The relative importance of chlorine and bromine radicals in the oxidation of atmospheric mercury at Barrow, Alaska

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[1] Mercury is a toxic environmental contaminant originating from both natural and anthropogenic sources. Gaseous elemental mercury (GEM) is relatively long lived in the midlatitudes and can be transported long distances in the atmosphere. In the Polar Regions, mercury can have a much shorter lifetime and is known to experience episodic depletions following polar sunrise in concert with ozone depletion events. A series of photochemically initiated reactions involving halogen radicals is believed to be the primary pathway responsible for converting elemental mercury to oxidized forms of reactive gaseous mercury (RGM) that are subsequently deposited to snow and ice surfaces. Using field measurements from the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) 2009 field campaign of GEM, RGM, ozone, and a large suite of both inorganic halogen and volatile organic compounds, we calculated steady state Br and Cl atom concentrations and investigated the contribution of Br, BrO, Cl, ClO, O₃, and OH to the observed decay of GEM for five cases of apparent first-order decay. The results of this study indicate that Br and BrO are the dominant oxidizers for Arctic mercury depletion events, with Br having the greatest overall contribution to GEM decay. Ozone is likely the primary factor controlling the relative contribution of Br and BrO, as BrO is a product of the reaction of Br with ozone, and reaction with O₃ can be the largest Br atom sink. Cl was not found to be significant in any of the studied events; however, this result is highly dependent on the rate constant, for which there is a large range in the literature. Modeled 48 h back trajectories of the mercury depletion events studied here indicate significant time spent over sea ice–covered regions, where the concentration of halogen radicals is likely higher than those estimated using local-scale chemical mole fractions.


1. Introduction

[2] Mercury is a naturally occurring heavy metal in the environment found globally in the air, oceans and soils.

Anthropogenic sources add to the atmospheric burden of gaseous mercury through industrial activities such as fossil fuel burning, gold mining, cement production and waste incineration [Pirrone et al., 2010; Steffen et al., 2008]. Unlike other heavy metals, elemental mercury is a liquid metal with a high vapor pressure at ambient temperatures, resulting in the atmosphere serving as a significant route for both transport and chemical transformation [Sommar et al., 2001].

[3] In the atmosphere, mercury exists primarily in its elemental state, Hg°. Gaseous elemental mercury (GEM) accounts for an estimated 95%–98% of airborne mercury, with oxidized forms, both gaseous and particulate, making up the rest [Lindberg et al., 2002; Steffen et al., 2008]. In midlatitudes, the residence time of GEM is estimated to be on the order of one year [Schroeder et al., 1998; Steffen et al., 2008], making it well distributed throughout the troposphere due to long-range transport, and effectively classifying it as a global pollutant. The northern hemispheric background of GEM is near 1.7–1.9 ng/m³, with somewhat lower background concentrations. GEM is not very reactive in the atmosphere and is important as a source of gaseous reactive mercury (RGM) that is subsequently deposited to snow and ice surfaces.

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values reported for the southern hemisphere and the poles [Nguyen et al., 2009; Slemr et al., 2003; Steffen et al., 2008]. The dry deposition and wet scavenging rates for RGM and particulate mercury species are about an order of magnitude higher than that of GEM [Lindberg et al., 2002], and thus they are expected to have a rather short lifetime in the atmosphere, in contrast to GEM, which can be transported far from sources and impact remote ecosystems such as the polar regions. Depending on its chemical form, mercury is also one of the most toxic elements found in nature [Ariya et al., 2002], and has been identified by the Arctic Monitoring and Assessment Programme (AMAP) as a “priority pollutant” in the Arctic of primary concern [AMAP, 2011].

[4] Current knowledge regarding the biogeochemical mercury cycle indicates numerous sources, but few known sinks. The global-scale chemical sinks for GEM have been determined to be higher than that of GEM [Simpson et al., 2007a], and from saline snowpacks [Foster et al., 2001]. The primary pathway for ozone destruction has been recognized to be reaction with bromine atoms resulting in the now well-known “bromine explosion.” In this mechanism, gas-phase Br reacts with O₃ to produce O₂ and BrO, followed by heterogeneous surface reactions that result in the autocatalytic release of additional reactive Br [Platt and Hönninger, 2003]. Consistent with this proposed mechanism, ground-based and satellite differential optical absorption spectroscopy (DOAS) measurements in the Arctic region have shown up to 41 ppt BrO during periods of active ozone depletions [Haasmann and Platt, 1994; Liao et al., 2011; Pöhler et al., 2010; Richter et al., 1998]. Surface DOAS measurements have corroborated this, with BrO generally observed to be negatively correlated with GEM in polar spring [Brooks et al., 2006; Ferrari et al., 2008]. Possible oxidation pathways for GEM thus include reactions (R1) and (R2).

(R1) \( \text{Br} + \text{Hg}^0 \rightarrow \text{products} \)

(R2) \( \text{BrO} + \text{Hg}^0 \rightarrow \text{products} \).

Field measurements have been unable to differentiate between Br and BrO as oxidants of GEM, however, because direct measurements of Br have not been achieved.

[7] The presence of aggressive chlorine atom chemistry in the Arctic has been well recognized [Ariya et al., 1998; Boudries and Bottenheim, 2000; Jobson et al., 1994; Keil and Shepson, 2006; Muthuramu et al., 1994; Ramacher et al., 1999; Rudolph et al., 1999]. Chlorine atoms can efficiently oxidize a wide range of volatile organic compounds. In the Arctic regions where water vapor and thus, the hydroxyl radical, are in low concentrations, chlorine atoms can serve as the primary sink for many of these species. Direct measurements of inorganic chlorine species other than chloride [Pszeny et al., 1993] are scarce, primarily due to a lack of suitable analytical techniques. Impey et al. [1997b] measured photolyzable chlorine (Cl₂ and HOCl) at Alert, Canada at concentrations up to 100 ppt. The ClO molecule (a product of chlorine atom reaction with ozone) has also been measured, though with high uncertainty, at levels between 3 and 20 ppt at Ny-Ålesund, Spitsbergen [Perner et al., 1999; Tuckermann et al., 1997]. Similar to the bromine radicals, Cl and ClO could serve as oxidizers of GEM [Ariya et al., 2002; Skov et al., 2004] as shown in reactions (R3) and (R4).

(R3) \( \text{Cl} + \text{Hg}^0 \rightarrow \text{products} \)

(R4) \( \text{ClO} + \text{Hg}^0 \rightarrow \text{products} \).

The potential contribution of chlorine radicals to the springtime depletion of mercury has not been elucidated due to the absence of chlorine radical measurements in the Arctic.

[8] Numerous laboratory investigations have been aimed at studying the kinetics of GEM oxidation with several oxygenated and halogenated species, and the results of these works are summarized in Table 1. The relatively slow rate of the gas-phase reaction of GEM with ozone [Hall, 1995; Pal and Ariya, 2004a; Spicer et al., 2002] indicates an
Table 1. Reported Second-Order Rate Constants From Previous Work for the Reactions of Hg° With Several Oxygenated and Halogenated Oxidants

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>( k ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_3)</td>
<td>(3 \times 10^{-20})</td>
<td>Hall [1995]</td>
</tr>
<tr>
<td></td>
<td>(9 \times 10^{-19})</td>
<td>Spencer et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>(7.5 \times 10^{-19})</td>
<td>Pal and Ariya [2004b]</td>
</tr>
<tr>
<td>OH</td>
<td>(8.7 \times 10^{-14})</td>
<td>Sommar et al. [2001]</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>(9.0 \times 10^{-14})</td>
<td>Ariya et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>(9.0 \times 10^{-14})</td>
<td>Pal and Ariya [2004a]</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>1.0 - 2.6 \times 10^{-18}</td>
<td>Ariya et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>(5 \times 10^{-17})</td>
<td>Spicer et al. [2002]</td>
</tr>
<tr>
<td>Br</td>
<td>3.2 (\pm 0.3) \times 10^{-12}</td>
<td>Ariya et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>9.7 \times 10^{-13}</td>
<td>Spicer et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>6.1 (\pm 2.2) \times 10^{-13}</td>
<td>Donohoue et al. [2006]</td>
</tr>
<tr>
<td>Cl</td>
<td>1.5 - 5.0 \times 10^{-11}</td>
<td>Horne et al. [1968]</td>
</tr>
<tr>
<td></td>
<td>1.0 (\pm 0.2) \times 10^{-11}</td>
<td>Ariya et al. [2002]</td>
</tr>
<tr>
<td></td>
<td>6.4 \times 10^{-11}</td>
<td>Spicer et al. [2002]</td>
</tr>
<tr>
<td>BrO</td>
<td>1.0 (\pm 0.7) \times 10^{-12}</td>
<td>Donohoue et al. [2005]</td>
</tr>
<tr>
<td></td>
<td>3.0 \times 10^{-14}</td>
<td>Spicer et al. [2002]</td>
</tr>
<tr>
<td>ClO</td>
<td>1.0 \times 10^{-13} - 1.0 \times 10^{-15}</td>
<td>Raofie and Ariya [2003]</td>
</tr>
<tr>
<td></td>
<td>3.6 \times 10^{-15}</td>
<td>Spicer et al. [2002]</td>
</tr>
</tbody>
</table>

*Experiments by Donohoue et al. [2005, 2006] performed in N\(_2\) bath gas; second-order rate constant calculated for 248 K from reported Arrhenius expression. Experiment by Horne et al. [1968] performed in Ar and CF\(_2\)Cl bath gas. Experiment by Ariya et al. [2002] performed in N\(_2\) bath gas.

atmospheric lifetime of GEM of between 20 days to over a year at 30 ppb ozone. Experimental evidence suggests, however, that heterogeneous reactions enhanced by surfaces or aerosols is the most probable mechanism for Hg\(^{0}\) oxidation by O\(_3\) rather than gas-phase reaction [Subir et al., 2011]. Indeed, product studies determined that solid mercuric oxide, HgO(\(_s\)), is the dominant product and HgO(\(_g\)) was not observed [Pal and Ariya, 2004a]. Reported rate coefficient values for the reaction of GEM with OH [Pal and Ariya, 2004b; Sommar et al., 2001] indicate an average GEM lifetime at global mean OH concentrations (~\(1 \times 10^{6}\) molecules/cm\(^3\) [Montzka et al., 2000]) of 4–7 months. Moreover, the lifetime of GEM against oxidation by H\(_2\)O\(_2\) is on the order of 1.5–3.7 years [Tokos et al., 1998], making this pathway considerably less important. It should be noted that these lifetime estimates are based only on the oxidation reactions to Hg\(^{0}\), and do not take into account reduction back to GEM. These studies indicate that consumption by the prominent atmospheric oxidants is unable to produce the fast destruction of GEM observed during AMDEs in the Arctic regions.

[5] Oxidation of elemental mercury by halogenated radicals is a likely possibility given the close correlation of AMDEs and ODEs and the observed photochemical behavior of RGM production. Ariya et al. [2002] used a relative rate approach to determine the rate constant for reaction of Cl\(_2\) atoms with GEM, and reported a value for \(k_3\) of \(1.0 (\pm 0.2) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), close to the 1.5 \times 10^{-11} derived by Horne et al. [1968]. The same authors determined the rate constant for GEM + Br (\(k_4\)) to be 3.2 (\pm 0.3) \times 10^{-12} cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). More recently, Donohoue et al. [2006] measured an effective second-order rate constant for \(k_1\) of 6.1 (\pm 2.2) \times 10^{-13} cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (calculated for 248 K) by an absolute method using pulsed laser induced fluorescence. The effective second-order rate constant for GEM + Cl was determined to be 1.0 (\pm 0.7) \times 10^{-12} cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) in N\(_2\) bath gas [Donohoue et al., 2005] by the same method. In the case of Cl atom reaction, the authors indicated an apparent rate coefficient 4 times faster when performed in air, presumably due to enhancement from reaction with radicals such as ClO and ClO\(_2\). This observation, as well as the inconsistent results obtained by Ariya et al. [2002] using different reference compounds, and their observations of the impacts of the presence of air, casts doubt on the use of the relative rate method for this particular reaction. Raofie and Ariya [2003] estimated a range for \(k_2\) (GEM + BrO) between \(1.0 \times 10^{-13}\) and \(1.0 \times 10^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Spicer et al. [2002] reported a value for \(k_2\) of 3.0 \times 10^{-14}. The only known study of reaction (R4) resulted in a rate constant of \(k_4 = 3.6 \times 10^{-17}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), significantly slower than for the other halogen radicals [Spicer et al., 2002]. The slow reaction kinetics observed in reactions of GEM with the molecular halogens, Cl\(_2\) and Br\(_2\), make these species unlikely sinks for GEM in the atmosphere [Ariya et al., 2002; Spicer et al., 2002].

[10] A number of theoretical studies have been performed to investigate the thermodynamics and energetics of gas phase Hg\(^{0}\) oxidation. The HgO molecule is predicted to be unstable, making O\(_3\) oxidation of Hg\(^{0}\) through O-atom transfer unfavorable [Castro et al., 2009; Tossell, 2003], and it is very unlikely that oxidation of Hg\(^{0}\) by O\(_3\) proceeds via homogeneous gas-phase reaction [Subir et al., 2011; Hynes et al., 2009]. Similarly, the reaction of GEM with BrO is predicted to be exergonic if it proceeds via O-atom transfer. Khalizov et al. [2003] drew a similar conclusion, stating that it is unlikely to form HgO directly from BrO oxidation. An ab initio study by Balabanov and Peterson [2003] found that while the O-atom transfer reaction (i.e., HgO\(^+\) + BrO → HgO + Br) is exothermic, the insertion reaction is endothermic (i.e., Hg\(^+\) + BrO → HgO(\(_g\))). The addition of a Br atom [Tossell, 2003] or Cl atom [Maron et al., 2008] to Hg\(^{0}\) is predicted to be exergonic, with the addition of a second halogen atom even more favorable than the first, at a rate constant close to the high-pressure limit [Goodsite et al., 2004]. HgBr\(_2\) and HgCl\(_2\) are more stable thermally than HgBr and HgCl, and thus are more likely candidates for RGM. Product studies by Ariya et al. [2002] confirm that HgCl\(_2\) and HgBr\(_2\) are the dominant products from reaction of mercury with the respective halogen atoms.

[11] Although the Cl-atom initiated reaction rate constant is larger than for Br or BrO reaction with GEM, many studies have concluded that Br is the most probable driver of Arctic AMDEs [Ariya et al., 2002, 2004; Brooks et al., 2006; Calvert and Lindberg, 2003, 2004; Goodsite et al., 2004; Skov et al., 2004], due to the larger estimated Br atom atmospheric abundances [Jobson et al., 1994; Keil and Shepson, 2006]. As there is currently no analytical technique able to measure Cl and Br atoms directly, several studies have calculated time-integrated concentrations based on rates of hydrocarbon decays [Ariya et al., 1998; Boudries and Bottenheim, 2000; Jobson et al., 1994; Ramacher et al., 1999; Rudolph et al., 1999] and an estimated reaction time of 1–20 days. The average bromine-atom-concentration derived from this method is approximately \(1 \times 10^4\) molecules/cm\(^3\), while the average chlorine-atom-concentration is about \(1 \times 10^3\) molecules/cm\(^3\). Therefore, using this method, [Br]/[Cl] ≈ 10\(^3\). However, time-integrated estimates calculate [Br] and [Cl] averaged over the lifetime of the VOCs, and do not
reflect fluctuations in [Br] and [Cl], or the near-surface concentrations. The [Br]/[Cl] ratio can thus increase or decrease in response to changing chemical or meteorological conditions. Keil and Shepson [2006] found that [Br]/[Cl] ranges from 80 to 990 during partial ODEs, thus on the low end of this ratio (i.e., when [Cl] is relatively high or [Br] is relatively low), Cl atoms might be able to compete in GEM depletion. It has also recently been shown that Cl2 can be produced by unknown chemistry involving O3 (J. Liao et al., Unexpected high levels of molecular chlorine detected in the Arctic and its impact on tropospheric ozone depletion, manuscript in preparation, 2012). Since O3 is the main sink for Br atoms, when O3 is high, Cl atom chemistry can be important, and when O3 is depleted, Br atom chemistry becomes relatively more important.

[12] In this study, we aim to investigate the quantitative contribution of the halogen radicals Br, BrO, Cl, and ClO to the depletion of GEM in the Arctic using data from the OASIS 2009 field campaign in Barrow, Alaska. During OASIS 2009, in situ measurements of GEM, RGM, particulate Hg (PHg), O3, OH, and numerous VOCs and inorganic halogen species, including Cl2, Br2, BrO and ClO were conducted. These data were used to calculate time-varying estimates of Br and Cl atom concentrations using a steady state approximation. We report here the relative contribution of possible gas-phase oxidation pathways for AMDEs observed during the OASIS campaign at Barrow, Alaska.

2. Experimental Setup

[13] Data used in the study were collected during the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS; www.oasishome.net) 2009 field campaign that took place from February to April of 2009 in Barrow, Alaska. Measurements of all species, with the exception of ClO, were conducted from portable trailers near the Barrow Arctic Research Center (BARC) building (71°19′0.02″N, 156°30′16″W), located 0.6 km southeast of the Chukchi Sea and 4 km northeast of the town of Barrow. CIO measurements were conducted at the KBRW radio tower (71°15′15″N, 156°30′27″W) located 10 km southeast of the Chukchi Sea. Instrumental methods for all measurements are described in detail elsewhere [Liao et al., 2011; Mauldin et al., 1999; Ridley et al., 1992; Schroeder and Munthe, 1998; Shetter and Müller, 1999]. For those species on which this analysis most heavily relies, a brief overview is included here.

[14] Three lines on a tower, with sample heights of 0.6, 1.8, and 5.4 m, were used to sample O3, with dwell times of 10 min at each of the 3 heights. O3 was measured using the chemiluminescence technique with a 1 s detection limit of 0.02 parts per billion by volume (ppbv), as described by Ridley et al. [1992]. Data were acquired at a 1 Hz sample rate.

[15] Gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle associated mercury (PHg) were determined during the OASIS 2009 campaign using automated Tekran 2537A, Tekran 1130, and Tekran 1135 instruments, respectively. GEM was measured using a Tekran 2537A mercury vapor analyzer. This method has been summarized by Steffen et al. [2008]. The Tekran 1130 and 1135 systems are front end modules that connect to the Tekran 2537A to collect RGM and PHg, respectively, and convert oxidized mercury forms to elemental mercury by pyrolysis. Because calibration with authentic RGM and PHg standards is currently not possible at this time, these two species must be considered, at best, operationally defined atmospheric species as presented in this publication, and are only used as relative concentrations.

[16] BrO, Br2, BrCl, HOBBr, and Cl2 were detected by chemical ionization mass spectrometry (CIMS). The CIMS was actively calibrated in the field using permeation sources of Br2 and Cl2. The CIMS instrument used during the OASIS campaign and the calibration procedures for BrO, Br2, and Cl2 are described in detail by Liao et al. [2011]. BrCl levels were calculated assuming a relative sensitivity of the CIMS to Br2 and BrCl that is identical to that reported by Neuman et al. [2010]. HOBr levels were calculated relative to Br2 levels. The relative sensitivity of HOBBr to Br2 was measured in the laboratory after the campaign. Gas-phase HOBr was synthesized in the laboratory by liberating HOBBr formed in solution by the hydrolysis of Br2 as shown in reaction (R5).

(R5) \[ \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HOBBr} + \text{Br}^- + \text{H}^+ \]

[17] The hydrolysis reaction is performed by flowing humidified N2 and Br2 in N2 over glass beads coated with AgNO3 as described by Neuman et al. [2010]. The concentration of HOBBr was determined by conversion back to Br2 via reaction with solid sodium bromide and subsequent measurement of Br2. The uncertainty of the Br2, Cl2, and BrCl measurements is estimated to be ±25%. The uncertainty of the HOBBr and BrO measurements is estimated to be ±35%.

[18] In situ measurements of ClO were performed using a flowing chemical reaction method that draws ambient air through a flow tube and quantitatively converts the reactive radical species to a stable halogenated acetone product using a reactive alkene as a halogen atom trap, similar to the method described by Impey et al. [1997a]. 1,1,1-trifluoroacetonitrile, a compound that is not present in ambient air, was used to scavenge the halogen atoms. The product, 1-chloro-3,3,3-trifluoroacetonitrile, is then separated and detected using a gas chromatograph with electron capture detection. Calibrations were performed both prior to deployment and weekly in the field using solutions of 1-chloro-3,3,3-trifluoroacetonitrile in diethyl ether. Field blanks were performed weekly by turning off the flow of 1,1,1-trifluoroacetonitrile to the flow tube. The limit of detection, calculated as three times the standard deviation of the blank, was 0.65 pptv. The propagated uncertainty of the measurements is calculated to be ±15%, taking into account loss of the radical on the reaction walls, reaction time and product yield of the chemical reaction, loss of the reaction product on the sample line, error in the calibration, and variability of the blanks. However, there could be unknown systematic errors that would lead to a larger uncertainty. Given the small value for k4 and the low ambient ClO concentrations observed, the conclusions discussed below will not be significantly impacted if this were the case.

[19] The Trace Organic Gas Analyzer (TOGA) using fast online gas chromatography coupled with mass spectrometry (GC-MS) was used to measure up to 30 different volatile organic compounds (VOCs) during OASIS as described by Apel et al. [2010]. The VOCs observed by TOGA during OASIS include NMHC (C4 and C5 alkanes, isoprene, benzene,
toluene, the C₈-aromatic VOCs), oxygenated VOCs (OVOCs; acetaldehyde (CH₃CHO), methanol (CH₃OH), ethanol (C₂H₅OH), acetone (CH₃COCH₃), propanal (C₃H₆O), butanal (C₄H₈O), methyl ethyl ketone (MEK; C₂H₅COCH₃) methyl tert-butyl ether (MTBE; C(CH₃)₃OCH₃)), halogenated VOCs (chloromethane (CH₃Cl), bromomethane (CH₃Br), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), tetrachloromethane (CCl₄)), acetonitrile (CH₃CN) and dimethylsulfide (DMS; CH₃SCH₃).

In addition, whole air samples were collected in electropolished stainless steel canisters through the same manifold used by TOGA. The canisters were typically pressurized to 2000 hPa. Approximately three samples were collected each day. The sample integration period was approximately 40 s. After collection, the canisters were transported back to NCAR or the University of New Hampshire and analyzed for more than 50 trace gases. At NCAR a subset of the samples were analyzed for NMHCs, selected halocarbons, and selected OVOCs. At the University of New Hampshire all samples were analyzed for NMHCs, halocarbons, DMS, alkyl nitrates, and selected OVOCs [Russo et al., 2010]. The reported detection limits are 3 pptv for most NMHC and sub-pptv for halocarbons. The precision of the C₂–C₄ NMHC analysis was ±3% when compared to NIST standards during the Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE) [Apel et al., 1994, 1999].

3. Results

In Barrow, Alaska, ozone concentrations began to exhibit depletion events in early February following polar sunrise. As the season progressed, stronger depletions with nearly complete destruction of ozone occurred through late March and April, and ceased after the onset of melt [Knepp et al., 2010]. Similar to observations at other Arctic locations, atmospheric mercury also exhibited depletion events during this time period in concert with ODEs. Figure 1a shows a portion of the time series profile of ozone and GEM measurements during the OASIS campaign. This time series covers background and fully depleted conditions, as well as periods of apparent GEM evasion from the tundra snowpack.

3.1. Steady State Calculations of Cl and Br Atom Concentrations

While the aim of this study was to investigate the relative contribution of halogen radicals to the GEM depletions observed in Barrow, there is currently no suitable
analytical technique capable of directly determining chlorine or bromine atom concentrations in the ambient air. Therefore, we applied a steady state approximation (certainly valid for these very short-lived atoms) to calculate the concentrations of Cl and Br using the time-resolved data sets described above. [Cl] and [Br] were calculated using known source (numerator) and sink (denominator) terms according to equations (1) and (2).

\[
\]

(1)

\[
\]

(2)

[23] Here, “J” represents the specific photodissociation rate coefficient for the species photolyzing at the appropriate time of day. The k in each case represents the second-order rate constant for the reaction producing or destroying the halogen atom. The self-reaction of ClO is estimated here to only regenerate 1 Cl atom based on the work of Horowitz et al. [1994], who found a 0.61 branching ratio for this product. The minority product is Cl2 (0.39 branching ratio), however, Cl2 is explicitly accounted for in our calculation from its known source of Cl and Br using the time-resolved data sets described above. Therefore, this reaction is not considered for Cl atom production. It should be noted that HOCI photolysis is not included because this compound was not measured during the campaign. We assume that [HOCI] is small for the purposes of this approximation; however, if [HOCI] is significant, we are likely underestimating [Cl].

[24] Alternatively, and as a means to assess uncertainties in the atom concentration estimates, Cl and Br atom concentrations can be calculated assuming a steady state on ClO and BrO, respectively, via equations (3) and (4).

\[
[Cl]_{ss} = \frac{(J[ClO] + k[ClO][BrO] + k[ClO][OH] + k[ClO][HO2] + k[ClO][NO] + k[ClO][NO2] + 2k[ClO][ClO])}{k[O3]}
\]

(3)

\[
\]

(4)

[25] Comparisons of the results from the two methods for each halogen (denoted Brss versus BrOss and Clss versus ClOss, respectively) yielded reasonably good agreement; however, the BrOss and ClOss methods yielded consistently higher halogen atom concentrations. Figure 2 illustrates the ratio of [Br] as calculated via the BrOss method and the Brss method, versus ambient ozone concentration. The ratio [Br]BrO-ss/[Br]Br-ss averages 1.8 at ozone concentrations greater than 1 ppbv. Below 1 ppbv, this relationship degrades rapidly, possibly due to other, unknown mechanisms for BrO production (e.g., Br2 + O). This reasonable agreement in [Br] between two mostly independent methods of calculation lends confidence to the estimations used in this analysis (for [O3] > 1 ppbv).

[26] There is a significantly larger discrepancy in [Cl] between the two methods of calculation, on average by a factor of 5 (data not shown). Similar to the case for BrOss/Brss, at low ozone concentrations, the ClOss/Clss drastically increases. However, the ClO data are much more limited; for this campaign, there is significantly more Cl2 data than ClO data, and thus the Clss method is preferred for this analysis. Note also that equations (1) and (2) are mostly dependent on measurement of stable (closed shell) species, while equations (3) and (4) rely more on measurements of radical species. We therefore use equations (1) and (2) for the following analysis of the GEM sinks. Since equation (2) yields significantly lower results than for equation (4), our results for the Cl atom contribution may be underestimated.

[27] Calculations were performed using equations (1) and (2) such that [Br] and [Cl] concentrations were generated hourly for the time period of 18 March through 5 April. Unless otherwise noted, rate constants were taken from the preferred values in the IUPAC Subcommittee for Gas Kinetic Data Evaluation [Atkinson et al., 2004, and references therein], and are listed in Table 2. A temperature of 248 K was used to calculate all rate constants, which is consistent with average temperatures in Barrow during the month of March. Photolysis rate coefficients (J values) used here were calculated using a modified version of the Tropospheric Ultraviolet and Visible (TUV) radiation model [Madronich and Flocke, 1999] for the duration of the campaign based on in situ measurements of downwelling actinic flux. The charged-coupled device Actinic Flux Spectroradiometer (CAMS) [Shetter and Müller, 1999] measured spectrally resolved downwelling actinic flux at 0.1 Hz. The upwelling was estimated as a function of solar zenith angle using the
TUV model under clear sky conditions. The sum of upwelling and downwelling actinic flux was used to calculate total photolysis frequencies.

[25] Short discontinuities in the various data sets were replaced with estimates interpolated based on concentrations immediately prior to and following the gap. Data gaps longer than half a day were left as breaks. Propagation of errors associated with both measurement uncertainties and rate constants, given the individual component variances, result in an overall average uncertainty for the steady state approximations of +38% to −33% for [Br] and +46% to −32% for [Cl] using equations (1) and (2).

[26] The resulting bromine and chlorine atom concentrations for the period of 20–29 March are illustrated in Figure 1c, along with observed [BrO]. Surface downwelling irradiance is shown in Figure 1b as a reference to solar intensity to illustrate time of day. Br atom concentrations peaked at levels of $1.6 \times 10^9$ molecules/cm$^3$, while Cl atoms reached $4 \times 10^5$ molecules/cm$^3$. [Br] attained its highest levels when severe ozone depletion was observed (i.e., when the rate of Br + O$_3$ is small), most notably during the 3 day event that began on 26 March. Some peaks in RGM/PHg (Figure 1a) occurred during this period, which suggests possible reoxidation of GEM emitted from the surface snowpack, as peaks in RGM production are indicative of local chemistry [Steen et al., 2011]. The Br and Cl concentrations calculated here are relatively large compared to those determined from VOC decays, possibly because they are calculated from near-surface layer data, while VOCs integrate the signal over their transport path, which includes a component aloft where halogen atom concentrations will be lower [Tackett et al., 2007]. Interestingly, Br and Cl fluctuate independently of each other. Notably, the extended ODE of 26 March is characterized by relatively high [Br] and relatively low [Cl]. However, this switches with the return of ozone on 29 March to a condition of relatively higher chlorine activity. This may be due to the fact that Br will tend to vary inversely with O$_3$, which is often its dominant sink, while it appears that O$_3$ is required for Cl$_2$ production (Liao et al., manuscript in preparation, 2012). That chlorine and bromine do not vary together is an observation that has also been noted in studies by Impey et al. [1997b] and Shepson et al. [1996], and is discussed by Liao et al. (manuscript in preparation, 2012) in reference to the OASIS field study.

3.2. Contribution of Atmospheric Oxidants to GEM Depletion

[30] To evaluate the contribution of the halogen radicals, O$_3$, and OH to the oxidation of GEM, the relative rates of GEM depletion by each oxidant were calculated during periods when GEM exhibited an apparent first-order decay, potentially indicative of significant local chemistry, the rate of which can be compared with the calculated rate. While it is quite possible that any observed decay event results from transport of previously depleted air from upwind, it is useful to be able to compare the observed rate and the calculated potential oxidative chemical depletion rate, given the locally measured oxidant concentrations and rate constants. Five such events in late March were chosen for this analysis: 20, 22, 23, 24 and 25 March. The peak in GEM on 24 March was likely a result of reemission from the snowpack, therefore, we use only the data when GEM was below background values. Meteorological data indicate wind speeds less than

![Figure 2. The ratio of [Br] calculated via equations (4) (BrO steady state method) and (2) (Br steady state method) versus ozone concentration. A 1:1 line for the bromine atom ratio is included.](image_url)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$ at 248 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$ + OH</td>
<td>$2.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>Cl + HO$_2$</td>
<td>$4.2 \times 10^{-11}$</td>
</tr>
<tr>
<td>Cl + O$_3$</td>
<td>$1.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>Cl + C$_2$H$_6$</td>
<td>$2.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>Cl + C$_2$H$_4$</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>Cl + C$_2$H$_2$</td>
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<tr>
<td>Cl + C$_3$H$_8$</td>
<td>$2.7 \times 10^{-10}$</td>
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<td>$1.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>Cl + C$_3$H$_10$</td>
<td>$1.3 \times 10^{-10b}$</td>
</tr>
<tr>
<td>Cl + nC$<em>4$H$</em>{10}$</td>
<td>$2.2 \times 10^{-10c}$</td>
</tr>
<tr>
<td>Cl + HCHO</td>
<td>$7.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Cl + CH$_3$CHO</td>
<td>$8.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>ClO + OH</td>
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</tr>
<tr>
<td>ClO + NO</td>
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</tr>
<tr>
<td>ClO + ClO</td>
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</tr>
<tr>
<td>ClO + BrO</td>
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</tr>
<tr>
<td>ClO + HO$_2$</td>
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</tr>
<tr>
<td>ClO + NO$_2$</td>
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</tr>
<tr>
<td>Br$_2$ + OH</td>
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</tr>
<tr>
<td>Br + HO$_2$</td>
<td>$1.3 \times 10^{-12}$</td>
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<tr>
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<td>$6.8 \times 10^{-13}$</td>
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<tr>
<td>Br + NO$_2$</td>
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</tr>
<tr>
<td>Br + HCHO</td>
<td>$7.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>Br + CH$_3$CHO</td>
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<tr>
<td>Br + C$_2$H$_6$</td>
<td>$3.7 \times 10^{-14}$</td>
</tr>
<tr>
<td>Br + C$_2$H$_4$</td>
<td>$1.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>Br + C$_2$H$_2$</td>
<td>$1.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>BrO + NO</td>
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</tr>
<tr>
<td>BrO + ClO</td>
<td>$1.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>BrO + BrO</td>
<td>$2.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>BrO + HO$_2$</td>
<td>$4.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>BrO + NO$_2$</td>
<td>$1.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>BrO + HO$_2$</td>
<td>$3.4 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

*All rate constants are derived from recommended values in the IUPAC Subcommittee for Gas Kinetic Data Evaluation [Atkinson et al., 2004] and calculated for 248 K unless otherwise specified.

*From Huang and Niki [1995] at 298 K.

*From Tyndall et al. [1997] at 298 K.
5 m/s or calm conditions for all five events (NOAA National Weather Service), increasing the likelihood that the event scale is local. Measurements of RGM and PHg for these periods (shown as the blue trace in Figure 1a) reveal a predominance of RGM over PHg, also consistent with the assumption of local chemistry. A greater relative concentration of PHg is expected in AMDEs of nonlocal origin [Cobbett et al., 2007; Lindberg et al., 2002; Steen et al., 2011], because of its longer lifetime. An example of the depletion for 20 March is shown in Figure 3a, which also shows some of the important observed or calculated halogen radical concentrations.

[31] Each depletion event was plotted as ln([GEM]) versus the time elapsed (in seconds) from the start of the observed depletion. If we assume first-order conditions (i.e., the oxidant concentrations are constant), then the negative of the slope of the linear regression is taken as the apparent first-order decay rate constant, \( k_{app} \). This \( k_{app} \) can then be compared to \( k_{calc} \), which is \( k_{calc} = k_{GEM+oxidant \_1[oxidant \_1]} + k_{GEM+oxidant \_2[oxidant \_2]} + \ldots \). The apparent first-order decay for the example case of 20 March is illustrated in Figure 3b.

[32] To determine the potential contribution of each known oxidant to Hg° decay during a depletion event, the calculated first-order decay rate constant, \( k_{calc} \), was determined as shown in equation (5) using the average oxidant concentration for the event, where each \( k \) represents the rate constant for the appropriate reaction of that oxidant with GEM.

\[
k_{calc} = k[Br] + k[Cl] + k[BrO] + k[ClO] + k[OH] + k[O_2]. \tag{5}
\]

[33] The rate constant for gas-phase Hg° reaction with Br, \( 6.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), was calculated for 248 K from Donohoue et al. [2006] using the reported Arrhenius expression. The Hg° + Cl rate constant, \( 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), was calculated from Donohoue et al. [2005]. While there is a large range in the reported rate constants between studies for the chlorine atom reaction (see Table 1 for a summary), we have chosen to use the Donohoue et al. values because this work was an absolute rate study performed in \( \text{N}_2 \) that demonstrated consistent results when performed with either Cl or Hg° in excess. Moreover, observational evidence suggests that \( \text{O}_2 \) may enhance the apparent rate constant through side reactions (perhaps \( \text{ClO}_2 + \text{Hg}^o \) [Donohoue et al., 2005; Hynes et al., 2009]), thus, relative rate studies performed in air may not be appropriate for this particular reaction. The rate constant for \( \text{O}_3 \), \( 7.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), was taken from Pal and Ariya [2004b], and those for BrO and ClO were from Spicer et al. [2002]. The rate constant for Hg° reaction with \( \text{OH} \), \( 8.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), was taken from Sommar et al. [2001]. We note that the rate constants for \( \text{OH} \) and \( \text{O}_3 \) should be taken as upper limits, given the computational results for HgO thermochemistry, discussed by Hynes et al. [2009]. The rate constants and their reported uncertainties are shown in Table 3. With the exception of Br and Cl, all rate constants used here were measured at room temperature. Atomic recombination reactions exhibit only very weak negative or no temperature dependence [Ariya et al., 2002; Goodsite et al., 2004], therefore, the rate constants used here are assumed to be valid in the low temperatures of the Arctic troposphere. The average concentrations for each oxidant for the period of decay for 20 March are also shown in Table 3, along with the resultant individual \( k_{oxidant} \).

[34] The \( k_{calc} \) obtained from equation (5) results in the total GEM depletion rate constant that can be accounted for by known gas-phase chemical transformation pathways. The individual and cumulative contributions for the oxidants are shown in Figure 4, plotted as the apparent first-order decay rate constant versus the calculated first-order rate for oxidation by Br, Br + BrO, Br + BrO + Cl, Br + BrO + Cl + ClO, and all oxidants combined (i.e., including \( \text{O}_3 \) and \( \text{OH} \)). Both axes are shown on logarithmic scales. A 1:1 line is included for comparison. These values are also listed in Table 4.

[35] For two of the cases considered here (22 and 25 March), the observed decay rate is not inconsistent with local-scale chemical loss via reaction with bromine atoms.
alone. However, in the remaining three cases, the calculated chemical loss rate is significantly less than the observed rate. This may be the case due to transport of an already-depleted air mass to the measurement site. That seems likely for a case such as 24 March, when $k_{\text{app}}$ is ~9 times greater than $k_{\text{calculated}}$. Interestingly, in four cases, BrO contributes a significant amount to the GEM decay. In no case studied here does Cl or ClO have a significant contribution to GEM depletion. This observation is especially interesting given the exceptionally high Cl$_2$ mole fractions observed in Barrow during this campaign, with some days reaching over 400 pptv, and Cl atom concentrations as high as 4 x 10$^9$ molecules/cm$^3$. It should be noted, however, that the Hg$^0$ + Cl rate constant used here is on the low end of all reported values, and it is possible that Cl could have a significant contribution if the rate constant were larger. For example, for 20 March, if the Cl atom rate constant were 1.0 x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [Ariya et al., 2002], it would contribute 8.1% of the total $k_{\text{app}}$.

[36] Heterogeneous reactions are not considered here, but it is not expected that such reactions contribute significantly to GEM depletion. Elemental mercury is only sparingly soluble in water [Shia et al., 1999] and aqueous phase reactions of Hg$^0$ with bromide and chloride are far too slow in comparison with gas-phase oxidation to be significant sinks [Lin and Pehkonen, 1998; Wang and Pehkonen, 2004]. Moreover, the low Henry’s Law equilibrium constant for Hg$^0$, 0.13 M/atm, results in a very small fraction of Hg$^0$ present in the aqueous phase. However, experimental evidence demonstrates that surface interactions can enhance reaction rate constants over that of pure gas phase, most notably for reactions of OH and O$_3$, wherein surfaces can stabilize the reaction intermediates. This would imply that GEM oxidation in the real atmosphere may occur more rapidly than suggested by gas-phase laboratory experiments [Subir et al., 2011]. Hedgcock et al. [2005] included heterogeneous chemistry on both maritime and continental cloud droplets in a modeling study, and found that aqueous phase oxidation could account for 2–30% of GEM oxidation. Due to the low OH mole fractions in the Arctic, and the much lower abundance of cloud droplets as compared to the mid-latitude MBL, it is likely that the aqueous phase does not contribute highly to oxidation in the Arctic.

[37] Since mixing and dilution of air masses should decrease the apparent rate of decay, any statistically significant differences between the observed and calculated rates of depletion can only arise from two possibilities: (1) depletion occurred upstream, followed by transport of the depleted air to the measurement site, and/or (2) we are missing a GEM sink. Although it is clear that some local chemistry was occurring for these events, given the radical concentrations, the first explanation seems more likely, in part because we have considered most known atmospheric oxidants. A faster apparent time scale can thus occur if the depleted region is well defined at the edges, and that air mass transits the measurement site. We note that the radical concentrations that apply to the upwind depletion of Hg$^0$ may be significantly different from those calculated for the measurement site at Barrow. This relates to the distinctly different time scales for the lifetime of the radical precursors (e.g., Br$_2$ and Cl$_2$) and the time scale for mercury depletion. On average, the latter is 5 h as measured at Barrow. For a 5 m/s wind speed, this corresponds to a transport distance of 90 km. Since all of the back trajectories shown in Figure 5 extend out over the sea ice, it is quite possible that due to the higher surface salinity on sea ice, the actual atmospheric surface layer halogen concentrations where some of the depletion is occurring are higher than operative at Barrow, and thus we underestimate the absolute atom concentrations. This is supported by the fact that periods of exceptionally high Cl$_2$ have similar back trajectories over the sea ice [Draxler and Rolph, 2012; Rolph, 2012], similar to that shown as an example in Figure 5.

[38] From the local-scale oxidant concentration measurements, we can determine the fractional contribution of each oxidant species to GEM decay. A 1:1 line is included for comparison.
oxidant to the total calculated decay. The results are shown in Figure 6, in the form of bar graphs constructed from the individual $k_{\text{oxidant}}$ values for Br, Cl, BrO, ClO, O3 and OH, relative to $k_{\text{calc}}$. The uncertainties in the fractional contributions are shown as error bars representing the possible range of percent contribution for each oxidant. The uncertainties reported here are based on the reported uncertainties in the rate coefficients used and propagated uncertainties in the steady state Br and Cl atom concentrations. Therefore, it is likely that these values underestimate the true uncertainties since they do not include uncertainties resulting from discrepancies in the [Br] and [Cl] estimation methods and given the range of reported rate constants in the literature (Table 1).

Figure 6 shows that of the total calculated decay, Br is the primary halogen radical driving the mercury loss for all events studied, consistent with the current hypotheses regarding AMDEs [Brooks et al., 2006; Calvert and Lindberg, 2003; Skov et al., 2004]. Though BrO does not dominate for any of the events, there is a significant contribution by BrO for the event on 23 March, with a smaller, though still significant, BrO contribution for 20, 24 and 25 March. This observation, and the relationship between Br and BrO, can help explain the temporal and spatial correlations sometimes seen between satellite BrO enhancements and ground level mercury depletion events [Lindberg et al., 2002; Lu et al., 2001]. Despite the high levels of Cl2 observed during this time, Cl atoms did not contribute significantly to any of the events studied. O3 also did not have a significant contribution due to the very slow rate constant, though there was a measurable contribution when ozone levels were higher. These days also correspond to days with higher BrO contribution, as would be expected since BrO is a product of Br reaction with ozone. Due to the very slow reaction rate constants for the $\text{Hg}^0 + \text{ClO}$ and $\text{Hg}^0 + \text{OH}$, these oxidation pathways did not contribute significantly to any of the studied events. We note that a small or perhaps zero contribution from OH and O3 reaction with GEM is expected from the discussion in the Hynes et al. [2009] work.

Table 4. Cumulative Oxidant Contributions for All Five Events (s $^{-1}$) in Comparison With $k_{\text{apparent}}$

<table>
<thead>
<tr>
<th>Day in March</th>
<th>$k_{\text{Br}}$</th>
<th>$k_{\text{Br}} + k_{\text{BrO}}$</th>
<th>$k_{\text{Br}} + k_{\text{BrO}} + k_{\text{Cl}}$</th>
<th>$k_{\text{Br}} + k_{\text{BrO}} + k_{\text{Cl}} + k_{\text{ClO}}$</th>
<th>$k_{\text{Br}} + k_{\text{BrO}} + k_{\text{Cl}} + k_{\text{ClO}} + k_{\text{O3}} + k_{\text{OH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>$4.2 \times 10^{-6}$</td>
<td>$6.2 \times 10^{-6}$</td>
<td>$6.3 \times 10^{-6}$</td>
<td>$6.3 \times 10^{-6}$</td>
<td>$6.7 (\pm 2.3) \times 10^{-6}$</td>
</tr>
<tr>
<td>22</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.4 (\pm 0.7) \times 10^{-4}$</td>
</tr>
<tr>
<td>23</td>
<td>$6.5 \times 10^{-6}$</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.3 (\pm 0.4) \times 10^{-5}$</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>24</td>
<td>$6.5 \times 10^{-6}$</td>
<td>$7.6 \times 10^{-6}$</td>
<td>$7.6 \times 10^{-6}$</td>
<td>$7.7 (\pm 3.4) \times 10^{-6}$</td>
<td>$7 \times 10^{-5}$</td>
</tr>
<tr>
<td>25</td>
<td>$5.0 \times 10^{-5}$</td>
<td>$5.6 \times 10^{-5}$</td>
<td>$5.6 \times 10^{-5}$</td>
<td>$5.6 (\pm 2.6) \times 10^{-5}$</td>
<td>$4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

[39] Figure 6 shows that of the total calculated decay, Br is the primary halogen radical driving the mercury loss for all events studied, consistent with the current hypotheses regarding AMDEs [Brooks et al., 2006; Calvert and Lindberg, 2003; Skov et al., 2004]. Though BrO does not dominate for any of the events, there is a significant contribution by BrO for the event on 23 March, with a smaller, though still significant, BrO contribution for 20, 24 and 25 March. This observation, and the relationship between Br and BrO, can help explain the temporal and spatial correlations sometimes seen between satellite BrO enhancements and ground level mercury depletion events [Lindberg et al., 2002; Lu et al., 2001]. Despite the high levels of Cl2 observed during this time, Cl atoms did not contribute significantly to any of the events studied. O3 also did not have a significant contribution due to the very slow rate constant, though there was a measurable contribution when ozone levels were higher. These days also correspond to days with higher BrO contribution, as would be expected since BrO is a product of Br reaction with ozone. Due to the very slow reaction rate constants for the $\text{Hg}^0 + \text{ClO}$ and $\text{Hg}^0 + \text{OH}$, these oxidation pathways did not contribute significantly to any of the studied events. We note that a small or perhaps zero contribution from OH and O3 reaction with GEM is expected from the discussion in the Hynes et al. [2009] work.

[40] As mentioned previously, the two different methods for calculating [Br] and [Cl] (i.e., Brss versus BrOss and Clss versus ClOss) result in estimations for the atom concentrations that differ by a factor of 1.8 and 5, respectively. In order to

Figure 5. Shown are 48 h back trajectories for the five events studied: 20 March (yellow), 22 March (pink), 23 March (red), 24 March (cyan), and 25 March (green), with a representative day with very high Cl2, 19 March, shown in orange.
determine whether this discrepancy would have any impact on the percent contribution results, the events for 20 and 22 March were recalculated using 5 times higher Cl atom concentrations. The date 22 March is a highly Br-dominant event, and using a higher [Cl] has no effect on the percent contribution calculated for Br. The date 20 March has a measurable Cl-atom contribution, and in this case, increasing [Cl] by a factor of five increases the Cl contribution from 0.9% to 4.3%, and decreases the Br contribution from 63% to 60%. In either case, the conclusion that Br is the dominant oxidizer of GEM for these events is not changed.

Figure 6. Bar graphs illustrating the percent contribution of the known gas-phase oxidation pathways to the depletion for which we can account. Error bars represent the high and low bounds as calculated from propagation of uncertainties associated with the oxidant concentrations and rate constants used.
[41] A much more significant source of error for this analysis is the wide range in reported rate constants for the Cl + GEM reaction, from $1.0 \times 10^{-12}$ to $6.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. We have chosen to use the Arrhenius expression for $k_5$ from Donohoue et al. [2005], which is one of the lowest reported values. We believe this value to be the most reliable because it was an absolute rate study performed in N$_2$ bath gas, and consistent results were obtained with either Cl or Hg$^{++}$ in excess. The authors report a fourfold increase in the apparent rate constant when performed in air, which they speculate to result from secondary reactions between Hg$^{++}$ and either ClO or ClO$_2$. Spicer et al. [2002] measured a very small rate constant for Hg$^{++}$ + ClO, $3.6 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and thus it is not likely that ClO is causing the observed enhancement. Because Hg$^{++}$ + Cl is a third-order reaction, it is possible that ClO$_2$ reaction could be a more efficient pathway to form HgCl because it carries with it its own third body in O$_2$ [Hynes et al., 2009]. In the relative rate studies performed by Ariya et al. [2002] the authors found inconsistent results depending on the reference compound used, and also observed nonlinearity in the relative rate plots, implying the possible effects of secondary chemistry. Based on these observations, relative rate studies performed in air are likely not appropriate for this particular reaction.

[42] The fourfold enhancement of the apparent Hg$^{++}$ + Cl reaction observed by Donohoue et al. [2005] in the presence of O$_2$ still does not account for the approximately 64-fold difference in the rate constant reported by Spicer et al. [2002]. The range in the reported rate constants is significant and it would have a dramatic impact on the results of this work if the larger values applied. For example, if the event on 20 March is recalculated using a rate constant of $6.4 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, the contribution of Cl atoms to GEM decay becomes 45%, and Br becomes 40%. In this case, Cl would be the dominant oxidizer of GEM. While, as we have stated, there are good reasons for assuming that the Donohoue et al. [2005] values for $k_5$ are valid, it is apparent that more laboratory studies on gas-phase Hg$^{++}$ reactions would be helpful to better constrain these rate constants.

[43] The contribution of the halogen radicals to AMDEs is dependent on both their concentrations and reaction kinetics. Because there is no method for measuring Br or Cl directly, time-integrated estimates have been performed in previous studies using observed hydrocarbon decays. Using time-integrated [Br] and [Cl] derived from hydrocarbon decay methods of $1 \times 10^9$ and $1 \times 10^8$ molecules/cm$^3$, respectively, as has been done in previous studies [Ariya et al., 2002, 2004; Goodsite et al., 2004; Skov et al., 2004], bromine-induced oxidation will always dominate mercury depletions. However, by examining the decay of GEM on a case-by-case basis, for conditions at the surface where most of the chemistry is likely occurring, it can be shown that as the relative concentrations of Br, Cl, and BrO fluctuate, and so too does their contribution to GEM oxidation. Though Cl itself does not display a significant direct contribution to GEM depletion based on our calculations (and chosen rate constants), it could be possible that the reaction of ClO$_2$ (formed by Cl + O$_2$) with Hg$^{++}$ may be a significant Hg$^{++}$ sink, thereby making Cl atoms indirectly important for AMDEs. Laboratory studies are needed to confirm this hypothesis. Note that while the hydrocarbon decay method explicitly integrates over a time scale corresponding to the lifetime of the VOCs, and thus potentially large spatial scales (including in the vertical direction), the halogen chemistry occurs in the very near surface environment [Bottenheim et al., 2002; Tackett et al., 2007]. Tackett et al. [2007] showed that chlorine chemistry and both ODEs (i.e., bromine chemistry) and AMDEs can occur in a shallow layer (~0–250 m) near the surface. This is also discussed by Frieß et al. [2011].

[44] The relative concentration of the halogen radicals appears to vary significantly, depending on [O$_3$]. When ozone is present, [BrO] is typically much greater than [Br], whereas during near-complete ozone depletion events, the ratio is shifted toward [Br] due to the removal of this major bromine atom sink. Indeed, there are cases when [Br] approaches 50 pptv, which is on the high end of all reported [BrO] measurements. Cl$_2$ observations from the OASIS field study show that molecular chlorine, the primary precursor of Cl, is only observed significantly above its detection limit when both ozone and radiation are present (Liao et al., manuscript in preparation, 2012), an observation similarly made by Impney et al. [1999] at Alert, Canada. This is also reflected in the Br and Cl steady state concentrations as mentioned previously, and well illustrated by the period of 26–29 March (Figure 1c). This points to an important role for ozone in mediating both the activation of chlorine, and the relative activity of the halogen radicals in mercury (and ozone) depletions. At high O$_3$, BrO (and potentially Cl atoms or ClO$_2$) will be important, but as O$_3$ concentrations deplete, the role of Br atoms will likely dominate. On the other hand, when O$_3$ is depleted, GEM is also typically nearly completely removed. Though ClO is also formed at high O$_3$, this is not a significant sink for GEM. Large Br atom concentrations calculated very late in an ODE/AMDE, i.e., when O$_3$ and GEM are effectively removed, will be the dominant oxidation pathway for GEM that is photochemically reemitted from the surface.

4. Discussion

[45] The results of this study imply that, in the polar regions, RGM will be composed of mostly Hg-Br compounds, though Hg-Cl compounds are possible. Because it is highly favorable for mercury to bind an additional atom in a two-step sequence, likely candidates for RGM would be HgBr$_2$, HgCl$_2$, HgBrO/HgBr, and/or HgBrCl. Coupling of the initially formed Hg$^+$ compound with a second ligand occurs in competition with thermal dissociation in a highly temperature-dependent manner. The cold temperatures of the Arctic can stabilize the initial Hg$^+$ compound such that generation of the Hg$^{II}$ product is more favorable than in the warmer temperatures of midlatitude regions. Product studies by Ariya et al. [2002] confirmed the formation of HgBr$_2$ and HgCl$_2$ upon reaction with only Br and only Cl atoms, respectively. However, in the atmosphere where numerous different species are present, it is likely that a significant portion of the RGM will be composed of Hg bound to two different atoms.

[46] Calvert and Lindberg [2004] suggested major RGM components to be OHgBr, BrHgOB and HHOgBr based on a modeling study simulating conditions in Barrow. Though direct OH oxidation of GEM is not expected to be significant due to the low rate of reaction of OH with gas-phase Hg$^{++}$, and
very rapid dissociation of Hg-OH [Goodsite et al., 2004], coupling of HgBr to OH is thought to be likely because of the similar bond strengths for BrHg-Br and BrHg-OH. However, the concentration of OH in the Arctic is generally quite low, 10$^3$–10$^6$ molecules/cm$^3$ based on measurements from OASIS, making it similar to the calculated levels of [Cl] and significantly less than [Br]. However, the Calvert and Lindberg study used only BrCl, at half the concentration of Br$_2$, as the chlorine atom source, and did not consider Cl$_2$. CIMS measurements of Cl$_2$ during OASIS indicate that molecular chlorine is much more prevalent than previously thought, and thus it is possible that more chlorinated-RGM products would be present in Barrow. An updated modeling study including a Cl$_2$ flux would be useful for investigating this situation.

[47] The presence of reactive iodine species (IO$_x$) has not been unambiguously detected in the High Arctic above instrumental detection limits; however, iodine-containing compounds have been observed in many coastal and low-latitude locations [Alicke et al., 1999; Stutz et al., 1999], and it is speculated that they could potentially influence mercury oxidation. The only known experimental study of gaseous Hg$^+$ reaction with iodine [Raofie et al., 2008] determined a rate constant for the Hg$^+$ + I$_2$ reaction of ≤1.27 (±0.58) × 10$^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, suggesting reaction with molecular iodine is too slow for rapid depletion of GEM. The same study determined the product of Hg$^+$ reaction with iodine atoms to be HgI$_2$, and that of Hg$^+$ reaction with IO to be HgIO/HgOI, however, the kinetics of these reactions were not determined. Goodsite et al. [2004] used Rice-Ramsperger-Kassel-Marcus (RRKM) theory to calculate a rate constant for the recombination of Hg and I and determined that it was 3–4 times slower than the recombination of Hg and Br. Thus, direct oxidation of mercury by iodine atoms is unlikely to be significant, with the possible exception of iodine-rich coastal locations with large algal populations [Saiz-Lopez et al., 2007]. However, iodine can enhance radical concentrations in the polar atmosphere through the very fast cross reactions of IO + BrO and IO + ClO [Platt and Hönninger, 2003]. Moreover, the bond strength of BrHg-I is very close to that of BrHg-Br, and the product HgBrI is extremely stable [Goodsite et al., 2004]. Due to the expected low concentrations of reactive iodine species in the Arctic, Calvert and Lindberg [2004] suggest that iodine-containing RGM species should be only minor products, and likely in the form of HgBrI, IOHgBr, or HgICl. IO has recently been detected in Antarctica at concentrations up to 20–50 ppt [Frieß et al., 2010; Saiz-Lopez et al., 2007]. The sub-Arctic location of Kuujjuarapik (Canada) has also been found to have IO present up to 3.4 pptv [Mahajan et al., 2010]. These locations are known to experience ozone and mercury depletion events [Dommergue et al., 2010; Steffen et al., 2005], and the iodine levels present could lead to greater formation of iodinated RGM compounds there. Based on the current lack of successful IO measurements in the High Arctic (limit of detection for LP-DOAS is 1–2 pptv [Saiz-Lopez et al., 2007]), it is not expected that iodine compounds would represent a significant fraction of RGM in this region.

[48] From the complex nature of RGM, it is crucial to develop methods to identify these compounds. However, given gas phase concentrations on the order of 100 ppqv for the total RGM, which is likely made up of multiple different reactive species, this is a very formidable challenge. Because the bond strengths and stabilities of various Hg$^+$ compounds can be quite different, their fate in the environment could also vary. Highly soluble Hg$^+$ compounds are readily scavenged to snow and ice surfaces and particles where they can be chemically transformed further. Mercury concentrations have been measured to reach 90–820 ng/L in surface snow during AMDEs [Douglas et al., 2005; Lindberg et al., 2002]. A portion of deposited RGM is photoreduced back to elemental mercury and reemitted to the atmosphere, though estimates of the fraction of mercury that is reemitted varies from slightly over half to upward of 92% [Brooks et al., 2006; Lalonde et al., 2002; Lindberg et al., 2002; Poulain et al., 2004]. Despite the large range, it is generally agreed that the Arctic acts as a net sink for atmospheric mercury [Ariya et al., 2004; Hirdman et al., 2009; Skov et al., 2004], and that some of the deposited Hg$^+$ is incorporated in the ecosystem during snowmelt in bioavailable forms [Lindberg et al., 2002]. Understanding the cycling and fate of mercury compounds in the environment, and their potential effects on the people and wildlife of the region, will require further investigation into the chemical composition of these species.

5. Conclusion

[49] Using in situ field measurements from Barrow, Alaska, this work has investigated the relative contribution of reactive halogen radicals to the rapid oxidation of atmospheric mercury during polar spring. Br is the dominant oxidation pathway for all events studied here, with significant contributions from BrO. No significant contribution was found from Cl atoms directly, though it is possible that Cl may have an indirect effect through ClO$_2$. It is also possible that we have underestimated the importance of Cl in mercury depletions given the large range in reported rate constants. The contribution of individual oxidants is of course dependent on their relative concentrations, thus, it is likely that RGM products in Barrow are not only highly complex, but also variable depending on the dominant oxidation mechanism involved, and represent a mixture of Hg$^+$ compounds. Both chemical and meteorological conditions are important mediators of the relative activities of the halogen radicals. When ozone is present, [BrO] > [Br], and [Cl] is relatively large, and thus they both contribute more to mercury depletion under those conditions. Interestingly, while O$_3$ is not itself an important GEM oxidant, its presence likely catalyzes the production of Cl (and possibly Br) atoms, and thus may have a significant indirect impact [Oum et al., 1998a, 1998b; Liao et al., manuscript in preparation, 2012]. The independent behavior of Br and Cl suggests a different source or different activation mechanism is controlling these two species. The results of this study highlight the importance of halogen chemistry in general in chemical cycling in the polar regions. Identification of RGM compounds is absolutely crucial because their chemical composition is likely to influence their fate and/or bioavailability in the environment. It is also imperative that the rate constants for the gas-phase oxidation of Hg$^+$ by halogen radicals, especially Cl and ClO$_2$, continue to be studied, including at temperatures relevant to the polar regions, since these values represent a large uncertainty in our knowledge of GEM
depletions. This work demonstrates through quantitative analysis that bromine chemistry is likely controlling AMDEs in the polar regions, corroborating current hypotheses. However, there is also a potentially important role of chlorine atoms in the oxidation of not only VOCs, but also GEM and ozone, thus, the mechanism for production of Cl2 also needs to be determined.

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References


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