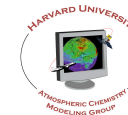


Thunderstorms increase mercury concentration in rainfall

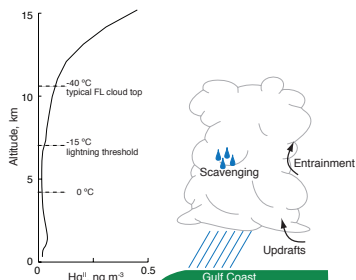
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1. Overview

Wet scavenging is a large source of mercury to the Eastern United States, especially the Gulf Coast. Long-term monitoring by the EPA Mercury Deposition Network (MDN) shows that most wet deposition occurs during the wet summer months. Previous studies have variously argued that mercury in rainwater derives primarily from nearby sources or from long-range transport at high altitude (e.g. Dvonch et al. 1998; Guentzel et al. 2001; Selin and Jacob 2008; Landing et al. 2010). We test the effects of storm type (thunderstorm vs. stratiform), convection altitude and rain intensity on mercury concentrations using a multiple regression model for individual rain events at 9 sites in the Eastern US. We find that thunderstorms have 44% higher mercury concentrations in rainwater, after accounting for dilution by larger rain depths. Cloud top altitude is uncorrelated with rainwater mercury concentration after controlling for

thunderstorm presence, but large radar reflectivities above 11 km is, suggesting that scavenging at high altitudes is a significant source of mercury. These precipitation characteristics explain 50% of the enhanced mercury deposition in the Gulf Coast vs. the Northeast US.

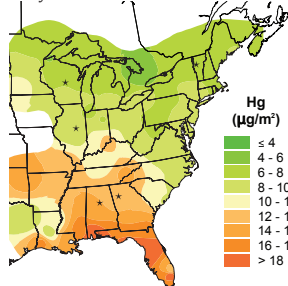


Vertical profile of Hg^{II} over Gulf region from GEOS-Chem global CTM (left). Key processes in wet scavenging (right).

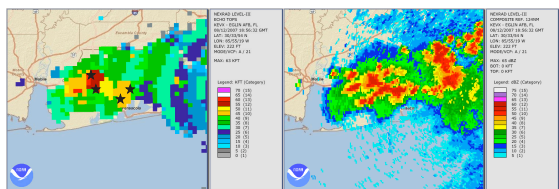
2. Data sources

- Mercury concentrations and precipitation depths from 806 individual rain events at 9 sites in the MDN and SEARCH networks, plus 3 FSU/UWF sites near Pensacola, FL (right). Pensacola rain samples were also analyzed for trace elements (Landing et al. 2009).
- Thunderstorm reports are collected from hourly METAR reports at the nearest airport. Rain events are classified based on observations in 36 hours prior to sample collection.
- Cloud-to-ground lightning strikes from the National Lightning Detection Network within 10 km of the site.

The map below shows mercury wet deposition in 2006. Stars show sites analyzed here

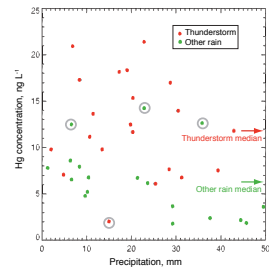


- Radar provides "echo tops" (maximum altitude of precipitation), reflectivity at 3 altitudes (0-8 km, 8-11 km, 11-21 km), plus "composite reflectivity" at all altitudes with 2 km and 5 minute resolution. Rain events are assigned extreme values observed within 10 km in 36 hours prior to sample collection.

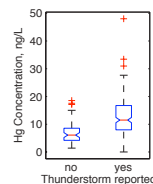


The figures above show "echo tops" (left) and "composite reflectivity" (right) in the Pensacola area on August 12, 2007. Multiple convective rain cells cover the region with intense rain, but only one cell generates echoes above 15 km. Stars indicate measurement sites.

3. Simple analyses



The figure at right shows large rain events (>20 mm) from all 9 sites and reinforces that thunderstorms have larger median mercury concentrations. Careful analysis must account for precipitation depth because of dilution in large rain events.



The figure at left shows mercury concentrations in summer rain events during 2005-2006 in Vermont. Concentrations are larger in thunderstorms, except under unusual conditions.

The smallest thunderstorm concentration occurred on the 3rd consecutive day of thunderstorms.

The largest non-thunderstorm concentrations occurred after several days without rain, often on days with towering cumulus.

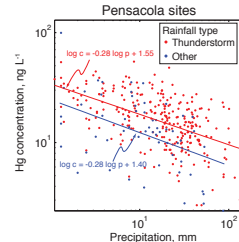
4. Multiple regression analysis

Mercury concentrations (*c*) obey a power law relationship with rain depth (*p*) at all sites, so we can fit all data with

$$\log c = \beta_0 + \beta_1 \log p + \sum \beta_i x_i$$

where *x_i* are additional predictor variables (below) and β_i are regression parameters. We use stepwise regression to test the significance of each predictor and interaction effects.

Predictor variable	Significant <i>p</i> <0.05
Storm type	yes
Rain depth	yes
Cloud top altitude	no
Radar reflectivity	
11-21 km	yes
8-11 km	not with 11-21 km
0-8 km	not with 11-21 km
Site differences	yes
Interaction effects	no



Major regression results

- Hg concentrations are 44% greater in thunderstorms than other rain.
- Hg concentrations are diluted 20% for each 2X increase in rain depth.
- Hg concentrations are 35% lower outside the Gulf region for the same storm type and rain depth.
- Hg concentrations correlate with high-altitude (11-21 km) radar reflectivity (i.e. rain rate) after accounting for other effects, but not with cloud top altitude, meaning that convection intensity is important, but not altitude.

Acknowledgements

We thank Brendan Hoch (Plymouth State University) for providing hourly METAR reports and Ken Knapp (NOAA NCDC) for providing HIRS/AT IR temperatures. This work has been funded by the Electrical Power Research Institute (EPRI) and an EPA-STAR Graduate Fellowship. The EPA has not officially endorsed this publication and the views expressed herein may not reflect those of the EPA.

Causes of higher Hg deposition to the Gulf region, from the regression model.

Cause	Enhancement Explained
Greater frequency of thunderstorms (75 vs. 50% of rain)	10-30%
Greater total rainfall (180 mm vs. 105 mm)	~20%
Other site differences	40-60%

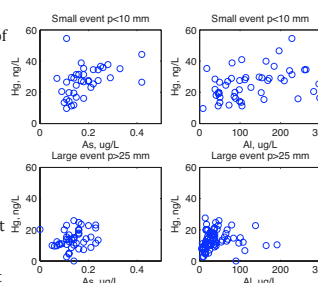
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5. Trace element correlations

Landing et al. (2010) estimated that coal combustion accounts for 20-40% of mercury in Pensacola rainwater, based on trace element correlations and PCA.

The figure at right shows that Hg correlates with As more strongly in small rain events (<10 mm) than in large events (>25 mm). Conversely, Hg correlates with Al more strongly in the large events. The same correlations occur other elemental indicators of dust and fossil fuel combustion.



Airmasses rich in dust account for most Hg in large rain events. These airmasses pass over the Sahara and through the sub-tropical Atlantic subsidence region and can mix with upper tropospheric air.

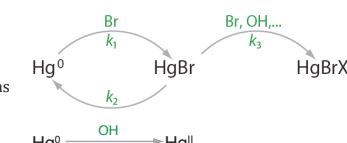
Mercury correlations with trace elements indicating fossil fuel and crustal sources.

A test of atmospheric mercury oxidation in Antarctica

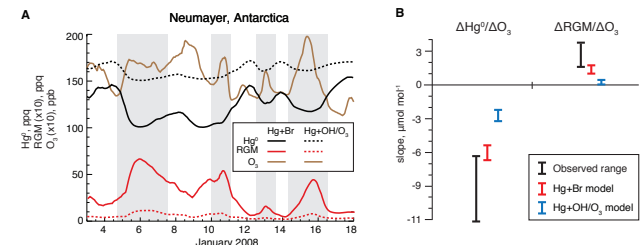
from C.D. Holmes, D.J. Jacob, E.S. Corbitt, X. Yang, R. Talbot, *Global atmospheric model for mercury including oxidation by bromine atoms.*

Observations at Antarctic sites show frequent summertime events of depleted Hg(0) and enhanced RGM together with elevated ozone (Sproveri et al. 2002; Temme et al. 2003). Correlations with O₃ and relative humidity indicate a subsidence source, unlike spring depletion events. Holmes et al. (2006) previously cited these

summer Antarctic events as qualitative evidence for Hg+Br chemistry. These observations provide a sensitive test for Hg(0) oxidation chemistry in the model because the cold, dry Antarctic atmosphere minimizes the confounding effect of aqueous reduction.



Two alternative oxidation mechanisms in the GEOS-Chem model.



Simulations with the Hg+Br oxidation mechanism include the observed range of ΔHg(0)/ΔO₃ enhancements, while the Hg+OH/O₃ mechanism does not.

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