



Increased atmospheric deposition of mercury in reference lakes near major urban areas

Peter C. Van Metre

U.S. Geological Survey, Austin, TX 78754, USA

ARTICLE INFO

Article history:

Received 28 March 2011

Received in revised form

27 September 2011

Accepted 6 November 2011

Keywords:

Mercury
Sediment
Urban
Lake
Core

ABSTRACT

Atmospheric deposition of Hg is the predominant pathway for Hg to reach sensitive ecosystems, but the importance of emissions on near-field deposition remains unclear. To better understand spatial variability in Hg deposition, mercury concentrations were analyzed in sediment cores from 12 lakes with undeveloped watersheds near to (<50 km) and remote from (>150 km) several major urban areas in the United States. Background and focusing corrected Hg fluxes and flux ratios (modern to background) in the near-urban lakes ($68 \pm 6.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ and 9.8 ± 4.8 , respectively) greatly exceed those in the remote lakes ($14 \pm 9.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ and 3.5 ± 1.0) and the fluxes are strongly related to distance from the nearest major urban area ($r^2 = 0.87$) and to population and Hg emissions within 50–100 km of the lakes. Comparison to monitored wet deposition suggests that dry deposition is a major contributor of Hg to lakes near major urban areas.

Published by Elsevier Ltd.

1. Introduction

Mercury is widely recognized as a global pollutant of concern because of its large anthropogenic emissions, ubiquitous occurrence, tendency to bioaccumulate, and toxicity to wildlife and humans (Clarkson and Magos, 2006; Landers et al., 1998; Pacyna et al., 2006). Although it is well accepted that atmospheric transport and deposition are the primary mechanisms by which Hg reaches sensitive ecosystems (Fitzgerald et al., 1998), understanding of the relative importance of various sources and emission-to-deposition cycling remains incomplete. Studies of gaseous and particulate Hg in air and Hg deposition modeling suggest that elevated deposition of Hg near major urban areas is occurring (e.g. Bullock et al., 2008; Manolopoulos et al., 2007; Rothenberg et al., 2010), however, because of the difficulty in quantifying dry deposition, and therefore total deposition, near-field (near source) deposition remains poorly understood (Lindberg et al., 2007).

About 80% of Americans live in urban areas (U.S. Census, 2000) and, because of the concentration of industry, power generation, waste incineration, and mobile sources, urban areas have higher levels of many contaminants than do rural areas (Mielke et al., 2004; Van Metre and Mahler, 2005). Urban areas have been shown to export contaminants via atmospheric pathways to

surrounding rural areas (Landis and Keeler, 2002; Mason et al., 2002) and to distant regions (Landers et al., 1998). Combustion of fossil fuels, in particular coal, accounts for as much as two-thirds of global anthropogenic emissions of mercury (Pacyna et al., 2006), although in the United States, large coal-fired power plants are not generally located in cities. In addition to major point sources such as industries and waste incineration, cities contain many diffuse sources of Hg. Wilson et al. (2006) used population distribution as a surrogate parameter for estimating distributed source Hg emissions, those from diffuse sources such as vehicular emissions and point-source emissions that are not accurately located. In North America distributed sources accounted for 27% of total emissions (Wilson et al., 2006).

A sizeable body of research suggests there is enhanced near-field Hg deposition. Elevated gaseous elemental (GEM), particulate (Hg(P)), and reactive gaseous Hg (RGM) in urban relative to rural air have been reported (Gildemeister et al., 2005; Liu et al., 2010; Manolopoulos et al., 2007; Rothenberg et al., 2010) and Hg(P) and RGM are primary contributors to near-field deposition (Lindberg et al., 2007). A source-receptor analysis of Hg in precipitation events in south Florida found that local sources strongly influenced wet deposition (Hg_{WET}) in storms across the region (Dvonch et al., 1998), although less local influence was suggested by Guentzel et al. (2001). South-to-north decreases in Hg_{WET} in Sweden (Iverfeldt, 1991) and in total Hg deposition reconstructed using lake-sediment cores in Canada (Muir et al., 2009) were attributed to greater emissions and near-field deposition from the more developed southern regions of both countries.

E-mail address: pcvanmet@usgs.gov.

Hg_{WET} in Chicago, Ill., was about 40–80% greater than to rural Lake Michigan sites in 1994–95 (Landis and Keeler, 2002).

Lake-sediment cores have been widely used as environmental archives of atmospheric deposition of Hg (Fitzgerald et al., 2005; Landers et al., 1998; Swain et al., 1992). To evaluate the effects of urbanization and of atmospheric deposition on contaminant trends, the U.S. Geological Survey (USGS) is using lake-sediment cores to evaluate trends for metals and persistent organic compounds (Mahler et al., 2006; Van Metre and Mahler, 2005). Lakes in undeveloped watersheds (reference lakes) were sampled both near to and remote from major urban areas to address these objectives. Here we present an analysis of Hg deposition rates and trends in 12 reference lakes as a function of distance from major metropolitan areas, population within different radii of the lake, and estimated Hg emissions in the area of the lake.

2. Methods

Sediment cores were collected from 12 widely distributed United States lakes to evaluate Hg deposition histories (Fig. 1; Supplementary Data Table S-1). These lakes are termed reference lakes because there is no or very little (e.g., a picnic ground) development in the watershed (see Supplementary Data Fig. S-1 for maps and aerial images of each lake). Lacking any significant development in the watershed, anthropogenic contaminants are assumed to arrive to the lake and watershed only by atmospheric deposition. Five of the lakes (near-urban lakes) are 50 km or less from the center of a major urban area (about 1,000,000 people or more). Six of the lakes (remote lakes) are 150–310 km from the center of the nearest major urban area. One lake is intermediate at 90 km from the nearest major urban area. The choice of nearest major urban area was made taking the prevailing wind direction into account using wind roses from near the lake or the major urban area (see Supplementary Data Fig. S-2).

2.1. Core collection

Cores were collected in most cases from the deepest part of the lake where post-depositional disturbance was assumed to be minimal. Box cores (14 × 14-cm and 20–50 cm tall) were collected from 11 of the 12 lakes and in two of these lakes (Cypress and Carlton Lakes) gravity cores (6.3 cm diameter) also were collected. A gravity core was collected from the 12th lake (Shoe Factory Pond). Cores were extruded vertically on site and sliced into intervals of 0.5–2 cm in most cases. Samples were analyzed for major and trace elements (only Hg presented here), ²¹⁰Pb, and ²²⁶Ra. Soil cores of up to 20 cm in length were collected from open meadows near two of the lakes (Todd Lake and Hobbs Lake) and were used to estimate excess ²¹⁰Pb fallout inventories for calculation of sediment focusing factors (*f_{fs}*) (Van Metre and Fuller, 2009).

2.2. Analytical methods

Samples were stored chilled (for up to six months) and were freeze dried and ground to a powder prior to analysis. Freeze-dried sediment and soil samples were analyzed for total ²¹⁰Pb and ²²⁶Ra by gamma spectrometry based on ASTM methods C 1402-98 and E 181-98, similar to methodology described by Fuller et al. (1999). Supported ²¹⁰Pb activity was calculated as the difference between total ²¹⁰Pb activity and ²²⁶Ra activity of each interval. Samples from 11 lakes were analyzed for Hg at

a USGS laboratory in Denver, Colo., and samples from Lake Elbert were analyzed for Hg at the USGS laboratory in Madison, Wis. The Denver laboratory used cold vapor atomic adsorption spectrometry (CVAAS) (Brown et al., 2003) for seven cores collected prior to 2007 and cold-vapor atomic fluorescence spectrometry (CVAFS) (Hageman, 2007) for four cores collected in 2007–2009. The Madison laboratory used CVAFS for the Lake Elbert core (Olund et al., 2004). Briefly, samples for analysis at the Denver laboratory were digested using a sodium dichromate-nitric acid solution. For CVAAS, the Hg in the digest was oxidized to Hg⁺² with air and a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution. For CVAFS, the Hg in the digest was oxidized using bromine monochloride then pre-reduced using hydroxylamine hydrochloride. At the Madison laboratory, samples were digested and oxidized using aqua regia, then pre-reduced using hydroxylamine hydrochloride. For all three methods, the Hg⁺² was reduced to Hg⁰ with stannous chloride in a continuous flow manifold and the mercury vapor was separated and measured using CVAAS or CVAFS. The reporting level for samples from the Denver laboratory is 0.02 μg g⁻¹ and from the Madison laboratory is 0.0006–0.006 μg g⁻¹, depending on sample mass, and there were no non-detections.

Quality assurance was provided for all three methods by determining Hg concentrations for a variety of geologic reference materials. A comparison of analyses of four soil standard reference materials by the two Denver laboratory methods indicates comparable analytical performance for the methods, with percent recoveries of 99–108% for the CVAFS method and 94–112% for the CVAAS method (Hageman, 2007). Repeated analyses of MESS-2, a marine sediment reference material, by the Madison laboratory method had a percent relative standard deviation (%RPD) of 11.9% (Olund et al., 2004), comparable to the %RPD of the Denver CVAFS method for the same material of 11.8% (Hageman, 2007). Hg data are presented in Supplementary Data (Table S-2).

2.3. Age-dating and calculation of Hg fluxes

The cores were age-dated using ²¹⁰Pb with the constant rate of supply (CRS) model, which provides an estimate of age and mass accumulation rate of sediment (MAR) for each core interval (Appleby and Oldfield, 1992). Excess ²¹⁰Pb profiles are shown in Supplementary Data Fig. S-3. Two of the lakes are reservoirs built in the late 1800s (South Reservoir and Turkey Hill Reservoir). The CRS model was applied to the two reservoirs after extending the ²¹⁰Pb record back to “supported” ²¹⁰Pb using the least-squares regression of cumulative mass in the core and the natural logarithm of excess ²¹⁰Pb (*r*² = 0.94 for South Reservoir and 0.89 for Turkey Hill Reservoir). The measured fraction of the total estimated excess ²¹⁰Pb inventory, parameter *A*₀ in CRS, in the South Reservoir core is 96% and in the Turkey Hill core is 98%. The uncertainty for age dating introduced by estimation of this small of a fraction of *A*₀ for post-1990s intervals, the focus of this paper, is very small. Varying the estimated part of *A*₀ for South Reservoir ±100% results in only a ±0.55 y change in the sample dated as 1989.6.

Estimation of the anthropogenic contribution to atmospheric deposition of an element using lake cores requires that natural background inputs be subtracted from total inputs. One approach to estimate the anthropogenic flux (H_{gA}) is to subtract the background Hg flux (H_{gB}), the product of the MAR and Hg concentration for the older, pre-industrial intervals, from the Hg flux of each more recent interval. Holding background-flux constant by this approach assumes that the dominant source of natural Hg to the lake is atmospheric deposition on the lake surface (Van Metre and Fuller, 2009). If, however, natural Hg is mainly associated with particle transport from the watershed, H_{gB} flux will scale proportionally to the MAR, underestimating natural Hg input when the MAR increases and overestimating it when the MAR decreases. Perry et al. (2005) addressed this concern using a sedimentation-rate correction factor to adjust H_{gB} for variations in the MAR. Their approach is mathematically equivalent to the Hg-concentration-based background correction used by Van Metre and Fuller (2009), in which the pre-industrial Hg concentration is subtracted from Hg concentration in each core interval prior to multiplying by the MAR to calculate H_{gA}. For most lakes, background inputs of Hg come from both the atmosphere and the watershed, therefore, both approaches are presented here.

The Mills Lake core and the two reservoir cores did not penetrate to pre-industrial (mid-1800s) sediment. H_{gB} to Mills Lake was estimated using the MAR for the deepest dated interval and a background Hg concentration of 0.04 μg g⁻¹, the median background Hg concentration in 35 U.S. lakes (Mahler et al., 2006) and similar to the background concentration at Lake Elbert (0.038 μg g⁻¹), also in the Colorado Rocky Mountains. H_{gB} in South and Turkey Hill Reservoirs was estimated using the MAR from the bottom of each core and the pre-industrial Hg concentration from Crocker Pond (0.06 μg g⁻¹), also in New England (northeastern USA).

The uncertainty in the estimation of modern H_{gA} depends on the choice of background correction approach, the relative magnitudes of H_{gB} and the modern Hg flux, and the uncertainty in the background Hg concentration and the pre-1900 MAR. These uncertainties lead to large uncertainty in the estimation of the flux-based H_{gB} even in the best of circumstances. An error analysis of age dating for the Hobbs Lake core indicated an uncertainty in the MAR of about 50% in 1900, increasing to >100% in the 1870s and before (Van Metre and Fuller, 2009). There is added uncertainty in the estimation of H_{gB} for the reservoir cores and Mills Lake because these cores did not record pre-industrial Hg concentrations. Estimated H_{gB}



Fig. 1. Lakes where sediment cores were collected and selected major cities.

accounts for 24%, 11%, and 9% of modern Hg flux for Turkey Hill Reservoir, Mills Lake, and South Reservoir, respectively, thus Turkey Hill Reservoir likely represents the highest uncertainty in Hg_A among the lakes sampled. Assuming 70% uncertainty for the MAR and 50% uncertainty for the estimated background Hg concentration for Turkey Hill Reservoir implies the modern Hg_A computed using a flux correction is $77 \pm 29 \mu\text{g m}^{-2} \text{yr}^{-1}$, and using the background-concentration correction, is $81 \pm 10 \mu\text{g m}^{-2} \text{yr}^{-1}$.

Estimation of anthropogenic atmospheric deposition using lake cores requires adjusting for two other potential sources of Hg to the core, focusing of sediment from other parts of the lake and transport of Hg from the watershed. A ^{210}Pb -based ff is typically used to adjust for focusing and, in systems where transport from the watershed is particle-associated, the ff also should adjust for watershed input; this was thought to be the case in Hobbs Lake (Van Metre and Fuller, 2009). However, where particulate concentrations are low and dissolved organic carbon (DOC) concentrations are high, Hg transport can be dominantly in the dissolved (filtered) phase (Shanley et al., 2008) and probably is not well represented by ^{210}Pb transport. Thus, focus correcting may only partially adjust Hg_A flux for watershed inputs in many systems. Because the sites studied here are widely distributed, using the relation between the ratio of drainage area to lake surface area (A_D/A_L) and Hg flux for multiple lakes to estimate watershed inputs is not applicable (Kamman and Engstrom, 2002; Swain et al., 1992). Thus, lacking an independent correction for watershed input, the background and focusing corrected flux ($Hg_{A,F}$) is taken as an upper estimate of anthropogenic atmospheric deposition flux. Although approach has been used as an estimate of atmospheric deposition in some studies (e.g., Perry et al., 2005), here it is recognized that $Hg_{A,F}$ probably exceeds atmospheric deposition in some of these lakes because of unaccounted for watershed inputs. The use of flux ratios to evaluate atmospheric deposition of Hg avoids the problem of watershed inputs by assuming that a constant proportion of atmospheric deposition is delivered from the watershed over time.

An ff was estimated for each core by dividing the excess ^{210}Pb inventory in the core by the estimated ^{210}Pb fallout inventory in the area (Supplementary Data Table S-1). The ff s range from 0.85 to 2.1 (median 1.34) and do not correlate to the A_D/A_L . The generally low MARs (0.0094–0.061 $\text{g cm}^{-2} \text{yr}^{-1}$) and ff s suggest that delivery of (particulate) material from these watersheds is relatively limited. The A_D/A_L ratio does not correlate to Hg flux in the cores or to distance from the nearest major city (a key explanatory variable).

3. Results

Modern $Hg_{A,F}$ (mean of post-1990 intervals) estimated using a background-flux correction varies from 5.6 to $77 \mu\text{g m}^{-2} \text{yr}^{-1}$ in the 12 lakes studied here, slightly higher than using background-concentration corrections (Table 1). The lowest $Hg_{A,F}$ is to Lake Elbert in northwestern Colorado and the highest is to South Reservoir in Boston. Historical trends in concentrations and estimated $Hg_{A,F}$ increase beginning about 1900 or before and have recent maxima (1994 or after) in 11 of 12 lakes (Fig. 2). Turkey Hill Reservoir had the highest $Hg_{A,F}$ of any of the lakes, peaking at $144 \mu\text{g m}^{-2} \text{yr}^{-1}$ in 1965. High Hg deposition during that time period could reflect emissions from industrial sources in the area that have been implicated in legacy Hg pollution (Clark and Benoit, 2009). In Carlton and Cypress Lakes, a single sample at or near the top of the core suggests ~50% decrease in $Hg_{A,F}$ relative to adjacent

samples (Fig. 2). Such rapid change in atmospheric deposition might occur but it is difficult to support such a conclusion based on a single sample. Recent decreases in $Hg_{A,F}$ are more clearly indicated by the cores from Palette and Arbutus Lakes, with a 37% decrease at Palette Lake since the mid-1990s and a 15% decrease at Arbutus Lake since about 2003. Recent decreases in Hg deposition have been reported elsewhere (Engstrom and Swain, 1997).

The near-urban lakes have much higher $Hg_{A,F}$ than the remote lakes, with modern $Hg_{A,F}$ in the near-urban lakes ranging from 60 to $77 \mu\text{g m}^{-2} \text{yr}^{-1}$ (mean of $68 \pm 6.9 \mu\text{g m}^{-2} \text{yr}^{-1}$) and those in the remote lakes ranging from 5.6 to $31 \mu\text{g m}^{-2} \text{yr}^{-1}$ ($14 \pm 9.3 \mu\text{g m}^{-2} \text{yr}^{-1}$) (Fig. 3). The difference in means is statistically significant (t -test; p -value < 0.0001). $Hg_{A,F}$ in Mills Lake, located 90 km from Denver and in the direction of the prevailing winds (Supplementary Data Fig. S-2), is intermediate at $25 \mu\text{g m}^{-2} \text{yr}^{-1}$, about 4 times greater than in Lake Elbert, located 190 km from Denver.

Hg flux ratios (post-1990 total Hg flux over background Hg flux) range from 2.4 (Lake Elbert) to 17 (Cyprus Lake). The mean flux ratio in the near-urban lakes is 9.8 ± 4.8 and it is 3.5 ± 1.0 in the remote lakes, excluding the high outlier of 12 at Crocker Pond. That was excluded because it mostly is caused by a relatively large recent increase in MAR that is an artifact of sediment mixing in upper parts of the core and the use of the CRS dating model (as with other remote lakes, the Hg fluxes to Crocker Pond are low). The mean flux ratio in the remote lakes is similar to flux ratios reported for other remote lakes (e.g. (Kamman and Engstrom, 2002)), and the difference in flux ratios between the near-urban and remote lakes is significant (t -test, p -value = 0.02). Distance from urban area explains 42% of the variance in flux ratio ($r^2 = 0.42$). The larger flux ratio in the near-urban lakes indicates that modern Hg atmospheric deposition is greater near these cities than in remote areas.

$Hg_{A,F}$ profiles computed using the background-flux correction and using the background-concentration correction are very similar in eight of the 12 lakes (Fig. 2) because MARs were relatively constant in these cores. In four lakes – Carlton Lake, Crocker Pond, Shoe Factory Pond, and Todd Lake – the flux-based background corrected $Hg_{A,F}$ is appreciably larger than the concentration-based background corrected $Hg_{A,F}$ because the MAR increased during the 20th century. On the basis of graphical comparisons of the two approaches, the general shape, timing, and direction of slope of the $Hg_{A,F}$ profiles are similar for these four lakes for the two approaches. There is not a clear answer as to which background correction method is best for assessing $Hg_{A,F}$. An increase in MAR during the 20th century, which causes the two approaches to differ, could be the result of watershed disturbance or increased dust deposition from more distant regions. If the increased sediment

Table 1

Summary of estimated Hg fluxes to 12 lakes. Lakes are sorted with increasing distance from the nearest major city. $Hg_{A,F}$ is post-1990 anthropogenic, focus-corrected Hg flux.

Lake	Nearest major city	Distance to city center (km)	$Hg_{A,F}^a$ ($\mu\text{g m}^{-2} \text{yr}^{-1}$)	$Hg_{A,F}^b$ ($\mu\text{g m}^{-2} \text{yr}^{-1}$)	Hg flux ratio Post-1990	Date of Hg peak
South Reservoir	Boston, Mass.	10	77	71	29	1999
Carlton Lake	Tampa, Fla.	34	72	55	5.9	2006
Turkey Hill Reservoir	New Haven, Conn.	36	63	66	3.6	1965
Shoe Factory Pond	Chicago, Ill.	50	66	41	7.3	2000
Cypress Lake	Orlando, Fla.	50	60	57	17	1987
Mills Lake	Denver, Colo.	92	25	21	4.5	1995
Arbutus Lake	Albany, N.Y.	150	31	28	4.4	2004
Todd Lake	Portland, Ore.	180	10	5.5	2.5	1999
Lake Elbert	Denver, Colo.	190	5.6	5.2	2.8	1986
Crocker Pond	Montreal, Canada	250	16	9.2	12 ^c	1999
Palette Lake	Minneapolis, Minn.	300	7.5	6.5	5.5	1997
Hobbs Lake	Salt Lake City, Utah	310	15	13	4.3	1999

^a $Hg_{A,F}$ uses a flux-based background correction.

^b $Hg_{A,F}$ uses a concentration-based background correction.

^c Outlier value affected by post-depositional sediment mixing leading to large (questionable) increase in MAR at the top of the core.

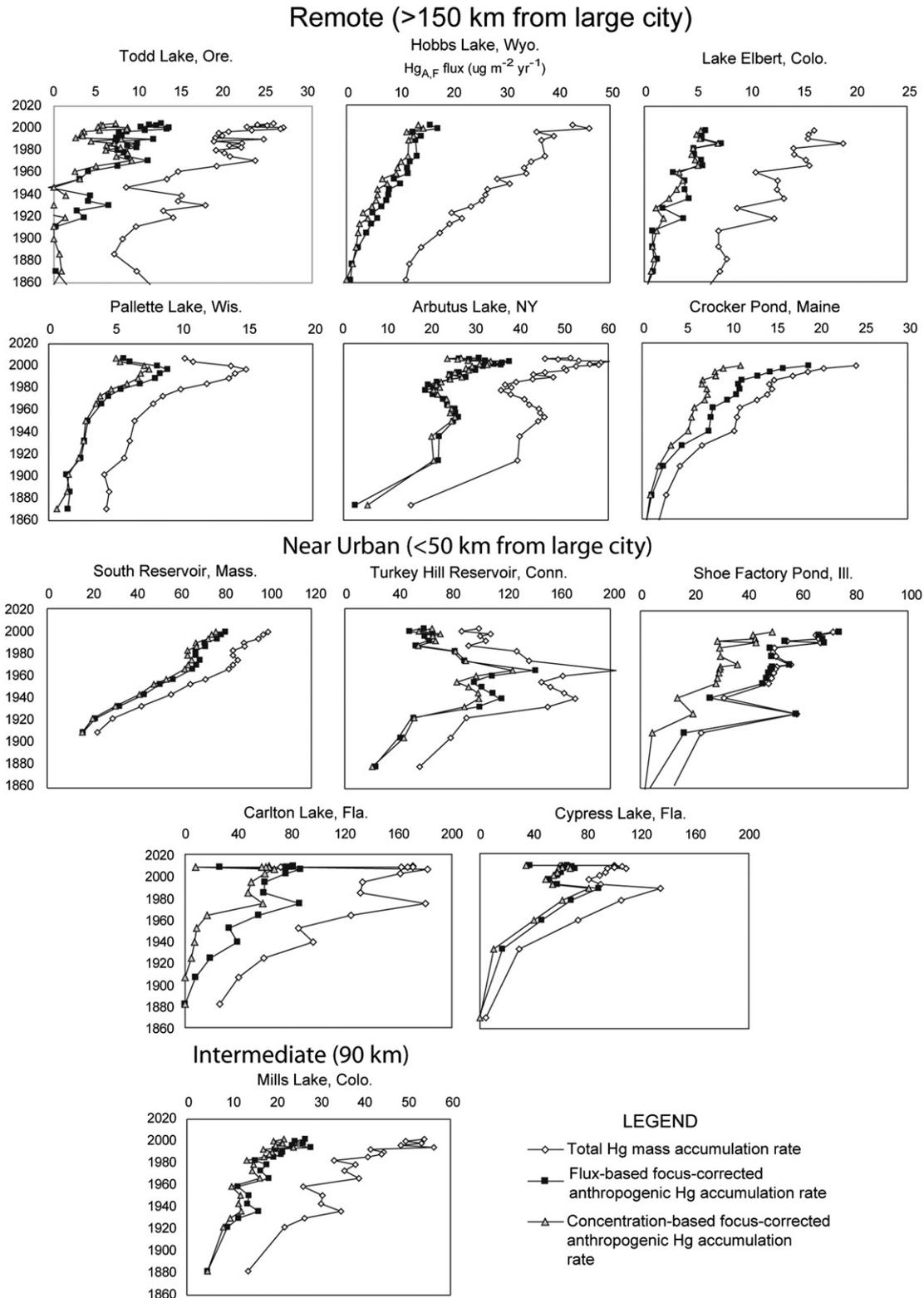


Fig. 2. Mercury mass accumulation rate and focus-corrected anthropogenic Hg accumulation rates for 12 lake-sediment cores.

loading carries with it naturally occurring Hg, then the concentration correction is favored. If on the other hand, a significant portion of the Hg associated with the increased sediment loading is from legacy anthropogenic sources, as was shown for a lake in Scotland (Yang et al., 2002), then this increased Hg loading is

anthropogenic. Following this reasoning, the flux-based correction results are used for subsequent analyses here.

Modern Hg_{A,F} is strongly related to the distance from the nearest major city (Fig. 3a), which explains 87% of the variance ($r^2 = 0.87$; std. error of the estimate = 10.9) in Hg_{A,F} in the lakes:

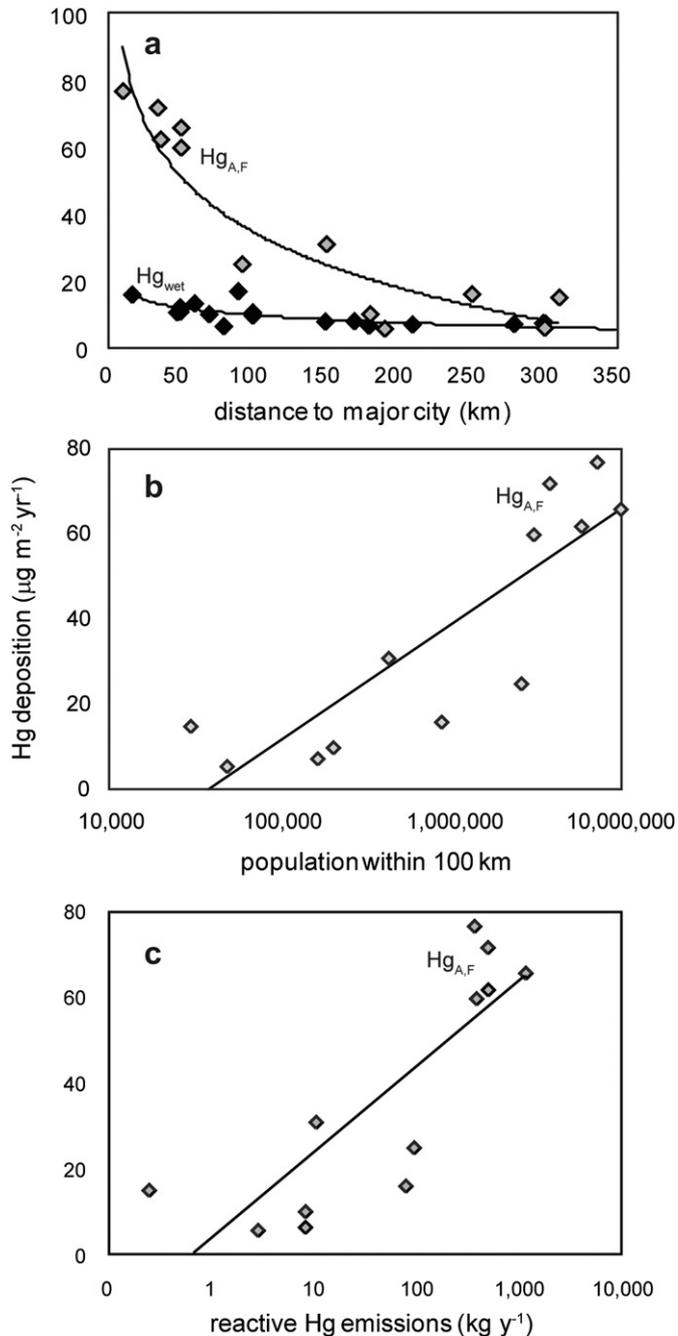


Fig. 3. Relations between three explanatory variables and Hg accumulation rates to 12 lakes. Graph a: distance from major urban area and $\text{Hg}_{\text{A,F}}$ (post-1990 anthropogenic focus-corrected Hg accumulation (gray diamond)) and Hg_{WET} (mean wet deposition from 2001 to 2008 for 18 MDN sites (black diamond)). Graph b: population within 100 km of the lake and $\text{Hg}_{\text{A,F}}$. Graph c: estimated reactive Hg (RGM and Hg(P)) emissions in the nine 0.5 degree cells over and around the lake and $\text{Hg}_{\text{A,F}}$.

$$\text{Hg}_{\text{A,F}} = 147 - 24.2 \cdot \ln(x) \quad (1)$$

where x = distance from the center of the nearest major city (km). The relation for Hg_{F} , focus-corrected but not background corrected Hg flux ($r^2 = 0.81$; std. error of the estimate = 14.6) is:

$$\text{Hg}_{\text{F}} = 163 - 26.4 \cdot \ln(x) \quad (2)$$

The apparent distance of influence of the urban “airshed” is on the order of 100 km (Fig. 3a). This apparent distance of influence is

supported by correlations for $\text{Hg}_{\text{A,F}}$ and the population within 50, 100, and 200 km radii of the lake ($r = 0.76, 0.85,$ and $0.68,$ respectively) (Fig. 3b); all of these correlations are significant (p -value < 0.05). The relation between population within 100 km (pop_{100} in eq. (3)) and $\text{Hg}_{\text{A,F}}$ ($r^2 = 0.74$; std. error of the estimate = 14.7) is:

$$\text{Hg}_{\text{A,F}} = 11.8 \cdot \ln(\text{pop}_{100}) - 125 \quad (3)$$

There are significant correlations between modern $\text{Hg}_{\text{A,F}}$ and local emissions of total mercury and reactive mercury (RM; the sum of RGM and Hg(P)). Wilson et al. (2006) estimated total Hg emissions then used “split factors” for Hg species reported by Pacyna et al. (2003) to estimate the portion of total as RGM and Hg(P). Local emissions are for 2000 (Wilson et al., 2006) and, as defined here, are the sum of emissions for the 0.5-degree grid cell where the lake is located and for the adjacent grid cells (9 cells total). In the central U.S., the 9-cell area is approximately 160 km (north–south) by 130 km (east–west). Correlations were tested between $\text{Hg}_{\text{A,F}}$ and local emissions of total Hg and RM from point sources, distributed sources, and the sum of the two. All of the relations tested are significant (p -value < 0.05), and there is a slightly stronger correlation to RM from point plus distributed sources ($r = 0.77$) (Fig. 3c) than for total Hg and RM from distributed sources (both $r = 0.75$). The relation between local emissions of RM (point plus distributed) and $\text{Hg}_{\text{A,F}}$ ($r^2 = 0.68$; std. error of the estimate = 16.3) is:

$$\text{Hg}_{\text{A,F}} = 8.84 \cdot \ln(\text{RM}) + 2.95 \quad (4)$$

These relations suggest that local emissions of RM are an important factor in elevated Hg deposition near urban areas. Note that equations (3) and (4) return negative values of $\text{Hg}_{\text{A,F}}$ for population and emissions approaching zero.

Precipitation can affect Hg deposition (Lindberg et al., 2007), however, mean annual precipitation for the 12 lakes (estimated using maps provided by the Oregon Climate Service: <http://www.wrcc.dri.edu/precip.html>) was not related to $\text{Hg}_{\text{A,F}}$ ($r = 0.02$). Mean annual precipitation for the six remote lakes (117 cm) was similar to mean annual precipitation for the five near-urban lakes (113 cm). All of the lakes, including the western mountain lakes, are in relatively wet areas. Although watershed inputs might be affecting (increasing) $\text{Hg}_{\text{A,F}}$, there is no indication that greater $\text{Hg}_{\text{A,F}}$ near urban areas is an artifact of greater watershed inputs to those lakes. $A_{\text{D}}/A_{\text{L}}$ ratios do not correlate to distance from urban area and the mean $A_{\text{D}}/A_{\text{L}}$ is smaller for the near-urban lakes (10.6) than in the remote lakes (15.3).

4. Discussion

Mercury trends and fluxes reported here generally are consistent with other studies based on lake and wetland sediment cores, although fluxes for reference lakes in or near major cities have rarely been reported. Modern Hg_{F} to the remote lakes of $18.7 \pm 11 \mu\text{g m}^{-2}\text{yr}^{-1}$ is in agreement with estimated average Hg deposition for North America of 14.3 – $19.8 \mu\text{g m}^{-2}\text{yr}^{-1}$ (Pirrone et al., 1998). It also is in the range of modern Hg deposition reported for lake cores in the upper Midwest ($12.5 \mu\text{g m}^{-2}\text{yr}^{-1}$) (Swain et al., 1992) and the northeastern USA ($21 \mu\text{g m}^{-2}\text{yr}^{-1}$) (Kamman and Engstrom, 2002); none of the lakes in those two studies appear to be near a major urban area. The range in $\text{Hg}_{\text{A,F}}$ reported here of 5.6 – $77 \mu\text{g m}^{-2}\text{yr}^{-1}$ is similar to the $\text{Hg}_{\text{A,F}}$ range reported for cores from 37 lakes in New England, USA (10.4 – $66.3 \mu\text{g m}^{-2}\text{yr}^{-1}$) (Perry et al., 2005) and for cores from 50 lakes from across eastern Canada (<0 – $61 \mu\text{g m}^{-2}\text{yr}^{-1}$) (Muir et al., 2009). Although these studies did not identify an urban airshed effect, Muir et al. (2009), did describe relations between Hg

deposition rates and the strong south-to-north trend in urban and industrial development in Canada.

Some researchers have noted that using multiple cores in a lake and developing a whole-lake Hg budget, and sampling multiple lakes in a single region is a more accurate approach to quantifying atmospheric Hg loading (Swain et al., 1992). In addition to bypassing the need for focusing correction, that approach allows for an estimate of watershed input of Hg. Because no correction was possible for watershed input to the lakes studied here, beyond any particle-related Hg transport that the ^{210}Pb *ff* might be correcting for, the $\text{Hg}_{\text{A,F}}$ probably over estimates atmospheric deposition at some of the sites. The $A_{\text{D}}/A_{\text{L}}$ within a single region has been shown to correlate to Hg flux to lakes in the region and thus has been used as a predictor of watershed inputs (Swain et al., 1992; Kamman and Engstrom, 2002). Among the lakes studied here, there is no relation between $A_{\text{D}}/A_{\text{L}}$ and $\text{Hg}_{\text{A,F}}$ or $A_{\text{D}}/A_{\text{L}}$ and distance from major city. Lack of these relations indicates that the elevated $\text{Hg}_{\text{A,F}}$ near major urban areas is not an artifact of greater watershed inputs to the near-urban lakes, and this conclusion is supported by the much larger Hg flux ratios to the near-urban lakes than to the remote lakes.

The predictive ability of equation (1) is good, with an r^2 of 0.86, and where there are differences between predicted and measured Hg deposition in the cores, those differences tend to be regional. Among the lakes >90 km from an urban area, the three that plot below the regression line on Fig. 3a (line described by equation (1)) are in the western U.S., where regional emissions are relatively low (Wilson et al., 2006). Two of the three plotting above the regression line are in the central and eastern U.S., where regional emissions are relatively high. The exception to this pattern is Hobbs Lake in Wyoming which, at 310 km (from Salt Lake City, Utah), is the furthest from a major urban area yet has higher than predicted Hg flux.

Modeling efforts have addressed remote and near-field Hg deposition including both wet and dry deposition (e.g. REMSAD model (USEPA, 2008)). Deposition modeled by REMSAD indicates increased deposition near and downwind from major cities and source areas. Modeled deposition to the areas of the remote lakes presented here, with the exception of Arbutus Lake, is similar to the Hg_{F} indicated by the lake cores, with estimates in the range of 8–20 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (USEPA, 2008). Modeled deposition near major cities, however, does not increase to the same degree as indicated by the near-urban lake cores. Modeled deposition, for example, is 28–32 $\mu\text{g m}^{-2} \text{yr}^{-1}$ in the Boston area where South Reservoir is located, compared to Hg_{F} of 80 $\mu\text{g m}^{-2} \text{yr}^{-1}$ in the core. In Florida, modeled deposition near Carlton Lake and Cypress Lake is >40 and 32–36 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (USEPA, 2008), respectively, compared with Hg_{F} of 86 and 64 $\mu\text{g m}^{-2} \text{yr}^{-1}$ for the lake cores. Because the Hg_{F} computed here does not account for all watershed input of Hg, it is unclear whether these differences are caused by underestimation of deposition by the models or overestimation of deposition by the lake cores caused by unaccounted for watershed inputs.

The increase in total Hg deposition indicated by the lake cores with decreasing distance from major urban areas is larger than the increase in wet deposition indicated by the MDN (Fig. 3). Annual Hg_{WET} for 2001–2008 (for those years with complete records) was averaged for 18 MDN sites in the same areas of the country as the lakes studied here (Supplementary Data Table S-3). Wet deposition at MDN sites that are 150 km or more from the nearest major city ($6.9 \pm 1.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ ($n = 7$)) is significantly less (t -test; $p = .001$) than wet deposition at MDN sites 100 km or less from the nearest city ($11.4 \pm 2.9 \mu\text{g m}^{-2} \text{yr}^{-1}$ ($n = 11$); only 3 sites are within 50 km)) (Fig. 3a). Wet deposition of Hg reported for a site in central London, UK (31.8 $\mu\text{g m}^{-2} \text{yr}^{-1}$) (Yang et al., 2009) and a site in central Chicago (26.9 $\mu\text{g m}^{-2} \text{yr}^{-1}$) (Landis and Keeler, 2002), however, is

considerably larger than the MDN wet deposition, suggesting that the increase may be greater than indicated by the mostly remote (from cities) MDN sites.

There are several factors that might contribute to greater Hg deposition to lakes in and near urban areas. These include large inputs of Hg to the urban atmosphere from point and diffuse sources (Wilson et al., 2006) and from emissions from historically-contaminated soils (Eckley and Branfireun, 2008), the presence of oxidants in urban air (Shon et al., 2007), and elevated Hg(P) in urban air (Keeler et al., 1995). Eckley and Branfireun (2008) measured Hg emissions from urban and rural soils and found that emissions from urban soils were about 6-times greater than from rural soils. Urban atmospheric pollutants (O_3 and other oxidants) could play a role in greater near-field Hg deposition by formation of RGM (Shon et al., 2007). Airborne Hg(P) is deposited relatively rapidly and in urban/industrialized areas can be an order of magnitude higher in concentration than in rural areas, sometimes approaching concentrations of GEM in the urban areas (Keeler et al., 1995).

Significantly greater atmospheric deposition of Hg within about 100 km of major urban areas could have important implications for risks associated with Hg deposition and for developing management responses to mitigate risks. Increased Hg loading and sediment Hg concentrations have been associated with water bodies with urban development in their watersheds (Chalmers et al., 2007; Engstrom et al., 2007; Mahler et al., 2006), but less is known about atmospheric deposition of Hg to undeveloped, near-urban water bodies. Quantifying the relation between major urban areas and Hg deposition to lakes could help constrain estimates of Hg deposition to larger water bodies as well, for example to the Great Lakes (Lai et al., 2007). Considering the relatively small number of samples (lakes) used here and the uncertainty about the effects of watershed inputs on Hg fluxes in the lake cores, additional research is warranted. Two important questions are how best to address watershed input in widely distributed lakes and what is the nature and role of dry deposition to the near-urban lakes.

Acknowledgments

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government. I thank Christopher Conway, Mark Brigham, Barbara Mahler, Dan Engstrom, and the anonymous peer reviewers for their many helpful comments on this manuscript.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.11.003.

References

- Appley, P.G., Oldfield, F., 1992. Application of lead-210 to sedimentation studies. In: Ivanovich, M., Harmon, S. (Eds.), Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences, 2nd Edition. Clarendon, Press, Oxford, p. 910.
- Brown, Z.A., O'Leary, R.M., Hageman, P.L., Crock, J.G., 2003. Mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic adsorption spectroscopy. In: Taggart, J.E.J. (Ed.), Analytical Methods for Chemical Analysis of Geologic and Other Materials, U.S. Geological Survey. U.S. Geological Survey, p. 11.
- Bullock, O.R., Atkinson, D., Braverman, T., Civerolo, K., Dastoor, A., Davignon, D., Ku, J.-Y., Lohman, K., Myers, T.C., Park, R.J., Seigneur, C., Selin, N.E., Sistla, G., Vijayaraghavan, K., 2008. The North American Mercury Model Intercomparison Study (NAMMIS): study description and model-to-model comparisons. *J. Geophys. Res.* 113, 17.
- Chalmers, A.T., Van Metre, P.C., Callender, E., 2007. The chemical response of particle-associated contaminants in aquatic sediments to urbanization in New England, U.S.A. *J. Contaminant Hydrology* 91, 4–25.

- Clark, H.F., Benoit, G., 2009. Legacy sources of mercury in an urbanised watershed. *Environ. Chem.* 6, 235–244.
- Clarkson, T.W., Magos, L., 2006. The toxicology of mercury and its chemical compounds. *Crit. Rev. Toxicol.* 36, 609–662.
- Dvonch, J.T., Graney, J.R., Marsik, E.J., Keeler, G.J., Stevens, R.K., 1998. An investigation of source–receptor relationships for mercury in south Florida using event precipitation data. *Sci. Total Environ.* 213, 95–108.
- Eckley, C.S., Branfireun, B., 2008. Gaseous mercury emissions from urban surfaces: controls and spatiotemporal trends. *Appl. Geochem.* 23, 369–383.
- Engstrom, D.R., Balogh, S.J., Swain, E.B., 2007. History of mercury inputs to Minnesota lakes: influences of watershed disturbance and localized atmospheric deposition. *Limnology and Oceanography* 52, 2467–2483.
- Engstrom, D.R., Swain, E.B., 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environ. Sci. Technol.* 31, 960–967.
- Fitzgerald, D.J., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* 32, 1–7.
- Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C.-M., Balcom, P.H., Hammerschmidt, C.R., 2005. Modern and historic atmospheric fluxes in Northern Alaska: global sources and arctic depletion. *Environ. Sci. Technol.* 39, 557–568.
- Fuller, C.C., van Geen, A., Baskaran, M., Anima, R., 1999. Sediment chronology in San Francisco Bay, California, defined by 210Pb, 234Th, 137Cs, and 239,240Pu. *Marine Chem.* 64, 7–27.
- Gildemeister, A.E., Graney, J.R., Keeler, G.J., 2005. Source proximity reflected in spatial and temporal variability in particulate and vapor phase Hg concentrations in Detroit, MI. *Atmos. Environ.* 39, 353–358.
- Guentzel, J.L., Landing, W.M., Gill, G.A., Pollman, C.D., 2001. Processes influencing rainfall deposition of mercury in Florida. *Environ. Sci. Technol.* 35, 863–873.
- Hageman, P.L., 2007. Determination of Mercury in Aqueous and Geologic Materials by Continuous Flow-cold Vapor-atomic Fluorescence Spectrometry (CVAFS). U.S. Geological Survey Techniques and Methods, book 5, chap. D2. U.S. Geological Survey, Denver, Colorado. 6.
- Iverfeldt, A., 1991. Occurrence and turnover of atmospheric mercury of the nordic countries. *Water Air Soil Pollut.* 56, 251–265.
- Kamman, N.C., Engstrom, D.R., 2002. Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from 210Pb dated sediment cores. *Atmos. Environ.* 36, 1599–1609.
- Keeler, G.J., Glinsorn, G., Pirrone, N., 1995. Particulate mercury in the atmosphere: its significance, transport, transformation, and sources. *Water Air Soil Pollut.* 80, 159–168.
- Lai, S.-O., Holsen, T.M., Han, Y.-J., Hopke, P.P., Yi, S.-M., Blanchard, P., Pagano, J.J., Milligan, M., 2007. Estimation of mercury loadings to Lake Ontario: results from the Lake Ontario atmospheric deposition study (LOADS). *Atmos. Environ.* 41, 8205–8218.
- Landers, D.H., Gubala, C.P., Verta, M., Lucotte, M., Johansson, K., Vlasova, T., Lockhard, W.L., 1998. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in Arctic and Boreal ecosystems. *Atmos. Environ.* 32, 919–928.
- Landis, M.S., Keeler, G.J., 2002. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study. *Environ. Sci. Technol.* 36, 4518–4524.
- Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D.R., Feng, X., Fitzgerald, W.F., Pirrone, N., Prestbo, E., Seigneur, C., 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* 36, 19–32.
- Liu, B., Keeler, G.J., Dvonch, J.T., Barres, J.A., Lynam, M.M., Marsik, F.J., Taylor Morgan, J., 2010. Urban-rural differences in atmospheric mercury speciation. *Atmos. Environ.* 44, 2013–2023.
- Mahler, B.J., Van Metre, P.C., Callender, E., 2006. Trends in metals in urban and reference lake sediments across the United States, 1975–2001. *Environ. Toxicol. Chem.* 25 (7), 1698–1709.
- Manolopoulos, H., Snyder, D.C., Schauer, J.J., Hill, J.S., Turner, J.R., Olson, M.L., Krabbenhoft, D.P., 2007. Sources of speciated atmospheric mercury at a residential neighborhood impacted by industrial sources. *Environ. Sci. Technol.* 41, 5626–5633.
- Mason, R.P., Lawson, N.M., Sheu, G.-R., 2002. The urban atmosphere: an important source of trace metals to nearby waters? In: Lipnick, R.L., Mason, R.P., Phillips, M.L. (Eds.), *Chemicals in the Environment*. American Chemical Society, Washington, D.C, pp. 203–222.
- Mielke, H.W., Wang, G., Gonzales, C.R., Powell, E.T., Le, B., Quach, V.N., 2004. PAHs and metals in the soils of inner-city and suburban New Orleans, Louisiana, USA. *Environ. Toxicol. Pharmacol.* 18, 243–247.
- Muir, D.C.G., Wang, X., Yang, F., Nguyen, N., Jackson, T.A., Evans, M.S., Douglas, M., Kock, G., Lamoureux, S., Pienitz, R., Smol, J.P., Vincent, W.F., Dastoor, A., 2009. Spatial trends and historical deposition of mercury in Eastern and Northern Canada inferred from lake sediment cores. *Environ. Sci. Technol.* 43, 4802–4809.
- Olund, S.D., DeWild, J.F., Olson, M.L., Tate, M.T., 2004. *Methods for the Preparation and Analysis of Solids and Suspended Solids for Total Mercury*. Techniques and Methods. U.S. Geological Survey, Reston, Virginia. 15.
- Pacyna, J.M., Pacyna, E.G., Steenhuisen, F., Wilson, S., 2003. Mapping 1995 global anthropogenic emissions of mercury. *Atmos. Environ.* 37-S, 109–117.
- Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* 40, 4048–4063.
- Perry, E., Norton, S.A., Kamman, N.C., Lorey, P.M., Driscoll, C.T., 2005. Deconstruction of historic mercury accumulation in lake sediments, Northeastern United States. *Ecotoxicology* 14, 85–99.
- Pirrone, N., Allegrini, I., Keeler, G.J., Nriagu, J.O., Rossmass, R., Robbins, J.A., 1998. Historical atmospheric mercury emissions and depositions in North America compared to mercury accumulations in sedimentary records. *Atmos. Environ.* 32, 929–940.
- Rothenberg, S.E., McKee, L., Gilbreath, A., Yee, D., Connor, M., Fu, X., 2010. Evidence for short-range transport of atmospheric mercury to a rural, inland site. *Atmos. Environ.* 44, 1263–1273.
- Shanley, J.B., Mast, M.A., Campbell, D.H., Aiken, G.R., Krabbenhoft, D.P., Hunt, R.J., Walker, J.F., Schuster, P.F., Chalmers, A., Aulenbach, B.T., Peters, N.E., Marvin-DiPasquale, M., Clow, D.W., Shafer, M.M., 2008. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. *Environ. Pollut.* 154, 143–154.
- Shon, Z.-H., Kim, K.-H., Song, S.-K., Kim, M.-Y., Lee, J.S., 2007. Environmental fate of gaseous elemental mercury at an urban monitoring site based on long-term measurements in Korea (1997–2005). *Atmos. Environ.* 42, 142–155.
- Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., Brezonik, P.L., 1992. Increasing rates of atmospheric mercury deposition in Midcontinental North America. *Science* 257, 784–787.
- USEPA, 2008. *Model-based Analysis and Tracking of Airborne Mercury Emissions to Assist in Watershed Planning*. Office of Wetlands, Oceans, and Watersheds, Washington, DC. 350.
- U.S. Census Bureau, 2002. *Census 2000 Basics*. U.S. Government Printing Office, Washington, D.C. MSO/02-C2KB, 19 p. Available at: <http://www.census.gov/main/www/cen2000.html>
- Van Metre, P.C., Fuller, C.C., 2009. Dual-core mass-balance approach for evaluating mercury and 210Pb atmospheric fallout and focusing to lakes. *Environ. Sci. Technol.* 43, 26–32.
- Van Metre, P.C., Mahler, B.J., 2005. Trends in hydrophobic organic contaminants in lake sediment across the United States, 1970–2001. *Environ. Sci. Technol.* 39, 5576–5574.
- Wilson, S.J., Steenhuisen, F., Pacyna, J.M., Pacyna, E.G., 2006. Mapping the spatial distribution of global anthropogenic mercury atmospheric emission inventories. *Atmos. Environ.* 40, 4621–4632.
- Yang, H., Berry, A., Rose, N.L., Berg, T., 2009. Decline in atmospheric mercury deposition in London. *J. Environ. Monit.* 11, 1518–1522.
- Yang, H., Rose, N.L., Battarbee, R.W., Boyle, J.F., 2002. Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. *Environ. Sci. Technol.* 36, 1383–1388.