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► **To cite this version:**

W. R. Simpson, U. Friess, Jennie L. Thomas, J. Lampel, U. Platt. Polar nighttime chemistry produces intense reactive bromine events. *Geophysical Research Letters*, 2018, 45 (18), pp.9987-9994. 10.1029/2018GL079444 . insu-01877525

HAL Id: insu-01877525

<https://insu.hal.science/insu-01877525>

Submitted on 3 Sep 2020

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Geophysical Research Letters

RESEARCH LETTER

10.1029/2018GL079444

Key Points:

- At polar sunrise, we observe a surface mixing ratio of 90-pmol/mol BrO, nearly doubling the prior peak observed in the Arctic
- Air that experienced little prior sunlight produced high BrO concentrations, consistent with a nocturnal source of photolabile precursors

Supporting Information:

- Supporting Information S1

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Citation:

Simpson, W. R., Frieß, U., Thomas, J. L., Lampel, J., & Platt, U. (2018). Polar nighttime chemistry produces intense reactive bromine events. *Geophysical Research Letters*, 45, 9987–9994. <https://doi.org/10.1029/2018GL079444>

Received 2 JUL 2018

Accepted 2 SEP 2018

Accepted article online 10 SEP 2018

Published online 23 SEP 2018

Polar Nighttime Chemistry Produces Intense Reactive Bromine Events

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Abstract By examining the origin of airmasses that arrive at Utqiagvik (formerly Barrow), Alaska, soon after polar sunrise (late January/early February), we identified periods when air arriving at Utqiagvik had previously resided primarily at higher latitudes in near total darkness. Upon illumination, these airmasses produced high concentrations of reactive bromine, which was detected by differential optical absorption spectroscopy as bromine monoxide (BrO). These observations are consistent with nighttime production of a photolabile reactive bromine precursor (e.g., Br₂ or BrCl). A large polar night source of photolabile reactive bromine precursors would contribute seed reactive bromine to daytime reactive bromine events and could export reactive halogens to lower latitudes and the free troposphere.

Plain Language Summary During the spring in the polar regions, unique halogen oxidizers dominate atmospheric chemistry, altering the fate of pollutants such as mercury. The sources of these oxidizers are not well understood, particularly during polar sunrise. Here we report the largest concentration ever detected of one of these species, bromine monoxide (BrO). We find these high concentrations occur when airmasses come out of the polar night, indicating a nocturnal source. Nocturnal production of reactive halogens could act as a *seed* source for subsequent reactive halogen photochemistry and could export reactive halogens from the polar night all winter.

1. Introduction

Polar springtime reactive halogen events (first reported by Tuckermann et al., 1997) and their impact on ozone depletion (first reported by Barrie et al., 1988) and mercury deposition (first reported by Schroeder et al., 1998) have been known for decades. Satellite observations show that reactive bromine is present in both the Arctic and Antarctic sea ice regions (Chance, 1998; Richter et al., 1998; Wagner & Platt, 1998). However, the mechanism of production and maintenance of high levels of reactive halogens, initiators of these events, and their environmental controls are still elusive (Abbatt et al., 2012; Simpson et al., 2015). A number of field campaigns (Frieß et al., 2011; Peterson et al., 2015; Pöhler et al., 2010; Pratt et al., 2013; Simpson et al., 2017) have been carried out to investigate this phenomenon, but few of those studies covered the full halogen activation season. The Canadian Polar Sunrise Experiments and the ALERT2000 field campaigns were exceptions, observing before and after polar sunrise, which is the time when the sun rises above the horizon for the first time since the prior fall. A key finding from ALERT2000 was that Br₂ and BrCl were produced in high concentrations right at the time of polar sunrise (Foster et al., 2001), potentially pointing to a nocturnal source of photolabile halogen species. More recently, studies using autonomous instrumentation and/or long-term monitoring sites have expanded our knowledge of reactive halogen events outside of the traditional peak months of March and April (Burd et al., 2017; Peterson et al., 2015, 2016). Specifically with respect to polar sunrise, Stohl (2006) showed that wintertime polar airmasses can remain for days to weeks in total darkness before being exposed to sunlight, which typically occurs by transport to lower latitudes. Therefore, we measured atmospheric BrO in late January/early February from 2013 to 2018 to quantify reactive bromine levels and couple those measurements with transport modeling to characterize air mass histories prior to sampling.

2. Methods

We calculated 3-day back trajectories using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT; Stein et al., 2015) and 1° resolution Global Data Assimilation System meteorology that arrive 50 m above sea

level at the Barrow Arctic Research Center (BARC) building (71.3°N 156°W) near Utqiagvik, Alaska, USA, for every hour in late January/February. At each hourly location along this trajectory, we calculated the local solar zenith angle that the parcel would have experienced. Because reactive bromine is produced by photolysis of precursors such as molecular bromine (Br_2), we calculated the photolysis rate coefficient for molecular bromine $J(\text{Br}_2)$ using a clear-sky parameterization that is a function of solar zenith angle (Madronich, 2017; Simpson et al., 2002; see supporting information). The product of $J(\text{Br}_2)$ times the duration of that time step (hour) is a unitless number describing the average number of photolytic exposures a Br_2 molecule would have experienced. We summed the photolysis over the 3-day duration to give a trajectory-integrated *clear-sky photoexposure* for that airmass at the arrival hour.

HYSPLIT calculations were used for routine hourly calculation of photoexposure throughout this period because they are rapid; however, HYSPLIT does not model the dispersion and mixing of airmasses. Therefore, we also use the FLEXible PARTicle dispersion model (FLEXPART) version 9.02 (Stohl et al., 1998, 2005; Stohl & Thomson, 1999) to study the potential emission source regions influencing measurements at Utqiagvik on specific dates of interest. For this application, FLEXPART is run in backward mode for specific days of interest with particles released at the surface from Utqiagvik (0–20 m above ground level) during a 1-hr period at local noon (release from 20:30 to 21:30 UTC, 11:30 to 12:30 AKST). We release 100,000 particles and follow them back for 10 days to have an airmass history. To drive the FLEXPART model we use the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalysis meteorology on a $0.75^\circ \times 0.75^\circ$ global grid (60 vertical levels) every 6 hr (00:00, 06:00, 12:00, and 18:00 UTC). We use the plume centroid locations to calculate the photochemical exposure analogous to the HYSPLIT method described above. We construct total column (0–20 km) and surface (0–200 m) potential emissions sensitivities (PESs) for 10 days. The total column PES indicates the region the air resided for the 10 days prior to arriving at Utqiagvik. The surface (0–200 m) PES indicates where air was in contact with the surface and potentially sensitive to surface emissions.

Bromine monoxide was detected by multiple axis differential optical absorption spectroscopy (MAX-DOAS) using an instrument on the roof of the BARC building via methods described previously (Frieß et al., 2011; Peterson et al., 2015; Simpson et al., 2017). Surface ozone was measured at the NOAA Earth Systems Research Laboratory Global Monitoring Division site near BARC (McClure-Begley et al., 2014).

3. Results

MAX-DOAS detects BrO by measuring scattered sunlight, so observations can only begin after polar sunrise at BARC, which happens around 22 January. Therefore, we looked for the first date of each year after polar sunrise at BARC when airmasses came southward toward BARC from the region of polar night. As the season progresses into February, the region of total polar night moves northward, and around the second week of February, the region of polar night has moved more than 500 km north of Utqiagvik, which is sufficiently far that transport from polar night to BARC is unlikely to occur in fewer than 24 hr. Therefore, only in the period from late January to mid-February is it possible to observe BrO in airmasses with low prior photoexposure. We identified the first date of arrival of minimum photoexposure (polar night) airmasses for each year from 2013 to 2018, which are shown in Table 1.

We find that on each of these polar night airmass arrival dates, high amounts of BrO were detected in the atmosphere. The peak BrO differential slant column density (dSCD) detected at 1° elevation viewing angle compared to the zenith view on that date is listed in Table 1. For comparison, note that five of these six events exceed the 90th percentile daily maximum BrO 1° dSCD from March–May 2012 to 2016, and the 2017 event is the largest ever observed at Utqiagvik. Figure 1 shows DOAS spectral fits for a composite of all daytime spectra observed on that date and shows BrO absorption that matches a laboratory-measured BrO reference spectrum, conclusively showing high levels of BrO. We additionally used the HeiPro optimal estimation method (Frieß et al., 2011; Peterson et al., 2015; Simpson et al., 2017) to model BrO lower tropospheric vertical column density (LT-VCD) and 0- to 200-m mixing ratio (MR), the results of which are shown in Table 1 and in supporting information Figure S3. The magnitude of these reactive bromine events are high compared to past observations (Morin et al., 2005; Peterson et al., 2015; Simpson et al., 2007), and 90 pmol/mol is double the prior highest observed surface MR (Pöhler et al., 2010). Although it has been noted that MAX-DOAS observations of surface MR can be systematically high during aerosol particle-rich or cloudy conditions (Frieß et al.,

Table 1
Arrival Dates of First Polar Night Airmasses With Peak BrO dSCD, LT-VCD, and MR and Photoexposures Prior to Arrival Day

Date (AKST)	BrO 1° dSCD (molecules per square centimeter)	BrO LT-VCD (molecules per square centimeter)	BrO 0- to 200-m MR (pmol/mol)	Prior photoexposure
1 Feb 2013	9×10^{14}	5×10^{13}	48	~10
7 Feb 2014	7×10^{14}	4×10^{13}	35	~5
3 Feb 2015	3×10^{14}	3×10^{13}	20	~20
6 Feb 2016	5×10^{14}	4×10^{13}	32	~20
9 Feb 2017	17×10^{14}	13×10^{13}	90	~20
30 Jan 2018	10×10^{14}	N/A	55	~10

Note. dSCD = differential slant column density; LT-VCD = lower tropospheric vertical column density; MR = mixing ratio.

2011), five of these six dates were low-aerosol cases with typical aerosol optical depth < 0.2 (supporting information Figure S3).

Figure 2 shows a FLEXPART simulation for particles arriving at BARC on 9 February 2017 and demonstrates that this airmass transported south from higher latitudes, where it was still polar night, before arriving at Utqiagvik. The shaded area shows the location of total polar night at the midpoint during the 10 days of the FLEXPART run, 4 February 2017. A great deal of the potential emission sensitivity of this simulation lies within this region of polar night, particularly the Arctic Ocean and adjacent Russian coastal areas, demonstrating that the air arriving at BARC had large influences from air that spent up to 10 days in polar night.

To examine the relationship between reactive halogen (BrO) events and prior airmass exposure to light, Figure 3 shows these quantities in the period 1–20 February 2017. The years 2013–2016 and 2018 are shown as supplemental figures. Top panel in Figure 3 shows that the minimum of the clear-sky photoexposure occurs on 9 February 2017 (AKST), with the airmass experiencing about 20 photoexposures on the prior part of the trajectory and that the airmass had been in near total darkness.

Figure 3 lower panel shows that BrO is highly elevated on this date, with a peak 1° dSCD of about 17×10^{14} molecules per square centimeter. Other BrO events occur after this first event, as is common during springtime, but those airmasses had been exposed to significantly more sun light (photoexposure) before their arrival at BARC, so they could have had BrO produced by typical springtime photochemistry as is common in March–May in the Arctic (e.g., Frieß et al., 2011; Hönninger & Platt, 2002; Peterson et al., 2016; Pöhler et al., 2010). The first event of the season, however, experienced only about 20 calculated clear-sky photoexposures before arrival at BARC, so somehow produced large amounts of BrO with relatively little prior photochemistry. Examining the other cases of first arrival of a polar night airmass in the years 2013–2016 and 2018

summarized in Table 1 and shown in supporting information Figures S5–S9, we see that the first event of the year commonly occurs with very low (< 20 clear-sky photoexposures) prior exposure to photolysis and is associated with high BrO abundance (Table 1). MAX-DOAS analysis also shows that NO_2 is low (within error of 0) on these dates, assuring that we are not sampling local pollution from Utqiagvik.

Late January/February ozone observations (supporting information Figure S10) were typically at background levels (30–40 nmol/mol) in the early part of the month and ozone depletion events ($\text{O}_3 < 20$ nmol/mol) do not typically occur until the last week of February, indicating that photochemistry is weak at the time of these late January/early February large BrO events. Specifically, the polar night airmass arrival dates (Table 1) showed non-depleted ozone levels (25–37 nmol/mol) at sunrise (see supporting information Figure S3) and ozone decay rates between 0 and ~ 4 nmol·mol⁻¹·hr⁻¹. The largest ozone loss rate occurred on 9 February 2017, the date of highest surface BrO MR. The non-depleted ozone levels on these dates indicates that the airmasses had not been highly processed by reactive halogen chemistry prior to arrival at Utqiagvik and are consistent with the airmasses being in the dark before arrival.

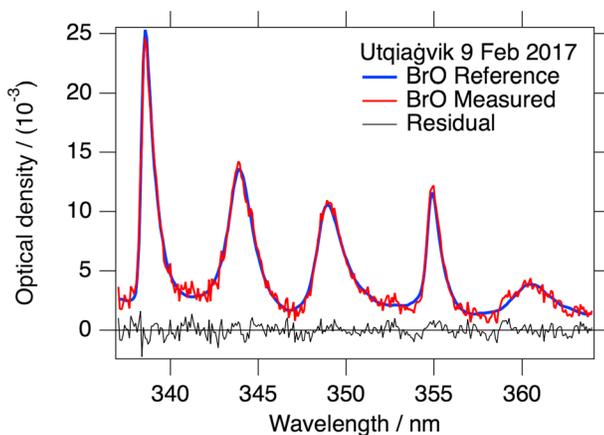


Figure 1. Spectral confirmation of BrO on 9 February 2017 using a composite of all daytime spectra. The BrO differential slant column density is 1.47×10^{15} molecules per square centimeter. See supporting information Figure S4 for fits to other gases.

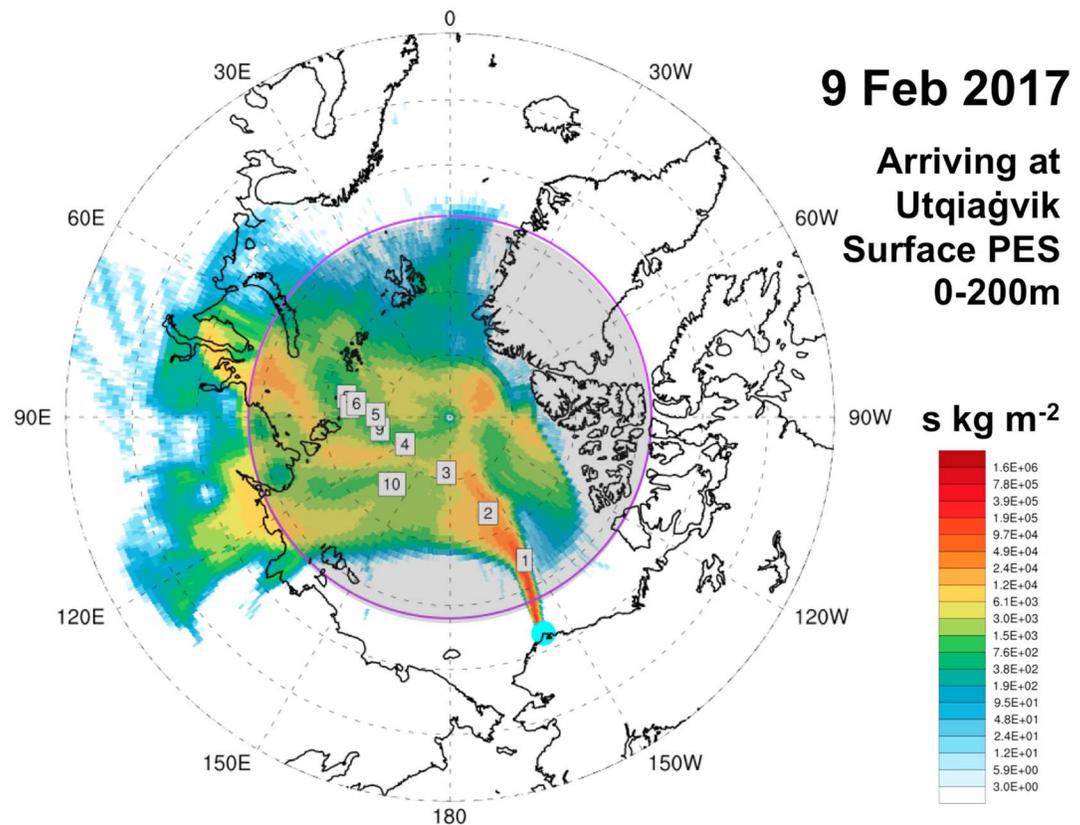


Figure 2. Ten-day surface potential emission sensitivity (PES) for particles arriving at Utqiagvik (BARC, light blue circle) at 12:00 on 9 February 2017 (AKST). The boxed numbers on the map show the position of the plume centroid location in days before the arrival at Utqiagvik. Within the shaded region, the sun has not yet risen at the midpoint of this calculation, 4 February 2017 ($>74^\circ\text{N}$).

To consider the degree to which these airmasses resided in the dark, we used the 10-day FLEXPART simulations to calculate photoexposure on longer timescales, where dispersion of the airmass will become more important. Figure 2 shows that the plume center remained for 10 days within the region of total polar night and that a large amount of the surface potential emission sensitivity was also within this circle of darkness. In the supporting information, Figure S11, we calculated integrated photoexposure for the peak BrO day on each year. We find that the exposure is between 4 days (2014) and >10 days (2013 and 2017) for <30 integrated Br₂ photoexposures. The lack of exposure to sunlight on this timescale is also visible in supporting information Figures S12 and S13, which show the FLEXPART simulations for each year.

4. Discussion

Reactions of nocturnal nitrogen oxides (e.g., N₂O₅) with NaBr (sea salt bromide) that produce photolabile bromine precursors (BrNO₂) have been studied and their atmospheric importance has been considered (Finlayson-Pitts et al., 1990). Similar reactions of N₂O₅ with chloride-containing particles that produce photolabile nitryl chloride have been definitively observed in the field through mass spectroscopy (Osthoff et al., 2008; Thornton et al., 2010), providing further evidence that nitrogen oxides can activate halogens through dark reactions (reactions not involving photolysis). Our MAX-DOAS observations episodically identified local NO_x pollution (coming from Utqiagvik, which lies 5 km southwest of BARC) at the $>1\text{-nmol/mol}$ level, but these specific dates of polar night airmass arrival are below NO_x detection limits (estimated to be $\sim 200\text{ pmol/mol}$), consistent with the airmasses arriving from the polar ice cap. However, below detection levels of NO_x, potentially from local pollution or produced by snowpack photochemistry before the airmass entered polar night (Honrath et al., 2002; Jones et al., 2001) or past exposure of these airmasses to NO_x could

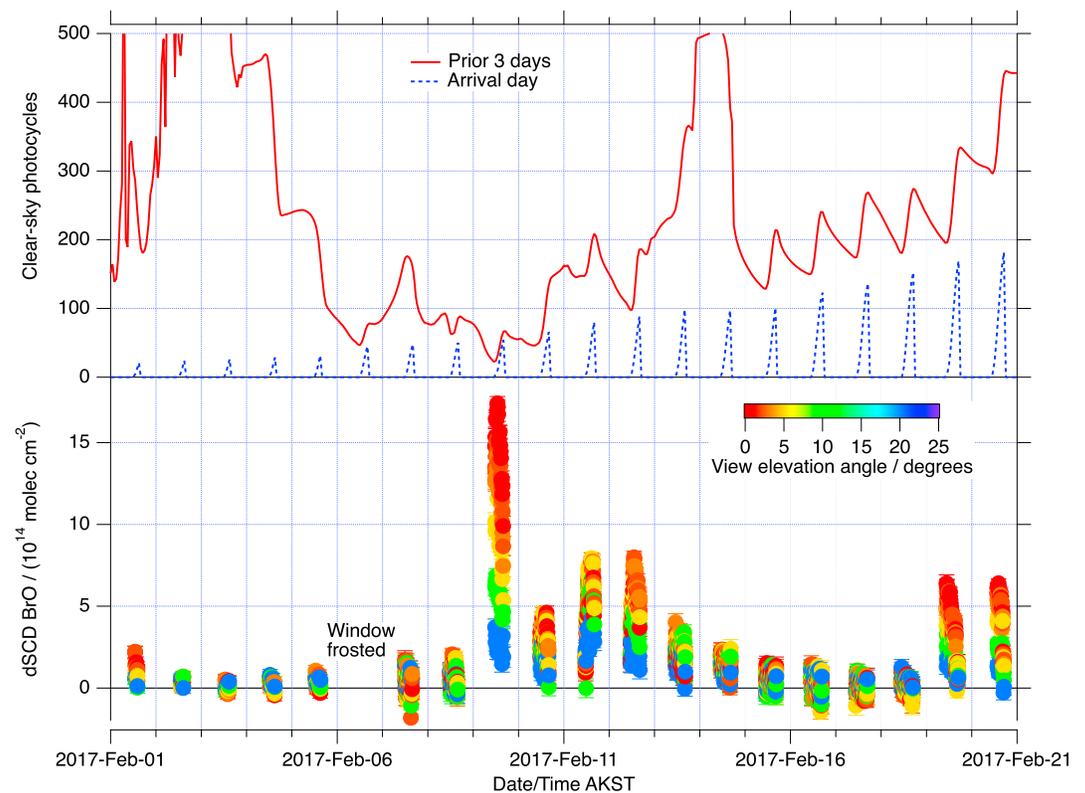


Figure 3. BrO observations related to prior exposure of air masses to photolysis. The top panel shows the clear-sky photoexposure calculated along a HYSPLIT 3-day back trajectory (red line) and on the day of arrival at BARC (blue dashed line). The bottom panel shows BrO dSCD as a function of view elevation angle versus time. dSCD = differential slant column density.

have produced photolabile bromine species via this mechanism. Therefore, dark reactions of nitrogen oxides with sea salt could be a mechanism consistent with our observations of high BrO in air masses arriving from the polar night.

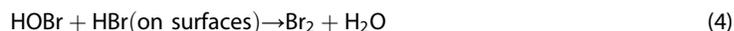
Oum et al. (1998) proposed that ozone oxidizes bromide (Br^-) on ice surfaces to produce Br_2 , providing another potential dark mechanism. Similar chemistry involving ozone oxidation of iodide at the sea water interface has been demonstrated (Carpenter et al., 2013) and provides analogous support for the mechanism of ozone oxidation of halides. Hirokawa et al. (1998) also observed that NaBr reacts with O_3 in the presence of water to produce Br_2 , and Hunt et al. (2004) provided evidence that this reaction may occur via a surface complex. Oum et al. (1998) estimate 0.6-pmol/mol Br_2 could be produced in 10 hr at an ozone exposure of 40 nmol/mol. Therefore, air masses that remain in the dark for 10 days could produce an estimated 14-pmol/mol Br_2 , which would photolyse and react with ozone to produce to ~ 28 -pmol/mol BrO, which is typically less than, but within an order of magnitude of, the observed BrO levels. In addition, polar air masses may reside in the dark for longer than 10 days due to the efficiency of the Polar Dome in inhibiting transport to lower latitudes, (Klonecki et al., 2003; Stohl, 2006) so even very slow dark reactions may be important. Further laboratory and modeling investigations of dark production mechanisms is clearly necessary, but it appears that these or other unknown mechanisms could produce photolabile bromine precursors that could explain the high BrO concentrations observed here.

Mass-spectroscopic field investigations (Foster et al., 2001) have shown evidence for production of photolabile bromine species at the time of polar sunrise near Alert, Canada. Foster et al. (2001) observed Br_2 MRs of up to 25 pmol/mol and BrCl of up to 35 pmol/mol. Production of either Br_2 or BrCl in the dark could build up a reservoir of photolabile bromine species over time, which then release reactive bromine upon exposure to sunlight through reactions 1 and 2.



Photolysis of Br_2 and BrCl at levels observed by Foster et al. (2001) followed by reaction of Br radicals with ozone would lead to 50- and 35-pmol/mol BrO, respectively, in qualitative agreement with the observed levels in this study (Table 1).

Typical springtime reactive bromine release is believed to proceed through reactions 1 and 2 followed by reaction of BrO with radicals (e.g., HO_2) to reform Br_2 in sequence below (Fan & Jacob, 1992; McConnell et al., 1992):



This *bromine explosion* (Platt & Janssen, 1995; Wennberg, 1999) sequence only amplifies reactive bromine during daytime, so it would not be responsible for nocturnal formation. It is possible that nocturnally formed reactive bromine precursors could be amplified on the day of detection via faster daytime photochemistry (Nissenson et al., 2014), but Figures 3 and S3 shows that most of these cases do not show an increase in BrO over the detection day. This traditional mechanism is also likely to be slowed under the low solar elevation conditions of late January/early February because HO_2 is produced photochemically and would be expected to be at low concentrations, so reaction 3 is likely to be slow. However, it is possible that there is nocturnal formation of HO_2 precursors that could photolyse to HO_2 radicals, which are then converted to reactive bromine radicals via reactions 4 + 1. To the extent that HOBr may be formed by these reactions or other dark mechanisms, it is likely to be converted to Br_2 by reaction 4, which has been shown to be fast in multiple studies (Fickert et al., 1999; Huff & Abbatt, 2002; Wachsmuth et al., 2002). Recently Nerentorp Mastromonaco et al. (2016) suggested a dark source of bromine could be responsible for observed mercury and ozone depletion in the Antarctic wintertime.

Ozone depletion occurs through reaction 2 followed by reactions of BrO that reform Br_2 , but because the sun is very low at this time of year, photolysis of Br_2 (reaction 1) limits the ozone depletion process. For example, on 9 February 2017, Br_2 experiences approximately 50 photoexposures, causing reaction 2 to occur 50 times for each BrO present (~90 pmol/mol), depleting 4.5-nmol/mol O_3 , which is consistent with the small ozone depletion observed on this date. Other dates have less reactive bromine and lower photoexposure, which is consistent with the lower observed ozone loss rates. Overall, these considerations indicate that these early season BrO events are different from typical ozone depletion events that occur under higher photoexposure in March–May. For these reasons, it appears that the formation of high BrO abundances in polar night airmasses is due to a dark mechanism rather than traditional bromine release chemistry.

5. Conclusions

We observe unprecedented levels of BrO, up to 90 pmol/mol and tropospheric vertical column density of 1.3×10^{14} molecules per square centimeter during February 2017 at Utqiagvik, Alaska. Four of the other five maxima also exceeded the 90th percentile of BrO observations from March–May 2012 to 2016, indicating that late January/early February often has episodes of very high BrO. Back trajectory analysis shows that these peak BrO measurements occurred in air that received minimum prior photolysis of Br_2 , indicating a nocturnal source of reactive bromine.

The observation of a nighttime formation mechanism of photolabile bromine species is important because it would imply that the wintertime Arctic Ocean could be producing high concentrations of photolabile bromine gases that would then transport southward to sunlight and release reactive bromine species. Although some of this photolabile bromine reservoir will be trapped under the polar dome, vertical mixing could loft these photolabile species where they could then inject reactive bromine into the lower-latitude free troposphere, potentially enhancing the free-tropospheric BrO loading. Nocturnally produced photolabile bromine would also provide *seed* reactive bromine for the traditional photochemical bromine release

mechanism on subsequent days. Direct measurement of Br₂ and BrCl in nighttime air masses and determination of the production mechanism and its rate are needed.

Acknowledgments

The authors indicate no conflicts of interest. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://www.ready.noaa.gov>) used in this publication. We also thank the team that has developed and provided FLEXPART to the community. Computing resources were provided by IDRIS HPC resources by the GENCI allocation A0030107141 and by the IPSL mesoscale computing center (CICLAD: Calcul Intensif pour le Climat, l'Atmosphère et la Dynamique). We thank NASA for support of this project under NNX16AQ43G and NSF for support under grant ARC-1602716. The financial support of the IUP Heidelberg by the German Research Association (DFG) in the framework of the HALOPOLE-III project (FR 2497/3-2) is gratefully acknowledged. We thank Ukpeagvik Iñupiat Corporation-Science and PolarField Services for providing space for the instrument in Utqiagvik. Data used in this study are accessible from the NSF sponsored archive, <http://arcticdata.io>; <https://doi.org/10.18739/A2222R550>.

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