Balancing the Mercury Inventory: Why Does 2006 Look Like 1750?

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1. Background

Recent work by Gustin et al. (2005) has indicated that background emissions of mercury (emissions of new native mercury from natural sources and re-emissions from legacy anthropogenic sources) may be about twice as great as previously believed, from an estimate of about 2200 Mg/y (range 800-3400 Mg/y) to something like 4000 Mg/y. The consequent constraints on the global mercury balance (measured background atmospheric concentrations and wet deposition rates, see Figure 1; atmospheric reservoir from concentration profiles; anthropogenic sources from measurements) leaves us with a quandary: how do we close the global balance? Conversely, if the anthropogenic and legacy inputs are discounted, an even more dire situation arises, with greater disparity between estimated preindustrial fluxes and the calculated reservoirs. One aspect of this is how to explain current locations in the industrialized Northern Hemisphere that experience mercury deposition apparently representative of pre-industrial levels, despite total fluxes and reservoirs now believed to be 3-5 times as great as in preindustrial times.

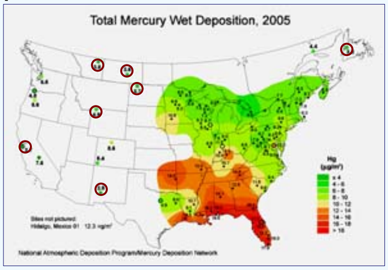

Fig. 1. Measured wet mercury deposition fluxes, µg m^{-2} y^{-1}, from Mercury Deposition Network. Circled stations show wet fluxes <5.

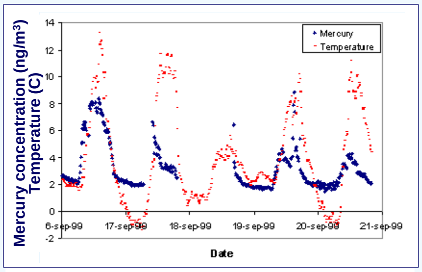

Fig. 2. Elemental mercury air concentrations vs. surface air temperature, Tasiusaq, Greenland (Brandt et al., 1999)

2. Methods

Measurements of concentration of mercury (ng/g) have been made in cored or stratified clean sections of peat bogs, lake-bottom sediments (nonlensing lakes), mountain glaciers and ice sheets, and soil horizons (Table 1). These are generally dated by radioisotope dating, such as 210Pb (with corrections for nuclear bomb-test excursions) or by simple counting of annual strata. Deposition rates are generally derived through date/depth correlations or by assumptions of uniformitarianism in precipitation and climate. The calculated deposition rates represent some location and environment-specific sum of mercury wet plus dry deposition (where, here, dry deposition of mercury is the sum of down-gradient transfer of gaseous elemental mercury and particulate-bound mercury gravitational deposition). These processes are known to be non-conservative; Brandt et al. (1999), Figure 2, have shown the loss of dry-deposited mercury over the Greenland ice sheet.

We have surveyed modeled values for mercury wet and dry deposition in the United States and adjacent sections of Canada and Mexico (Figure 3) because of the collocation of the extensive Mercury Deposition Network (MDN) wet deposition stations. Comparison of those modeled values with documented levels of fish exceedances of the U.S. EPA human health criterion fish tissue level of 0.3 ppm, and with locations where MDN values are consistently <5 µg m^{-2} yr^{-1}, were selected to accommodate the (unmeasureable and unknown) dry deposition values of roughly the same magnitude. These locations then represent points where total (wet+dry) mercury deposition is no more than 10 µg m^{-2} yr^{-1}, within the range thought to be prevalent during preindustrial times, that is, 1750 and earlier in Europe or 1850 and before in North America.

3. "Pre-industrial" Mercury Fluxes

Rood et al. (1995) measured mercury in soil cores and samples from the Florida Everglades, finding post-1985 deposition rates 0f 53 µg m^{-2} y^{-1}, cited as a mean increase of 4.9-fold over the early 20[th] century. Hence, in this location, a "pre-industrial" deposition rate of ~10.8 µg m^{-2} y^{-1} is calculated.

Meili (1995) noted that sediment cores used to estimate pre-industrial rates of atmospheric mercury deposition may be subject to overestimation, due in part to Hg inputs from the catchment and in part because of horizontal redistribution of sediments within lakes.

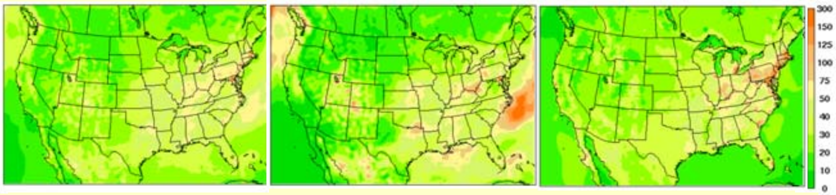

Fig. 3. Total, wet, dry (left-right) mercury depositio, µg m^{-2} y^{-1}, North America; EPRI CMAQ-MADRID model.

Meili (1995) noted that sediment cores may be subject to overestimation, due to Hg inputs from the catchment and horizontal redistribution of sediments within lakes. Peat core Hg may undergo vertical migration due to water table fluctuations. He suggests that "natural" mercury deposition rates from the lower part of the range of values are most reasonable estimates, 2 vs. a range of 3-12 µg m^{-2} y^{-1}. As a result, Meili (1995) suggests recent anthropogenic contributions to deposition may be underestimated by comparison to unreasonably high pre-industrial levels.

4. Dry, Wet, Total Deposition

Of the total deposition in boreal areas, Meili estimates that about 1/3 of 2 µg m^{-2} y^{-1} is due to dry deposition. This contrasts with the estimate of Lucotte et al. (1995) that Hg in Quebec shield lakes is due primarily to dry deposition of Hg^0 and Hg_p. Lucotte also notes the apparent later increase in mercury deposition there, dating it to the 1940s, rather than the 1860s U.S. date of Schuster et al. (2002).

In that case, glacial cores from the Lower Fremont Glacier, Wyoming, U.S.A., showed pre-industrial levels of 2-5 µg m^{-2} y^{-1} except during such as Tambora (1815) [Table 1]. Clear evidence of an industrial-era rise is not evident before about 1870, following an unexplained drop in mercury deposition rates following an extended multi-decade rise to about 10-17 µg m^{-2} y^{-1} cited as the California gold rush. Historically, this is not explainable by Gold Rush placer mining per se, since mercury was not used extensively during that period. Heavy mercury use began later in the 19[th] century as placer deposits were depleted.

Table 1. From Schuster et al., 2002

site	sample media	episode (Schuster et al., 2002, reference)	year(s)	average [Hg] (ng/L)	deposition[a] (µg/m^2/year)	change from preindustrial (multiplier)
UFG	ice	Clean Air Act	1986-1993	9	11.4	11
UFG	ice	industrial max	1984	20	20.3	20
UFG	ice	Mt. St. Helens	1980	11[b]	12.7[§]	12
UFG	ice	industrial	1900-1993	10	11.0	11
UFG	ice	WWII	1938-1946	7	4.73	5
UFG	ice	Krakatau	1883	21[c]	18.2[§]	18
UFG	ice	Gold Rush	1850-1878	8	4.84	5
UFG	ice	Tambora	1815	10	8.60[§]	8
UFG	ice	preindustrial	1719-1847	3	0.78	na[d]
Minnesota	wet ppt	(49)	1997-1999	14	6.99	7
Colorado	wet ppt	(49)	1999	10	9.20	9
			<1880	na	80.0	na
Minnesota	lake sed**	(48)	>1880	na	170	2[#]
			<1850	na	3.70	na
Minnesota	lake sed	(45)	modern	na	12.5	3

a Deposition calculated using age-depth correction factor.
b Preindustrial and industrial inputs subtracted to isolate volcanic signal; maximum input reported.
c Preindustrial input subtracted to isolate volcanic signal; maximum input reported.
d Not applicable or not available.
e Wet precipitation.
§ Age-depth correction factor not used to calculate deposition rate.
** Sediment.
# Change measured from "preindustrial" dated cores from cited study.

In sum, for North American sites, "pre-industrial" deposition rates in the range of 2-10 µg m^{-2} y^{-1} are shown in repeated measurements. The dating of the rise in mercury deposition varies between regions, reflecting regional histories of settlement. Nonetheless, North American mercury rates prior to 1850 or so can be considered "pre-industrial." Yet there are areas with both these preindustrial levels of total deposition, and wild fish stocks with mercury levels in consumable portions above what are considered health thresholds (Figure 4).

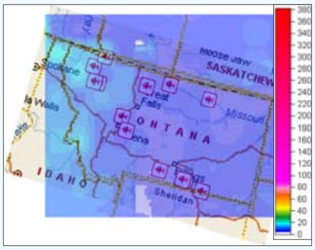

Fig. 4. Tinting: Hg_{TOT} deposition <10 µg m^{-2} y^{-1} (EPRI TEAM model); base map: Montana waters with fish levels > 0.3 ppm Hg (icons)

Mercury in each of its deposition reservoirs – ice, peat, lake sediment – may undergo chemical transformation or migration. In lakes, diagenesis may transform precipitable reactive mercury to elemental mercury, subject to re-volatilization loss to the atmosphere. Dry-deposited mercury may undergo oxidation or ligandization. Surface uptake by flora can enhance the dry-depositional component of total deposition. Fitzgerald et al. (2005) calculate, for Alaskan lakes, dry deposition about 7% that of wet deposition. Alternatively, Seigneur et al. model dry deposition rates roughly equivalent to those of wet deposition (Figure 3).

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