Reactive Gaseous Mercury (RGM) Measurements using KCl-Coated Denuders

Tony Hynes and James Remeika
Two Forms of Gas-Phase Hg in Atmosphere

• Gaseous Elemental Mercury (GEM)
  – Not very soluble
  – Long lifetime in atmosphere

• Reactive Gaseous Mercury (RGM)
  – All Hg(II) species
  – Water Soluble
  – “Sticky”: enhanced dry deposition

→ While [RGM] << [GEM], RGM could significantly influence Hg uptake in ecosystems.
How is GEM oxidized?

• Very challenging problem; we can’t yet speciate RGM in the atmosphere!

• **Traditional Process:** Hg oxidized by OH, O$_3$
  – Used in most current models
  – Product is HgO
  – Challenged by recent thermodynamic calculations

• **Alternative Process:** Hg oxidized by Bromine atoms
  – Consistent with recent field experiments
Field Observations

• Mercury Depletion Events
  – Observed in Arctic, Antarctic, Dead Sea (Schroeder, Linberg, Brooks, Peleg)
  – Strong correlation observed between Hg, O$_3$ depletion
  – Halogen chemistry implicated

• Previous High Altitude Measurements
  – Elevated RGM observed in upper troposphere.
    • Aircraft Measurements (Landis, Hynes)
    • High altitude ground sites (Schwartzendruber, Landis)
If Br is important on global scale look for RGM in the upper troposphere.

\[ \text{Hg} + \text{Br} + \text{M} \leftrightarrow \text{HgBr} + \text{M} \]
\[ \text{HgBr} + \text{Br} \rightarrow \text{HgBr}_2 \]

- Br : BrO ratio most favorable
- Recombination reaction faster at lower temp but slower at lower P so not much gain
- Lifetime of HgBr is much longer at lower T
Experimental Setup
Collection System (In-Plane)

- Teflon inlet @ 50°C
- Teflon manifold
- Manual valve
- KCl-coated annular denuder
- Mass Flow Controller (10 LPM)
- Pump
Analysis System

- Argon Supply
- Tube Furnace @ 500°C
- KCl coated annular denuder
- Tekran 2537B
Flight #1: 6 May 2010

Elapsed Time (seconds)
Altitude (ft)
Flight #1: 6 May 2010
0.00 0.01 0.02 0.03 0.04
[RGM] (Arbitrary Units)
Calibration / QA

• Daily Calibrations of Tekran GEM analyzer
  – Internal and External sources
• Installation and flight blanks of denuders
  – Daily installation blanks
  – ?? Flight blanks
Challenges / Open Qs

- Clean working area on ground
- Shared inlet protocol