Atmospheric Mercury Cycling: Constraints from INTEX-B and GEOS-Chem

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Summary

During INTEX-B the DC-8 and UWB-Duchess measured vertical profiles of Hg^0 over the mid-latitude ocean for the first time. In contrast to observations over land, where surface air is enriched in Hg^0 relative to the free troposphere [e.g. *Banic et al.*, 2003], the marine columns showed *decreasing* Hg^0 in the marine boundary layer (MBL) (Section 1). The GEOS-Chem Hg CTM [*Selin et al.*, 2007], does not reproduce these profiles (Section 4), suggesting that some aspect of the atmospheric budget needs revision.

As oxidation of Hg^0 to Hg(II) (followed by deposition) by halogens is one possible explanation of the low MBL Hg^0 observations, we studied the sensitivity of the vertical profile to halogen oxidants. Among the reactive halogens, Br has the largest impact on Hg^0 [*Holmes et al.*, 2006]. Because the vertical gradients of Br are not well known, we use several plausible scenarios (Section 4).

While adding Hg-Br chemistry and strong MBL Br enhancements improves the simulated vertical profile of Hg^0 in GEOS-Chem, the slope remains incorrect, suggesting that other processes, such as source errors are responsible.

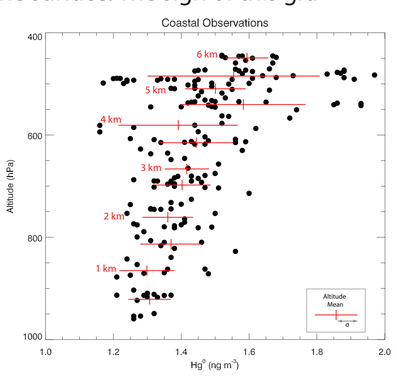
1. Hg^0 Observations

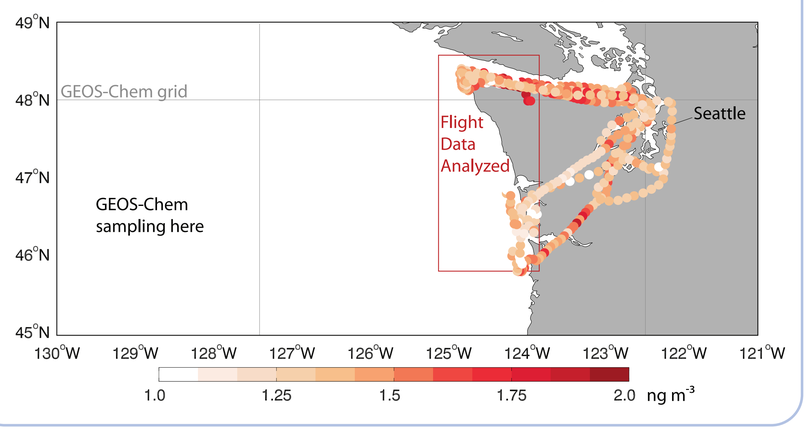
The UWB Duchess aircraft measured vertical profiles of Hg^0 in marine airmasses on 8 flights, shown below. This study examines only the marine coastal observations, shown in the red box.

On all flights, Hg^0 decreased from ~1.7 ng m^{-3}, typical for the mid northern latitudes, to 1.3 ng m^{-3} near the surface. The sign of this gradient is the primary focus of this work.

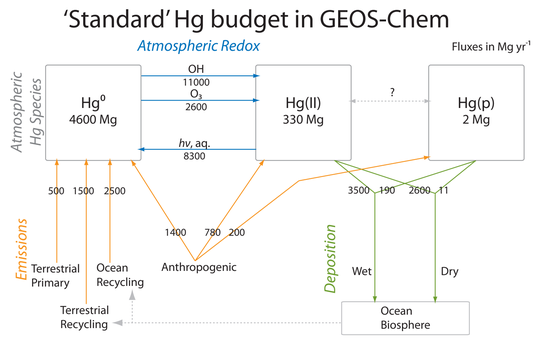
The samples have primarily marine histories, according to HYSPLIT back-trajectories [Chand *et al.*, 2006].

In order to avoid sampling terrestrial sources in the model, and because the vertical profile appears marine in origin, we sample GEOS-Chem in adjacent land-free grid domains.

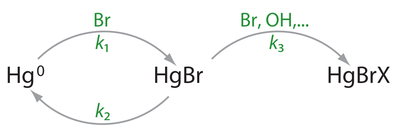




2. GEOS-Chem Hg Budget



Additional reactions (at right) may affect the atmospheric redox state of Hg. The Hg-Br reaction is a two-step recombination in competition with the thermal dissociation of the reactive intermediate (HgBr) [*Holmes et al.*, 2006].

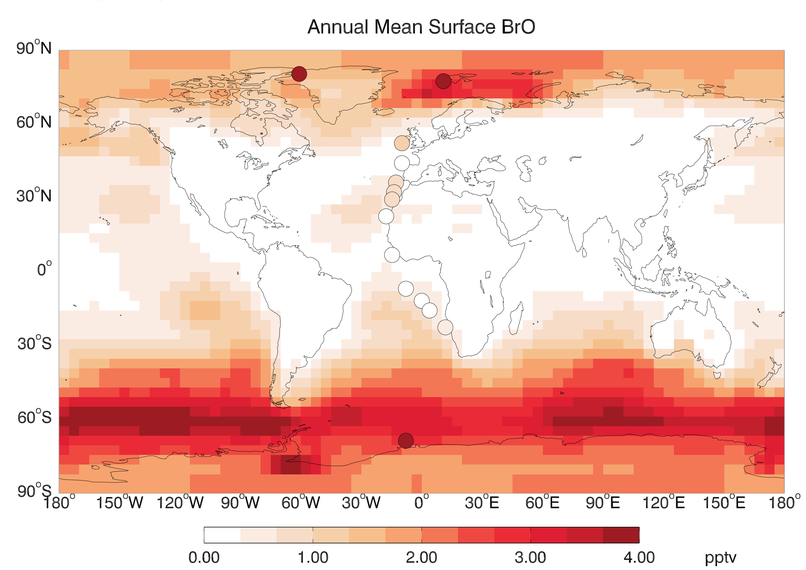


Cl and OCl^- abundances are too small to affect Hg, while the BrO reaction is likely endothermic.

$Hg^0 + Cl \rightarrow$ Hg(II) products
$Hg^0_{(aq)} + OCl^- \rightarrow$ Hg(II) products
$Hg^0 + BrO \rightarrow$ Hg(II) products

3. Tropospheric Br Distribution

The map shows modeled (TOMCAT) surface BrO mixing ratios, derived from inorganic bromine released by sea salt aerosol photochemistry and the decay of brominated VOCs [*Yang et al.*, 2005]. Observations are overlaid. This model version includes recyling of Br reservoir species to Br_2 by heterogeneous reactions. We used this and the 'base' model (without recycling) for the sensitivity analysis (Section 4).



4. Sensitivity Results

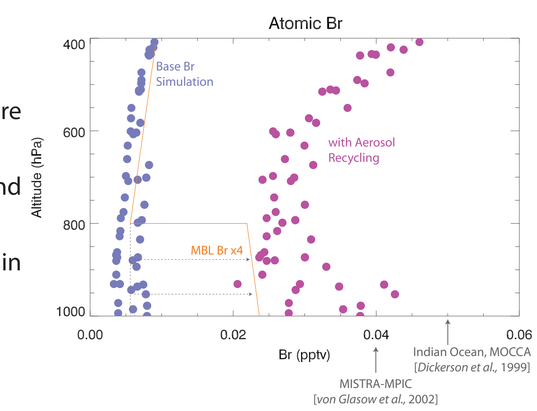
	Sensitivity Test	Hg^0 oxidants	Outcome
1	'Standard' Chemistry	OH, O_3	Hg^0 increases in MBL
2	Hg-Br Chemistry	Br, O_3	Hg^0 increases in MBL
3	Hg-Br Chemistry with aerosol Br recycling	Br, O_3	$Hg^0 \approx 0.6$ ng m^{-3} Hg^0 increases in MBL
4	Hg-Br Chemistry with 4X MBL Br	Br, O_3	Hg^0 increases in MBL, but less than in 1 and 2

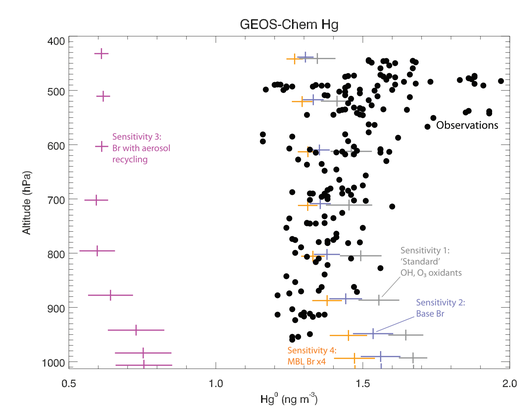
Sensitivity tests with the standard Hg chemistry (Section 2), Hg-Br chemistry, and different Br distributions (below right), show limited improvements in reproducing the decrease of Hg^0 in the MBL (bottom). MBL atomic Br concentrations are unlikely to be much higher, implicating other atmospheric processes.

Key issues for future research:

- the vertical profile of Br and Br(inorg)

- Oceanic Hg^0 emissions in the eastern Pacific





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