1. Introduction

Most mercury (Hg) emission is the elemental gas Hg^0, which is transported globally in the atmosphere. It is eventually oxidized to divalent Hg^2+ salts, which are highly water-soluble, can partition into the aerosol, and are efficiently removed from the atmosphere by wet and dry deposition. Hg^2+ can also be reduced back to Hg^0. Understanding the redox chemistry of atmospheric Hg is critical to determining the patterns of deposition to surface environments, where Hg can be transformed to toxic and bioaccumulative methylmercury. Here we present a state-of-the-science redox mechanism for use in atmospheric models, and implement it in the GEOS-Chem model to evaluate against atmospheric observations and examine the implications for Hg deposition.

2. Atmospheric Mercury Chemistry

Oxidation by Br atoms is known to cause atmospheric mercury depletion events in the Arctic boundary layer in spring. Holmes et al. (2010) suggested that Br atoms oxidize Hg^0 to Hg^2+ in the atmosphere. With the new emissions inventory, declining atmospheric concentrations can be explained by the phase-out of Hg from commercial products and by shifts in the speciation of Hg emissions driven by air pollution control technologies.

3. Improved Emissions Inventory & Model Setup

A longstanding conundrum has been the apparent disconnect between increasing global emissions trends and measured declines in atmospheric mercury in North America and Europe. We construct an improved global emission inventory for the period 1990-2010 accounting for emissions from commercial products, emission controls on coal-fired utilities, and trends in ASGM and find a 20% decrease in total Hg emissions and a 30% decrease in anthropogenic Hg^2+ emissions, with much larger decreases in North America and Europe offsetting the effect of increasing emissions in Asia.

4. Results: Hg^2+ Production

Gas-phase Br-initiated Hg oxidation dominates in the troposphere and stratosphere. The most important pathways are NO_2 and NO_3, due to their greater abundance relative to other halogen radicals and OH (Fig. 3).

5. Implication for Wet Deposition & Surface Ocean

Changes in wet deposition are due to a combination of:
- changes in Br distribution (Schmidt et al. 2015) – less deposition over the Southern Ocean
- additional second step oxidants like HO_2 that have greater abundance in the tropics – increased deposition to the tropics
- changes in Hg reduction – distributions of Hg^2+ are related to spatial pattern of OA. Now, differences between Br – initiated oxidation and OH/O_3 oxidation are slightly muted with respect to Hg^2+ wet deposition.

6. 30- Second Summary

- Observed decreasing trends in atmospheric Hg^2+ can be explained by changes in domestic emissions – based on recently available data
- Atmospheric redox reactions determine where emitted Hg will be deposited to surface environments
- Br is dominant oxidant in troposphere and stratosphere. Abundant radicals (HOCI, NO_3) dominate overall oxidation pathways
- Hg^2+ reduction pathway is needed, even given uncertainty in Hg^2+ lifetime from observations, even within uncertainty in oxidation reaction rates (+/- 50%)

Selected References:
- Holmes et al., ACP, 2012
- Streets et al., JAS, 2011
- Zhang et al., PNAS, in press

We use v9-02 of the global GEOS-Chem Hg model including atmosphere-ocean-land interactions. 3-D atmospheric transport is driven by GEOS-5 assimilated meteorological data from NASA GMAO, degraded to 4° x 5° horizontal resolution. There are three Hg tracers transported in the atmosphere: Hg^2+, gas-phase Hg^0, and aerosol-phase Hg^0. With the new emissions inventory, declining atmospheric concentrations can be explained by the phase-out of Hg from commercial products and by shifts in the speciation of Hg emissions driven by air pollution control technologies.

Figure 5: Global annual Hg budget. Hg^2+ lifetime against oxidation + deposition: Model: 7 months. Observational constraints: 5 – 12 months

Due to additional and more abundant 2nd step oxidants, Hg^2+ reduction is needed to comply with constraint on Hg^2+ lifetime from observations, even within uncertainty in oxidation reaction rates (+/- 50%).

Figure 6. Hg wet deposition. Percent change is after including improved Hg redox mechanism and emission inventory. Changes in wet deposition are due to a combination of:
- changes in Br distribution (Schmidt et al. 2015) – less deposition over the Southern Ocean
- additional second step oxidants like HO_2 that have greater abundance in the tropics – increased deposition to the tropics
- changes in Hg reduction – distributions of Hg^2+ are related to spatial pattern of OA. Now, differences between Br – initiated oxidation and OH/O_3 oxidation are slightly muted with respect to Hg^2+ wet deposition.

Figure 7. Average 2009-2011 model emissions. Hg emissions are related to spatial pattern of OA.

Most Hg oxidation occurs in the upper troposphere (Fig. 4) due to the distribution of oxidants. Lower altitude oxidation is primarily due to the presence of HO_2 and NO_3. Br – initiated oxidation also dominates in the stratosphere, consistent with aircraft observations in the UTLS (not shown).