

# ANTHROPOGENIC INFLUENCES ON THE GLOBAL MERCURY CYCLE: A MODEL-BASED ANALYSIS

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**Abstract:** A model of the global Hg cycle is presented and applied to analyze modern Hg budgets and historical changes in deposition. Our modeling suggests that mixing into the ocean interior is a significant sink of Hg and likely has limited any anthropogenically-caused increase in surface ocean Hg concentrations to about 50% above natural levels rather than 200% as has recently been argued. Additionally, both the increase in air pollutants during the industrial era and their recent decrease in North America likely have affected atmospheric Hg scavenging and the resulting records of Hg deposition rates in lake and bog sediments.

## 1. Introduction

The anthropogenic influence on the global Hg cycle is evident from the 2- to 5-fold higher current rates of Hg accumulation in lake sediments (Swain *et al.*, 1992), and peat bogs (Benoit *et al.*, 1994) relative to preindustrial fluxes. Although in some cases a decline in deposition is evident over the past 20 years, global atmospheric Hg<sup>0</sup> concentrations appear to have increased at an annual rate of 1.2 to 1.5 percent between 1977 and 1990 (Slemr and Langer, 1992). Recently, Mason, Fitzgerald and Morel (MFM, 1994) argued that Hg in the surface ocean is now 3-times the natural level and, consequently, two-thirds of oceanic Hg emissions are actually anthropogenic in origin. MFM concluded that two-thirds of all Hg now entering the atmosphere each year is ultimately derived from anthropogenic sources.

To understand the link between anthropogenic emissions, atmospheric concentrations, and deposition of Hg, models of regional and global Hg transport and deposition are needed. To date, modeling of the global Hg cycle has primarily consisted of budgets of natural and anthropogenic fluxes to and from the atmosphere. Although a mechanistic Hg cycle model was developed by Milward (1982), that work predated the recent significant revisions in geochemical data. In this paper, we present a Global Mercury Cycling Model (G-MCM) calibrated using the MFM synthesis of recent global Hg budgets and use it to identify key assumptions that influence the response of the Hg cycle to anthropogenic activities over the past few centuries.

## 2. A Global Mercury Cycling Model (G-MCM)

Since Hg is an atmophilic element, the principal global transport fluxes occur through the atmosphere. Inputs to the atmospheric Hg<sup>0</sup> pool  $A_{Hg}$  include a constant flux from volcanoes  $W_{atmo}$  and variable emissions from terrestrial systems  $E_{terra}$ , the oceans  $E_{ocean}$ , and anthropogenic activities  $E_{anthro}$ . Atmospheric Hg<sup>0</sup> removal is approximated

as a first-order process with rate coefficients  $k_{terra}^D$  and  $k_{ocean}^D$  defining the rate of wet plus dry deposition of  $Hg^{II}$  to terrestrial systems  $D_{terra}$  ( $= k_{terra}^D \times A_{Hg}$ ) and to the oceans  $D_{ocean}$  ( $= k_{ocean}^D \times A_{Hg}$ ). The resulting mass balance for a single box atmosphere is:

$$\frac{dA_{Hg}}{dt} = W_{atmo} + E_{terra} + E_{ocean} + E_{anthro} - D_{terra} - D_{ocean} \quad (1)$$

Hg in terrestrial systems  $T_{Hg}$  exists primarily as  $Hg^{II}$  in soils (Hg in vegetation is not well quantified at present, but the limited data available suggest that it is insignificant in mass compared to Hg in soils). The sinks for  $T_{Hg}$ , reduction and subsequent evasion of  $Hg^0$  from soils  $E_{terra}$  ( $= k_{terra}^E \times T_{Hg}$ ), burial in inland drainages and deltaic sediments  $B_{terra}$  ( $= k_{terra}^B \times T_{Hg}$ ), and fluvial export to the oceans  $X_{terra}$  ( $= k_{terra}^X \times T_{Hg}$ ), are all first-order processes. The mass balance for the single box terrestrial system is:

$$\frac{dT_{Hg}}{dt} = D_{terra} + W_{terra} - E_{terra} - X_{terra} - B_{terra} \quad (2)$$

where  $W_{terra}$  is the constant rate of mercury input to soils from weathering.

In the oceans, G-MCM represents the cycling of both  $Hg^0$  and  $Hg^{II}$ , but not mono- and dimethylmercury since they do not contribute significantly to the exchange of Hg between the oceans and atmosphere (Mason and Fitzgerald, 1993). Oceanic mixing and circulation is parameterized according to a multilayer, box-diffusion model calibrated for the oceanic uptake of  $^{14}C$  and cycling of  $\Sigma CO_2$ , ALK, DOC, and P (Hudson *et al.*, 1994). Since  $Hg^{II}$  sorbs on settling particles in proportion to its concentration, scavenging generates a downward flux out of each layer and a net burial in pelagic sediments  $B_{ocean}$ , which depends on the particle flux and the  $Hg^{II}$  concentration at the sea bottom. The rate of  $Hg^{II}$  reduction to  $Hg^0$  in surface waters  $R$  ( $= k_{ocean}^R \times O_{Hg^{II}}^{surface}$ ) is proportional to the amount of  $Hg^{II}$  present  $O_{Hg^{II}}^{surface}$ . The net  $Hg^0$  efflux to the atmosphere  $E_{ocean}$  is calculated according to standard equations (Liss, 1983). The mass balance on total Hg in the oceans  $O_{Hg}$  ( $= O_{Hg^{II}} + O_{Hg^0}$ ) may be expressed as:

$$\frac{dO_{Hg}}{dt} = D_{ocean} + X_{terra} - E_{ocean} - B_{ocean} \quad (3)$$

G-MCM solves these differential equations (1-3) and others for the ocean interior using a fully implicit solution technique with one-half year timesteps. It was developed for personal computers using Extend™ (Imagine That, San Jose, CA).

### 3. Model Calibration

Recognizing that the uncertainties in all global Hg budgets are significant, we take MFM as our starting point (Table 1). For each process in the Hg cycle, the rate coefficients are calculated from the modern ratio of its rate to the size of the Hg pool the process draws upon, e.g.,  $k_{ocean}^D = D_{ocean}/A_{Hg} = 10 \text{ Mmol yr}^{-1}/25 \text{ Mmol} = 0.4 \text{ yr}^{-1}$ . We then calibrate G-MCM by forcing our reconstruction of the past to be consistent with the present and with our assumptions about the history of anthropogenic influences on the Hg cycle. Some adjustments to MFM are necessary, however, to account for our different

TABLE I  
Modern (circa 1990) global Hg cycle fluxes and derived model rate parameters.

Flux/Pool	Global Hg Cycle Fluxes (Mmol yr <sup>-1</sup> )			Rate coefficient <sup>a</sup> (yr <sup>-1</sup> )	
	MFM	Simulation I	Simulation II	Simulation I	Simulation II
$D_{ocean}$	10	10.0	10.2	0.398	0.398
$D_{terra}$	15	12.0	13.8	0.482	0.545
$E_{ocean} \approx R$	10	7.5	9.2	0.181 <sup>b</sup>	0.218 <sup>b</sup>
$E_{terra}$	5.0	4.7	4.6	0.00094	0.00094
$W_{atmo}$	—	0.3	0.3	—	—
$W_{terra}$	—	0.7	0.7	—	—
$B_{ocean}$	1.0	0.4	0.5	—	—
$B_{terra}$	—	0.7	0.6	0.000135	0.00012
$X_{terra}$	1.0	0.8	0.8	0.000165	0.00017
$E_{anthro}$	10	10	10	—	—
$dA_{Hg}/dt$	+0.2	+0.4	+0.1	—	—
$dO_{Hg}/dt$	+0.4	+2.9	+1.2	—	—
$dT_{Hg}/dt$	+9.4	+6.5	+8.5	—	—

<sup>a</sup> Calculated assuming  $A_{Hg} \approx 25$ ,  $O_{HgII}^{surface} \approx 40$  for 75 m deep surface layer, and  $T_{Hg} \approx 5000$ .

<sup>b</sup> Parameter shown is  $k_{ocean}^R$ .

representations of terrestrial and oceanic Hg cycling.

First, MFM did not clearly quantify the inputs of Hg from weathering as required for G-MCM. Fitzgerald (1986) estimated volcanic inputs to the atmosphere  $W_{atmo}$  of 0.3 Mmol yr<sup>-1</sup>. We next assume that Hg from weathering of soils  $W_{terra}$  is 0.7 Mmol yr<sup>-1</sup> in order for weathering to balance MFM's estimate of the current oceanic Hg sedimentation flux. Actual rates of weathering may be 2.5 Mmol yr<sup>-1</sup> or more (Lindquist, 1991), but adopting this value would require a careful evaluation of geochemical data to determine  $B_{terra}$  and  $B_{ocean}$ , a task beyond the scope of this paper. Finally, we adjust the relative values of  $B_{terra}$  and  $B_{ocean}$  in order to obtain unperturbed levels of  $T_{Hg}$  that are consistent with modern surface soils, which contain ~5000 Mmol Hg (Lindquist, 1991), and our estimates of cumulative anthropogenic deposition to soils, 900-1000 Mmol.

Our second adjustment involves accounting for mixing into the ocean interior, which is neglected in MFM. We find that  $dO_{Hg}/dt$  should be ~3 Mmol yr<sup>-1</sup> at present given the emissions history assumed below. To accommodate this change in the oceanic Hg budget, we decrease  $E_{ocean}$  by 2.5 Mmol yr<sup>-1</sup> from the MFM budget since  $D_{ocean}$  is better constrained by measurements than is  $E_{ocean}$  and 10 Mmol yr<sup>-1</sup> is likely an upper bound on the true  $D_{ocean}$  (R. Mason, personal communication). To maintain the atmospheric Hg balance we also decrease  $D_{terra}$  by ~3 Mmol yr<sup>-1</sup>. We refer to the results based on these recalculated parameters as Simulation I (Table 1).

Scavenging by particles is a second process that transports  $\text{Hg}^{\text{II}}$  downward into the ocean interior. MFM estimated a modern flux to the deep ocean (>1000 m depth) of  $1 \text{ Mmol yr}^{-1}$ . Since the bulk of settling POM has decayed by this depth, the scavenging removal from the surface layer should be considerably larger. If we apply the MFM ratio of  $\text{Hg}:\text{C}$  in oceanic particulate matter ( $0.6 \mu\text{g Hg/g C}$ ) to current estimates of export production,  $10\text{--}18 \text{ Pg C yr}^{-1}$  (see references in Hudson *et al.*, 1994), a scavenging removal from the surface layer of  $>30 \text{ Mmol yr}^{-1}$  is obtained. Tests with scavenging included in the model indicate that the shape of the  $\text{Hg}$  concentration profile is sensitive to this process. However, in the presence of mixing, scavenging only causes minor increases in the oceanic  $\text{Hg}$  uptake rate. Scavenging may become more important when our present representation of the process as an equilibrium sorption reaction is modified to include the kinetics of particle aggregation and settling.

#### 4. Reconstructing Historical Changes in the Global Hg Cycle

Reconstructing historical changes in the global  $\text{Hg}$  cycle requires that we develop estimates of both the natural, "pretechnological" state of the global  $\text{Hg}$  cycle and the historical evolution of  $E_{\text{anthro}}$ . At present, the paleochemical data are too limited to give an independent estimate of the natural conditions. Therefore, in order to estimate the initial state, we assumed that (a)  $E_{\text{anthro}} = 0$ , (b) steady-state conditions prevailed, (c) changes in  $A_{\text{Hg}}$ ,  $T_{\text{Hg}}$  and  $O_{\text{Hg}}$  are consistent with model formulations and emissions histories, and (d) modern values of process rate parameters apply throughout the time period, except as discussed below.

For the purposes of this paper, we approximate  $E_{\text{anthro}}$  as having two components: (1) emissions from gold and silver mining in the Americas and (2) emissions from coal combustion, municipal waste incineration, and other industrial activities (Figure 1).  $\text{Hg}$  con

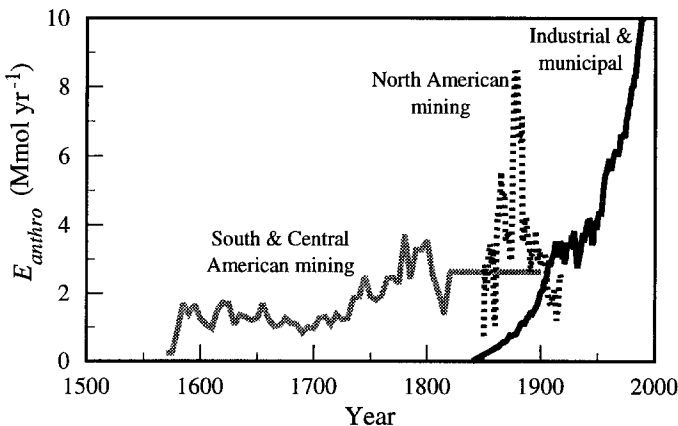


Fig. 1. Historical anthropogenic Hg emissions.

sumption in precious metal mining was substantial from about 1570 to 1920 and about 60 percent of the total amount of  $\text{Hg}$  consumed in the *patio* process may have been

emitted to the atmosphere (Nriagu, 1994). Since much of the industrial and municipal Hg emissions currently derive from coal combustion (Nriagu, 1989), we approximate their historical evolution by assuming they have increased in constant proportion to global CO<sub>2</sub> emissions from coal combustion (Keeling, 1990; Marland 1990), i.e., 4.17 Mmol-Hg Pg-C<sup>-1</sup>. The surprising implication is that mining emissions at the height of the North American gold rush, 11 Mmol yr<sup>-1</sup>, may have been greater than the modern anthropogenic emissions rate of 10 Mmol yr<sup>-1</sup>.

The assumptions of Simulation I imply that the “pretechnological” levels of Hg in the environment were somewhat higher than MFM suggest. Due to mixing into the ocean interior,  $O_{\text{HgII}}^{\text{surface}}$  increased by only 54% rather than 200% as in MFM, implying that currently about 36% of the oceanic and 60% of the total Hg emissions are anthropogenic in origin. At present, about 44% of the total emissions come directly from anthropogenic activities. The modern  $D_{\text{terra}}$  is 2.8 times the pretechnological flux, similar to the ratio of 3 proposed by MFM. An important assumption in calibrating G-MCM is the size of the  $T_{\text{Hg}}$  pool. As represented here, a ~20% increase in  $E_{\text{terra}}$  is obtained. If terrestrial systems have smaller, more rapidly cycled pools of Hg, a greater terrestrial response to anthropogenic emissions would be expected.

TABLE II  
Reconstructed historical global Hg cycle fluxes (Mmol y<sup>-1</sup>) and pools (Mmol).

Flux/Pool	Pre 1890	Pretechnological ( <i>ante</i> 1570)		Preindustrial ( <i>circa</i> 1800) <sup>b</sup>	
	MFM	Simulation I	Simulation II	Simulation I	Simulation II
$D_{\text{ocean}}$	3	3.6	6.1	5.7	9.4
$D_{\text{terra}}$	5	4.3	4.2	6.9	6.4
$E_{\text{ocean}}$	3	4.8	6.2	5.0	8.1
$E_{\text{terra}}$	4.7	3.8	3.7	4.1	3.9
$B_{\text{ocean}}$	0.3	0.5	0.5	0.5	0.5
$B_{\text{terra}}$	0.0	0.6	0.5	0.6	0.5
$X_{\text{terra}}$	0.3	0.67	0.7	0.7	0.7
$A_{\text{Hg}}$	8	9.0	15.3	14.4	23.5
$O_{\text{HgII}}^{\text{surface}}$	13.5 <sup>a</sup>	25.9	28.4	27.7	37.1
$T_{\text{Hg}}$	—	4070	3980	4320	4190

<sup>a</sup> Value normalized to 75 m deep surface layer; equal to 18 for 100 m as in MFM (1994).

<sup>b</sup>  $E_{\text{anthro}} = 3.5 \text{ Mmol y}^{-1}$

With these extrapolated initial conditions and emissions histories, we use G-MCM to reconstruct the expected evolution of the global Hg cycle and of atmospheric deposition to terrestrial systems  $D_{\text{terra}}$  (Figure 2). Unlike CO<sub>2</sub>, there exist no reliable measurements of atmospheric Hg concentrations prior to the late 1970's nor any paleochemical record of atmospheric Hg concentrations. At present, the best indicators of the historical changes in the Hg cycle consist of the records of deposition over the past few centuries preserved in lake sediments (e.g., Swain *et al.*, 1992) and bogs (Benoit *et al.*, 1994). To facilitate

comparison with the model results, figure 2 also shows the changes in Hg deposition rates relative to the 1800-1850 average inferred from sediment Hg accumulation rates measured in seven lakes in the upper midwest of the United States (Swain *et al.*, 1992). While simulation I does predict the observed generally increasing rates of deposition from pretechnological to modern times, it does not match the details well. Most notably, it predicts modern deposition rates that are 1.8-times "preindustrial" (*circa* 1800), as compared to the observation of 3.7-times higher rates. In addition, the predicted peak due to North American mining centered at about 1880 is too prominent. The ratio of modern/pretechnological values of  $D_{terra}$ , 2.7, is closer to the observed modern/preindustrial ratio. The two would be more consistent if the impact of Hg mining emissions during the 1800's was moderated.

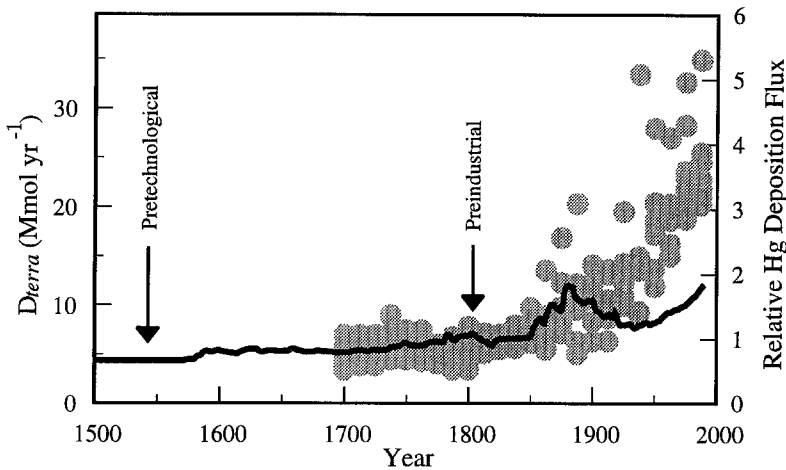


Fig. 2. Simulation I: modeled changes in the global average terrestrial Hg deposition compared to Hg deposition recorded in lake sediments. Historical data are cores from 7 lakes normalized to mean modern/preindustrial ratio for each lake (Swain *et al.*, 1992).

The appropriate way to compare Hg deposition at a particular site to global averages needs to be carefully considered. Variability in deposition rates around the world reflects both the effects of proximity to regional and hemispheric sources as well as the differences in atmospheric chemistry and precipitation volume that influence deposition fluxes. For now, we can only hope that the relative change at a particular site removed from regional sources should compare well to the relative change in global average deposition. (This may not be the case, if as we argue below, changes in atmospheric chemistry may also influence deposition.) This approach has been used by Engstrom *et al.* (1994), who found that modern Hg accumulation rates in the sediments of two Alaskan lakes were 2.5-times the 1800-1850 level and suggested that about one-third of the deposition to the midwest was regional in origin.

The changes in atmospheric chemistry over the past century due to anthropogenic emissions of particles,  $\text{SO}_2$ , and oxidants also have the potential to influence the global transport of Hg (Munthe and McElroy, 1992). It is likely that these changes have altered

the atmospheric residence time of Hg and possibly the relative rates of deposition to the oceans and to land, where most air pollutants are generated. A detailed consideration of the changes in atmospheric chemistry is beyond the scope of this paper, but we wish to examine how such changes might affect deposition histories. First, we note that changes in the atmospheric residence time will affect  $A_{\text{Hg}}$ , but not  $D_{\text{terra}}$  or  $D_{\text{ocean}}$ , as long as the ratio  $k_{\text{terra}}^D/k_{\text{ocean}}^D$  remains constant. Changes in the relative values of  $k_{\text{terra}}^D$  and  $k_{\text{ocean}}^D$  will, however, significantly alter the historical reconstruction since different amounts will accumulate on land and in the oceans.

To examine this question using G-MCM, we hypothesize that  $k_{\text{terra}}^D$  has increased by a factor of two since 1840, in parallel with coal combustion rates, while  $k_{\text{ocean}}^D$  has remained nearly constant (Simulation II). In this case, the modern  $dO_{\text{Hg}}/dt$  is less than for Simulation I (Table I), a change requiring readjustment of the global Hg budget as above. All modern fluxes in Simulation II are close to MFM values. However, pretechnological  $A_{\text{Hg}}$  and  $O_{\text{Hg}}^{\text{surface}}$  are only 39% and 45% below their respective modern levels and most surprisingly both are within 10% of modern by 1800. About one-third of  $E_{\text{ocean}}$  and 58% of total emissions is anthropogenic in origin, with  $E_{\text{anthro}}$  currently accounting for 42%. The modern/pretechnological and modern/preindustrial ratios of  $D_{\text{terra}}$  are 3.3 and 2.2 respectively, which agree with the sediment records more closely than Simulation I does. Most notably, the overall increase from preindustrial conditions to the present is greater and the maximum at 1880 is lower than current rates of deposition. Although this historical reconstruction does not prove that the hypothesized changes happened, it does suggest that anthropogenic influences on deposition processes should be considered in any historical reconstruction of the global Hg cycle. Changes in  $k_{\text{terra}}^D$  are likely to vary significantly by region and could contribute to the observed decreases in recent deposition to the upper midwest of the United States (Benoit *et al.*, 1994).

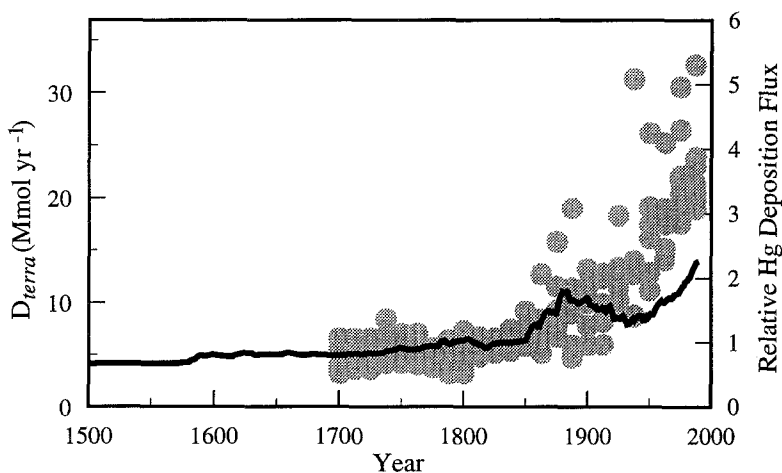


Fig. 3. Simulation II compared to Hg deposition inferred from lake sediments as in Figure 2.

## 5. Conclusions

We have developed a mechanistic model of the global Hg cycle (G-MCM) and calibrated it using recent estimates of global Hg fluxes and reconstructions of anthropogenic emissions history. Our results suggest the following conclusions:

(a) Global Hg budgets should account for transport of Hg into the ocean's interior. Current transport rates depend on the history of anthropogenic influences on the Hg cycle.

(b) At present, direct anthropogenic emissions account for about 40% of the total Hg input to the atmosphere. An additional 20% results from past anthropogenic emissions being reemitted from oceans and terrestrial systems.

(c) Assuming that changes in Hg emissions alone have caused the observed variations in Hg accumulation rates in lake sediments leads to simulations that do not fit the observations well. An increase in terrestrial relative to oceanic Hg deposition over the period 1850-1990, as might be caused by anthropogenic emissions of SO<sub>2</sub>, oxidants, and particles, improves simulations of terrestrial deposition fluxes.

(d) Conversely, a recent decrease in other air pollutants, especially particulate matter, for North America could explain the apparent conflict between increasing atmospheric Hg and apparent decreases in Hg deposition since 1960 (Benoit *et al.*, 1994).

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