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

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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 ± 6.9 µg m^{-2} yr^{-1} and 9.8 ± 4.8, respectively) greatly exceed those in the remote lakes (14 ± 9.3 µg m^{-2} 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.

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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.

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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), ^{210}Pb, and ^{226}Ra. 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 ^{210}Pb fallout inventories for calculation of sediment focusing factors (ffs) (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 ^{210}Pb and ^{226}Ra by gamma spectrometry based on ASTM methods C 1402-98 and E 181-98, similar to methodology described by Fuller et al. (1999). Supported ^{210}Pb activity was calculated as the difference between total ^{210}Pb activity and ^{226}Ra 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 Hg^0 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 ^{210}Pb 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 ^{210}Pb 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 ^{210}Pb record back to "supported" ^{210}Pb using the least-squares regression of cumulative mass in the core and the natural logarithm of excess ^{210}Pb ($r^2 = 0.94$ for South Reservoir and 0.89 for Turkey Hill Reservoir). The measured fraction of the total estimated excess ^{210}Pb 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 (Hg$_A$) is to subtract the background Hg flux (Hg$_B$), 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, Hg$_B$ 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 Hg$_B$ 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 Hg$_A$. 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. Hg$_B$ 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. Hg$_B$ 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 Hg$_A$ depends on the choice of background correction approach, the relative magnitudes of Hg$_B$ 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 Hg$_B$ 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 Hg$_B$ for the reservoir cores and Mills Lake because these cores did not record pre-industrial Hg concentrations. Estimated Hg$_B$

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