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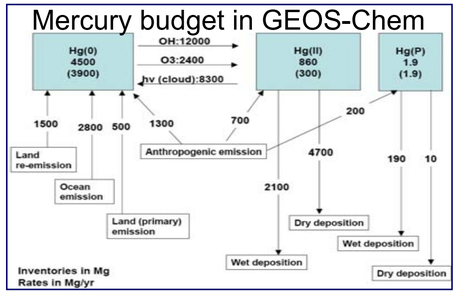
Chemical cycling and deposition of atmospheric mercury: Global constraints from observations

For further information, see: *Selin et al.* [2006], *Journal of Geophysical Research*, in press
http://www.as.harvard.edu/chemistry/trop/publications/selin2006a.pdf

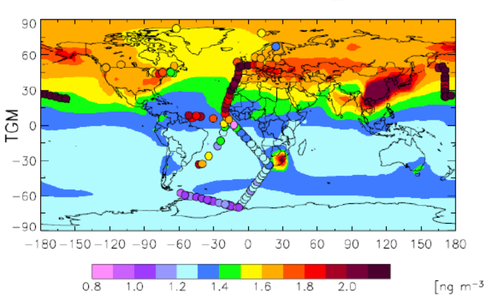
Abstract: We use a global 3-D model of atmospheric mercury (GEOS-Chem) to interpret worldwide observations of total gaseous mercury (TGM) and reactive gaseous mercury (RGM) in terms of the constraints they provide on the chemical cycling and deposition of mercury. Our simulation including a global mercury source of 7000 Mg y-1 and a TGM lifetime of 0.8 y reproduces the magnitude and large-scale variability of TGM observations at land sites. However, it cannot capture observations of high TGM from ship cruises, implying a problem either in the measurements or in our fundamental understanding of mercury sources. Observed TGM seasonal variation at northern mid-latitudes is consistent with a photochemical oxidation for Hg(0) partly balanced by photochemical reduction of Hg(II). Observations of increasing RGM with altitude imply a long lifetime of Hg(II) in the free troposphere. We find in the model that Hg(II) dominates over Hg(0) in the upper troposphere and stratosphere, and that subsidence is the principal source of Hg(II) at remote surface sites. RGM observations at Okinawa Island (Japan) show large diurnal variability implying fast deposition, which we propose is due to RGM uptake by sea-salt aerosols. Observed mercury wet deposition fluxes in the United States show a maximum in the southeast, which we attribute to photochemical oxidation of the global Hg(0) pool. They also show a secondary maximum in the industrial Midwest due to regional emissions that is underestimated in the model, possibly because of excessive dry deposition relative to wet (dry deposition accounts for 68% of total mercury deposition in the United States in the model, but this is sensitive to the assumed phase of Hg(II)). We estimate that North American anthropogenic emissions contribute on average 20% to U.S. mercury deposition.

1. GEOS-Chem Model Description

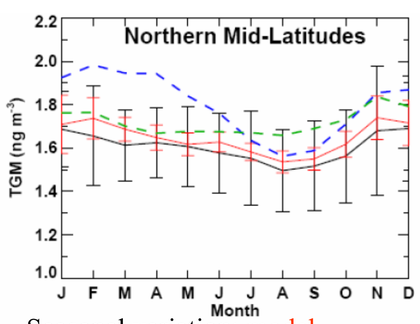


- GEOS-Chem v. 7.04 [*1*], 4°x5°, assimilated meteorology, NASA Goddard Earth Observing System (GEOS-4)
- GEIA 2000 emissions [*2,3*]
- Coupled ocean-atmosphere model [*4*]
- Hg(0) oxidation by OH and O_3 [*5,6,7*]), Hg(II) aqueous, photochemical reduction
- Wet & dry deposition of Hg(II), Hg(P) [*8,9,10*]
- Hg(0) dry deposition to ocean [*4*]

2. Global Atmospheric Distribution

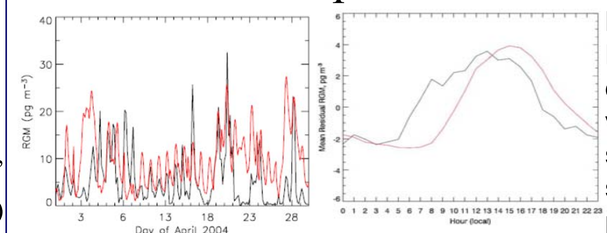


Model captures interhemispheric gradient and global distribution of mercury, but underestimates high cruise data over oceans



Seasonal variation: model, measurements, OH oxidation only, O3 oxidation only

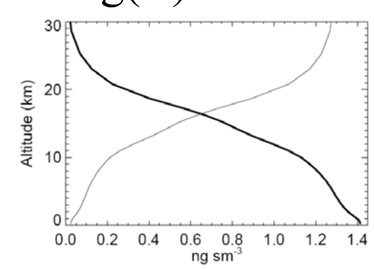
3. Okinawa Comparison: Sea-Salt?



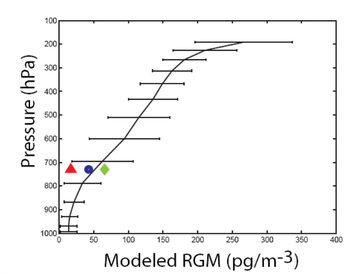
Measurements at Okinawa, Japan [11] show diurnal variation in RGM

Magnitude of RGM and its diurnal variation suggest fast sink: we propose sea-salt uptake [*14*]

4. Hg(II) Increase with Altitude

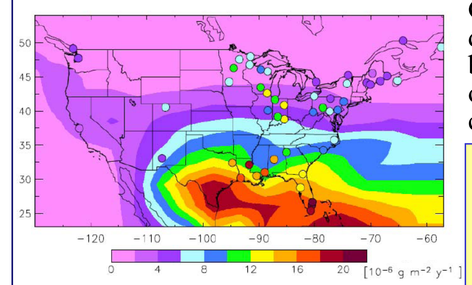


Hg(II) is the dominant form of mercury in the model at high altitude. This is supported by measurements [*12,13*].



Comparison to measurements at Mt. Bachelor, OR [*12*].
▲=day, ● =all, ◊ = night

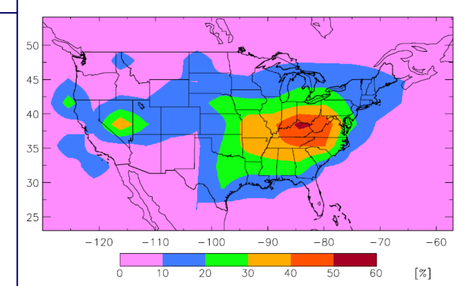
5. Deposition to the US: Two Patterns



GEOS-Chem annual wet deposition flux, 2003-04, background, compared with observations from MDN [*15*], circles.

Two patterns:
- latitudinal gradient (driven by OH oxidation in sunny, wet areas) and
- regional enhancement (Midwest US).

Average N. American contribution to U.S. total deposition: 20%.



Simulated % contributions from North American primary anthropogenic sources to total (wet + dry) annual deposition in GEOS-Chem for 2003 (excluding re-emission), from simulation with these sources shut off

References: [1] I. Bey et al. 2001, *Journal of Geophysical Research-Atmospheres*, *106*, 23073-23095; [2] J. Pacyna et al. 2006, *Atmospheric Environment 40*, 4048-4063; [3] S. Wilson and F. Steenhuisen 2006, *Atmospheric Environment 40,* 4621-4632; [4] S. Strode et al. 2006, *Global Biogeochemical Cycles*, submitted; [5] B. Pal and P. A. Ariya 2004, *Physical Chemistry Chemical Physics*, *6*, 572-579; [6] J. Sommar et al. 2001, *Atmospheric Environment*, *35*, 3049-3054; [7] B. Hall 1995, *Water, Air, and Soil Pollution*, *80*, 301-315; [8] H. Liu et al. 2001, *Journal of Geophysical Research*, *106*, 12,109-112,128; [9] Y. Wang et al. 1998, *Journal of Geophysical Research*, *103(D9)*, 10,713-710,726; [10] M. L. Wesley 1989, *Atmospheric Environment*, *23*, 1293-1304; [11] D. Jaffe et al. 2006 *Atmospheric Environment 39*: 3029-3038;[12] P. Swartzendruber et al. 2006, *Journal of Geophysical* Research, in press; [13] D.M. Murphy et al. *Environmental Science and Technology 40,* 3163-3167; [14] E.M. Malcolm et al. 2003, *Journal of Geophysical Research* 108, 4357; [15] National Atmospheric Deposition Program, 2003

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