Investigating the Kinetics of Mercury Oxidation and the Contribution of Halogen Radicals from Field Measurements in Barrow, Alaska

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Atmospheric Mercury in the Arctic

Gaseous elemental mercury (GEM) is emitted into the atmosphere from both natural and anthropogenic sources. In mid-latitudes, GEM is believed to persist in the atmosphere for 6-24 months, with little spatial variability. The long residence of GEM allows it to be transported to the remote Polar Regions where it can undergo rapid oxidation and loss to the surface, which happens in concert with surface level ozone depletion events (ODEs). At Alert, Canada in 1995 it was observed that GEM undergoes rapid, episodic depletions (atmospheric mercury depletion events (AMDEs)) following Polar Sunrise. AMDEs have been observed to be limited to a chellone (e.g. 100-200m) layer near the surface in the very high Arctic (see Antarctica) boundary layer. Though evidence exists that halogens are the drivers of AMDEs, the nature of the dominant halogen oxidant has yet to be definitively proven. Correlations with ODEs and the knowledge that Br atoms are the main species involved in ODEs have led to the hypothesis that Br atoms (and/or BrO) are responsible. Some laboratory evidence indicates that Cl atoms could also be important. During March and April 2009, the Ocean-Atmosphere Sea Ice- Snowpack (OASIS) study occurred at Barrow, AK, at which measurements of GEM and a range of halogen radicals and radical precursors were made. Here we discuss how these data can be used to determine the relative importance of the various mercury oxidants.

Methods

To investigate the contribution of halogen radicals to the destruction of GEM, we compared the apparent first-order decay of GEM at Barrow with that calculated based on a steady state analysis, given the pressure and sink concentrations. Included in this analysis are calculated/measured concentrations of Br, Cl, BrO, ClO, OH, and O$_3$. GEM was measured during OASIS at Barrow, AK, using a Tekran 2537A Mercury Vapor Analyzer. Br, Cl$_2$, BrO, and HOBr measurements were conducted with a chemiluminescent mass spectrometer. CDI radicale was measured with a flowing chemical reaction method using a gas chromatograph with electron-capture detector. [Br] and [Cl] concentrations were calculated using the following steady-state approximations:

$$
\text{BrO} + \text{H} + \text{O}_3 \rightarrow \text{Br} + \text{HO}_2
$$

$$
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$$

$$
\text{Br} \rightarrow \text{Br}^+ + \text{e}^- \quad \text{rate} = k\text{[Br]}
$$

The resulting Br and Cl atom concentrations are plotted below for the period March 20 through 29, along with observed GEM and BrO concentrations.

Determination of Oxidant Contributions

Table 1: Sample Values for Calculations, Day 78

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Average Concentration (nmol/mol)</th>
<th>A Value (nmol/mol S)$^{-1}$</th>
<th>Time Elapsed (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>1.4e+9</td>
<td>8.9e-5</td>
<td>5.0 e+5</td>
</tr>
<tr>
<td>ClO$_3$</td>
<td>1.5e+9</td>
<td>2.0e-5</td>
<td>3.0 e+5</td>
</tr>
<tr>
<td>ClO$_2$</td>
<td>1.5e+9</td>
<td>2.0e-5</td>
<td>3.0 e+5</td>
</tr>
<tr>
<td>ClO</td>
<td>1.5e+9</td>
<td>2.0e-5</td>
<td>3.0 e+5</td>
</tr>
</tbody>
</table>

Figure 2: Cumulative contribution of known oxidants to GEM decay on Day 78 for apparent first-order rate constant.

Figure 3: First-order decay of GEM for Day 78 with apparent first-order rate constant.

Relative Rate Determination

The pseudo-first order rate approach assumes that the decay is a result of local-locale chemistry rather than transport. However, the effects of transport can be effectively removed using a relative rate approach. Figure 8 shows a relative rate analysis for March 20 (Day 75) and March 25 (Day 80) using ozone as a reference compound, since O$_3$ is believed to be mostly consumed by Br. The slope of the line represents the relative rate constant for O$_3$, or if they were both removed by Br atoms, the relative second-order rate constant. Using $k_{\text{ClO}_3}=8.9 \times 10^{-5}$ cm$^3$/molecule/s, we would yield $k_{\text{ClO}_3} \times 5.0 \times 10^{-5}$ for March 20, and $9.5 \times 10^{-5}$ for March 25 (in cm$^3$/molecule/s), somewhat smaller than the laboratory determined $k_{\text{ClO}_3} = 9.7 \times 10^{-5}$, though the uncertainty with this method is very large.

Discussion

In mid-latitudes, GEM exhibits a long atmospheric residence time due to its slow rate of removal by O$_3$ and OH. This is also reflected in this study, as these oxidants contribute very little to the observed decay of GEM for the four periods illustrated here. The results of this study show that the halogen radical BC$_2$ and BrO$_3$ contribute significantly to GEM consumption. However, the primary oxidant is not consistent across depletion events, and the relative importance of each varies depending on $k_{\text{ClO}_3}$. These results imply that in the polar regions, Reactive Gas Phase Mercury (RGM) may be composed of both Br$_2$ and BC$_2$ compounds. It is clear that the rate constants for reaction of Cl$_2$, Br$_2$, and BC$_2$ with O$_3$ must all be carefully measured, and that work on development of methods to speciate RGM should be a high priority. This work and the work of Liao et al. assist to an important role of chlorine atoms in the oxidation of BC$_2$ in ClO$_3$ and in ODEs. Thus the mechanism for production of BC$_2$ also needs to be determined.

References