

# Global lifetime of anthropogenic and background mercury against oxidation by atomic bromine in the free troposphere

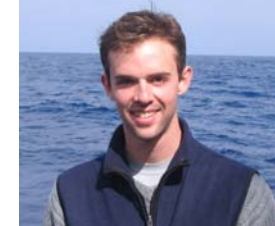
Christopher D. Holmes (*holmes2@fas.harvard.edu*)

Xin Yang

Daniel J. Jacob, Noelle E. Selin

Department of Earth & Planetary Sciences  
Harvard University

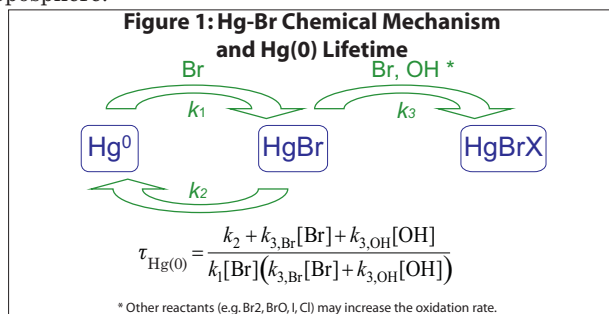
Centre for Atmospheric Science  
University of Cambridge



C. Holmes

## Background

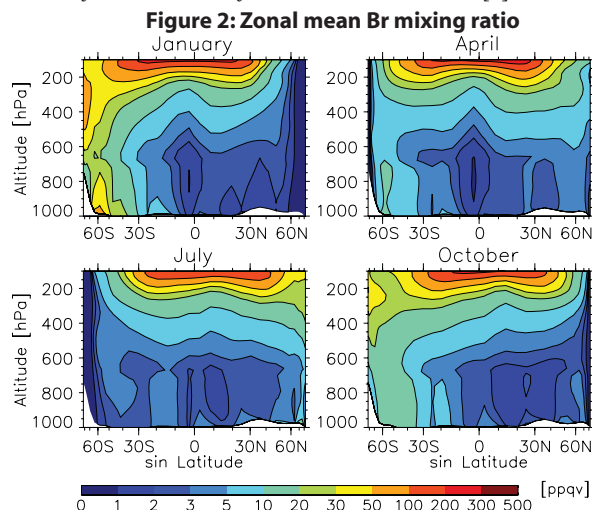
Current global models identify hydroxyl (OH) as the main global oxidant of Hg(0) [3], but this is questionable in light of the rapid expected decomposition of HgOH [4]. The main sink for Hg(0) is photochemical and therefore not ozone [3]. We examine whether atomic Br, a major oxidant of Hg(0) in the marine boundary layer, is the “missing oxidant” in the free troposphere.



The Hg-Br reaction mechanism is a two-step recombination of Hg(0) with Br, in competition with thermal dissociation of the reactive intermediate HgBr (figure 1) [2].

## 1. Atomic Br in the Troposphere

Figure 2 shows modelled atomic Br mixing ratios, derived from inorganic bromine released by sea salt aerosol photochemistry and the decay of brominated VOCs [5].



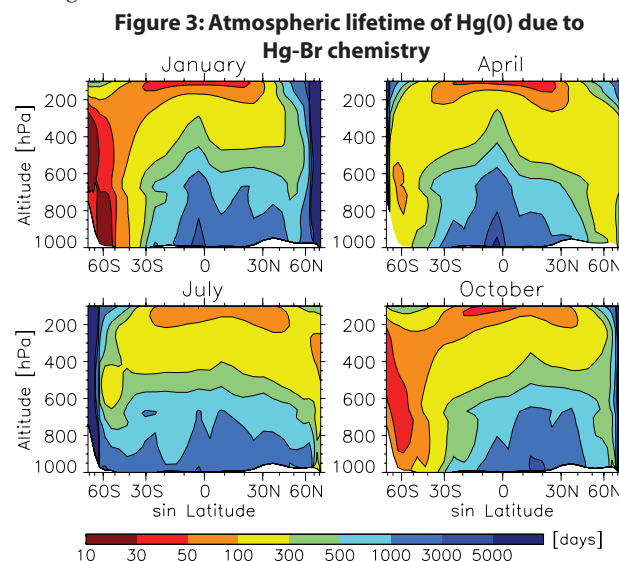
The model provides a conservative estimate of bromine abundance, as compared to satellite BrO columns.

## Summary

We calculate the global atmospheric lifetime of elemental mercury (Hg(0)) against oxidation by atomic bromine (Br) in the troposphere by combining recent kinetic data for the Hg-Br system with estimated global distributions of tropospheric Br [1]. Most of the oxidation takes place in the middle and upper troposphere. We obtain a Hg(0) lifetime of 0.5-1.5 years, implying that oxidation by Br is a major, and possibly dominant, global pathway for Hg(0) oxidation and eventual deposition of atmospheric mercury.

## 2. Tropospheric Hg(0) Lifetime

Figure 3 shows  $\tau_{\text{Hg}(0)}$  calculated with ab initio rate constants [2], and global distributions of Br (figure 2), OH, and temperature. Most oxidation takes place in the middle and upper troposphere, where Br concentrations are high and where cold temperatures suppress thermal decomposition of the Hg-Br intermediate.

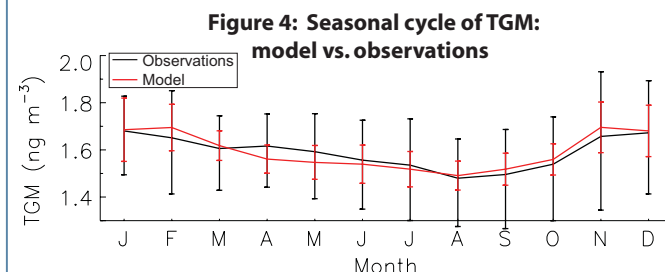


• The Hg-Br mechanism gives a mass-weighted, global-mean tropospheric  $\tau_{\text{Hg}(0)}$  of 200 days. Other published rate constants [6,7] imply a range of 160-510 days.

This work was supported by the Atmospheric Chemistry Program of the U.S. NSF; and by the STAR Graduate Fellowship Program of the U.S. EPA. EPA has not officially endorsed this publication.

## 3. Observational Comparison

• Figure 4 shows that the Hg-Br mechanism reproduces the seasonal cycle of TGM at an ensemble of 12 northern mid-latitude sites in a global chemistry and transport model (CTM). Results from the GEOS-Chem CTM [3], using laboratory rate constants [6].



• Rapid summertime oxidation of Hg(0) ( $\tau = 10\text{-}50$  days) at all altitudes in Antarctic summer (figure 3) is consistent with observations of high gaseous Hg(II) during November-January [8,9].

## 4. Implications

- Oxidation of Hg(0) by Br is potentially faster than by ozone ( $\tau_{\text{Hg}(0)+\text{O}_3} > 320$  days).
- The Hg-Br mechanism reconciles observational evidence that Hg(0) oxidation is photochemically mediated with the evidence against a major role for oxidation by OH.
- Atmospheric Hg models should include Hg-Br chemistry.
- Better measurements of Br in the free troposphere are needed to test this mechanism.

## References

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