Observations of inorganic bromine (HOBr, BrO, and Br₂) speciation at Barrow, Alaska, in spring 2009

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[1] Inorganic bromine plays a critical role in ozone and mercury depletions events (ODEs and MDEs) in the Arctic marine boundary layer. Direct observations of bromine species other than bromine oxide (BrO) during ODEs are very limited. Here we report the first direct measurements of hypobromous acid (HOBr) as well as observations of BrO and molecular bromine (Br₂) by chemical ionization mass spectrometry at Barrow, Alaska in spring 2009 during the Ocean-Atmospheric-Sea Ice-Snowpack (OASIS) campaign. Diurnal profiles of HOBr with maximum concentrations near local noon and no significant concentrations at night were observed. The measured average daytime HOBr mixing ratio was 10 pptv with a maximum value of 26 pptv. The observed HOBr was reasonably well correlated ($R^2 = 0.57$) with predictions from a simple steady state photochemical model constrained to observed BrO and HO₂ at wind speeds $< 6 \text{ m s}^{-1}$. However, predicted HOBr levels were considerably higher than observations at higher wind speeds. This may be due to enhanced heterogeneous loss of HOBr on blowing snow coincident with higher wind speeds. BrO levels were also found to be higher at elevated wind speeds. Br₂ was observed in significant mixing ratios (maximum = 46 ppty; average = 13 ppty) at night and was strongly anti-correlated with ozone. The diurnal speciation of observed gas phase inorganic bromine species can be predicted by a time-dependent box model that includes efficient heterogeneous recycling of HOBr, hydrogen bromide (HBr), and bromine nitrate (BrONO₂) back to more reactive forms of bromine.

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1. Introduction

[2] Surface ozone depletion events (ODEs), where ozone drops from 30 to 40 ppbv to below 10 ppbv, have been frequently observed in spring in polar regions [e.g., *Oltmans*, 1981; *Bottenheim et al.*, 2009; *Jones et al.*, 2010]. The importance of bromine chemistry in catalyzing ozone depletion has been established by field observations of

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filterable bromide and bromine oxide (BrO) during ODEs [e.g., *Barrie et al.*, 1988; *Hausmann and Platt*, 1994].

[3] BrO is a key species that impacts ozone loss rates during ODEs. Br atoms efficiently react with O₃ to form BrO and O₂ (R1). The self reaction of BrO ((R2a) and (R2b)) reforms Br atoms, molecular bromine (Br₂) and O₂, which in combination with reaction (R1) effectively converts O₃ to O₂. The reaction of BrO with HO₂ (R3) followed by photolysis of HOBr (R6) also reforms Br atoms without reforming ozone and in this way active bromine species lead to ozone destruction. BrO photolysis (R4) and reaction with NO (R5), followed by photolysis of NO₂, reform O₃ and do not contribute to net O₃ loss [e.g., *Simpson et al.*, 2007].

$$(R1) Br + O_3 \rightarrow BrO + O_2$$

 $(R2a) \qquad \qquad BrO+BrO \rightarrow 2Br+O_2$

 $(R2b) \qquad \longrightarrow Br_2 + O_2$

$$BrO + HO_2 \rightarrow HOBr + O_2$$

(R3)

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$$(R4) BrO + hv \rightarrow Br + O$$

$$(R5) \qquad BrO + NO \rightarrow Br + NO_2 \qquad (R12)$$

[4] BrO has been detected in numerous ground based campaigns at mixing ratios of up to 30-40 pptv [e.g., Tuckermann et al., 1997; Pöhler et al., 2010] in the Arctic marine boundary layer (MBL) and up to 20 pptv in the Antarctic MBL [e.g., Saiz-Lopez et al., 2007], primarily by differential optical absorption spectroscopy (DOAS). Airborne observations of up to \sim 7 pptv [Liao et al., 2011b; Neuman et al., 2010] in the Arctic MBL by chemical ionization mass spectrometry (CIMS) have been reported. Recently, a comparison of CIMS and long path DOAS (LP-DOAS) demonstrated that both instruments could sensitively and accurately measure BrO [Liao et al., 2011a]. Diurnal patterns of BrO with maxima in the daytime have been observed [e.g., Hausmann and Platt, 1994; Saiz-Lopez et al., 2007; Pöhler et al., 2010; Liao et al., 2011a], which confirmed that BrO is a photochemically generated species with a short lifetime [e.g., Evans et al., 2003; Fan and Jacob, 1992]. BrO is the dominant bromine radical when O_3 is not severely depleted ($O_3 > 1$ ppbv), and observations of this species are crucial for understanding the chemical processing that leads to ODEs [e.g., Sander et al., 1997; von Glasow et al., 2002; Jones et al., 2009; Yang et al., 2010].

[5] Br and BrO are rapidly converted into the non-radical bromine reservoirs hypobromous acid (HOBr), bromine nitrate (BrONO₂) and hydrogen bromide (HBr) via reactions (R3), (R8), (R11) and (R12). HOBr is a short-lived reservoir (photolysis lifetime ~ 10 min) of active bromine (R3), as it can both photolyze to reform Br atoms (R6) and react on surfaces with Br⁻ to generate reactive gas phase bromine (e.g., Br₂) (R7) [Fan and Jacob, 1992]. BrONO₂ is also a short-lived active bromine reservoir as it photolyzes to form active bromine (photolysis lifetime ~ 20 min) and undergoes heterogeneous reactions that eventually form molecular bromine ((R10) and (R7)) [Fan and Jacob, 1992]. HBr is mainly lost by uptake on surfaces. The dissolved HBr can react with HOBr in the condensed phase to generate Br₂ (R7). Small amounts of HBr can be converted back to Br atoms via reaction (R13).

$$(R6) \qquad \qquad HOBr + hv \rightarrow Br + OH$$

(R7)
$$HOBr_{(aq)} + Br_{(aq)}^- + H_{(aq)}^+ \rightarrow Br_2 + H_2O$$

$$(R8) BrO + NO_2 \rightarrow BrONO_2$$

(R9a)
$$BrONO_2 + hv \rightarrow BrO + NO_2$$

$$(R9b) \rightarrow Br + NO_3$$

(R10)
$$BrONO_2 + H_2O(s/aq) \rightarrow HOBr(aq) + HNO_3$$

$$(R11) Br + HO_2 \rightarrow HBr + O_2$$

$$(R12) Br + CH_2O \rightarrow HBr + HCO$$

$$(R13) \qquad \qquad HBr + OH \rightarrow H_2O + Br$$

The reactions (R3) and (R8) followed by the condensed phase reactions (R10) and (R7) and Br₂ photolysis (R14) lead to bromine activation. The recycling rates of nonradical bromine to radical bromine through heterogeneous reactions largely determine the active bromine concentrations and ozone loss. However, the rates of the heterogeneous processes (R7) and (R10) are not well known. Observations of the concentrations and diurnal behaviors of HOBr, BrONO₂ and HBr allow the examination of current bromine mechanisms. Impey et al. [1999] reported HOBr up to ~ 260 pptv inferred from the measurements of total photolyzable bromine (Br₂ and HOBr) in the springtime Arctic boundary layer. Beine et al. [2001] and Ianniello et al. [2002] reported in situ HBr up to \sim 20 pptv measured by denuder. However, to our knowledge there are no in situ measurements of HOBr and BrONO₂.

[6] Br₂ is photolyzed rapidly by sun light to form Br atoms (R14) (lifetime = ~ 30 s) which can initiate the bromine catalyzed ozone depletion cycles. Br₂ is likely a precursor of bromine radicals at sunrise and a reservoir of reactive gas phase bromine at night [e.g., *Fan and Jacob*, 1992].

$$(R14) Br_2 + hv \rightarrow 2Br$$

Accurately measuring Br₂ is challenging because HOBr easily converts to Br₂ on inlet surfaces [Neuman et al., 2010]. Br₂ mixing ratios of up to 27 pptv in the daytime and up to 15 pptv at night were measured in the Arctic boundary layer by Foster et al. [2001]. Br₂ mixing ratios of up to 4 pptv in the daytime and up to 9 pptv at night were observed in Pacific MBL by Finley and Saltzman [2008]. The sum of Br₂ and HOBr was measured as high as 20 pptv in the daytime by Neuman et al. [2010] onboard the NOAA P-3 over the Arctic Ocean in spring 2008. However, all these measurements of high levels of Br₂ in the daytime are likely susceptible to interference from conversion of HOBr on inlet surfaces [Neuman et al., 2010]. Efficient conversion of HOBr to Br₂ on the walls of sampling inlets demands a sampling system with limited wall interaction and the consideration of the potential role of HOBr as an interference to achieve accurate measurement of Br₂.

[7] An intensive field study took place at Barrow, Alaska in spring 2009 during the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) campaign (http://www.oasishome.net/ barrow2009.php) to investigate air-surface interactions in the Arctic and their evolution in future climates. This provided a unique opportunity to further study halogen chemistry in the Arctic. In this paper, the first simultaneous measurements of BrO, HOBr and Br₂ are reported. Molecular chlorine (Cl₂) and bromine monochloride (BrCl) were also observed during the same campaign and are reported by J. Liao et al. (Observations of very high levels of molecular chlorine at Barrow, AK, manuscript in

Species and Parameters	Instrument	Uncertainty	Detection Limits (10 min)	Reference
BrO	CIMS	$\pm 34\%$	1.1 pptv	Liao et al. [2011a]
HOBr	CIMS	+44%/-30%	2.0 pptv	this paper
Br ₂	CIMS	+7%/-26%	2.0 pptv	this paper
O ₃	chemiluminescence	$\pm 5\%$	<1 ppbv	Weinheimer et al. [1998]
NOv	chemiluminescence	$\pm 15\%$	10 pptv	Weinheimer et al. [1998]
NO/NO ₂	chemiluminescence	$\pm 10\%$	2 pptv	Weinheimer et al. [1998]
HO ₂	CIMS	$\pm 30\%$	0.1 pptv	Edwards et al. [2003] and Cantrell et al. [2003]
OH	CIMS	$\pm 30\%$	0.01pptv	Mauldin et al. [2004]
CO	CO instrument	$\pm 5\%$	10 ppbv	
CH ₂ O	Tunable Diode	$\pm 21\%$	59 pptv	Fried et al. [2003]
	Laser Spectroscopy			
Aerosol number density	Scanning Mobility	$\pm 10\%$		Woo et al. [2001]
Aerosol	Scanning Mobility	+15%		We at al $[2001]$
surface area	Particle Sizer	1570		100 ei ul. [2001]
i values	NCAR CCD Actinic	$\sim\pm$ 12%		Shetter and Muller [1999]
5	Flux Spectroradiometer	(Molecular dependent)		
Wind speeds	Sonic	±6%		

Table 1. Summary of the Measurements Used in This Study^a

^aThe measurement frequency is higher than every 10 min for all the species and parameters listed in Table 1.

preparation, 2012). HOBr observations are compared to a photochemical model and the diurnal speciation of inorganic bromine species is investigated by comparison with a time dependent box model.

2. Methods

2.1. Measurements

[8] BrO, HOBr, and Br₂ were measured by a CIMS in March and April 2009 at Barrow, AK. Measurements of other trace gases (NO, NO₂, NO_y, O₃, CO and CH₂O) and actinic fluxes were also obtained at the same site. The measurement of aerosol size distributions was carried out at a site \sim 700 m northwest. The observations of wind speed and wind direction were made 28 m southeast of the chemical measurements. The layout of the instruments is provided by *Liao et al.* [2011a]. The measurements used in this study are summarized in Table 1.

2.2. CIMS Measurements

[9] The details of the CIMS instrument and inlet configuration to measure halogen species are described in detail by *Liao et al.* [2011a]. The sampling inlet consisted of a custom three way valve connected to two short sampling tubes *[Huey et al.*, 2004]. All surfaces exposed to ambient air were made of Teflon. In the normal operating configuration the inlet was effectively a 25 cm long, 0.65 cm ID Teflon tube. HOBr can be converted to Br₂ on the wall of the Teflon sampling inlet and minimizing the length of the inlet decreases the impact of this process [*Neuman et al.*, 2010]. Hydrated I⁻ was used to selectively ionize the halogen species including BrO, HOBr, and Br₂.

 $(R15) BrO + I^- \rightarrow IBrO^-$

(R16)
$$HOBr + I^- \rightarrow IHOBr^-$$

$$(R17) \qquad \qquad Br_2 + I^- \rightarrow IBr_2^-$$

The mass resolution of the CIMS was better than 1 amu, which allowed HOBr (at 223 and 225 amu) to be distinguished from BrO (at 222 and 224 amu).

2.2.1. Measurements of Background Signals

[10] Instrument background signals were measured and subtracted from the total signals to determine the contributions from halogen species in the ambient atmosphere. The instrumental background levels for the halogen measurements were determined periodically (every 20 min) by scrubbing ambient air with glass wool [Liao et al., 2011a]. Lab experiments showed that glass wool effectively removes many halogen species with greater than 95% efficiency (e.g., BrO, HOBr and Br₂) from a gas stream, which was also validated by tests in the field by scrubbing the output of a Br₂ permeation tube [Neuman et al., 2010]. An example of typical raw signals of Br₂ (287 amu) and HOBr (223 amu) with a series of background measurements is shown in Figure 1. The background for the Br₂ measurement was more unstable for a few days in the later period of the campaign. These measurements with reduced accuracy were removed from the data set. The reason for the variance in the Br₂ background measurements especially later in the campaign is not understood at this time. The raw signal obtained for BrO (224 amu) has been previously shown by Liao et al. [2011a].

2.2.2. Calibration

[11] Br₂ and Cl₂ permeation tubes (Kin-tek) were used as the primary calibration standards for the OASIS campaign. Known amounts of the standard gases were periodically added to the CIMS inlet. The details of the calibration procedures and the verification of the output rates of the permeation tubes are provided by *Liao et al.* [2011a]. An example of the raw signals for the Br₂ standard addition is displayed in the top panel of Figure 1. The typical sensitivity of Br₂ during OASIS was 12 ± 4 Hz per pptv. The concentrations of other halogen species were determined from the sensitivity of these specific halogens relative to that of Br₂ or Cl₂. The sensitivity of BrO relative to Br₂ was determined in laboratory experiments to be 0.47 \pm 25%. BrO was produced from the thermal dissociation of Br₂ to Br



Figure 1. Raw signals (Hz) of IBr_2^- (black) and $IHOBr^-$ (blue) at mass 287 amu and 223 amu. Open squares with a cross in the middle represent the average calibration signal when 1.47 ppbv of Br_2 was added. Note the time scales of the x axes are different. Red squares denote the average background signals (shaded areas) when sampled air went through the glass wool scrubber.

atoms in excess O_3 . The detailed experiment method is described by *Liao et al.* [2011a]. The sensitivity of HOBr relative to Br_2 was also determined in laboratory experiments to be $0.5 \pm 25\%$. HOBr was synthesized by the reaction of liquid Br_2 with a silver nitrate solution (AgNO₃). The HOBr source was calibrated relative to Br_2 by conversion of HOBr back to Br_2 on humidified sodium bromide (NaBr). The details of this method are described by *Liao et al.* [2011b]. The typical sensitivity for BrO and HOBr was about 6 Hz/pptv.

2.2.3. Limits of Detection

[12] Measurement precision and background stability affected the limit of detection for each compound. The absolute difference between successive one minute average background measurements of HOBr was essentially normally distributed with a median of 1.3 pptv. The detection limit (3σ) of HOBr is then estimated to be 3.9 pptv for 1 min data. This variance is very close to that due to the counting statistics of the background level which was 121 Hz (~20 pptv). For this reason, we expect the detection limit to decrease as approximately the square root of the averaging time. However, as it is difficult to determine the non statistical component of the background variance we estimate the detection limit (3σ) of HOBr to be 2.0 pptv for 10 min data, assuming that the non statistical component of the background variance does not decrease with averaging and the statistical variation decreases as the square root of the averaging time. Similarly, the detection limit (3σ) for Br₂ is estimated to be ~2.0 pptv for 10 min data before April 8 2009 and ~4.0 pptv for 10 min data after April 8 2009. The variance of the background signal is the major factor that determines the detection limit and the variance of the Br₂ background was greater than that of HOBr background. The estimated detection limit for BrO is 1.1 pptv (3σ) for 10 min data according to *Liao et al.* [2011a]. **2.2.4.** Accuracy

[13] The accuracy of the Br₂ measurements, when operating well above detection limits, is estimated to be 7% due to the uncertainty in the permeation rate of the calibration source [*Liao et al.*, 2011a]. However, daytime mixing ratios of observed Br₂ higher than below detection limit were almost certainly due to the conversion of HOBr on the wall of the sampling inlet. We estimate that on average less than 20% of HOBr was converted to Br₂ on the 25 cm long Teflon inlet based on lab studies. Combining the uncertainties in the sensitivity ratio of HOBr to Br₂ (\pm 25%), the output of permeation tubes (\pm 7%) and the interferences of the conversion of HOBr to Br₂ on the sampling inlet (-0%/+20%), the uncertainty in the HOBr measurements is



Figure 2. The raw ambient signal of HOBr at mass 223 amu (Hz) versus 225 amu (Hz). The correlation coefficient is 0.85 (R^2) with a slope of 1.05 and an intercept of 1.68 Hz or 0.28 pptv when periods with NO_x levels above 10 ppbv (gray) are excluded.

estimated to be -30%/+44%. The accuracy of the BrO measurements is estimated to be 30% [Liao et al., 2011a]. 2.2.5. Isotope Comparison

[14] Bromine has two naturally occurring isotopes of

almost equal abundance which enables the detection of a bromine species at two (or more) different masses by the CIMS. In many cases this provides a valuable test of the quality of the bromine measurements. The raw ambient signals for mass 223 amu (IHO⁷⁹Br⁻) are plotted against the signals at mass 225 amu (IHO⁸¹Br⁻) in Figure 2. The correlation is very good ($R^2 = 0.85$) except for a few polluted periods (gray dots) when NO_x levels were higher than 10 ppbv. Unknown chemical compounds from polluted plumes (high NO_x periods) appeared at mass 225 and decreased the correlation between the signal at mass 223 and 225. An equally weighted bivariate regression applied to the filtered data yielded a slope of 1.05 and an intercept of 1.68 Hz (0.28 pptv). This is a strong indication that HOBr is being detected at these masses. Because of the interference at 225 amu, mass 223 was used to derive the HOBr concentrations. The signal of Br₂ at mass 287 (I⁷⁹Br⁸¹Br⁻) was correlated well with that at mass 285 $(I^{79}Br^{79}Br^{-})$ (R² = 0.84) and mass 289 ($I^{81}Br^{81}Br^{-}$) (R² = 0.91). The most abundant isotope at mass 287 did not have significant interferences and was used to derive the concentrations of Br₂. The correlation between mass 222 (I⁷⁹BrO⁻) and 224 (I⁸¹BrO⁻) amu was illustrated by *Liao* et al. [2011a].

2.3. Models

[15] The observations are compared to two models. A simple steady state photochemical model run with and without HOBr loss on aerosol surfaces is used to analyze the HOBr observations. A time-dependent model prediction is compared to the average temporal evolution of the observed halogen species. The steady state model is highly constrained by BrO measurements and only used to calculate the concentrations of HOBr. The time dependent model is unconstrained by bromine species measurements and is used to model the diurnal bromine speciation based on the chemical mechanism.

2.3.1. Steady State Calculation of HOBr

[16] HOBr concentrations were predicted using the steady state assumption as its lifetime due to photolysis is relatively short (~ 10 min in the daytime). The calculation was constrained to measured BrO and HO₂. The heterogeneous formation of HOBr via reaction (R10) is not included as BrONO₂ levels are not expected to be high and the resultant HOBr(aq) from this reaction may also react with Br⁻ in solution to form Br₂. The predictions considered two cases: case (a): no heterogeneous loss of HOBr on surfaces; and case (b): inclusion of loss of HOBr on aerosol surfaces.

$$ase(a): [HOBr]_{pred_{noaeroloss}} = \frac{k_3 [HO_2] [BrO]}{J_{HOBr}}$$
(1)

$$case(b): [HOBr]_{pred} = \frac{k_3[HO_2][BrO]}{J_{HOBr} + k_a}.$$
 (2)

k_a is the loss rate of HOBr on aerosol surfaces and is calculated by formula below.

 $k_a = 4\pi R_p D_g f.$ where

R_p: Particle radius

с

- D_{g} : Diffusivity of gas species in air f: Transition regime formula $\frac{0.75\alpha(1+Kn)}{Kn^2+Kn+0.283Kn.\alpha+0.75\alpha}$ [Fuchs and Sutugin, 1971]
- α : Mass accommodation coefficient; Kn = $\lambda/(2R_p)$; λ = $3D_g/c$; $c = \sqrt{\frac{8kT}{\pi m}}$. D_g is assumed to be 0.1 cm² s⁻¹.

[17] The mass accommodation coefficient of HOBr on aerosol particles in the calculation of k_a is estimated to be 0.6 [Wachsmuth et al., 2002]. The rate coefficient for reaction (R3), k₃, is taken from a kinetics database [Sander et al., 2006]. The photolysis rate, J_{HOBr}, was derived from actinic fluxes measurements. BrO levels were obtained from CIMS observations. HO₂ concentrations were from the NCAR CIMS measurements [Cantrell et al., 2003].

[18] As the CIMS BrO measurements used in the calculation are in agreement with BrO measurements by LP-DOAS [Liao et al., 2011a], the uncertainty of the HOBr calculation is likely dominated by the uncertainty in HO₂ measurements and the loss rate of HOBr on heterogeneous surfaces.

2.3.2. Time Dependent Box Model

[19] A time dependent box model is used to simulate the average diurnal speciation of bromine during the OASIS campaign. The model only incorporates gas phase and heterogeneous phase reactions (R1)-(R14) and loss of HBr to aerosol surfaces. Because HOBr is rapidly converted to Br_2 on surfaces, the heterogeneous reaction rates of (R7) and (R10) are assumed to be the loss rate of gas phase

 Table 2. The Observed Levels of the Input Species of the Time

 Dependent Model

Input Species	Average Levels	Range of the Levels
O ₃ CH ₂ O NO NO ₂	13 ppbv 203 pptv 5 pptv 7 pptv	10–18 ppbv 149–322 pptv 4–8 pptv 5–10 pptv
HO ₂ OH Aerosol surfaces	$6.9 \times 10^{7} \text{ molec.cm}^{-3}$ $4.4 \times 10^{5} \text{ molec.cm}^{-3}$ $51 \ \mu \text{m}^2 \text{ cm}^{-3}$	$\begin{array}{c} 0-2.1\times10^8 \text{ molec.cm}^{-3} \\ 0-1.9\times10^6 \text{ molec.cm}^{-3} \\ 9-400 \ \mu\text{m}^2 \text{ cm}^{-3} \end{array}$

non-radical bromine (HOBr and BrONO₂) on aerosols. The time dependent model does not include detailed heterogeneous reaction processes because key parameters of aerosols (e.g., liquid water contents and pH) and snow surface (e.g., area) are not well known. The diurnal evolution of the boundary layer height or the bromine recycling on blowing snow surfaces is not included in the model.

[20] Bromine species including Br₂, BrO, HOBr, BrONO₂, HBr, and Br are predicted in the model. The inputs are 10 min average diurnal data (e.g., j values and NO). The typical concentrations of the diurnal data used as model inputs are given in Table 2. Because high levels of NO and NO₂ detected at Barrow were likely due to local pollution, the NO and NO₂ measurements with exclusion of the periods when NO > 20 pptv and NO₂ > 20 pptv were used to calculate the average diurnal profile of NO and NO₂ as the time dependent model input. The average NO and NO₂ mixing ratios were 5 pptv and 7 pptv, respectively. The initial mixing ratio of Br₂ is specified to be 15 pptv, based on the average Br₂ mixing ratios observed at 12:00 A.M. The initial concentrations of other bromine species are assumed to be zero. The gas phase reaction rate constants, photolysis rates, and HOBr mass accommodation coefficients are from the same sources as in section 2.3.1. The mass accommodation coefficient of HBr on aerosol particles is estimated to be 0.3 from the data measured for HOBr relative to HBr in work by Fluckiger and Rossi [2003]. The mass accommodation coefficient of BrONO₂ is estimated to be 0.8 [Sander et al., 2006; Deiber et al., 2004; Hanson et al., 1996].

[21] As the concentrations of Br^- available for reaction (R7) are not well known, the following assumptions are made. HOBr and BrONO₂ are efficiently (100%) recycled back to Br_2 when Br^- supplied from the heterogeneous loss of HBr is abundant. When the heterogeneous loss of HOBr and BrONO₂ are higher than the Br^- supplied from the heterogeneous loss of HBr, the production rate of Br_2 is assumed to be equal to the heterogeneous loss rate of HBr plus 50% of the difference between the sum of the heterogeneous loss rate of HOBr and BrONO₂ and HBr.

This assumes that HOBr and BrONO2 still react to form Br2

to the gaseous phase with 50% efficiency when Br^- from HBr is depleted.

3. Results and Discussion

3.1. BrO, HOBr, and Br₂ Measurements By CIMS

[22] Ten minutes averages of the BrO, HOBr, Br₂, and O₃ observations from March 18 to April 14, 2009 during the OASIS campaign are shown in a time series plot in Figure 3. The Br₂ and HOBr data shown have not been corrected for conversion of HOBr to Br₂. The hourly average diurnal profile mixing ratios of Br₂ and HOBr corrected for conversion of HOBr to Br₂ assuming 20% conversion in the inlet are shown in Figure 4. The daytime Br₂ measurements during April 9–April 13 2009 were assumed to be zero in Figure 4. The gaps in BrO and HOBr measurements are due to the malfunction of the instrument and power outages. The extra gaps in the Br₂ measurements are due to unstable Br₂ background measurements leading to observations that are below detection limits.

3.1.1. BrO Measurements

[23] The hourly average diurnal profile of BrO from March 18th to April 14th is shown in Figure 4. BrO concentrations increase at sunrise and decrease at sunset as expected. BrO mixing ratios are relatively flat during the day without a clear noontime peak, similar to the observations in Cape Verde [Read et al., 2008] and the Arctic [Pöhler et al., 2010]. This BrO pattern had been explained based on model simulations for the marine boundary layer by von Glasow et al. [2002]. The daytime (9 A.M.–6 P.M.) BrO mixing ratios on days with significant BrO (maximum BrO > =10 pptv) observed and low NO (<100 pptv) have an average value of 11.9 pptv and ranged up to 37 pptv. The BrO concentrations observed by CIMS were correlated well with that measured by a nearly co-located LP DOAS during the OASIS campaign [Liao et al., 2011a]. No simple relationship between BrO and ozone was observed (Figure 7, middle), similar to that provided by *Pöhler et al.* [2010]. The observed BrO levels were often not large enough to explain the O_3 loss at Barrow by (R2) and (R3). O_3 levels were also observed to decrease at night (e.g., 4 April and 6 April), which also indicates that the concentrations of O₃ at Barrow are impacted by transport as well as local chemical loss.

3.1.2. HOBr Measurements and Predictions

[24] The hourly average diurnal profile of HOBr from March 18 to April 14 is also shown in Figure 4. Approximately 9.8 pptv of HOBr were observed in the daytime (9 A.M.–6 P.M.) on average during the campaign. Up to ~26 pptv of HOBr were detected for the 10 min average data (Figure 3). HOBr has similar diurnal patterns to BrO with maximum in the daytime and no evidence of significant nighttime concentrations. This is consistent with the production of HOBr by the reaction of photochemically shortlived species BrO and HO₂ (R3), and the rapid loss of HOBr from the gas phase. The concentrations of HOBr increased

Heterogeneous Br2production rate

$$= \begin{cases} k_{HBr}[HBr] + 0.5(k_{HOBr}[HOBr] + k_{BrONO2}[BrONO_2] - k_{HBr}[HBr]) & (k_{HOBr}[HOBr] + k_{BrONO2}[BrONO_2] > k_{HBr}[HBr]) \\ k_{HOBr}[HOBr] + k_{BrONO2}[BrONO_2]) & (k_{HOBr}[HOBr] + k_{BrONO2}[BrONO_2] < k_{HBr}[HBr]) \end{cases}$$
(3)



Figure 3. A time series of measurements of BrO (red), HOBr (blue), Br_2 (black), O_3 (green) and j values of Br_2 (gray) averaged to 10 min from March 18 to April 14 2009 during the OASIS campaign. Ticks on the bottom axis represent the starting time 00:00 of each day.

slightly later than BrO at sunrise and decreased slightly earlier than BrO at sunset. This is consistent with the mechanism that HOBr is formed by reaction of BrO and HO_2 , which increased later than BrO at sunrise and decreased earlier than BrO at sunset.

[25] A steady state model was used to test the consistency of measured HOBr mixing ratios (section 2.3.1) with known chemical processes. The steady state box model predictions of HOBr in case (a) and case (b) (see 2.3.1) plotted against the HOBr measurements are shown in Figures 5a and 5b. respectively. HOBr data taken under polluted conditions (NO > 100 pptv) are excluded from the comparison. HOBr predictions are reasonably well correlated ($R^2 = 0.53$ in case a; $R^2 = 0.57$ in case b) with HOBr measurements at low wind speeds ($< 6 \text{ m s}^{-1}$) with a slope of 2.85 for case (a) and 1.67 for case (b) from equally weighted bivariate linear regressions through zero. The average ratio of HOBr_{pred} to $HOBr_{obs}$ (when $[HOBr]_{obs} > 2$ pptv) is 2.88 with a standard deviation of 1.91 for case (a) at wind speeds $< 6 \text{ m s}^{-1}$. The average ratio of HOBr_{pred} to HOBr_{obs} (when [HOBr]_{obs} > 2 pptv) is 1.49 with a standard deviation of 1.18 for case (b) at wind speeds $< 6 \text{ m s}^{-1}$. As the HOBr measurement has a +45% error bar and the HO₂ has an error bar of $\pm -30\%$, the calculated HOBr is well within the combined error bars of these parameters alone.

[26] The model overpredicted HOBr at high wind speeds. Because the HOBr predictions were highly constrained by BrO measurements, the overprediction of HOBr at high wind speeds is likely due to enhanced deposition of HOBr on blowing snow surfaces. It is likely that blowing snow at high wind speeds provided more surface area for HOBr loss which regenerates active bromine and eventually BrO. The correlation between HOBr predictions and measurements also indicates that HOBr can be predicted in the Arctic at low wind speeds by relatively simple models that include the heterogeneous loss of HOBr on aerosol surfaces.

[27] The impact of wind speeds on bromine recycling is further illustrated in Figure 6. The mixing ratios of BrO and HOBr in the daytime (9 A.M.–6 P.M.) are binned according to wind speed. The average values of BrO and HOBr in each bin are shown as the heights of the bins. The average BrO mixing ratios increase at higher wind speeds (>6 m s⁻¹); however, HOBr levels remained relatively constant as a



Figure 4. Hourly average diurnal profiles of observed BrO (red), HOBr (blue) and Br_2 (black). The measured Br_2 and HOBr mixing ratios were corrected for the conversion of HOBr to Br_2 on instrument sampling lines.



Figure 5. The predicted HOBr plotted versus the observed HOBr (a) without and (b) with the heterogeneous loss of HOBr on aerosol surfaces. The plots were color coded with wind speeds. An equally weighted bivariate regression through zero gives a correlation coefficient (R^2) of 0.37 and a slope of 3.78 for all the data, and $R^2 = 0.53$ and a slope of 2.85 for the data at low wind speeds (wind speeds <6 m s⁻¹) for Figure 5a. The same regression gives a correlation coefficient of 0.44 and a slope of 2.07 for all the data, and $R^2 = 0.57$ and a slope of 1.67 for the data at wind speeds <6 m s⁻¹ for Figure 5b.

function of wind speed. This is consistent with blowing snow at high wind speeds increasing the efficiency for regenerating active bromine (e.g., BrO) by providing more surfaces for heterogeneous loss of HOBr. Higher production rates of HOBr due to enhanced BrO present at higher wind speeds seemed to be balanced by higher loss rates of HOBr on the blowing snow and resulted in a relatively constant HOBr mixing ratio as a function of wind speed. It should also be noted that the sum of BrO and HOBr was also enhanced at higher wind speeds. These results provide direct evidence for the important role of high wind and possibly blowing snow in activating bromine including potentially producing higher total inorganic gas phase bromine species. Jones et al. [2009] also found that enhanced BrO levels from satellite observations coincide with high wind speeds. Active bromine and BrO levels measured over the Arctic Ocean were highest when wind speeds were the greatest [Neuman et al., 2010]. Begoin et al. [2010] suggested that the activation of BrO was linked to a cyclone with very high surface wind speeds probably associated with blowing snow and that the transported aerosols and snow can also provide surfaces for BrO recycling within the BrO plume. The model of Yang et al. [2010] also showed that a bromine source from blowing snow is needed to explain the bromine "explosion" events.

3.1.3. Br₂ Measurements

[28] Diurnal variations of Br_2 were observed with maximum concentrations at night (Figure 3). On average about 13 pptv of Br_2 was observed at night (10 P.M.–4 P.M.) with a maximum value of 46 pptv (Figure 4). Observed Br_2 concentrations decreased rapidly as the sun rose. This is consistent with Br_2 accumulation at night followed by photolysis to produce bromine atoms at sunrise. Small but

detectable levels of daytime Br_2 (see Figure 3) were due to the conversion of HOBr on the Teflon inlet wall [*Neuman et al.*, 2010] and the uncertainty in background signal measurements. The Br_2 measurements at night were without interference from HOBr as this species was not observed in the dark.

[29] Nighttime Br_2 was clearly anti-correlated with O_3 . The mixing ratios of nighttime Br₂ binned as a function of O₃ mixing ratios are shown in Figure 7. These observations are consistent with the transport of active bromine at night as Br₂ in ozone depleted air masses. The data also suggest that the magnitude of active bromine in the air mass is proportional to the loss of ozone. This observation is somewhat surprising as ozone destruction rates are often assumed to be dominated by the BrO self reaction (R2) which could lead to a quadratic dependence on bromine levels. However, the BrO self reaction (R2) is not dominant at Barrow. Based on noontime HO₂ concentrations ranging from 2×10^8 molec. cm^{-3} to 5 × 10⁸ molec. cm^{-3} , the O₃ loss rate due to the reaction of BrO with HO₂ (R3) was higher than reaction (R2) except for periods when BrO mixing ratios were higher than 33 pptv. The O_3 loss rate due to self reaction of BrO was \sim 35% of the O₃ loss rate due to reaction of BrO with HO₂ on average at Barrow during OASIS. This is consistent with the linear anticorrelation of O₃ with Br₂.

3.2. Diurnal Patterns of Bromine Compounds

[30] A time dependent model (see 2.3.2) is used to simulate the observed diurnal patterns of bromine species at Barrow (Figure 4). The model reproduces the average diurnal patterns of gas phase HOBr, BrO and Br₂ reasonably well. The initial gas phase bromine (15 pptv) needs to be recycled very efficiently (\sim 39 times in 24 h) from



Figure 6. The average mixing ratios of daytime (9 am-6 pm) (top) BrO and (bottom) HOBr for a 1 min average base are binned according to wind speed. One standard deviation $(\pm 1\sigma)$ of the bromine measurement is denoted as the error bar. Each wind speed bin contains at least 400 measurements except for 11–12 m s⁻¹ with 80 measurements.

heterogeneous phase to gas phase Br_2 to maintain the gas phase bromine concentrations. The lifetime of HOBr, BrONO₂ and HBr due to loss on observed aerosol surface is estimated to be 12 min, 20 min and 11 min and is even shorter with more heterogeneous surface. The method to calculate the loss rates and the parameters are provided in section 2.3.1 and 2.3.2. All of the gas phase bromine species HOBr, HBr, and BrONO₂ must be recycled to sustain the observed bromine concentrations.

[31] The predicted Br_2 with an initial mixing ratio of 15 pptv at night, decreases to below 1 pptv at sunrise and builds back up to near original levels after sunset. The predicted average daytime (9 A.M.-6 P.M.) BrO and HOBr mixing ratios were 8.1 pptv and 10.0 pptv (Figure 8), which are comparable to the observations. The predicted HOBr concentrations also increased slightly later than BrO at sunrise and decreased slightly earlier than BrO at sunset, similar to the observations. It should be noted that for simplicity this analysis assumes only aerosol surfaces are involved in recycling bromine. The surface of the snowpack may also be important for recycling bromine as simulated in previous studies [Michalowski et al., 2000; Piot and von Glasow, 2008]. The model did not consider the dilution of chemical species due to evolution of boundary layer height, which may also contribute to the differences between observed and predicted diurnal patterns.

[32] No observations of HBr and $BrONO_2$ were available to compare to the model predictions. The ratios of predicted HBr to BrO and HOBr were within the range of previous predictions [*Evans et al.*, 2003] in the Arctic, and the diurnal pattern of predicted HBr was similar to that predicted by *Fan and Jacob* [1992]. The predicted diurnal pattern of BrONO₂ had an early morning and a late afternoon peak with a local minimum at noon, which is likely due to the sharp peak in the BrONO₂ photolysis rate ($\sim 0.0015 \text{ s}^{-1}$) around noon.

[33] In the marine boundary layer when high levels of NO_x are present, its coupling with halogen chemistry is important to fully study the bromine catalyzed ozone depletions in the MBL. With average NO_2 mixing ratios of 7 pptv used in the model, the early morning and late afternoon peaks of BrONO₂ were predicted to be 6 pptv and noon time BrONO₂ was predicted to be 4 pptv. This indicates that the impact of NO_x on bromine can be significant in the early morning and late afternoon in the MBL when significant NO_2 is present. The predicted BrONO₂ diurnal profile is consistent with that predicted by *Sander et al.* [1999].

4. Conclusions

[34] The simultaneous measurements of BrO, HOBr, and Br₂ at Barrow, AK by CIMS reveal gas phase bromine



Figure 7. (top) The average nighttime (6 P.M.–9 A.M.) mixing ratios of Br_2 and the daytime (9 A.M.–6 P.M.) mixing ratios of (middle) BrO and (bottom) HOBr for a 1 min average are binned according to different ozone levels. The error bar represents ± 1 standard deviation of the bromine measurements.



Figure 8. Prediction of hourly average diurnal profiles of bromine species (BrO, HOBr, Br_2 , Br, $BrONO_2$ and HBr) from a time dependent model. Input parameters used in the model are summarized in Table 2.

speciation in the Arctic MBL. The first direct observations of HOBr were achieved and were found to agree reasonably well ($R^2 = 0.57$; mean ratio of predicted to observed = 1.49) at low wind speeds (<6 m s⁻¹) with a simple photochemical model constrained to BrO observations. The BrO mixing ratios were enhanced relative to HOBr at higher wind speeds. This indicated that high wind speeds, likely inducing blowing snow, favored bromine activation and provided more surfaces for HOBr heterogeneous loss. Nighttime levels of Br₂ were anti-correlated with O₃ at Barrow, which indicates that the extent of O₃ loss is proportional to total bromine levels. The average diurnal patterns of observed HOBr, BrO and Br₂ are consistent with predictions from a simple time dependent model that efficient recycles HBr, HOBr, and BrONO₂. Further observations of inorganic bromine species (e.g., HBr and BrONO₂) are needed to confirm the details of the bromine catalyzed ozone depletion mechanisms.

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