Mercury deposition to the Gulf Coast region from deep convection and long-range atmospheric transport

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Abstract A53D-0308

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Summary

Wet scavenging is a large source of mercury deposition in the Gulf Coast of the United States. Following concern about mercury's impact on ecosystems and humans, the US EPA Mercury Deposition Network (MDN) makes ongoing weekly wet deposition measurements at 10 sites in the Gulf region. Deposition in this area peaks in the summer months when rain is its most frequent and intense. Previous studies have variously argued that mercury in rainwater derives primarily from nearby sources or from long-range transport at high altitude. As a new test for high-altitude wet scavenging contributing to mercury deposition, we use lightning counts from the National Lightning Detection Network (NLDN) and cloud top temperatures from the International Satellite Cloud Climatology Project (ISCCP-B1) as proxies for deep convection. We find a significant correlation between lightning and mercury deposition, after accounting for precipitation depth. This implies that scavenging of mercury from the global mercury pool in the upper troposphere is a significant source of mercury deposition in the Gulf region.

1. Possible sources of Hg in rainwater

The Gulf Coast has the highest Hg deposition in the US (right), but its sources are debated. Dvonch et al. (1998) attributed most deposition in south Florida to regional sources, while Guentzel et al. (2001) found a large contribution from long-range transport. Mercury transport models predict that convective thunderstorms scanvenge soluble Hg^{II} from the upper troposphere in the subsiding branch of the Hadley circulation (Selin et al. 2008).

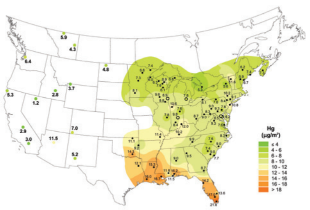

Figure 1: Total mercury wet deposition, 2007 (EPA MDN)

HYPOTHESIS: If susidence from the upper troposphere supplies Hg^{II} from the upper troposphere to the Gulf region, then Hg wet deposition should be correlated with convection height, after controlling for precipitation amount.

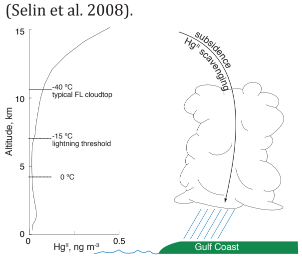

Figure 2: Vertical profile of Hg^{II} over Gulf region simulated by GEOS-Chem global CTM (left). Hypothesized dominant mercury scavenging pathway for the Gulf region (right).

2. Data sources

- US EPA Mercury Deposition Network weekly totals at 12 Gulf-region sites June-September 2001-2006
- Lightning: NLDN cloud-to-ground strikes within 10km of MDN site
- Cloud-top temperature (CTT): GOES 11μm channel within 20km of MDN site every 3 hours

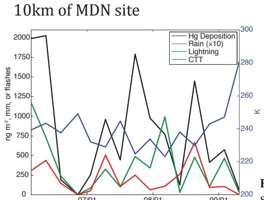

Figure 3: MDN site FL05 (near Tampa, FL) for summer 2003.

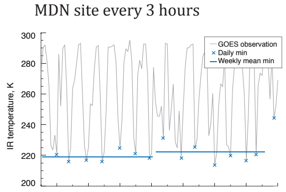

Figure 4: Weekly cloud-top temperatures calculated as the mean of daily minimum GOES temperature.

3. Correlation results

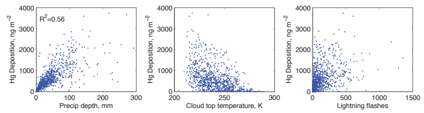

Figure 5: Mercury deposition in the Gulf region during summer correlates with precipitation depth, cold cloud tops and lightning flashes, all of which are associated with thunderstorms. N=889

Mercury deposition increases in the presence of lightning and cold cloud tops at all MDN sites in the Gulf, even after accounting for precipiation depth (Figure 6). The relationship between Hg deposition, lightning, and CTT may not be linear, so we next regress subsets of the data.

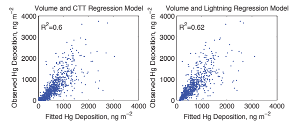

Figure 6: Adding CTT (left), lightning (right), or both (not shown) to a multiple regression model improves the model fit (p<0.01) despite only a small increase in R^2.

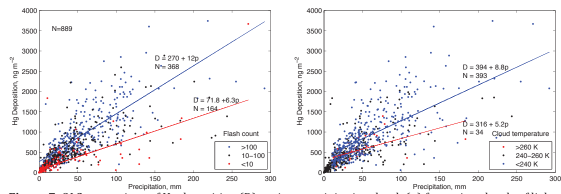

Figure 7: OLS regressions of Hg deposition (D) against precipitation depth (p) for various levels of lightning (left) or cloud-top temperature (right). Data for all Gulf-region sites during summer 2001-2006. N=889

Within the Gulf region weeks with frequent lightning (>100 flashes) experience nearly twice as much Hg deposition as weeks with low flash rates (<10 flashes) for the same amount of precipitation. Since lightning flashes are correlated with cloud-top height, this supports our hypothesis. Hg deposition, however, shows only a slight increase for the coldest clouds (<240 K) vs. the warmest ones (>260 K).

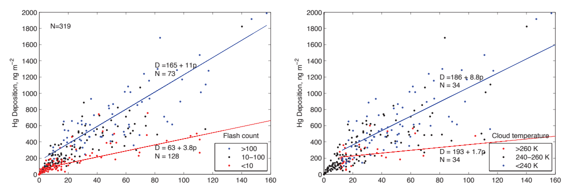

Figure 8: Same as Figure 7, except data from 3 MDN sites with low Hg deposition in Georgia and South Carolina during summer 2001-2006. N=319

Sites outside the Gulf region experience similarly high Hg depostion in the presence of frequent lightning or cold cloud tops, but lower deposition in their absence. This suggests similar supplies of Hg^{II} in the upper troposphere over the Gulf and regions further north, with differences in total deposition due to thunderstorm frequency rather than subsidence, contra hypothesis.

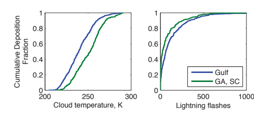

Figure 9: Cumulative Hg deposition associated with cloud-top temperature and lightning.

REFERENCES

Dvonch, J.T. et al. (1998) Sci. Total Environ. 213, 95-108.

Guentzel, J.L. et al. (2001) Environ. Sci. Technol. 35, 863-873.

Holmes, C.D. et al. (2008) Atmos. Environ. in review.

Selin, N.E. et al. (2008) Atmos. Environ. 42, 5193-5204.

Considine, D.B. et al. (2008) Atmos. Chem. Phys. 8, 2365-2385.

Yang, X. et al. (2008) J. Geophys. Res., in press.

Zeng, T. et al. (2003) Geophys. Res. Lett. 30, 2298

Hynes, A. et al. (2008) UNEP Global Mercury Partnership.

Holmes, C. et al. (2006) Geophys. Res. Lett. 33, L20808.

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4. Implications and open questions

- Since lightning frequency has a stronger association with Hg deposition than CTT (Figure 7), scavenging microphysics or convection vigor may be more important than scavenging altitude. If so, then what is the scavenging mechanism?
- Is lightning a better predictor of Hg deposition than CTT for individual storms?
- We find no evidence of subsiding Hg^{II} unique to the Gulf region.
- Are deep convective events at higher latitudes equally large sources of Hg deposition?

5. A global Hg+Br chemistry simulation

We are evaluating the impact of Hg+Br chemistry on the global mercury cycle within the GEOS-Chem global land-ocean-atmosphere model. Recent kinetic studies suggest that OH and O_3 are minor oxidants of Hg^0 under atmospheric conditions (Hynes et al. 2008), but that atomic Br could be important globally (Holmes et al. 2006).

The CTM includes the two-step oxidation

$$Hg^0 + Br + X \rightarrow HgBrX \quad (X = Br, OH)$$

We specify Br concentrations derived from the major sources:

- Biogenic bromocarbons ($CHBr_3$, CH_3Br, CH_2Br_2,...) from the pTOMCAT CTM (Yang et al. 2008)
- Halons from the GMI CTM (Considine et al. 2008)
- Sea-salt aerosols from photochemical steady-state with 1.6 ppt BrO (Holmes et al. 2008)
- Polar bromine explosion from photochemical steady-state with GOME BrO (Zeng et al. 2003)

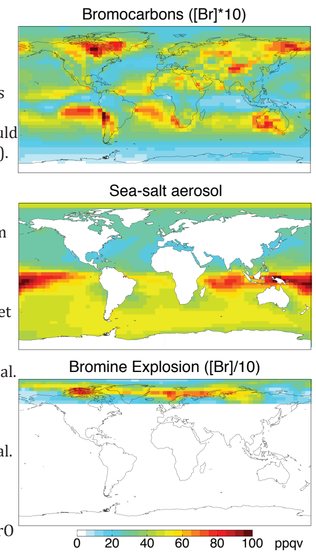

Figure 10: Surface concentrations of atomic bromine from various sources. All figures show April mean.

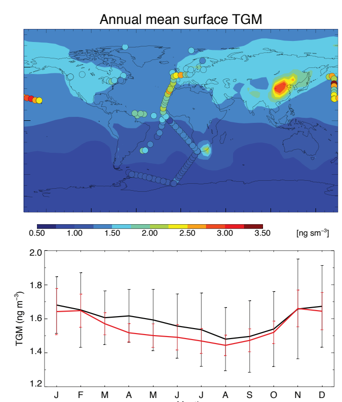

Figure 11: Simulated surface concentration of total gaseous mercury (top) compared with ship measurements and annual-means at surface stations. Seasonal cycle of TGM observed (black) and simulated (red) at 12 northern mid-latitude sites.

We now calculate scavenging of Hg^{II} by sea-salt aerosols using a physical mechanism based on wind speed and humidity (Holmes et al. 2008). This increases Hg deposition to high-latitude marine ecosystems.

Oxidation of Hg^0 by Br and O_3 can explain the meridional gradient and seasonal cycle found in atmospheric Hg observations (Figure 11). The model does not require aqueous photoreduction.

Global budgets with Br and OH oxidants are similar because both species increase with altitude, especially in the tropics, and are minimum in winter.

Further model evaluation will include aircraft observations in the Arctic and Pacific (from NASA ARCTAS and INTEX-B experiments).