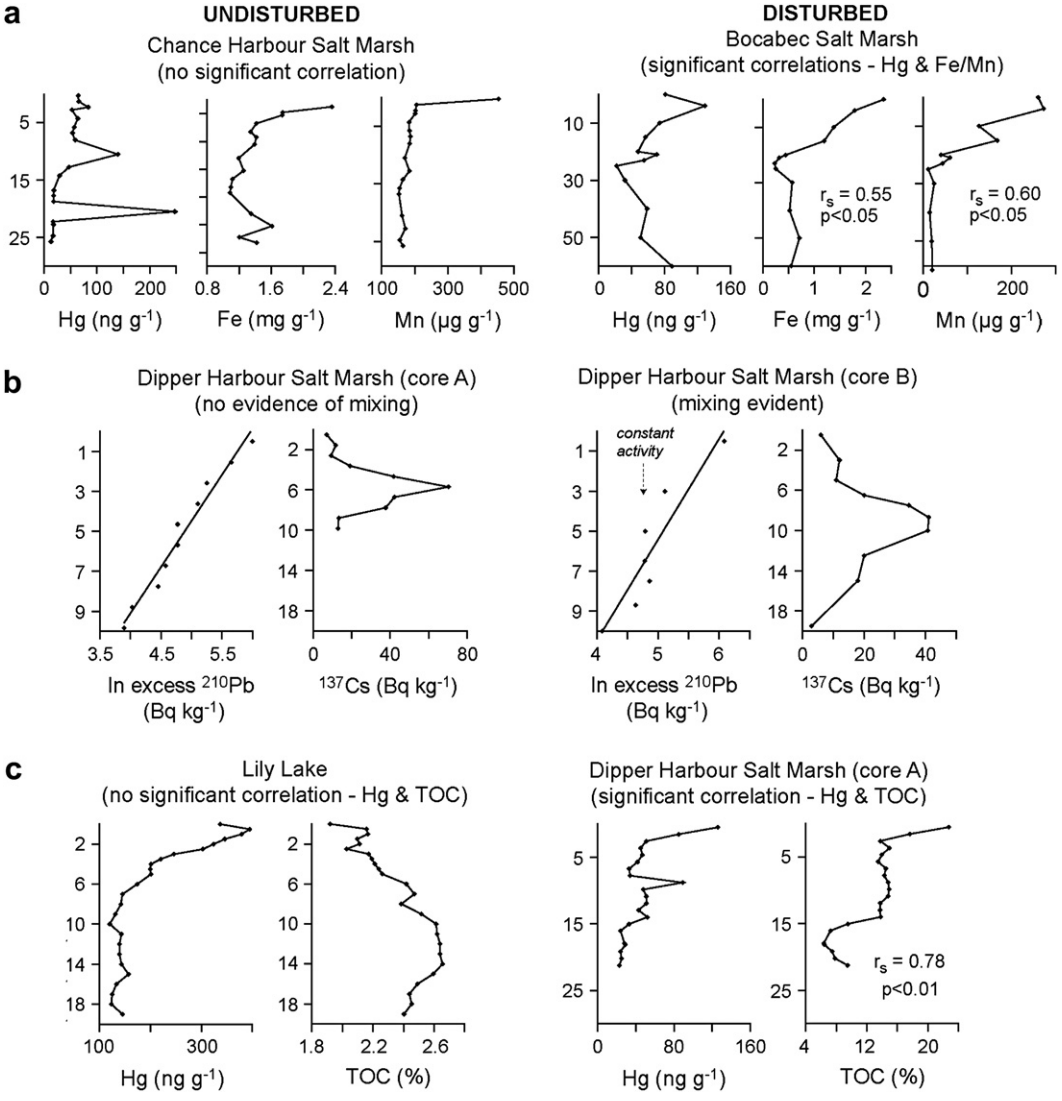

Fig. 2. Examples of sediment Hg profiles in undisturbed and disturbed sediments through: (a) redox related mobility of Hg in sediment column, (b) physical and biological mixing indicated by radionuclide data, and (c) coincident enrichment of Hg in surface sediments with total organic carbon (TOC). Spearman rank correlation coefficients (r_s) between Hg and ancillary sediment data are shown next to Fe, Mn and TOC profile data. For ^{210}Pb data, the straight line next to the unsupported isotope activity shows the ''ideal'' decay. For ^{137}Cs, a perfectly preserved profile appears as a narrow pulse beginning in 1950, with a primary peak in 1958 and an overall maximum in 1963 followed by a rapid decline (Charles and Hites, 1987).

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Mn or Eh (Fig. 2a, Supplementary Figs. 1 and 2). Fluctuations in redox status can remobilize Hg under reducing conditions by releasing divalent mercury (Hg(II)), which is subsequently strongly sorbed to the surface of Fe and Mn hydroxides/oxides in oxic environments (Benoit et al., 1998; Bricker, 1993).

Radionuclide data (^{137}Cs, ^{210}Pb) used to date sediment cores can also be used to indicate physical and biological disturbances (Fig. 2b). For example, Dipper Harbour salt marsh core B has a rounded and drawn out ^{137}Cs profile compared to core A (Fig. 2b). In addition, the ^{210}Pb profiles from both Dipper Harbour (core B) and St. Patrick's Lake and show zones of constant activity with depth rather than the expected exponential decay (Fig. 2b, Supplementary Fig. 2).

Contemporary Hg fluxes derived from sediment cores may reflect an enrichment of organic matter rather than enhanced Hg atmospheric deposition. For example, Dipper Harbour salt marsh (core A) shows a coincident rise in surface sediment Hg concentrations with total organic carbon (TOC) content (Fig. 2c). Several other studies show an abundance of easily degradable organic matter in surface sediments can result in a corresponding peak in Hg concentrations (Kainz et al., 2003; Sanei and Goodarzi, 2006).

In summary, a variety of diagenetic processes have altered the Hg profiles in three out of seven sediment cores included in our analysis (Bocabec salt marsh, St. Patrick's Lake, Dipper Harbour salt marsh (core B)). We therefore exclude these cores from further analysis. In addition, surface enrichment of both Hg and TOC in Dipper Harbour salt marsh (core A) suggests this core does not reliably indicate recent Hg deposition. Cores from Chance Harbour salt marsh and Lily Lake show the least evidence of disturbance through diagenetic processes (Fig. 2, Supplementary Figs. 1 and 2). We were unable to determine the suitability of data from the Caribou Bog core because ancillary information needed to assess controls on Hg distribution were not available.

2.1.2. Correction factors for atmospheric deposition

To infer atmospheric deposition rates from sediment data, other studies commonly use correction factors for sediment focusing (preferential accumulation of sediment in certain regions) (Charles and Hites, 1987; Perry et al., 2005). Such corrections are derived from the ratio between atmospherically deposited (excess) ^{210}Pb fluxes and directly measured atmospheric ^{210}Pb deposition (e.g., Charles and Hites, 1987; Engstrom and Swain, 1997; Lamborg et al., 2002; Perry et al., 2005). We estimate atmospheric ^{210}Pb deposition in the Bay of Fundy is $\sim$0.01 Bq cm^{-2} year^{-1} using rainfall data from St. Andrews, NB between 1996 and 2002 (NADP, 2007) and measured ^{210}Pb concentrations in precipitation from Nova Scotia (Lamborg et al., 2002). This is the same as reported regional data on ^{210}Pb deposition (Oldfield and Appleby, 1984). Using these data, we derive sediment focusing correction factors for Lily Lake (0.145) and Dipper Harbour (core A) (0.435). Measured excess ^{210}Pb flux in surface sediments from the Chance Harbour core (0.013 Bq cm^{-2} year^{-1}) falls within the range of expected atmospheric deposition and therefore requires no correction factor. Such correction factors are not necessary for ombrotrophic bogs (e.g., Caribou Bog), which receive all of their nutrients and water directly from atmospheric deposition (Shotyk, 1988).

Many studies also apply correction factors for watershed/tidal delivery of atmospherically deposited Hg (e.g., Bricker, 1993, 1996; Engstrom et al., 1994; Engstrom and Swain, 1997; Kamman and Engstrom, 2002; Lamborg et al., 2002 and references therein). Watershed delivery of atmospherically deposited Hg to lake sediments varies widely depending on watershed characteristics and can be estimated empirically using data from multiple sediment cores within a lake basin (Engstrom et al., 1994; Engstrom and Swain, 1997). Because multiple cores are not available for Lily Lake, we use the catchment to water surface area ratio (4:1) to derive the watershed correction factor (0.454) based on an estimated 30% watershed delivery for other lakes in the region with similar ecological characteristics (Lamborg et al., 2002). For Dipper Harbour (core A) and Chance Harbour salt marsh cores, we correct for tidal inputs based on mass balance calculations (supporting Table 1) using the methodology developed by Bricker (1996). As noted above, such corrections are not required for ombrotropic bogs.

2.1.3. Corrected sediment data

Fig. 3 shows corrected atmospheric Hg deposition rates for sediment cores from Chance Harbour salt marsh, Lily Lake

Table 1
Pre-industrial atmospheric Hg deposition estimates for the Bay of Fundy region

Data source	Description	Temporal resolution	Spatial resolution	Deposition (μg m^{-2} year^{-1})	Reference
GEOS-Chem pre-industrial simulation	Global Eulerian model	Pre-industrial mercury cycle (zero emissions human sources)	4° × 5° (44–48°N 62.5–67.5°W)	3.4	Selin et al. (in press)
Chance Harbour salt marsh core	Dated deep sediments	ca. 1800–1850 (average)	Point estimate 45.1°N 66.1°W	3.8	This study
Lily Lake core	Dated deep sediments	ca. 1800–1850 (average)	Point estimate 45.3°N 66.3°W	3.1	Kainz et al. (1998)
Caribou Bog core	Dated deep sediments	ca. 1835	Point estimate 45.5°N 65.0°W	1.4	Rutherford and Matthews (1998)
Dipper Harbour salt marsh core	Dated deep sediments	ca. 1800–1850 (average)	Point estimate 45.0°N 66.3°W	3.3	This study

See supplementary Tables 1 and 2 for details of sediment correction factors applied and anthropogenic enrichment factors (AEFs).

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and Caribou Bog. We use these cores to interpret contemporary (ca. 1990–1996) and pre-industrial deposition (ca. 1800–1850) in the Bay of Fundy region (Tables 1 and 2).

We assume that pre-industrial Hg deposition (ca. 1800–1850) in this region is approximately representative of deposition from natural sources, although this may include a small component of recycled anthropogenic Hg from historic global sources (Roos-Barraclough et al., 2002). Comparing modern deposition rates (surface sediments) to pre-industrial loading rates (deep sediments) indicates anthropogenic enrichment of Hg deposited in this region (supplementary Table 2). Anthropogenic Enrichment Factors (AEFs) in cores presented here range between 3.0 and 13.9. The high end of this range is from the Chance Harbour core, where no data were available to assess the significance of diagenetic remobilization of Hg. A number of other studies have found ^{210}Pb migration and corresponding mobility and loss of Hg in the sediment column of other peat cores, suggesting this is potentially a problem in the Caribou Bog core (Biester et al., 2007; Lamborg et al., 2002; Shotyk, 1988). For example, Biester et al. (2007) show that anthropogenic Hg enrichment is often overestimated in peat archives compared to lake sediments because of upward diffusion of Hg in peat cores. However, in the absence of additional information for analysis, such discussion remains equivocal. AEFs from Lily Lake and Chance Harbour salt marsh sediments range between 3.0 and 4.9, which agrees well with other studies in the region showing AEFs range between 2.1 and 6.9 (average 3.9) in the New England region (Kamman and Engstrom, 2002; Perry et al., 2005) and 5.0 in Nova Scotia (Lamborg et al., 2002).

Despite corrections for non-atmospheric Hg sources and sediment focusing, temporal patterns of Hg deposition differ among bog, lake and salt marsh cores (Fig. 3). In part, this reflects the degree to which Hg deposition is temporally averaged in sediments (supplementary Table 3). For the cores shown in Fig. 3, Lily Lake sediments have the lowest temporal resolution (8–17 years) compared to salt marsh sediments (3–5 years) and bog sediments (~7 years). Accordingly, Chance Harbour salt marsh sediments show the most detailed temporal differences in Hg accumulation. Although the Chance Harbour core shows an increase in Hg deposition around WWII and ca. 1883 (potentially from historic gold

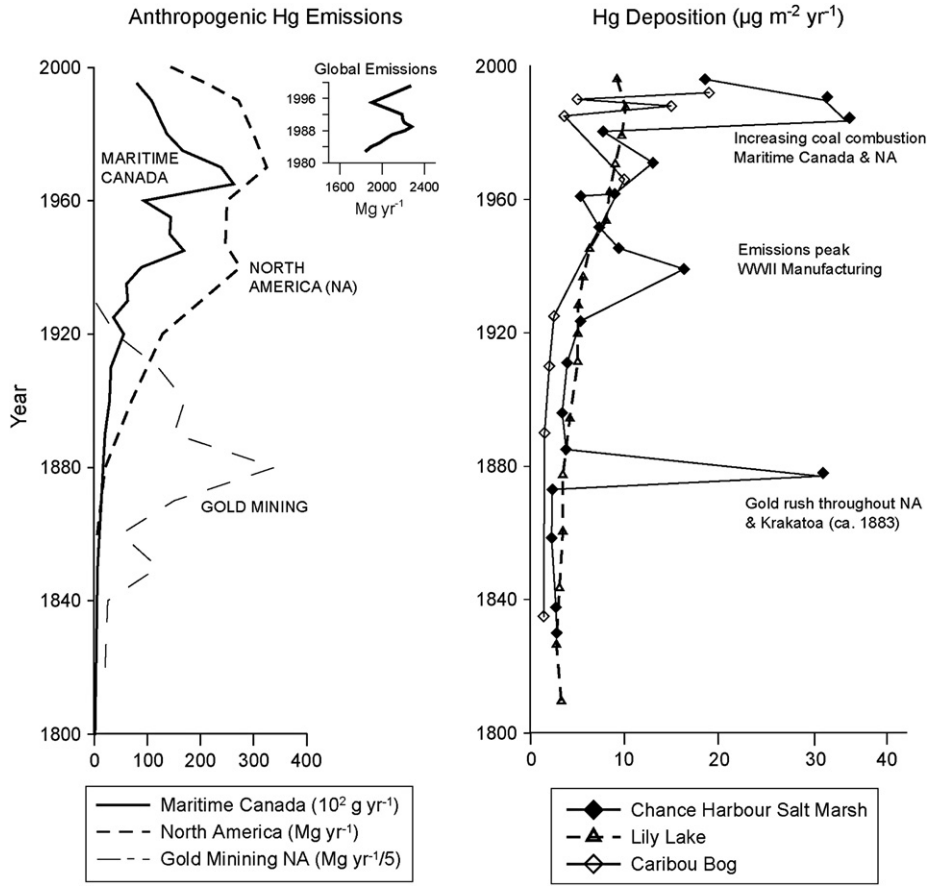

Fig. 3. Comparison between historical emissions from anthropogenic sources on the local (Maritime Canada), regional (North America) and global scales and atmospheric deposition recorded in sediments from Chance Harbour and Lily Lake sediment cores. Enrichment factors for both cores are also shown from 1880 to present. [a]Global emissions are from Pirrone et al. (1998), Pacyna and Pacyna (2002), and Pacyna et al. (2006). [b]Anthropogenic emissions in Maritime Canada are from Sunderland and Chmura (2000). [c]North American emissions are for "modern sources" (all sources but gold mining estimates) by Pirrone et al. (1998) up to 1980, and Pai et al. (2000), Pacyna and Pacyna (2002), Seigneur et al. (2004) and Pacyna et al. (2006). [d]Emissions from gold mining in North America are from Pirrone et al. (1998).

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Table 2
Contemporary Hg deposition estimates for the Bay of Fundy region

Data source	Description	Temporal resolution[a]	Spatial resolution	Deposition ($\mu g\ m^{-2}\ year^{-1}$)	Reference[b]
ca. 1990–1996					
HYSPLIT 1990–1996 simulation	Regional scale Lagrangian model of US/Canada human sources	1990–1996 US and Canada emissions; 1996 meteorology	Gulf of Maine area receptor, centroid location 43.59°N, 67.91°W	7.8	This study; Cohen et al. (2004)
Chance Harbour salt marsh core	Surface sediments collected 1996	ca. 1993–1996	Point estimate 45.1°N 66.1°W	18.6	This study
Lily Lake sediment core	Surface sediments collected 1996	ca. 1986–1996	Point estimate 45.3°N 66.3°W	9.2	Kainz et al. (1998)
Caribou Bog sediment core	Surface sediments collected 1993	ca. 1989–1993	Point estimate 45.5°N 65.0°W	19.0	Rutherford and Matthews, (1998)
ca. 1999–2001					
CMAQ 2001 simulation	Regional Eulerian model	1999–2001 US and Canada emissions; 2001 meteorology GEOS-Chem boundary conditions	36 km^2 (area aggregated for analysis: 44.3–45.2°N, 65.8–67.4°W)	12.0	USEPA (2005)
GEOS-Chem 2000–2003 simulation	Global Eulerian model	2000 global emissions; 2003 meteorology	4° × 5° (44–48°N 62.5–67.5°W)	10.0	Selin et al. (2007)
HYSPLIT 1999-2001 simulation	Regional scale Lagrangian model of US/Canada human sources	1999–2001 US and Canada emissions; 1996 meteorology	Gulf of Maine area receptor, centroid location 43.59°N, 67.91°W	3.3	This study; Cohen et al. (2004)

n/a, not applicable.
[a] Resolution of surface sediment data is based on calculations shown in supporting Table 3.
[b] References provide additional details of data collection and analysis (sediments) and model formulation/evaluation.

mining and/or volcanic activity) that agrees well with observations from ice core records (Schuster et al., 2002), such data must be interpreted with caution since they only appear in one sediment core from this region.

2.2. Modeling data sources

2.2.1. Global (GEOS-Chem)

GEOS-Chem is a global atmospheric chemistry transport model adapted for mercury by Selin et al. (2007). Contemporary GEOS-Chem results presented in Fig. 4 are from model version 7.04 (http://www-as.harvard.edu/chemistry/trop/geos/), have a horizontal resolution of 4° × 5°, and are based on year 2000 global anthropogenic emissions and 2003 meteorological data from the NASA Goddard Earth Observing Systems (GEOS-4) (Table 2). We also use results from a GEOS-Chem simulation of the pre-industrial global Hg cycle (Table 1) (Selin et al., in press).

2.2.2. Regional Eulerian (CMAQ)

CMAQ (community multi-scale air quality model) is an Eulerian regional scale atmospheric model for North America. Mercury deposition results shown in Fig. 4 are for the year 2001 from model version 4.3, which was developed for the Clean Air Mercury Rule using a 36 km horizontal grid cell spatial resolution (USEPA, 2005). CMAQ inputs include a detailed mercury emissions inventory for the US and Canada and global boundary conditions from the GEOS-Chem model (Table 2).

2.2.3. Regional Lagrangian (HYSPLIT)

Cohen et al. (2004) created a specialized version of the NOAA HYSPLIT_4 model (hybrid single particle Lagrangian integrated trajectory model, Version 4) to simulate the atmospheric fate and transport of mercury. HYSPLIT is a Lagrangian model that is well suited to examine source–receptor relationships. Source–receptor data used in our analysis (Table 2) are based on 1996 meteorology and anthropogenic Hg emissions inventories in the US and Canada for two periods (1990–1996 and 1999–2001). We consider results for two receptors: (1) the entire Gulf of Maine region, including the Bay of Fundy and (2) the MDN (NB-02) station in St. Andrews. Results from the HYSPLIT model for the MDN NB-02 point receptor and the Gulf of Maine area receptor are similar, suggesting minor variability in source–receptor relationships.

2.2.4. Comparison of modeled and measured wet Hg deposition

Other studies describe underlying assumptions and evaluation of all models presented here for a variety of applications (Cohen et al., 2004; Selin et al., 2007; USEPA, 2005). We investigate the site specific performance of each model by comparing the results to all wet deposition data available from the MDN station (NB-02) located in St. Andrews, NB for the duration of its operation between 1996 and 2003 (Fig. 5). Observed differences between modeled results and measurements reflect uncertainties in model representations of mercury chemistry and deposition processes as well as differences among the spatial domains of the models, sources considered, emissions inventories, and meteorological data.

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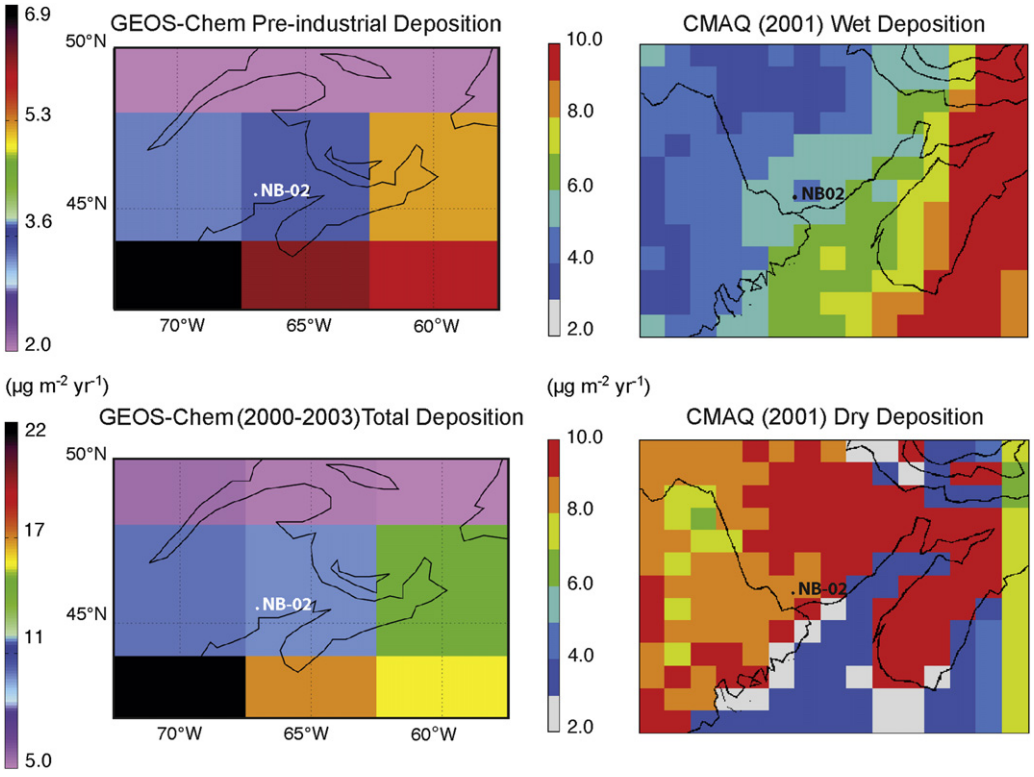

Fig. 4. Modeled contemporary and pre-industrial atmospheric mercury deposition rates for the Bay of Fundy region of Canada. Model resolution is 36 km^2 for each CMAQ grid cell and 4° × 5° for each GEOS-Chem grid cell.

As expected, HYSPLIT wet deposition results for the NB-02 point receptor are less than measured values because the model only considers deposition originating from Canadian and US anthropogenic Hg sources and does not include global or natural sources. Although the temporal resolution of HYSPLIT results (1990–1996; 1999–2001) and measured deposition values (1995–2003) are not directly comparable, both modeled and measured values seem to indicate a decline in wet deposition after 1999 (Fig. 5). This pattern has been observed at a number of MDN sites in the midwestern and northeastern US (Butler et al., in press).

CMAQ model results for the 36 km^2 grid cell surrounding the MDN NB-02 station compare favorably with 2001 measurements (Fig. 5). No local estimates for wet deposition are available from GEOS-Chem as the spatial resolution of the model is 4° × 5°. Thus it is perhaps inappropriate to compare the GEOS-Chem wet deposition to the measured deposition at NB-02. While the overall model-estimated wet deposition in the grid cell that contains NB-02 is lower than measured, modeled total Hg deposition (dry + wet) using CMAQ and GEOS-Chem are very similar (10–12 μg m^{-2} year^{-1}) (Fig. 4). The GEOS-Chem model is known to underpredict the wet vs. dry deposition fraction, as discussed in Selin et al. (2007). Such differences are a common finding when comparing models (e.g., Ryaboshapko et al., 2007). We note that all of the models discussed here have been evaluated against available ambient data (Cohen et al., 2004; Selin et al., 2007; USEPA, 2005) and have generally been found to reproduce patterns of wet deposition with reasonable accuracy.

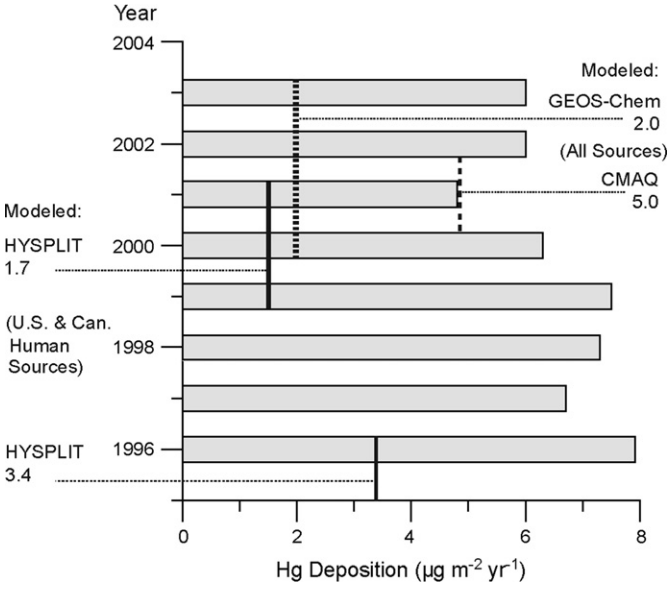

Fig. 5. Comparison of measured wet Hg deposition at Mercury Deposition Network (MDN) station NB-02 and CMAQ, GEOS-Chem, and HYSPLIT modeling results. Gray bars in the figure showing annual measured MDN data represent volume-weighted deposition from Beauchamp (1998) for 1996 and 1997 and NADP (2007) for 1998–2003. HYSPLIT results are for wet deposition from US and Canadian anthropogenic sources at the point receptor NB-02 based on emissions for the periods 1990–1996 and 1999–2001 and 1996 meteorology. CMAQ results are for wet deposition at the 36 km^2 grid cell corresponding to the MDN station based on 1999–2001emissions and meteorology. GEOS-Chem results are for the 4° × 5°grid cell that includes the NB-02 MDN station based on 2000 global anthropogenic emissions and 2003 meteorology.

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3. Results and discussion

3.1. Contemporary Hg deposition

Decreasing total Hg deposition beginning in the mid-to-late 1990s in the Bay of Fundy region is suggested by measured wet deposition (discussed above), and combined sediment and modeling data. Both Lily Lake and Chance Harbour salt marsh sediments show a pattern of declining Hg deposition in surface sediments. In addition, average Hg deposition for the early to mid-1990s estimated from sediments is 15.6 μg m^{-2} $year^{-1}$ compared to 10–12 μg m^{-2} $year^{-1}$ from models for 2001–2003 (Table 2). High and low ranges for total deposition presented in Fig. 6 are based on variability among cores and models for these two time periods (Table 2).

3.2. Source-attribution of Hg deposition

Contributions to atmospheric deposition from pre-industrial sources estimated from sediment data range between 1.4 and 3.8 μg m^{-2} $year^{-1}$, which is consistent with the modeled pre-industrial deposition from GEOS-Chem of 3.4 μg m^{-2} $year^{-1}$ (Table 1). By assuming pre-industrial deposition rates (Table 1) are approximately representative of the natural fraction of atmospheric Hg deposition, we estimate that natural sources account for between 14 and 32% in the Bay of Fundy region (Fig. 6).

We estimate contributions to deposition from US and Canadian sources using HYSPLIT model results from both the early-mid 1990s and late 1990s/2000 (Tables 1 and 2). In the early to mid-1990s, anthropogenic emissions sources in the US and Canada accounted for approximately half (average 50%, range 41–85%) of the total atmospheric deposition, compared to about one-third (28–30%) by the end of the decade (Fig. 6). Although HYSPLIT results do not include deposition from Mexican sources, contributions from US and Canadian sources observed here are comparable to other recent modeling efforts that attribute 20–30% of atmospheric Hg deposition across the entire US to North American sources (Seigneur et al., 2004; Selin et al., 2007). Detailed source–receptor information from the HYSPLIT model indicates that declines in Hg deposition in the Bay of Fundy region from US and Canadian sources are mainly due to reduced emissions from incinerators, achieved through phase-outs of mercury in waste streams, closure of older facilities, and installation of additional pollution control equipment (Fig. 7).

Global contributions to atmospheric deposition in the Bay of Fundy region (Fig. 6) were estimated using two methods. For the late 1990s/early 2000s, we used the results of a contemporary GEOS-Chem simulation with North American sources removed (total deposition 8.7 μg m^{-2} $year^{-1}$) and subtracted the simulated pre-industrial (3.4 μg m^{-2} $year^{-1}$) deposition (Table 1) to estimate global background (5.3 μg m^{-2} $year^{-1}$) (Selin et al., in press). For other years and to derive ranges in values shown in Fig. 6, we calculated relative contributions of global sources to deposition by subtracting US/Canadian anthropogenic and pre-industrial sources described above from estimated total deposition for 2000–2003. Our analysis suggests that relative contributions of global sources as a fraction of total deposition increased between the early and late 1990s, reaching approximately half of total deposition (range 41–53%, Fig. 6).

3.3. Combined modeling and sediment data

Observed declines in Hg deposition in the Bay of Fundy region in the mid-to-late 1990s points to the success of various regional measures aimed at reducing mercury releases in the northeastern states and eastern Canada as well as emission reductions in the midwestern US over this same time period (Butler et al., in press). For example, an agreement between the New England Governors and Eastern Canadian Premiers established in the mid-1990s with a goal of reducing anthropogenic emissions in their region by 90% by 2010 has already resulted in emissions reductions of greater than 50% (NEG-ECP, 2003). However, as regional sources decrease, the relative significance of global sources has increased (Fig. 6). Such patterns are consistent with the most recent global inventory showing that mercury emissions from Asian countries are continuing to rise and now account for approximately 52% of total global emissions (Pacyna et al., 2006). Although

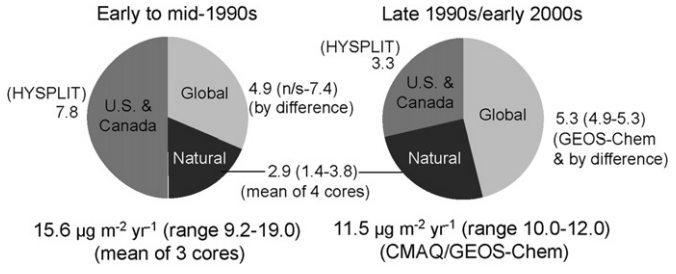

Fig. 6. Relative contributions to atmospheric mercury deposition from pre-industrial, global and Canadian/US sources estimated by combining modeling and sediment data. Figure shows mean values (μg m^{-2} $year^{-1}$) derived from sediment data and model results with ranges in brackets. n/s, not significant.

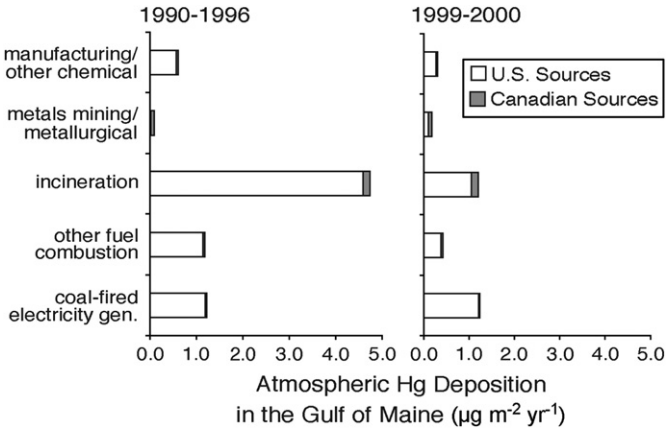

Fig. 7. Estimated contributions of US and Canadian anthropogenic source sectors to deposition in the Gulf of Maine/Bay of Fundy region from the HYSPLIT model.

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modeling and sediment data from the Bay of Fundy region illustrate the success of regional and continental Hg emission controls (Figs. 6 and 7), we conclude that further reductions in Hg deposition will be most effective if they take place on multiple geographic scales, supporting the call for a global treaty on mercury releases (Selin and Selin, 2006).

4. Dealing with uncertainty in models and measurements

Despite our efforts to develop temporally coherent estimates of atmospheric Hg deposition from a variety of modeling and sediment data, significant uncertainties remain. Direct comparison of results among different modeling frameworks and to sediment data are confounded by differences in temporal and spatial resolution. Limited data on dry deposition restrict our ability to corroborate modeling results with directly measured atmospheric Hg deposition rates. Although we show that comparing sediment data and modeling results for total Hg deposition is possible, sediments represent a temporally averaged signal of mercury deposition at a single location whereas models provide temporally explicit data that are often averaged over a larger region of interest. Our analysis also highlights challenges faced by policy makers and analysts considering results from multiple models, where simulations based on comparable input data (emissions, meteorology) and with comparable and/or desired spatial resolution are generally not available due to resource constraints.

Our analysis shows that over 40% (3/7) of the sediment cores considered did not provide reliable data on historical Hg deposition, reinforcing how easily such data can be misinterpreted as records of historical Hg deposition if effects of diagenetic processes are not identified. When data to assess the effects of sediment diagenesis are not available (e.g., Caribou Bog), constraining historical atmospheric Hg deposition estimates is extremely challenging and usually results in wide variation in Hg fluxes and AEFs among sediment cores and archive types.

Despite these limitations, we assert that using all available modeled and measured data on atmospheric Hg deposition allows a useful, weight-of-evidence approach for estimating temporal trends and source attribution that would not be possible otherwise. In addition, ranges in estimates across models and data types helps to quantify uncertainty in present atmospheric Hg deposition estimates. Future research aimed at improving our confidence in atmospheric Hg deposition models and measurements would benefit from consistent application of methods to correct for sediment diagenesis, improved spatial resolution of modeling results, improved availability and accuracy of model input data, and data on dry deposition that can be used to evaluate model performance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2008.01.021.

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