

Reviewer Response: acp-2016-1141

We thank Anonymous Referee #1 for the constructive comments on this manuscript. In our response, we first address the overarching concerns of the reviewer, followed by addressing individual comments. Our response to points that the reviewer raises is denoted with bold text. All line numbers in our responses refer to the attached tracked change manuscript.

This paper presents a detailed analysis of a bromine activation event that took place over Barrow in March 2012. This event was probed by BrO and supporting measurements at the surface (in situ and MAX-DOAS), from aircraft (MAX-DOAS), and from satellite. A spectacular finding is the observation of a BrO plume aloft at 0.5-1 km altitude, implying that BrO can be sustained through reservoir recycling reactions within the atmosphere presumably through aerosols. This is a major new finding not only for understanding elevated BrO in Arctic spring but also for explaining the BrO tropospheric background. This paper certainly deserves publication in ACP. The paper can be published pretty much as is in my opinion (I do think the abstract needs some tweaking, see below). However, I found it a struggle to go through because of all the complicated plots of near-raw data forcing me through (I thought) unnecessary details. In my view, Figure 11 makes the paper. The authors might consider cutting back on the figures or simplifying them. This is just a suggestion, however, because the authors might feel that the detail is necessary. Readers like me will be discouraged by the detail and go straight to the abstract, and that's OK.

Based on the reviewer's suggestion, Figs. 2 and 5 have been moved to the supplemental information. In addition, the now Fig. 9 has been modified to show the LT-VCD as well as the BrO profile to facilitate comparisons between figures.

I do think that the authors can (and should) broaden the impact of their paper by linking their results to background tropospheric BrO. As they know, there is a lot of current interest in understanding the ~ 1 ppt BrO observed in the troposphere with implications for ozone, OH, and Hg. Heterogeneous recycling in aerosols similar to the springtime Arctic (but at a slower pace) has been proposed to explain the sustained background tropospheric BrO levels but without direct evidence (Parrella et al., ACP 12, 6723- 6740, 2012; Schmidt et al., JGR 121, 11819-11835, 2016; sorry to be pushing my own literature). The present paper offer strong support for this heterogeneous recycling. It would be a neat way to connect the Arctic spring chemistry to the global picture. Brief statements in the Abstract, intro, and conclusions is all that would take.

This is an excellent point. As suggested, we have added brief statements to the abstract (pg. 1, line 15), intro (pg. 2, line 19) and conclusions (pg. 15, line 5) discussing the implications of this finding for the tropospheric background as

suggested by the reviewer.

Specific comments: (page, line) 1. Abstract, line 9: disconnected from the surface is vague, I would point out that the plume is at 0.5-1 km altitude.

We changed this sentence to specify the plume altitude.

Abstract, lines 10-11: I dont think that the authors can claim as fact that the recycling took place on the co-located supermicron aerosol particles. They can claim evidence that it did. Its too bad that the aircraft didnt carry in situ instrumentation that would provide more correlative information including BrO reservoirs and ozone as well as aerosols. Maybe for the next campaign?

We have modified this sentence to suggest this recycling took place rather than explicitly say this took place. While the plane did carry an ozone monitor, it was unfortunately not functional for this flight. We are intending to pursue more detailed gas and aerosol chemistry measurements in the future.

Abstract, line 12: increases the spatial extent of bromine chemistry This is vague. We already know that BrO events extend for great distances horizontally. Maybe the authors mean vertical extent? That would definitely be an appropriate statement.

The mechanism allows for transport far from the source region, which extends the impacts of this halogen chemistry in both the horizontal and vertical dimension. While we already know BrO events extend for large distances horizontally, these results provide evidence for a likely process governing the BrO spatial extents observed by satellite measurements. This is now clarified in the abstract.

Abstract, line 14: must be considered in the interpretation of satellite observations Vague, how is that? I didnt see reference to this in the text.

We argue that the existence of plumes disconnected from the surface would alter the interpretation of satellite observations of enhanced LT-VCDs. We now clarify that we are referring to column observations

Page 7, line 7: give the source of the tropospheric BrO satellite data (a website can be a useful reference). How was the stratosphere removed?

We have modified the text in the methods (pg. 4, lines 15-16) to clarify the answer to these questions.

Page 11: a spectacular observation from this paper is that BrO is killed by ozone depletion at the surface but apparently not at 0.5-1 km. This led me to search through the paper for any indication of ozone data aloft but I didnt find any. Presumably there were no ozone measurements from the aircraft? That would be worth stating. No ozonesondes? Does the general ozonesonde climatology in the Arctic have information on the vertical structure of ozone depletion in the lowest 2 km?

We have added a statement (pg. 6, line 1) that no ozone measurements aloft are available for this flight. Oltmans et al. (2012) showed that ODEs can vary between hundreds of meters to 2km in thickness and the transition between completely depleted air near the surface and non depleted air aloft is typically gradual.

As an example of making figures more user-friendly, it would help if the LT-VCD data and the fraction below 200 m were expressed in units of ppb BrO.

We have modified Fig. 9 to include LT-VCD information to facilitate comparison to other figures. However, converting a LT-VCD to a mixing ratio requires one to make assumptions about the vertical distribution of BrO, which we show in this paper is quite variable. Thus, we do not feel it is appropriate to make conversions between LT-VCDs and mole fractions in the absence of detailed vertical profile information (figures other than Fig. 9).

More generally, anything you can do to cut back on the number of figures (or panels within figures) or simplify them would (I think) be appreciated by the reader.

The original figures 2 and 5 have been moved to the supplement.

We thank Anonymous Referee #2 for the constructive comments on this manuscript. Our response to points that the reviewer raises is denoted with bold text.

Section 3.1: I am not too impressed to the presentation order of Figure 4-7. The story telling in Section 3.1 begins with referral to Figures 5 and 7, followed by Figures 7 and 6 and then Figure 4. I felt uneasy while flipping pages back and forth many times until I understood the basic story. I suggest the authors to reorganize either the figure presentation order or the sentence order in Section 3.1 if at all possible.

We have reorganized the presentation order of the figures to match the referrals in the text.

Section 3.2, second paragraph: The description of the atmospheric stability on March 11 and 12 and its link to the mixing of BrO could be more specific. From the vertical gradient of potential temperatures, I can see that the lowest 200 meters of air was well mixed on March 11 and the lowest 300 meters on March 12. On March 11, however, there was a second layer between 300 and 800 meters where the air appears to have been mixed relatively well. If the authors believe that this second layer carried a significant amount of surface-sourced reactive bromine, they should say so explicitly.

Ground based measurements (Fig. 5) showed the majority of the BrO was in the lowest 200 m of the atmosphere, thus we do not believe this layer observed on the 11th carried a significant amount of surface-sourced bromine.

Section 3.3: You can make more sense of the vertical profile of BrO mixing ratios during the aircraft takeoff shown in Figure 11 by integrating over 0-2km altitudes and then comparing with the values of BrO LT-VCDs shown in Figure 9.

We modified the now Figure 9 to include LT-VCD information.

Section 3.4: It is not always clear to me what the authors mean by heterogeneous recycling, especially when they refer to the Hara et al. (2002) study at the end of the second paragraph. I normally use the term recycling when referring to conversion of gaseous halogen species into a more photolabile one, e.g., $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$. If you refer to the reaction $\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ where the bromide anion is directly provided from sea salt, I would call it a bromine explosion. I would like the authors to state this difference a little more clearly in Section 3.4. The abundance of the super-micron aerosols measured in-situ at 700-1000 meters aloft (Fig. 11) does seem to imply these particles are relatively fresh having been emitted either from open leads or snow-covered surfaces, even though I understand the reservations by the authors as discussed in detail.

Heterogeneous recycling in this context refers to heterogeneous reactions that regenerate BrO_x from HOBr and HBr that has deposited on particles. We have modified the text (pg. 12, line 21) in this section to clarify this point.

P2, L13 & L16: e.g ->e.g.

We made this change.

P2, L28-29: Add a comma between that and during.

We made this change.

P4, L12: Sihler et al. (2012) ->(Sihler et al., 2012)

We made this change.

P10, Figure 8 caption: Add the arrival date (March 13th) and time (either in UT or AKST) of the trajectories over Utqiagvik. Also, add the height (750 m) of central trajectory arrival.

We made this change.

P10, L19: daily soundings ->daily meteorological soundings

We made this change.

P12, Figure 10b (x-axis title): West Wind ->Westward Wind

We made this change.

P12, L17: Fig. 11 ->Fig. 11a

We made this change.

P12, L17: show ->shows

We made this change.

P12, L18: Fig. 11 ->Fig. 11b

We made this change.

P12, L21: Fig. 11 ->Fig. 11c

We made this change.

P13, Figure 11: Change the x-axis title BrO Molar Ratio ->BrO Mixing Ratio.

We changed this title to "BrO Mole Fraction" to match the text.

P13, L12: an initial ->a primary

We made this change.

P13, L14: Remove the comma after particles.

We made this change.

P15, the top line: or ->and

We made this change.

References

Oltmans, S. J., Johnson, B. J., and Harris, J. M.: Springtime boundary layer ozone depletion at Barrow, Alaska: Meteorological influence, year-to-year variation, and long-term change, *Journal of Geophysical Research*, 117, D00R18, doi:10.1029/2011JD016889, URL <http://doi.wiley.com/10.1029/2011JD016889>, 2012.

Observations of Bromine Monoxide Transport In the Arctic Sustained on Aerosol Particles

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Abstract. The return of sunlight in the polar spring leads to production of reactive halogen species from the surface snowpack, significantly altering the chemical composition of the Arctic near-surface atmosphere and the fate of long-range transported pollutants, including mercury. Recent work has shown the initial production of reactive bromine at the Arctic surface snowpack; however, we have limited knowledge of the vertical extent of this chemistry, as well as the lifetime and possible transport of reactive bromine aloft. Here, we present bromine monoxide (BrO) and aerosol particle measurements obtained during the March 2012 Bromine Ozone Mercury Experiment (BROMEX) near Utqiaġvik (Barrow), AK. The airborne differential optical absorption spectroscopy (DOAS) measurements provided an unprecedented level of spatial resolution, over two orders of magnitude greater than satellite observations and with vertical resolution unable to be achieved by satellite methods, for BrO in the Arctic. This novel method provided quantitative identification of a BrO plume, ~~disconnected from the surface~~ between 500 m and 1 km aloft, moving at the speed of the air mass. ~~This~~ Concurrent aerosol particle measurements suggest this lofted reactive bromine plume was transported and maintained at elevated levels through heterogeneous reactions on co-located supermicron aerosol particles, independently of surface snowpack bromine chemistry. This chemical transport mechanism ~~significantly increases the spatial extent of this~~ explains the large spatial extents often observed for reactive bromine chemistry, ~~impacting which impacts~~ atmospheric composition and pollutant fate across the Arctic region, beyond ~~the area~~ areas of initial snowpack halogen production. ~~This process must~~ The possibility of BrO enhancements disconnected from the surface potentially contributes to sustaining BrO in the free troposphere and must also be considered in the interpretation of satellite

BrO ~~observations and examined~~ column observations, particularly in the context of the rapidly changing Arctic sea ice and snowpack.

1 Introduction

With the return of sunlight in the polar spring, production of reactive halogen species radically changes the chemical processes in the Arctic atmospheric boundary layer (Simpson et al., 2007b). Bromine radical chemistry, in particular, is implicated in widespread episodic depletion of boundary layer ozone (Barrie et al., 1988; McConnell et al., 1992; Simpson et al., 2007b), and altered oxidation of atmospheric pollutants, including mercury (Schroeder et al., 1998; Steffen et al., 2008). Satellite observations have given a coarse depiction of the spatial extent of these events (e.g. Richter et al., 1998; Wagner and Platt, 1998; Sihler et al., 2012; Choi et al., 2012), showing that millions of square km are affected by this chemistry. However, many uncertainties remain regarding the initiation of this halogen chemistry and its vertical distribution, as well as the transport and sustained recycling of reactive halogens aloft (Simpson et al., 2015).

Satellite-based observations have shown large plumes (1000s of km) of BrO commonly occurring over sea ice regions in the spring (Wagner and Platt, 1998; Richter et al., 1998). While these plumes could potentially be stratospheric in origin or related to variations in tropopause height (Theys et al., 2009; Salawitch et al., 2010), a variety of tropospheric BrO retrievals (e.g. Theys et al., 2011; Sihler et al., 2012; Koo et al., 2012) (e.g. Theys et al., 2011; Sihler et al., 2012; Koo et al., 2012), which use various ~~teehniques~~ techniques to subtract the stratospheric BrO contribution and calculate a tropospheric BrO column, continue to show these large BrO plumes over the Arctic. However, during both the ARCTAS and ARCPAC campaigns, flight measurements showed enhancements in tropospheric BrO above the convective boundary layer (e.g. Salawitch et al., 2010; Choi et al., 2012), (e.g. Salawitch et al., 2010; Choi et al., 2012), potentially sustained on aerosol particles (e.g. Parrella et al., 2012; Schmidt et al., 2016), suggesting some of this BrO column may not be due to boundary layer halogen activation chemistry in sea ice regions.

Ground-based measurements also show a relationship between BrO and sea ice regions (Simpson et al., 2007a); however, the low short-term correlation between time an air mass spends in sea ice regions and the amount of BrO observed suggests while an air mass origin in sea ice regions is important, other environmental factors control the release of reactive bromine (Peterson et al., 2016). Given the short lifetime of BrO in sunlit conditions, heterogeneous reactions are required to explain the amount of reactive bromine observed in the Arctic spring (McConnell et al., 1992; Platt and Hönninger, 2003). While the snowpack provides an abundant surface for these reactions near the ground, both ground-based (Frieß et al., 2011; Peterson et al., 2015) and airborne (McElroy et al., 1999; Prados-Roman et al., 2011; Choi et al., 2012) observations have shown active halogen chemistry also occurring aloft. Concurrent observations of aerosol particle extinction and BrO by Frieß et al. (2011) showed increases in near surface BrO occurring concurrently with high wind speeds and increased aerosol extinction. They interpret this as wind-abraded snow dispersed aloft and providing additional surface area for this chemistry to occur. This process occurred concurrently with snowpack driven halogen chemistry. In contrast, Peterson et al. (2015) observed that, during the spring of 2012, aerosol particle extinction did not depend solely on wind speed, and events occurred with BrO aloft in the absence of enhancements in near-surface aerosol particle extinction. Thus, the mechanism for sustaining such halogen

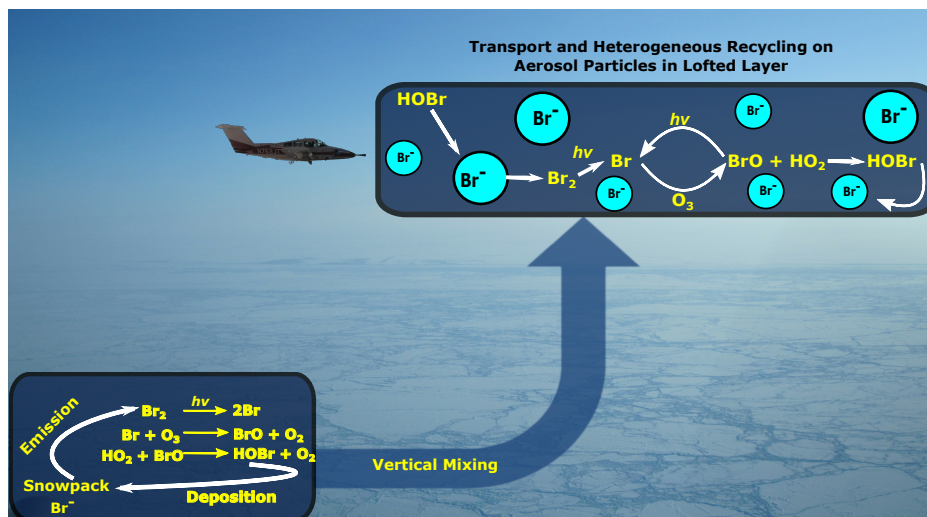


Figure 1. Overview of processes observed in this study. Bromide (Br^-) is converted to reactive bromine (e.g. Br_2 , BrO , HOBr) through heterogeneous reactions occurring in the surface snowpack leading to the release of Br_2 into the overlying atmosphere. This Br_2 undergoes photolysis, creating bromine atoms and leading to ozone depletion. As increased mixing is observed, the bromine enriched air mass moves aloft. On the day of the flight, we observed sustained BrO levels in a lofted layer concurrently with aerosol particles, indicating heterogeneous recycling of reactive bromine aloft, decoupled from the initial snowpack activation processes.

chemistry aloft, independently of the snowpack, remains an open question. While aerosol particles represent a potential surface for these reactions to take place aloft (Fan and Jacob, 1992), there is currently no observational evidence for this phenomenon occurring solely aloft, independently of concurrent snowpack driven halogen activation chemistry.

During the March 2012 BROMine Ozone Mercury EXperiment (BROMEX) near Utqiagvik (Barrow), Alaska, we investigated the activation (i.e. conversion of Br^- to reactive bromine: e.g. Br atoms, BrO , or HOBr (Fig. 1)) and subsequent transport of reactive bromine with a combination of satellite, airborne, and ground-based measurements (Nghiem et al., 2013). While the spatial extent of this reactive bromine chemistry can be characterized from satellite measurements at a spatial resolution of tens of km, the vertical distribution of BrO in the atmospheric boundary layer cannot be determined via satellite, complicating identification of the source, mechanism of initial activation, subsequent transport scales, and chemical transformation of the reactive bromine. In contrast, ground-based differential optical absorption spectroscopy (DOAS) enables determination of the amount of BrO both near the surface, and in the lowest 2 km of the atmosphere with high temporal resolution (Frieß et al., 2011; Peterson et al., 2015), while airborne DOAS measurements allow determination of spatial distribution of BrO with 100 m vertical and horizontal resolution (General et al., 2014), enabling detailed observation of moving BrO plumes. The combination of these techniques in the current study allowed observations of the evolution of the vertical and horizontal distribution of reactive bromine chemistry with an unprecedented level of detail, enabling identification of the mechanisms driving the transport of reactive bromine aloft.

2 Methods

~~Location of ground-based measurements with flight track overlaid. Locations of the Barrow MAX-DOAS instrument (BARC), the two icelanders (IL1 and IL2) as well as the location of the chemical ionization mass spectrometry measurements are shown. The location of Utqiagvik (Barrow) is shown on the inset map of Alaska with a yellow star.~~

5 2.1 DOAS Measurements

Airborne BrO measurements were made using the Purdue University Airborne Laboratory for Atmospheric Research (ALAR). The 13 March flight took off from the Utqiagvik (Barrow) airport located at 71.2853° N, 156.7658° W. ALAR carried the Heidelberg Imaging DOAS instrument (HAIDI), allowing for simultaneous measurements in both scanning nadir view and limb view (General et al., 2014). The initial DOAS fitting of the HAIDI spectra and subsequent analysis of the nadir viewing measurements have been described extensively in previous literature (Pratt et al., 2013; General et al., 2014). Limb viewing measurements allowed for retrieval of BrO and aerosol particle extinction profiles (e.g. Prados-Roman et al., 2011) during ALAR ascent and descent. After the initial DOAS fitting, the limb measurements of O₄ and BrO were used in a two step optimal estimation procedure to retrieve BrO profiles (Frieß et al., 2011). Averaging kernels, error bars, and further details of these retrievals are given in the supplemental information. Satellite based BrO lower tropospheric vertical column densities (LT-VCDs) ~~are retrieved from~~ were determined using Level 1 GOME-2 spectra data provided by EUMETSAT. The stratospheric subtraction to obtain a LT-VCD was completed using previously published techniques ~~Sihler et al. (2012)~~ (Sihler et al., 2012).

Ground based MAX-DOAS measurements were conducted at three sites during BROMEX. The instrument at Utqiagvik (Barrow) was placed on top of the Barrow Arctic Research Consortium building, located at 71.325° N, 156.668° W with a viewing azimuth of 27° east of true north. Additional MAX-DOAS instruments were deployed at two sea ice locations as part of the Icelander platform, an autonomous platform designed to be rapidly deployed via helicopter and conduct chemical and meteorological measurements at remote locations (Peterson et al., 2015). The first Icelander (IL1) was deployed east of Utqiagvik (Barrow) at 71.355° N, 155.668° W with a view azimuth of 2° east of true north, while the second Icelander (IL2) was deployed to the west at 71.274° N, 157.395° W with a view azimuth of 12° east of true north.

These MAX-DOAS data were analyzed using previously published techniques (Frieß et al., 2011; Peterson et al., 2015). Briefly, solar spectra at telescope elevation angles of 1, 2, 5, 10, and 20° were analyzed using a temporally located zenith spectra as a reference for DOAS fitting to retrieve differential slant columns (dSCDs) of BrO and O₄. These dSCDs were used to retrieve mole fractions of BrO from the surface up to 2 km with optimal estimation assuming an a priori BrO profile with 10 pmol mol⁻¹ at the surface exponentially decaying with a scale height of 250 m. The retrieved profiles represent 20 pieces of information; however, the typical degrees of freedom for signal in our retrievals ranges between 1 and 2 independent pieces of information. Thus, rather than using the retrieved profile, we report a VCD in the lowest 200 m, and if visibility permits, a LT-VCD for 0-2 km (Peterson et al., 2015).

2.2 Chemical Ionization Mass Spectrometry

Measurements of Br₂, BrO, and HOBr were conducted using chemical ionization mass spectrometry (CIMS) (Peterson et al., 2015) at a site (71.275° N, 156.6405° W) ~5 km inland and southeast of Utqiagvik (Barrow), AK. Using I(H₂O)_n⁻ reagent ions, Br₂ was monitored as I⁷⁹Br⁸¹Br⁻ (287 amu) and I⁸¹Br⁸¹Br⁻ (289 amu), BrO as I⁷⁹BrO⁻ (222 amu) and I⁸¹BrO⁻ (224 amu),
5 and HOBr as IH⁷⁹BrO⁻ (223 amu) and IH⁸¹BrO⁻ (225 amu). For 11-13 March 2012, the limit of detection for 1 h averaging is estimated at 0.4 pmol mol⁻¹ for Br₂, BrO, and HOBr, with the associated uncertainties calculated to be (14% +0.4 pmol mol⁻¹), (63% +0.4 pmol mol⁻¹), and (50% +0.4 pmol mol⁻¹), respectively. Additional sampling details are provided in the Supplementary Information.

2.3 Aerosol Particle Measurements

10 Size resolved aerosol particle number concentrations were measured with six second temporal resolution using a Grimm 1.109 optical particle counter (Grimm Aerosol Technik GmbH), which measured particles from 0.25 to 32 μm in 31 size bins. A size resolved model of inlet transmission was used to correct the measured number concentrations for expected aircraft inlet losses as a function of particle diameter. Details of this model are given in the supplement. After correcting for inlet efficiency, only particles up to 4 μm (optical diameter) were considered in further analysis. Surface area concentrations were estimated
15 assuming all measured particles were spherical with a diameter equal to the midpoint of the size bin.

2.4 Envisat ASAR Sea Ice Images

Satellite radar images were acquired by the Advanced Synthetic Aperture Radar (ASAR) aboard the European Space Agency (ESA)'s Environmental Satellite (Envisat) to support BROMEX. For the period of analysis in this paper, an Envisat ASAR scene was obtained on 11 March 2012 over the BROMEX study domain including the Chukchi Sea and the Beaufort Sea
20 (Figure 2). This ASAR scene was collected in the Wide Swath Medium-resolution mode (ASA_WSM_1P) with the horizontal polarization. ASA_WSM_1P has a geometric resolution of approximately 150 m by 150 m with a pixel spacing of 75 m by 75 m over a swath width of 400 km along a stripe of 4000 km in the maximum extent (European Space Agency, 2007). In the data processing, the precise orbits were used before calibration and terrain correction to achieve accurate backscatter with an excellent geolocation. The ASAR data allowed an excellent observation of sea ice with the all-weather capability regardless of
25 solar lighting and cloud cover conditions.

2.5 Supporting Ozone and Meteorological Measurements

Ozone mole fractions and meteorological data were obtained from the NOAA Global Monitoring Division site near Utqiagvik (Barrow), Alaska. Twice daily meteorological soundings (03:00 and 15:00 AKST) were conducted at the Utqiagvik (Barrow) Airport. The 72 h backward air mass trajectories were calculated using the NOAA Hybrid Single Particle Lagrangian Integrated
30 Trajectory (HYSPLIT) model (Stein et al., 2015). These trajectories were calculated in an ensemble configuration using an arrival heights of 750 m agl and one degree GDAS meteorology. Meteorological measurements aboard ALAR were obtained

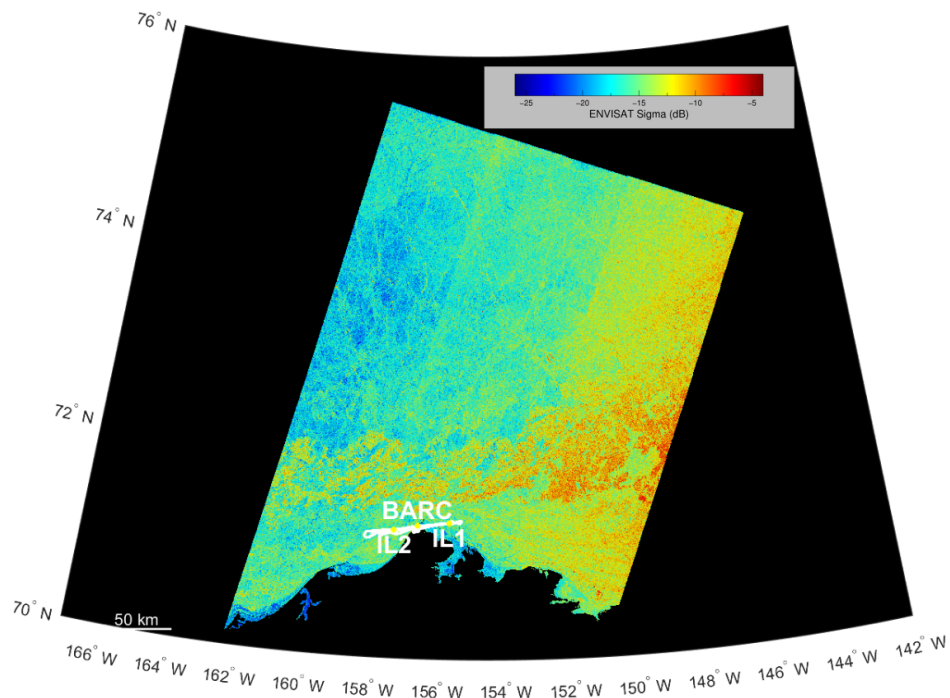


Figure 2. Sea ice imagery from Envisat Advanced Synthetic Aperture Radar (ASAR) backscatter data (Sigma in dB). Flight track and measurement locations; Barrow Arctic Research Consortium (BARC) building, Icелander 1 (IL1), and Icелander 2 (IL2) are shown. Multi-year ice is shown in darker red and first-year ice in orange to green and blue colors.

using a "Best Air Turbulence" (BAT) probe (Garman et al., 2006). [Due to an instrumental issue, airborne O₃ measurements were not available during this flight.](#)

~~Meteorological and in-situ ozone measurements from Barrow. a) Daytime soundings from the Barrow Airport. b) Near-surface ozone mixing ratios from the NOAA/GMD site. c) Wind speeds and directions from the NOAA/GMD site. On panels b and c, the rectangle indicates when the flight took place.~~

3 Results and Discussion

Here we show observations of an intense synoptic scale halogen activation event observed at Utqiaġvik (Barrow), Alaska on 11-13 March. We describe the details of this event chronologically and show the process by which snowpack Br₂ production and evolving boundary layer stability later led to the decoupled recycling of reactive bromine on aerosol particles aloft (Fig.

10 1).

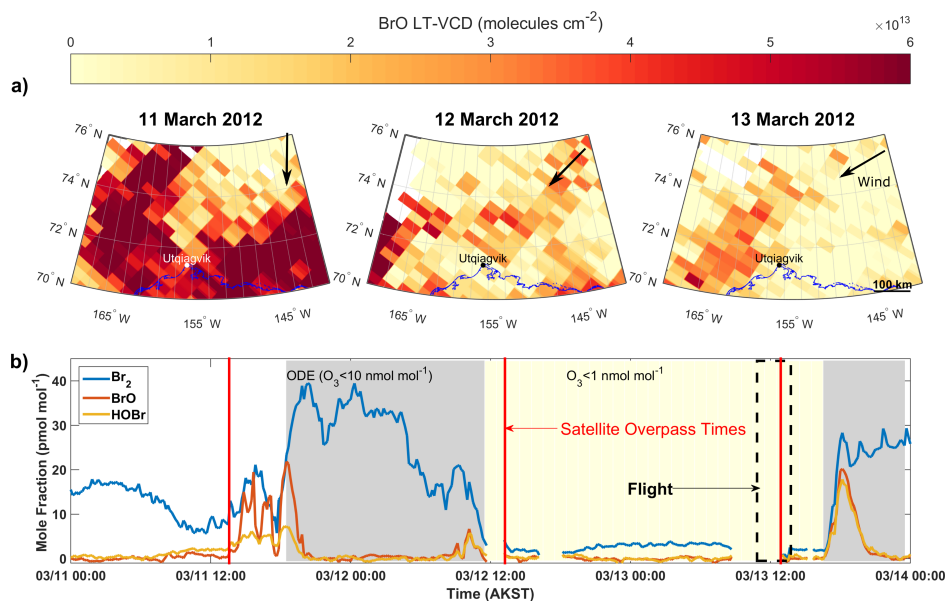


Figure 3. Pan-Arctic tropospheric Summary of a) satellite based BrO LT-VCDs on 11 March 2012 derived observations over northern Alaska and b) ground-based reactive bromine measurements at the Utqiagvik (Barrow) tundra site. a) BrO lower tropospheric vertical column densities (LT-VCD) from the GOME-2 spectra satellite are shown from 11-13 March 2012, with the location of Utqiagvik (Barrow), Alaska denoted. The top portion of the map is the Arctic Ocean, while the bottom portion is snow covered tundra. The wind direction at Utqiagvik (Barrow) is shown with black arrows. b) Gas phase bromine species (Br_2 , BrO , HOBr) mole fractions measured with chemical ionization mass spectrometry are shown for 11-13 March 2012. Data gaps represent time periods of separate experiments (Pratt et al., 2013). Times when an ODE ($\text{O}_3 < 10 \text{ nmol mol}^{-1}$) was observed at Utqiagvik (Barrow) are shaded in gray; times when ozone was titrated ($\text{O}_3 < 1 \text{ nmol mol}^{-1}$) to the point of inhibiting BrO formation are shaded in yellow. The flight time is outlined with a black box, and the times of satellite overpasses are denoted with red lines.

3.1 Initial Snowpack-Driven Bromine Activation

3.1 Initial Snowpack-Driven Bromine Activation

During BROMEX, GOME-2 satellite observations of BrO on 11 March 2012 showed an intense synoptic scale halogen activation event over the northern coast of Alaska and Canada, including Utqiagvik (Barrow), Alaska (Figs. ??, Fig. 3a). Ground-based BrO measurements at both sea ice and tundra sites near Utqiagvik (Barrow) show this event initiated near the snowpack (Figs. 3b, 4), with 30-40% of the observed BrO column in the lowest 200 m. At Utqiagvik (Barrow), winds were out of the northeast with speeds below 6 m s^{-1} (Fig. 5c) which likely enabled movement of air from the snowpack to the overlying atmosphere through wind pumping (Peterson et al., 2015), but were too low to induce blowing snow (Jones et al., 2009; Yang et al., 2010). Further evidence of snowpack sourced reactive bromine is provided by observed enhanced near-surface (1 m)

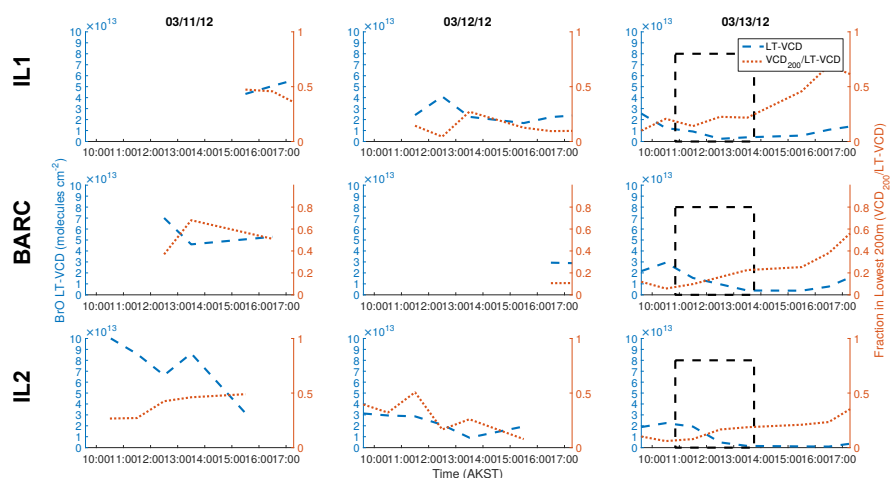


Figure 4. Summary of ground based MAX-DOAS BrO observations near Barrow, all times are local. Observations are from IL1 (top row), the BARC building (middle), and IL2 (bottom row). The blue lines show the LT-VCD measured from the ground, and the red lines show the fraction in the lowest 200 m. LT-VCDs are not shown when the degrees of freedom aloft is below 0.7, indicating reduced visibility.

mole fractions of Br_2 , BrO, and HOBr (Fig. 3). Together, these findings indicate that this event originated at the snow surface, which is consistent with a snowpack source of Br_2 (Pratt et al., 2013).

At 17:00 AKST on 11 March, near surface ozone mole fractions sharply decreased at Utqiagvik (Barrow) from 20 to 8 nmol mol^{-1} over a one hour time period (Fig. 5b). This rapid ozone loss cannot be explained solely by bromine chemistry occurring at Utqiagvik (Barrow) (Hausmann and Platt, 1994) and likely indicated the advection of a boundary layer ozone depletion event (ODE) into the study area. By 20:00 AKST ozone levels had fallen to near-zero levels (Fig. 5b), which has been shown to inhibit BrO production (Helmig et al., 2012), and is reflected in the BrO observations during this study (Fig. 3b). Inhibition of BrO formation also hindered the formation of HOBr, as shown in Fig. 3b, halting the heterogeneous recycling (Fig. 1) needed to sustain high levels of reactive bromine in the Arctic boundary layer (Fan and Jacob, 1992). The lack of recycling leads to the observed decrease in Br_2 production (Pratt et al., 2013), effectively ending snowpack production of reactive bromine (Fig. 3b). This reduction of reactive bromine near the surface is also observed via decreasing BrO column densities observed from GOME-2 on 12 and 13 March (Fig. 3a). Continuous determination of the vertical distribution of BrO by concurrent ground-based DOAS measurements showed the reduction in reactive bromine near the surface was accompanied by movement of BrO aloft on 12 March, transitioning to BrO being observed exclusively aloft on 13 March (Figs. 4, 3b, 3b, 4).

15 3.2 Movement of BrO Aloft

Given that the most probable initial source of the observed reactive bromine was the surface snowpack, as discussed above, subsequent observations of BrO aloft raise the question of how the BrO was lofted to ~ 750 m where the plume was observed. Previously proposed mechanisms for enhancing the vertical extent of BrO events include blowing snow events, where high

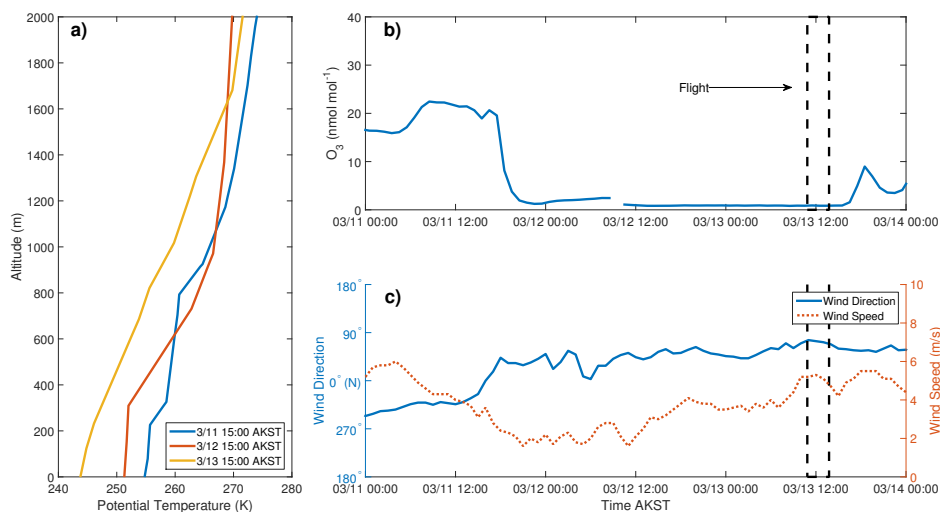


Figure 5. Summary of a) satellite-based BrO observations over northern Alaska [Meteorological](#) and b) ground-based reactive bromine [in-situ ozone](#) measurements at the [from](#) Utqiagvik (Barrow) [tundra](#) site. a) BrO lower-tropospheric-vertical column densities (LT-VCD) [Daytime soundings](#) from the GOME-2 satellite are shown from 11-13 March 2012, with the location of Utqiagvik (Barrow), Alaska denoted [Airport](#). The top portion of the map is the Arctic ocean, while the bottom portion is snow covered tundra. The wind direction at Utqiagvik (Barrow) is shown with black arrows. b) Gas phase bromine species (Br₂, BrO, HOBr) [Near-surface ozone](#) mole fractions measured with chemical ionization mass spectrometry are shown for 11-13 March 2012. Data-gaps represent time periods of separate experiments (Pratt et al., 2013). Times when an ODE was observed at Utqiagvik ([from the NOAA/GMD Barrow Observatory](#), c) are shaded in gray; times when ozone was titrated to [Wind speeds and directions](#) from the point of inhibiting BrO formation are shaded in yellow [NOAA/GMD Barrow Observatory](#). The flight time is outlined with a black box. On panels b and c, rectangles indicate when the times of satellite overpasses are denoted with red lines [flight took place](#).

wind speeds lead to activation of bromine from dispersed snow aloft (Yang et al., 2010; Jones et al., 2009; Frieß et al., 2011), wind pumping events, where increased ventilation of the snowpack in a turbulent atmosphere potentially allows the propagation of BrO aloft (Peterson et al., 2015; Toyota et al., 2014), uplifting of bromine enriched air masses due to synoptic scale meteorological conditions (Frieß et al., 2004; Begoin et al., 2010), and the opening of sea ice leads which are associated with enhanced vertical mixing (Wagner et al., 2007; Moore et al., 2014) and have been proposed to lead to increases in BrO aloft (McElroy et al., 1999).

Backward air mass trajectories (Fig. 6) also suggest the observed lofted bromine originated near the snowpack in sea ice regions as part of the large scale activation event observed on 11 March. These trajectories, along with NCEP reanalysis data (Figs. 6, S4) from 11 March are also consistent with the BrO plume being uplifted from the surface prior to arriving over Utqiagvik (Barrow) on 13 March. Sea ice imagery (Fig. 2) shows no indication of open sea ice leads near or upwind of Utqiagvik (Barrow), ruling out local sea ice dynamics as an explanation for the presence of BrO aloft observed in this study. The vertical distribution of BrO is closely tied to atmospheric stability, with shallow layers associated with thermal inversions, where most of the BrO is in the lowest 200 m, compared to well mixed atmospheres, which allow for propagation of BrO

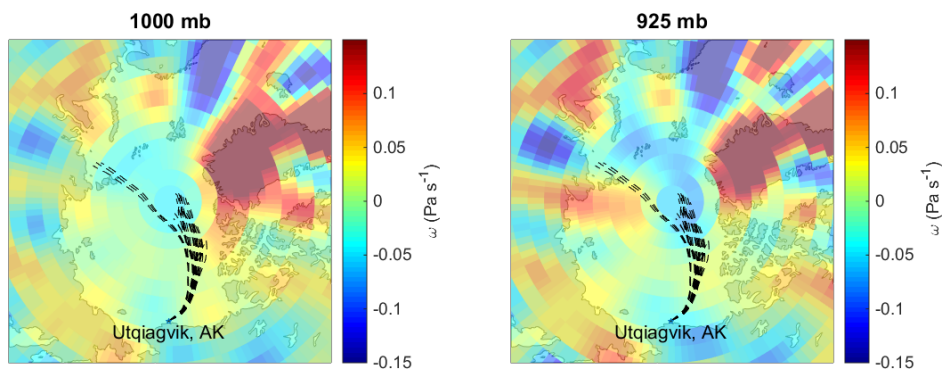


Figure 6. NOAA generated HYSPLIT backward air mass trajectories for the plume overlaid on daily averaged NCEP reanalysis data for 11 March 2012. All panels show an ensemble of ~~27~~ twenty seven 72 h trajectories arriving at Utqiagvik on 13 March 2012 at noon local time. The central trajectory had an arrival height of 750 m. The ensemble is generated by offsetting the modeled meteorology used to calculate the trajectory by 1° horizontally and ~ 250 m vertically prior to running HYSPLIT. The blue regions on the map reflect regions where air was moving upward, while red regions reflect regions where air was moving downward.

aloft leading to a lower fraction of the observed BrO residing near the surface snowpack (Peterson et al., 2015). Despite the absence of leads, daily meteorological soundings (Fig. 5a) from 11 and 12 March (15:00 AKST) at the Utqiagvik (Barrow) airport show increased atmospheric mixing allowing BrO to propagate aloft prior to the day of the flight, as seen with the ground-based MAX-DOAS measurements (Fig. 4). On 13 March, the potential temperature profile at flight takeoff showed inhibited atmospheric mixing due to a surface based inversion (Fig. 8), decoupling the chemistry occurring in the plume aloft from the snowpack.

3.3 Observed Transport of Reactive Bromine Aloft

On 13 March, individual satellite overpasses (Fig. 7a) showed a tropospheric BrO plume linked to the event described above moving to the west over Utqiagvik (Barrow). Concurrently, airborne measurements probed both the vertical profile and horizontal distribution of this BrO plume from 10:53 to 13:33 AKST. Figure 9 shows when the aircraft took off from Utqiagvik (Barrow), BrO mole fractions were near-zero at the surface increasing to 15-20 pmol mol⁻¹ between 500 m and 1 km aloft, indicating that the BrO observed by the satellite during the flight corresponded to a lofted reactive bromine plume. Ground-based MAX-DOAS measurements at Utqiagvik (Barrow) and two sea ice sites in a linear array spanning ~ 60 km also confirmed the observed BrO remained aloft as the plume moved westward over the course of the flight (Fig. 7c). Similarly, near-surface measurements of Br₂, HOBr, and BrO (Fig. 3b) confirmed that little active halogen chemistry was occurring above the snowpack surface on 13 March, and that any BrO observed during the flight time period was solely due to bromine activation chemistry occurring aloft.

Airborne transects (Fig. ~~???~~ 7) enabled detailed characterization of the lofted BrO plume as it moved west. The largest observed BrO lower tropospheric vertical column density (LT-VCD, within the lowest ~ 2 km) during each airborne transect

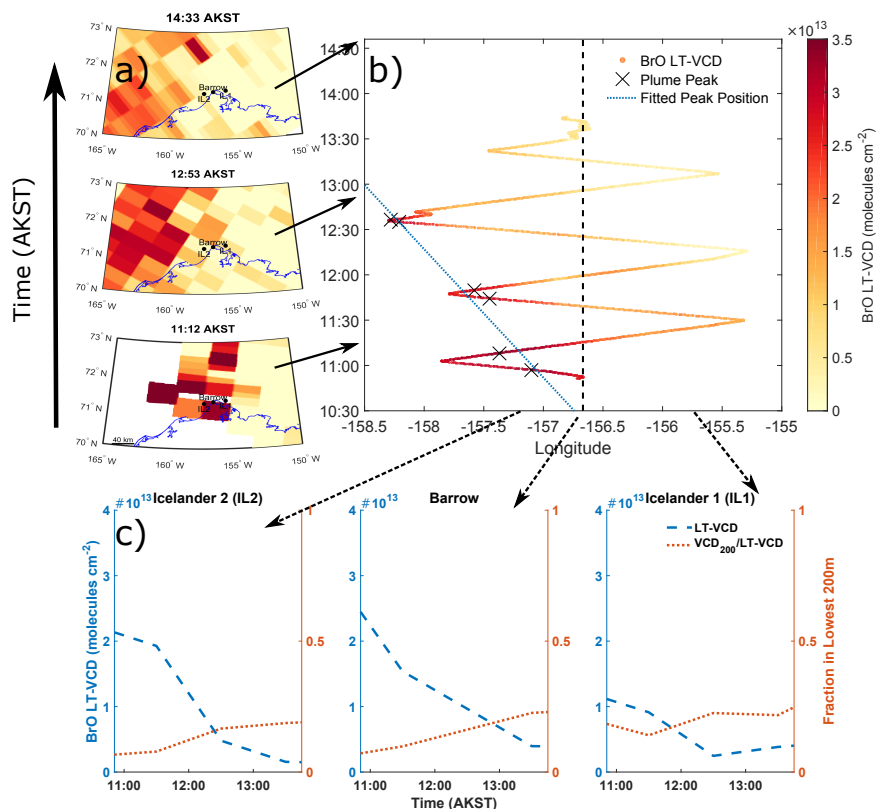


Figure 7. Summary of BrO plume motion over Utqiagvik (Barrow) on 13 March. a) BrO plume motion from east to west as observed by individual overpasses of the GOME-2 satellite as well as the locations of ground-based measurement sites. The blue line denotes the Alaska coastline. b) BrO plume motion as observed by airborne DOAS. The dashed black line indicates the longitude of Utqiagvik (Barrow). The black crosses show the observed peak BrO positions for each transect, while the blue line gives the fitted plume peak location as a function of time. c) Ground-based MAX-DOAS measurements at each site during the flight arranged from west to east.

ranged from 2.8 to 3.3×10^{13} molecules cm^{-2} (Fig. 7b). A linear fit of the plume peak position versus flight time (Fig 7b) for the six plume transects ($R=0.97$) showed the BrO plume was moving westward with a velocity of 7 m s^{-1} , consistent with measured wind speeds of 6 - 10.5 m s^{-1} to the west at altitudes of 500 m to 1 km during initial flight ascent (Fig. 8). The plume moving with the wind indicates these observations reflect transport of a reactive bromine feature, rather than the plane flying over areas with variable amounts of recycling or primary bromine emission from the snowpack. The vertical profile of BrO obtained just prior to the end of the flight (Fig. 9) showed that the BrO plume was no longer present above Utqiagvik (Barrow), consistent with ground-based and satellite observations (Figs. 7a,c).

~~Vertical profiles of BrO mole fractions, aerosol particle extinction, and supermicron (1 - $4 \mu\text{m}$ optical diameter) aerosol particle surface area concentrations during takeoff and landing on the 13 March 2012 flight. Error bars on the remote sensing measurements have been omitted for clarity and are shown in the supplemental information.~~

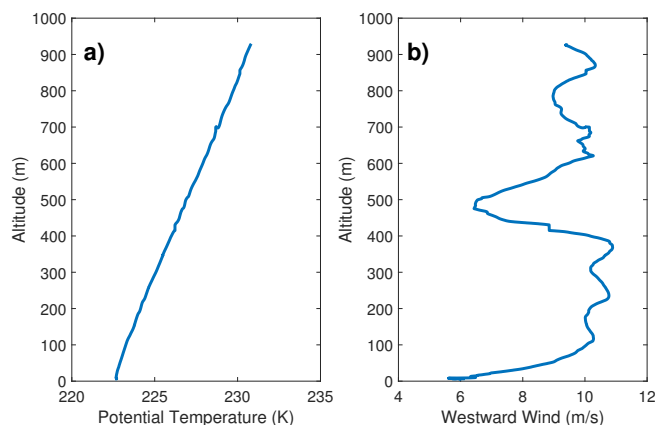


Figure 8. Potential temperature (a) and east-west component of wind speed profiles (b) from the BAT probe during aircraft ascent on 13 March 2012 at 10:53 AKST.

3.4 Role of Aerosol Particles

During plume transport, the peak BrO LT-VCD observed during each transect did not decay during the flight, indicating sustained BrO levels of $\sim 20 \text{ pmol mol}^{-1}$ (Fig. 9a). Examination of aerosol particle extinction vertical profiles ~~show~~ shows the beginning of the flight was marked by a lofted aerosol layer at the altitude of the BrO plume (Fig. 9b) over Utqiagvik (Barrow). Like the BrO plume, this lofted aerosol layer was not observed over Utqiagvik (Barrow) at the end of the flight. The enhanced aerosol particle extinction aloft is consistent with observed enhancements in supermicron ($> 1 \mu\text{m}$) aerosol surface area concentrations at 800-900 m (Fig. 9c). During the two transects of the plume conducted in the altitude range where the plume was observed, in situ aerosol particle measurements within the plume showed peaks in supermicron aerosol particle surface area concentrations occurring concurrently with peaks in BrO. For the first transect, both measurements peaked at a longitude of 157.10°W . For the second transect, the BrO peaked at a longitude of 157.31°W , with supermicron aerosol particle surface area peaking at a longitude of 157.36°W , showing the aerosol particle plume and BrO plume were moving together with the wind.

Over the course of this flight, submicron ($0.25\text{-}1.0 \mu\text{m}$) aerosol particle number concentrations had a median value of 26.5 cm^{-3} with a standard deviation of 16.8 cm^{-3} . At altitudes where the plume was observed, the variations of submicron aerosol particle number concentrations within and outside the plume were not significantly different at the 95% confidence level (Smirnov, 1939). Supermicron ($>1.0 \mu\text{m}$) aerosol particle number concentrations had a median value of 1.2 cm^{-3} with a standard deviation of 6.3 cm^{-3} . In contrast to the submicron aerosol, the variability of supermicron aerosol particle number concentrations within and outside the plume were significantly different at the 95% confidence level (Smirnov, 1939), with increasing supermicron aerosol surface area observed with increasing BrO LT-VCDs (Fig. 10). This finding indicates it is unlikely that variations in submicron aerosol particles were ~~an initial a primary~~ controlling factor in the heterogeneous recycling of reactive bromine on particles aloft. However, within the BrO plume, it is likely bromide propagated, through multiphase

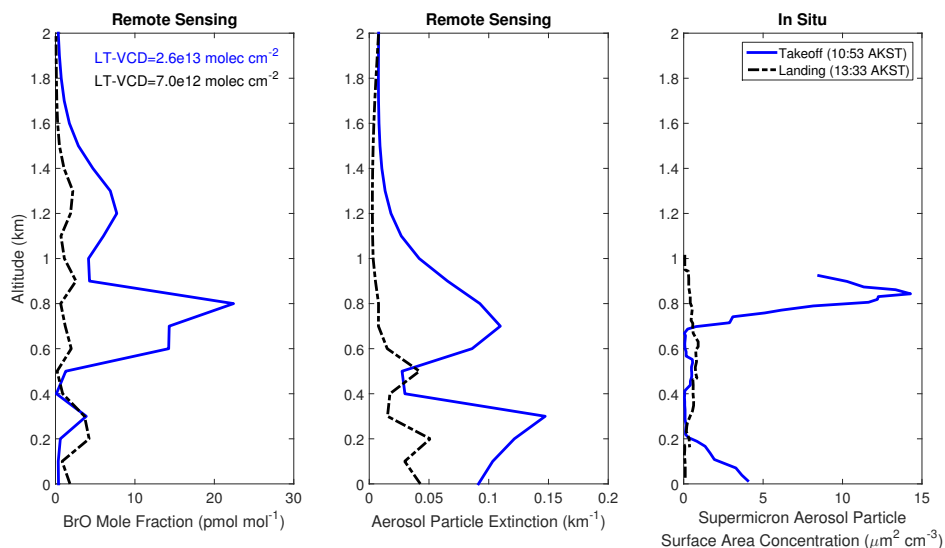


Figure 9. Vertical profiles of BrO mole fractions with the corresponding LT-VCD, aerosol particle extinction, and supermicron (1-4 μm optical diameter) aerosol particle surface area concentrations during takeoff and landing on the 13 March 2012 flight. Error bars on the remote sensing measurements have been omitted for clarity and are shown in the supplemental information.

reactions and subsequent gas-particle partitioning, from supermicron aerosol particles to submicron aerosol particles (Hara et al., 2002) such that these particles may also have provided additional bromide-enriched surface area for heterogeneous recycling.

Previous studies have shown the majority of supermicron particles in the springtime Arctic boundary layer are sea salt aerosol particles (Brock et al., 2011), which have the potential to be a source of reactive bromine (Fan and Jacob, 1992; Hara et al., 2002). Calculations of the reaction rate of HOBr with bromide based on the measured aerosol particle surface area concentrations and detailed in the supplemental information, suggest the observed surface areas are likely sufficient to enable heterogeneous recycling of reactive bromine aloft. Recent literature (e.g. Yang et al., 2010; Jones et al., 2009) has suggested that wind dispersed saline snow during high wind events could be an important source of bromide-containing aerosol particles. However, Peterson et al. (2015) showed that near surface aerosol particle extinction is not dependent on near surface wind speed at Utqiagvik and that episodes of enhanced particle extinction and BrO occur most often at lower wind speeds than typically cited as needed for blowing snow (Jones et al., 2009). Recent work by May et al. (2016) showed enhancements in supermicron sea salt aerosol particle number concentrations at Utqiagvik when wind speeds were greater than 4 m s^{-1} in the presence of open water or sea ice leads; these enhancements were not observed for closed ice conditions. While sea ice imagery (Fig. 2) shows no local lead activity, the lack of available sea ice imagery closer to the origin of the lofted layer (Fig.6) means we can not rule out the possibility of open leads and associated sea salt aerosol production where the observed lofted plume initiated. Given these limitations, we are unable to distinguish between a blowing snow source from consolidated sea ice and sea salt aerosol production from open leads as the source of the sea salt aerosol particles sustaining the BrO plume.

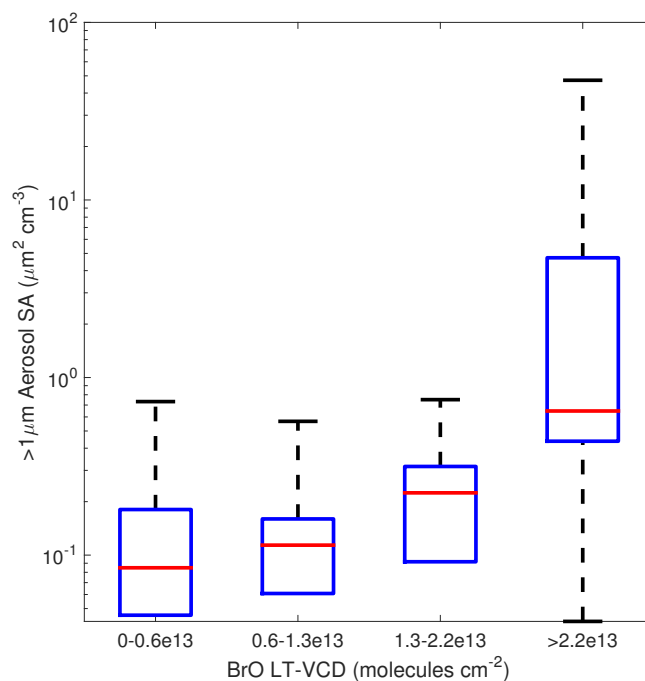


Figure 10. Box and whisker plot of supermicron particle surface area concentrations as a function of BrO LT-VCD. The red line represents the median, the blue box outlines the inner quartiles, and the whiskers represent the outer quartiles. In some cases, the difference between the lowest aerosol observation and the 25th percentile is too small to draw a lower whisker. These aerosol observations are restricted to altitudes where the plume was observed on takeoff and binned by dividing the BrO observations into quartiles.

These coincident observations of an aerosol layer and BrO recycling aloft suggest heterogeneous reactions on these aerosol particles played a key role in sustaining the observed enhanced levels of BrO aloft. Although this mechanism was previously proposed (McConnell et al., 1992; Fan and Jacob, 1992), our measurements constitute the first direct observation of this process occurring aloft, decoupled from the snowpack.

5 4 Conclusions

The Arctic is currently undergoing rapid changes, including loss of perennial sea ice (Maslanik et al., 2011) and decreasing snow depth in sea ice regions (Blanchard-Wrigglesworth et al., 2015), which impact atmospheric composition through multiphase halogen chemistry (Simpson et al., 2007b). During BROMEX, the horizontal and vertical distribution of reactive bromine, in the form of BrO, was quantified by airborne DOAS at unprecedented spatial resolution, over two orders of magnitude higher than satellite-based measurements. While a pan-Arctic scale view of BrO can be obtained from satellites, this three-dimensional view of the BrO spatial extent, obtained for the first time in the Arctic, combined with higher temporal resolution compared to satellites, provided a process-level view of bromine activation. As summarized in Fig. 1, a synoptic scale BrO event was observed together with snowpack bromine activation, releasing reactive bromine into the Arctic boundary

layer. Evolving boundary layer stability allowed the reactive bromine to propagate aloft where it underwent sustained transport enabled by recycling on aerosol particles independently of snowpack driven halogen activation. The observation of aerosol recycling of reactive bromine enabling the transport of a lofted BrO plume provides a mechanism by which active halogen chemistry alters the fate and transport of atmospheric pollutants far beyond the immediate area where snowpack sourced halogen activation occurs. This [mechanism also provides a means of sustaining bromine chemistry in the free troposphere, potentially explaining previous observations of BrO in the Arctic free troposphere \(e.g. Salawitch et al., 2010; Choi et al., 2012\)](#). This chemical transport mechanism is likely prevalent throughout the springtime Arctic, and the identification of this phenomenon improves our ability to evaluate changes in atmospheric composition related to rapidly changing Arctic sea ice.

5 Data availability

10 Data from the BROMEX field campaign are accessible at: <https://nex.nasa.gov/nex/projects/1388/> and/or by contacting the corresponding author.

Author contributions. P.K.P. and K.A.P. led data integration, analysis, and interpretation. P.K.P. prepared the initial version of the manuscript and figures. P.K.P. and W.R.S. conducted the ground-based BrO measurements with assistance from U.F., J.Z., and U.P. P.B.S., D.P., S.G., J.Z., K.A.P. and B.H.S. conducted the aircraft-based measurements. H.S. and T.W. provided the satellite based BrO measurements. S.V.N. provided the sea ice measurements. K.A.P. and P.B.S. conducted the measurements using chemical ionization mass spectrometry. K.A.P., P.K.P., S.D., and J.D.F. contributed to the aerosol data collection and analysis. D.R.C. contributed to the analysis of aircraft based meteorological measurements. S.V.N. led the 2012 field campaign along with P.B.S. and W.R.S. All authors reviewed and commented on the paper.

Competing interests. The authors declare that they have no competing financial interests.

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