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# Comparison of model and ground observations finds snowpack and blowing snow both contribute to Arctic tropospheric reactive bromine

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## Abstract

Reactive halogens play a prominent role in the atmospheric chemistry of the Arctic during springtime. Field measurements and models studies suggest that halogens are emitted to the atmosphere from snowpack and reactions on wind-blown snow. The relative importance of snowpack and blowing snow sources is still debated, both at local scales and regionally throughout the Arctic. To understand implications of these halogen sources on a pan-Arctic scale, we simulate Arctic reactive bromine chemistry in the atmospheric chemical transport model GEOS-Chem. Two mechanisms are included: 1) a blowing snow sea salt aerosol formation mechanism and 2) a snowpack mechanism assuming uniform molecular bromine production from all snow surfaces. We compare simulations including neither mechanism, each mechanism individually, and both mechanisms to examine conditions where one process may dominate or the mechanisms may interact. We compare the models using these mechanisms to observations of bromine monoxide (BrO) derived from multiple-axis differential optical absorption spectroscopy (MAX-DOAS) instruments on O-Buoy platforms on the sea ice and at a coastal site in Utqiaġvik, Alaska during spring 2015. Model estimations of hourly and monthly average BrO are improved by assuming a constant yield of 0.1% molecular bromine from all snowpack surfaces on ozone deposition. The blowing snow mechanism increases BrO by providing more surface area for reactive bromine recycling. The snowpack mechanism led to increased BrO across the Arctic Ocean with maximum production in coastal regions, whereas the blowing snow mechanism increases BrO in specific areas due to high surface windspeeds. Our uniform snowpack source has a greater impact on BrO mixing ratios than the blowing snow source. Model results best replicate several features of BrO observations during spring 2015 when using both mechanisms in conjunction, adding evidence that these mechanisms are both active during the Arctic Spring. Extending our transport model throughout the entire year leads to predictions of enhanced fall BrO that are not supported by observations.

## 1. Introduction

Simulating Arctic halogen chemistry is a persistent problem for global models because processes appear to differ between the Arctic and middle latitudes (Parrella et al., 2012; Schmidt et al., 2016). Space-based instruments observe large column densities of reactive bromine across swaths of the Arctic Ocean during the Arctic spring (Chance, 1998; Richter et al., 1998; Wagner and Platt, 1998). Increased levels of tropospheric reactive bromine are associated with ozone depletion events (Barrie et al., 1988; Foster et al., 2001; Koo et al., 2012; Halfacre et al., 2014) as well as oxidation of gaseous elemental mercury (Schroeder et al., 1998; Nghiem, 2013; Moore et al., 2014). Bromine radicals have been observed to lead directly to ozone depletion and mercury oxidation (Wang et al., 2019a). Deposition of oxidized mercury to the snowpack can have deleterious effects on the health of Arctic humans and animals (AMAP, 2011). Arctic reactive bromine chemistry impacts tropospheric oxidative chemistry but is not typically accounted for in global models. Model studies have found that reactive halogen chemistry can explain the oxidation of gaseous elemental mercury (Holmes et al., 2010) and reduce radiative forcing from ozone (Sherwen et al., 2016c). Replicating reactive halogen chemistry in models requires inclusion of multi-phase chemical reactions as well as mechanisms affecting sea salt aerosol particle production and chemical reactions within the snowpack.

These increased levels of tropospheric reactive bromine radicals are a product of heterogeneous photochemical reactions at the interface between air and saline surfaces such as surface snowpack and sea salt aerosols (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Figure 1 depicts the gas-phase, heterogeneous, and photochemical reactions thought to control tropospheric bromine, all of which are included in the model and results presented in this manuscript. Bromine radicals (Br) are produced by photolysis of molecular bromine (P1) and react with ozone to form bromine monoxide (BrO) (R2). Under sunlit conditions, BrO is most often photolyzed back to Br radicals and an oxygen atom (P2) that then most often reforms ozone, resulting in a null cycle. Due to this rapid interchange of Br and BrO, these two compounds form the $BrO_x$ family. If processes other than BrO photolysis (P1) convert BrO back to Br without producing ozone, the imbalance between these other processes and P1 result in net ozone depletion. For example, ozone is depleted through R6 or R7 when BrO reacts with another halogen oxide to form either $Br_2$ or BrCl, or through other more extended processes. A reactive halogen activating cycle occurs when a BrO radical reacts with a hydroperoxy ($HO_2$) radical in R5 to form gaseous hypobromous acid (HOBr). Heterogeneous chemistry can occur on a saline surface between HOBr and particulate bromide (p-$Br^-$) in HR1 forming $Br_2$ or particle chloride (p-$Cl^-$) in HR6 forming BrCl. For each cycle of reactions P1, R2, R5, and HR1, one hydroperoxy radical is removed from the atmosphere, one bromine radical is released to the atmosphere, and one ozone molecule is destroyed. This process of activation of particulate bromide to $Br_2$ by consuming other radicals (e.g. $HO_2$) is known as the "bromine explosion" (Wennberg, 1999). Ground-based instruments have observed sharp increases in reactive bromine levels over the course of a single day from below 2 pmol/mol up to a maximum of 41 pmol/mol (Pöhler et al., 2010). Reactions may also sequester reactive bromine into more stable bromine reservoir species. BrO may react with nitrogen dioxide ($NO_2$) in R8 to form bromine nitrate ($BrNO_3$), which can also undergo hydrolysis on a saline surface to form HOBr as in HR3.

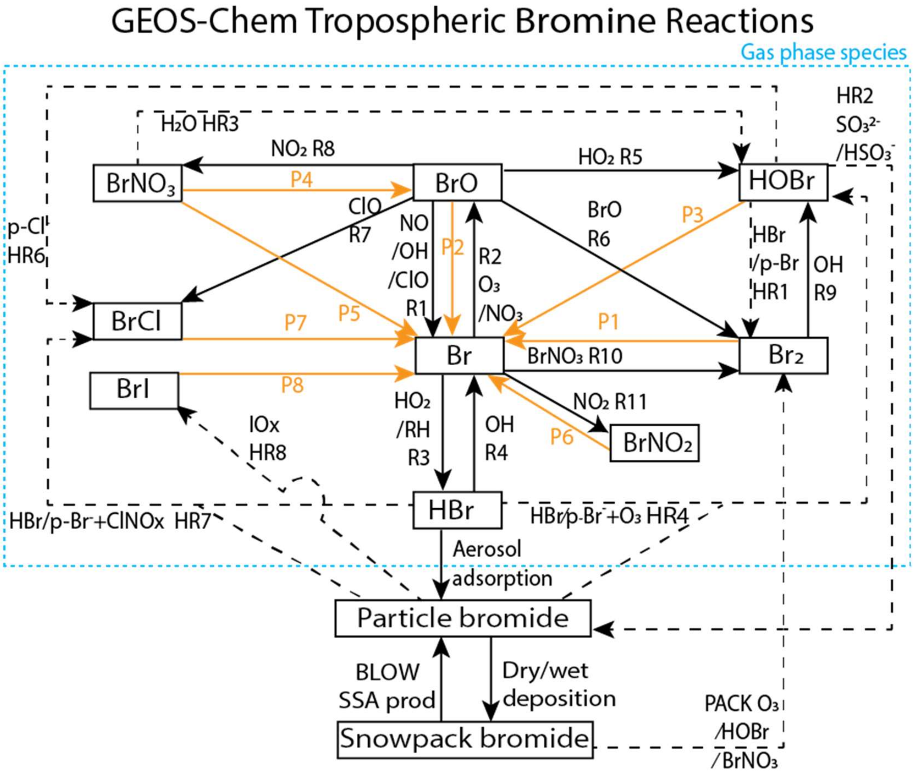

**Figure 1: GEOS-Chem tropospheric bromine reactions.** Tropospheric bromide reservoirs shown in black boxes, with attached lines indicating reactions. Solid black lines R1-R11 indicate gas phase

chemical reactions, solid orange lines P1-P8 indicate photolysis reactions, and dashed black lines HR1-HR8 indicate heterogeneous reactions. All gaseous species may undergo wet and dry deposition. Additional sources of tropospheric bromine include the production of particulate bromide by the BLOW mechanisms and the production of $Br_2$ by the PACK mechanism, as well as the degradation of organobromines to form Br (OR1).

A potentially important competitor for recycling of reactive bromine through HOBr is its reaction with sulfur (IV) species, such as the reaction between $HSO_3^-$ and HOBr in HR2 (Chen et al., 2017). To the extent that this reaction competes with HR1, it can slow the release of bromide from surfaces and reduce gas-phase reactive bromine (e.g., reduce BrO). Deposition of the HBr formed from HOBr by HR2 can remove reactive bromine from the troposphere. In general, the termination of this chemistry leads to formation of HBr, which undergoes gas-particulate uptake to particulate bromide (p-$Br^-$).

Ozone deposited to a saline surface can oxidize $Br^-$ to form HOBr (similar to p-$Br^-$ reactions HR4a and HR4b) which is then converted to $Br_2$ or another dihalogen (e.g., BrCl). Production of reactive bromine during ozone deposition does not require light and can occur at night (Oum et al., 1998; Artiglia et al., 2017). The production of $Br_2$ is increased at low pH levels (Halfacre et al., 2019).

We define the inorganic bromine family, $Br_y$, in this manuscript as the sum of the bromine species: Br, BrO, HOBr, $BrNO_3$, $2xBr_2$, BrCl, BrI, and HBr, excluding p-$Br^-$. The release of bromine from sea salt aerosol particles was found to be the dominant global source of reactive bromine (Sander et al., 2003; Zhu et al., 2019). Sea salt aerosol particles (SSA) sourced from the bursting of bubbles in oceanic whitecaps and other sources and are one of the most abundant aerosol particle types present in the troposphere (De Leeuw et al., 2011). Due to their abundance, SSA particles greatly increase the surface area available for heterogeneous reactive bromine chemistry. Debromination of acidified aerosol increases reactive bromine by 30%, although global models may underestimate Arctic reactive bromine when considering only open ocean-sourced SSA (Schmidt et al., 2016). Initial literature on Arctic reactive bromine chemistry identified aerosol particles as a potential saline surface for reactive bromine photochemistry (Fan and Jacob, 1992; Vogt et al., 1996). If one supposes that SSA can only be produced from the open ocean source of SSA, the lack of Arctic Ocean open water during the winter/spring is at odds with observations of high SSA concentrations observed during the winter months in polar regions (Wagenbach et al., 1998; Huang et al., 2018). The formation of SSA from the sublimation of blowing snow particles over the Arctic Ocean was proposed as an alternate SSA production mechanism (Yang et al., 2008, 2010, 2019). Recent field studies have confirmed the direct production of SSA from blowing snow (Frey et al., 2020). A blowing snow mechanism was implemented in the global chemical model GEOS-Chem and was able to explain wintertime SSA enhancements over the Arctic (Huang and Jaeglé,

2017) as well CALIOP-detected aerosol particle abundance (Huang et al., 2018) and high levels of Arctic BrO detected by satellites in spring (Huang et al., 2020).

Snowpack containing bromide salts was also identified as a source of reactive bromine (Tang and McConnell, 1996). Molecular bromine was measured above the snowpack at levels up to 25 pmol/mol (Foster et al., 2001). Field experiments demonstrate that the snowpack emits $Br_2$, $Cl_2$, and BrCl, with emission affected by ambient ozone levels, the snowpack ratio of bromide to chloride, and exposure to sunlight (Pratt et al., 2013; Custard et al., 2017). Box modeling found that the flux of reactive bromine from the surface of the Arctic Ocean sea ice is a prerequisite for bromine activation (Lehrer et al., 2004). Box modeling found that both HOBr and $BrNO_3$ can be converted to $Br_2$ in the snowpack (Wang and Pratt, 2017). Detailed one dimensional models of the snowpack-air interface find that reactive bromine production can occur in the interstitial air between snowpack grains (Thomas et al., 2011; Toyota et al., 2014), with ozone depletion events arising from snowpack reactive bromine production (Thomas et al., 2011; Cao et al., 2016). However, a detailed snowpack model coupled to an atmospheric model would be sensitive to important parameters such as snowpack bromide content and acidity of the air-ice interface that are highly variable across the Arctic (Toom-Sauntry and Barrie, 2002; Krnavek et al., 2012). A mechanism to parameterize the release of molecular bromine from snowpack upon deposition of ozone, HOBr, and $BrNO_3$ was implemented in the GEM-AQ model and captured many of the observed features of reactive bromine in the Arctic troposphere (Toyota et al., 2011). The mechanisms from Toyota et al. (2011) assumes a 100% yield of molecular bromine on deposition of HOBr or $BrNO_3$ (see Figure 1 PACK) and a diurnally varying yield of $Br_2$ on ozone deposition of 7.5% during the daytime (solar elevation angle > 5°) and 0.1% during the nighttime (solar elevation angle < 5°) (see Figure 1 PACK). In the Toyota et al. (2011) parameterization, the daytime yield of $Br_2$ from ozone was increased to 7.5% to match surface ozone depletion observations and is based on the assumption that photochemical reactions in the snowpack would trigger a bromine explosion and amplify the net release of $Br_2$ (Toyota et al., 2011). Herrmann et al (2021) implemented the Toyota et al. (2011) mechanism in WRF-Chem and found snowpack $Br_2$ production was capable of replicating ozone depletion events observed in multiple datasets. Marelle et al. (2021) implemented a surface snowpack mechanism based on Toyota et al. (2011) and a blowing snow mechanism based on Yang et al. (2008) and Huang and Jaeglé (2017) and found improved prediction of ozone depletion events, the majority of which were triggered by the snowpack mechanism. The Toyota et al. (2011) mechanism was also implemented in the EMAC model and replicated many of the features of reactive bromine events observed by satellite-based GOME sensor (Falk and Sinnhuber, 2018).

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Field campaigns have directly observed the production of SSA from blowing snow (Frey et al., 2020) as well as production of $Br_2$ from the snowpack (Pratt et al., 2013) in the environment. This manuscript uses both production mechanisms for the first time in the global chemical model GEOS-Chem. We devised a set of six model runs to test each mechanism individually and together as well as one control run using neither mechanism. We compare BrO simulated in each model run against extensive ground-based observations of BrO made from February to June 2015. This set of modeling scenarios allows identification of the effects of each mechanism on BrO as well as the synergistic effects of both mechanisms working together.

## 2. Data sources and methods

### 2.1 MAX-DOAS observation platforms

Multiple axis differential optical absorption spectroscopy (MAX-DOAS) remotely measures the vertical profile of BrO (Hönninger and Platt, 2002; Carlson et al., 2010; Frieβ et al., 2011; Peterson et al., 2015; Simpson et al., 2017). BrO is commonly used as a proxy for total tropospheric reactive bromine (Chance, 1998; Richter et al., 1998; Wagner and Platt, 1998; Theys et al., 2011; Choi et al., 2012). MAX-DOAS instruments were mounted on all of the fifteen floating autonomous platforms (O-Buoys) deployed in the Arctic sea ice as a part of the National Science Foundation-funded Arctic Observing Network project (Knepp et al., 2010). Since MAX-DOAS requires sunlight to operate, measurements are not available in winter. Spring observations on the O-Buoys typically begin in April when there is enough O-Buoy solar power to defrost the MAX-DOAS viewport. Figure 2 shows the O-Buoys active during 2015. O-Buoy 10 was deployed into sea ice in fall 2013 and measured reactive halogen chemistry in spring 2014 and 2015. Most O-Buoys were destroyed in the summer, crushed between fragments of melting sea ice. However, O-Buoy 10 survived summer 2014 in an intact ice floe, survived the winter of 2014-15, and re-started MAX-DOAS observations in April 2015. O-Buoys 11 and 12 were deployed in fall 2014 and also re-started observing BrO in April 2015. Figure 2 shows the GPS-derived tracks of the O-Buoys for their full deployment and highlights the O-Buoy locations from April to June 2015 when the BrO observations considered in this analysis were gathered. A MAX-DOAS instrument of the same design was deployed at the Barrow Arctic Research Center (BARC) on the coast of the Arctic Ocean located at 156.6679°W, 71.3249°N near Utqiaġvik, AK (Simpson, 2018), also shown in Figure 2. Unlike the O-Buoy MAX-DOAS systems, which were powered by batteries and solar panels, the BARC MAX-DOAS was powered from local utilities and was able to defrost its viewport to gather BrO observations earlier in the year, including February and March 2015. The BARC MAX-DOAS data was compared with two O-Buoy style MAX-DOAS instruments deployed on Icelander platforms (deployed on top of sea ice instead of within) and measurements from the various MAX-DOAS systems were found to be comparable (Simpson et al., 2017). The reactive bromine season ends when the BrO slant column densities fall below the instrument detection limit and do not recover, which we call the seasonal end date (Burd et al., 2017). All O-Buoy and BARC (Utqiaġvik) data are available at arcticdata.io (Simpson et al., 2009) (Simpson, 2018). More information on the time periods of spring BrO observations can be found in Swanson et al. (2020) and Burd et al. (2017). For comparison to the MAX-DOAS BrO observations, GEOS-Chem model simulations are sampled along the GPS-derived paths of O-Buoys 10, 11 and 12 as well as at BARC.

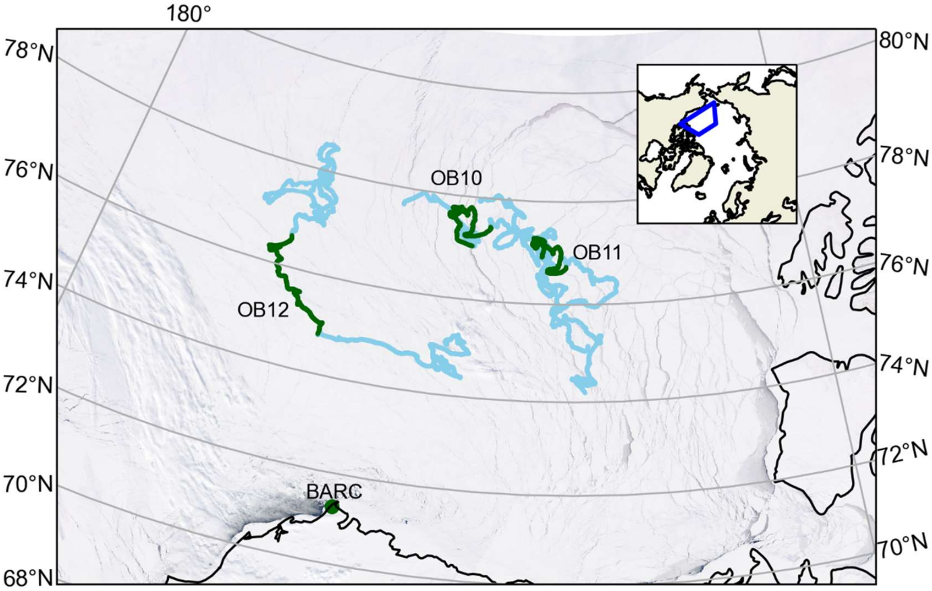

**Figure 2: Locations of MAX-DOAS BrO observations used in this work.**

Blue lines show the drift tracks of O-Buoys, with green showing the locations with valid BrO measurements in spring 2015. Location of Barrow Arctic Research Center (BARC) in Utqiaġvik indicated by green dot. Inset map shows True color MODIS imagery on 1 April 2015 shows typical sea ice coverage (NASA 2015).

### 2.2 MAX-DOAS profile retrieval

Vertical profiles of BrO were derived from MAX-DOAS observations by means of optimal estimation inversion procedures detailed in Peterson et al. (2015) with settings detailed in Simpson et al. (2017). The HeiPro optimal estimation algorithm (Frieß et al., 2006, 2019) is used to retrieve a vertical profiles of BrO between the surface and 4km from the MAX-DOAS observations. Examination of the averaging kernels from each MAX-DOAS retrieval finds the retrieved vertical profile of BrO is best represented by two quantities: the vertical column density of BrO in the lowest 200 m, and the vertical column density of BrO in the lowest 2000 m of the troposphere referred to in this manuscript as $BrO_{LTcol}$ (Peterson et al., 2015). We approximate surface mixing ratio by assuming well mixed constant distribution of BrO throughout the lowest 200 m. This mixing ratio is reported as $BrO_{pptv200}$ (Simpson et al 2009, Simpson 2018). It was shown in Peterson et al. (2015) that these two quantities were largely independent of each other, were fairly insensitive to variations in the assumed prior profile, and represented the ~2-3 degrees of freedom for signal indicated by the optimal estimation retrieval. An important consideration of this method is that when the visibility is poor, the MAX-DOAS is unable to traverse the lowest 2000m AGL and the $BrO_{LTcol}$ cannot be measured accurately. Therefore, our quality-control algorithm eliminates $BrO_{LTcol}$ observations when the degrees of freedom for signal in the lofted (200m - 2000m AGL) layer were below 0.5 (Simpson et al., 2017). The average fitting error (1σ error) of $BrO_{LTcol}$ during spring 2015 was $5.6*10^{12}$ molecules/cm$^2$.

### 2.3 SSA production from open ocean

Seafoam from breaking waves and bursting of bubbles forms aerosol droplets suspended in the marine boundary layer (Lewis and Schwartz, 2004). We calculate emission of sea salt aerosol particles from the open ocean as a function of wind speed and sea surface temperature (SST) using the mechanism initially described in Jaeglé et al. (2011) and updated with decreased emissions over cold (SST < 5°C) ocean waters (Huang and Jaeglé, 2017). Two separate SSA tracers are transported: accumulation mode SSA ($r_{dry}$ = 0.01−0.5 µm) and coarse mode SSA ($r_{dry}$ = 0.5–8 µm). Sea salt bromide is emitted assuming bromine content of $2.11\times10^{-3}$ kg Br per kg of dry SSA (primarily NaCl) based on the mean ionic composition of sea water (Sander et al., 2003). Bromide content is tracked separately on accumulation mode SSA and on coarse mode SSA. Heterogeneous chemical reactions can convert SSA-transported bromide into gaseous reactive bromine species in the atmosphere. We run our open ocean SSA calculations at 0.5° latitude x 0.625° longitude spatial resolution using the harmonized emissions component (HEMCO) for highest possible detail (Keller et al., 2014; Lin et al., 2021) including cold water corrections used in Jaeglé et al. (2011) . Production of SSA from open oceans which can lead to Arctic reactive bromine recycling on advected open ocean SSA within GEOS-Chem. Each of our model runs reads the dataset generated offline by HEMCO rather than spend computational time replicating open ocean SSA emissions. We call our control run using only open ocean SSA emissions BASE.

### 2.4 Blowing snow SSA production

Snow can be lofted from the snowpack into the lowest layers of the troposphere by high windspeeds, where it can undergo saltation (bouncing leading to fragmentation) and sublimation to form SSA (Yang et al., 2008, 2010; Frey et al., 2020). This process is modeled as a function of humidity, ambient temperature, windspeed, and the salinity of the blowing snow (Yang et al., 2008, 2010). Three thresholds must be met for SSA production from blowing snow (Dery and Yau, 1999; Déry and Yau, 2001). A temperature threshold restricts SSA production from blowing snow to temperatures below freezing. The humidity threshold is based on relative humidity with respect to ice. Sublimation from snow crystals cannot occur if the air is saturated, and no SSA is produced if $RH_{ice}$ is greater than 100%. The windspeed threshold requires ten-meter wind speed to be greater than a threshold value defined in Equation 1 for any production of SSA (Dery and Yau, 1999; Déry and Yau, 2001).

$$U_t = 6.975 + 0.0033(T_s + 27.27)^2 \tag{1}$$

The wind speed threshold ($U_t$) is dependent on surface temperature ($T_s$) in Celsius with a minimum threshold of 6.975 m/s at -27.27 C° and a maximum threshold at 0 C° of 9.429 m/s. The ten-meter windspeed threshold is the most stringent and often controls the production of SSA from blowing snow.

Production of blowing snow and SSA is highly sensitive to surface windspeed. We use the highest resolution surface windspeed dataset to ensure the most accurate modeling of SSA and reactive bromine. The MERRA-2 Global Reanalysis Product has a 0.5° latitude x 0.625° longitude resolution which is typically re-gridded to a lower resolution for global chemical modeling. Previous use of the snowpack blowing snow mechanism has simulated blowing snow with MERRA-2 data re-gridded to either 2°x2.5° or 4°x5° latitude and longitude (Huang and Jaeglé, 2017; Huang et al., 2018, 2020). Re-gridding to coarser spatial resolution may smooth out the highest ten-meter windspeeds by averaging them with lower windspeeds in the grid cell. The Utqiaġvik MERRA-2 ten-meter windspeeds at different spatial resolutions are shown in Supplemental Figures S1, S2 and S3 to illustrate this effect. Average Utqiaġvik ten-meter windspeeds for 2015 are 5.3 m/s at 2°x2.5° resolution and 5.5 m/s at 0.5°x0.625° resolution. The maximum Utqiaġvik ten meter windspeed at MERRA-2 2x2.5 is 16.3 m/s, while the maximum windspeed at MERRA-2 0.5°x0.625° is 19.3 m/s. These extremely high windspeed events are more common at higher spatial resolution and can contribute an outsized amount of SSA to the marine boundary layer. Supplemental Figure S4 shows the measured ten-meter windspeed at BARC, along with daily average threshold windspeed (Equation 1). Spikes in daily averaged windspeed at BARC in April can contribute to SSA formation and justify the use of high-resolution MERRA-2 wind speed data.

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Snow salinity is influenced by snow age and the material underlying the snow (Krnavek et al., 2012). The median surface snowpack salinity near Utqiaġvik was measured at 0.67 practical salinity units (PSU)PSU for 2-3 weeks old sea ice, 0.12 PSU for thicker first year ice, and 0.01 PSU for multi-year ice (MYI) (Krnavek et al., 2012). Snow salinity is also a function of snow depth above sea ice, with blowing surface snow having much lower salinity than snow at depth that is in contact with the sea ice (Frey et al., 2020). Domine et al**.** (2004) measured median salinity at 0.1 PSU on snowpack over first year ice and 0.02 PSU on snowpack over multi-year ice. In this analysis we use a salinity of 0.1 PSU on first-year sea ice as in Huang et al. (2020). The production of reactive bromine from sea ice types is entirely dependent on PSU in this parameterization. Previous modeling efforts have used 0.01 PSU for MYI (Huang et al., 2018) and underestimate BrO production in high Arctic areas with increased MYI coverage. The bromide content of surface snow over MYI is enriched by deposition of SSA and trace gases, and MYI regions may play a role in springtime halogen chemistry (Peterson et al., 2019). Previous analysis of O-Buoy data found no statistically significant differences in springtime BrO between regions of the Arctic (Swanson et al., 2020). We use 0.05 PSU for snowpack on MYI as in Huang et al. (2020).

Another important parameter for SSA formation is the number of SSA particles formed from each blowing snowflake. A value of 5 particles per snowflake was used in Huang and Jaeglé (2017) based on wintertime observations of supermicron and sub-micron SSA at Barrow. Values of 1 and 20 particles per snowflake have been tested (Yang et al., 2019) but it is unclear which value was more realistic. We use a particle formation value of 5 particles per snow grain as in Huang et al. (2020).

Snowpack may be enriched or depleted in bromide compared to seawater, which is thought to be an effect of atmospheric deposition or release of bromine from snowpack (Krnavek et al., 2012). Snowpack enrichment due to atmospheric deposition is less pronounced when snowpack salinity is high, with snowpack containing 1000 µM $Na^+$ (approximately 0.06 PSU) or more never exceeding twice the seawater ratio of bromine to chloride (Krnavek et al., 2012). Domine et al. (2004) found an increased enrichment factor of five times seawater in snow with a salinity of 100 µM $Cl^-$ (approximately 0.006 PSU). We use a snowpack enrichment factor of bromide five times that of seawater as in Huang et al. (2020) where this enrichment best agreed with GOME-2 observations. However, we note that a bromide enrichment factors five times seawater exceeds enrichment factors of two measured in snowpack with a salinity of 0.1 PSU (Krnavek et al., 2012).

Our choice of model input settings is similar to Huang et al. (2020) but we will be running the blowing snow mechanism in HEMCO at a 0.5° latitude x 0.625° longitude spatial resolution. The model run using the results of our high-resolution blowing snow SSA HEMCO simulation is called BLOW.

### 2.5 Snowpack emissions of molecular bromine

We base our $Br_2$ emissions scheme on Toyota et al. (2011) and Marelle et al. (2021), which prescribe a yield of $Br_2$ upon snowpack deposition of ozone, $BrNO_3$ and HOBr. In other modeling studies, this simplified deposition-based mechanism captured the synoptic-scale behavior of reactive bromine production across the Arctic (Toyota et al., 2011; Falk and Sinnhuber, 2018; Herrmann et al., 2021; Marelle et al., 2021). These modeling studies used different yields of $Br_2$ upon deposition over land snowpack, multi-year ice, and first year ice, restricting the production of molecular bromine from ozone deposition to first year ice surfaces. None of these studies were coupled to a snowpack model tracking snow bromide, and effectively assume an infinite bromide reservoir with $Br_2$ production limited only by the deposition flux and $Br_2$ yield.

Field studies indicate that snowpack over multi-year ice, first-year ice, and land regions may contribute to reactive bromine chemistry. Krnavek et al. (2012) found snow bromide content spanning six orders of magnitude, with individual samples taken from multi-year ice, first-year ice, and land regions showing variability of up to three orders of magnitude for each region. Analysis of variance in tropospheric BrO from 2011-2016 found no statistically significant differences in tropospheric BrO between different regions of the Arctic (Swanson et al., 2020). Both coastal snowpack and multi-year ice regions may produce reactive bromine. Molecular bromine production has been observed from coastal snowpack on exposure to ozone (Pratt et al., 2013; Custard et al., 2017). Airborne sampling has observed enhanced BrO up to 200 km inland (Peterson et al., 2018). Snow above multi-year sea ice regions is depleted in bromide, indicating that it may play a role in Arctic bromine chemistry (Peterson et al., 2019).

Our modeling study tests the hypothesis that all snow has a uniform ability to produce molecular bromine, effectively assuming an infinite bromide reservoir with $Br_2$ production limited only by the deposition flux. We differ from previous model parameterizations in allowing uniform $Br_2$ production upon snowpack deposition of ozone, $BrNO_3$ and HOBr over all sea ice surfaces and selected coastal snowpack regions. We expect higher predictions of snowpack molecular bromine production than recent modeling efforts (Herrmann et al., 2021; Marelle et al., 2021) in which ozone deposition over land and multi-year ice surfaces did not produce molecular bromine.

#### 2.5.1 Snowpack $Br_2$ production over sea ice

We assume a uniform production of $Br_2$ on deposition to snowpack over oceanic ice whether the ice is first-year sea or multi-year sea ice. We use MERRA-2 fractional ocean ice coverage fields, which introduces some artifacts. MERRA-2 classifies the freshwater Great Lakes as ocean, but sea ice and snowpack on those frozen lakes is unlikely to have sufficient bromide to support large $Br_2$ fluxes due to its distance from the ocean. Therefore, we specifically prohibit snowpack $Br_2$ emissions in the Great

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Lakes region (between 41° N and 49° N latitude and 75° W and 93° W longitude). This choice is in agreement with McNamara et al. (2020), who found road salt derived aerosol particles are responsible for 80-100% of atmospheric $ClNO_2$ in Michigan with no mention of a source of reactive halogens from nearby Great Lakes.

### 2.5.2 Snowpack $Br_2$ production over land

We wish to only enable production of $Br_2$ over land if the snowpack is sufficiently enriched in bromide. Snowpack over land surfaces and glaciers may be enriched in bromide by oceanic SSA sources (Jacobi et al., 2012, 2019). The distance that SSA may be transported inland from the coast is limited by geographical features such as mountains. Based on direct observations of reactive bromine chemistry up to 200 km from the Alaskan coastline (Peterson et al., 2018), we include unlimited production of $Br_2$ from specific land grid cells within 200 km of the coast upon deposition of ozone, HOBr, and $BrNO_3$. We only allow the fraction of each grid cell that is within 200 km of the coastline (Group and Stumpf, 2021) to produce molecular bromine. We further restrict snowpack $Br_2$ emissions to locations that are less than 500 m above sea level, because higher elevation locations are unlikely to be enriched by sea spray. This altitude screen eliminates $Br_2$ emissions from coastal mountains such as the Alaskan Rockies, the Brooks Range in Alaska, and the Scandinavian Mountains as well as from the Greenland Plateau. Halogen chemistry may occur over the Greenland ice sheet (Stutz et al., 2011) contrary to this screen, but this will have minimal impact on the regions of interest in this manuscript.

Our final screen is based on the average snow depth in each land grid cell. Both modeling studies (Thomas et al., 2011; Toyota et al., 2014) and field studies (Domine et al., 2004; Pratt et al., 2013; Custard et al., 2017; Frey et al., 2020) agree that bromine chemistry can occur in the better ventilated and illuminated top  of the snowpack. Regions with less than 10 cm of snowpack may not have sufficient snow for reactive bromine chemistry, thus we only produce snowpack $Br_2$ when the average snow depth in a land grid cell is 10 cm or greater. This screen prevents molecular bromine production in the lower latitude regions with minimal snow coverage and is necessary because ozone deposition to plants in snow-free grid cells often exceeds the slow deposition of ozone to snowpack and would not be expected to produce $Br_2$.

### 2.5.3 Diurnal yield of $Br_2$ on ozone deposition

We choose two alternate assumptions for the yield of $Br_2$ during the day. Toyota et al. (2011) initially assumed a constant yield of $Br_2$ from ozone deposition of 0.1% based on laboratory observations of nighttime bromine activation on ozone deposition (Oum et al., 1998; Wren et al., 2010, 2013) and then adjusted the daytime yield of $Br_2$ on ozone deposition to 7.5% to better match surface ozone mixing ratios measured at coastal stations. This increased daytime yield value was chosen based on the assumption that photochemistry may trigger an autocatalytic cycle leading to a 75-fold increase in $Br_2$ yield. The PHOTOPACK runs uses the increased daytime $Br_2$ yield of 7.5% when the solar elevation angle is 5° or greater. Previous implementations of the snowpack mechanism (Toyota et al., 2011; Herrmann et al., 2021; Marelle et al., 2021) predict ozone deposition velocities over Arctic sea ice on the order of 0.01 cm/s. Our model predicts similar ozone deposition rates over polar open ocean of 0.009 cm/s (Pound et al., 2020), but our model currently predicts deposition velocities over Arctic sea ice between 0.02 cm/s and 0.1 cm/s based on the month (see Supplemental Figure S5), with higher values influenced by proximity to the coast as described in Bariteau et al. (2010).. Thus, our PHOTOPACK run may predict much higher Br emissions than previous snowpack predictions despite the same yield values due to differences in deposition. To match out magnitude of $Br_2$ production with previous implementations of the snowpack mechanism (Toyota et al., 2011; Herrmann et al., 2021; Marelle et al., 2021) we add two PACK runs with a constant $Br_2$ yield on ozone deposition of 0.1% based on yield values in Toyota et al. (2011). Both PACK and PHOTOPACK runs assume 100% conversion of deposited HOBr and $BrNO_3$ to $Br_2$. Table 1 shows further model run yield details.

**Table 1 Model run settings**

Sea salt aerosol particles are produced from blowing snow as detailed in Section 2.5. Daytime is defined as when the solar elevation angle is greater than 5°, nighttime is defined as when the solar elevation angle is less than 5°.

| Model Run | Blowing snow SSA produced | Millimoles Br yielded per mole O3 deposited (daytime) | Millimoles Br yielded per mole O3 deposited (nighttime) |
|---|---|---|---|
| BASE | FALSE | 0 | 0 |
| BLOW | TRUE | 0 | 0 |
| PACK | FALSE | 1 | 1 |
| BLOW+PACK | TRUE | 1 | 1 |
| PHOTOPACK | FALSE | 75 | 1 |
| BLOW+PHOTOPACK | TRUE | 75 | 1 |

## 2.6 GEOS-Chem chemistry and transport model

The GEOS-Chem global atmospheric chemistry and transport model (Bey et al., 2001) simulates emissions, transport, and chemistry of atmospheric trace gases and aerosols, including halogens. The chemical mechanism in GEOS-Chem 12.9.3 (http://www.geos-chem.org, last access 29 October 2019, DOI:10.5281/zenodo.3974569) includes $HO_x$-$NO_x$-VOC-$O_3$-halogen-aerosol tropospheric chemistry (Mao et al., 2013; Fischer et al., 2014; Fisher et al., 2016; Travis et al., 2016; Wang et al., 2021). The model has been regularly and consistently updated to reflect current understanding of heterogeneous and gas-phase halogen chemistry.

Halogens in the troposphere may be sourced from photooxidation of halocarbons, emissions of iodine from the ocean surface, downward transport of halogens from the stratosphere, and release of halogens through heterogeneous chemistry on SSA.  Figure 1 shows a simplified version of the GEOS-Chem reaction scheme focusing on tropospheric bromine reactions and reservoirs. Heterogeneous reactions for release of reactive bromine from aerosol surfaces were added to GEOS-Chem (Parrella et al., 2012) and have been updated to include multiphase reactions and reactions between bromine, chlorine and iodine species (Schmidt et al., 2016; Sherwen et al., 2016a; Wang et al., 2019b) as well as input from the stratosphere (Eastham et al., 2014). Recent updates also include reactions between sulfur (IV) species and HOBr, which lead to a 50% decrease in $Br_y$ due to the scavenging of HOBr on aerosol surfaces containing sulfur (Chen et al., 2017). These HOBr-sulfur(IV) reactions are critical in moderating tropospheric BrO in the mid latitudes (Zhu et al., 2019). In GEOS-Chem 12.9 the halogen chemical mechanism was modified extensively to include chlorine chemistry as detailed in Wang et al. (2019b) with update halogen-sulfur (IV) rates (Liu et al., 2021) as well as improved cloud pH calculation from Shah et al. (2020).  For the simulations here, GEOS-Chem uses the Modern-Era Retrospective Analysis for Research and Applications, version 2 (MERRA-2) assimilated meteorological fields (Gelaro et al., 2017) re-gridded from native resolution of 0.5°x0.625° latitude and longitude to 2°x2.5° using a reduced vertical grid of 47 layers.

We initialize our model in October 2014 from a full-chemistry benchmark file, allowing for 6 months of spinup before our period of interest spanning from March to November 2015. We run six different model simulations with settings detailed in Table 1. The base model (BASE) includes the halogen sources described above but no Arctic-specific halogen sources. The BLOW simulation adds SSA production from blowing snow following Huang et al (2020) but using a more recent version of GEOS-Chem. The PACK simulation adds snowpack $Br_2$ emissions using a constant yield from $O_3$ deposition. The PHOTOPACK simulation also emits $Br_2$ from snowpack but increases the $Br_2$ yield from $O_3$ deposition under sunlight. These blowing snow and snowpack sources are combined in the BLOW+PACK and BLOW+PHOTOPACK simulations.

### 2.7 Comparing GEOS-Chem results to MAX-DOAS vertical column densities

GEOS-Chem simulates BrO mixing ratios for each of its 47 atmospheric layers.  Reducing the vertical resolution of the more-resolved GEOS-Chem predictions to be comparable to the coarser MAX-DOAS data is necessary for appropriate comparison (Rodgers and Connor, 2003).  To compare the GEOS-Chem profiles with these two grid-coarsened quantities, we grid-coarsen the averaging kernels produced by the HeiPro retrieval algorithm using Supplemental Equation S1 from Payne et al. (2009) to the partial column averaging kernels shown in Figure 3. We use the average of all April averaging kernels

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that pass our quality criteria (>0.5 DOFS in the lofted layer), which generally represents non-cloudy conditions. We calculate modeled $BrO_{LTcol}$ by applying the partial column averaging kernels shown in Figure 3 to the GEOS-Chem modeled vertical BrO profiles.

Figure 3 shows the average partial column averaging kernel for the surface layer (0-200m AGL) has near unit sensitivity to BrO at the ground, decaying to about 0.5 at 200m AGL then to zero at about 400m AGL, as desired. The sensitivity of the $BrO_{LTcol}$ is near unity from about the surface to 600m AGL, then slowly decays with 0.5 sensitivity at 2000m AGL. The resulting sensitivity to mid-tropospheric BrO means that free-tropospheric BrO produced by the GEOS-Chem model contributes to modeled $BrO_{LTcol}$, albeit at 50% or lower sensitivity, even if the GEOS-Chem-predicted free-tropospheric BrO is above the nominal 2000m top of the integration window. The residual sensitivity of the $BrO_{LTcol}$ averaging kernel above 2000m is caused by the limited ability of ground-based MAX-DOAS to distinguish the true altitude of BrO at non-tangent geometries (higher viewing elevation angles) that are required to view BrO at these higher altitudes. Figure 3 shows that BrO above 4 km makes only a small contribution to the modeled $BrO_{LTcol}$, which was not included in the $BrO_{LTcol}$.

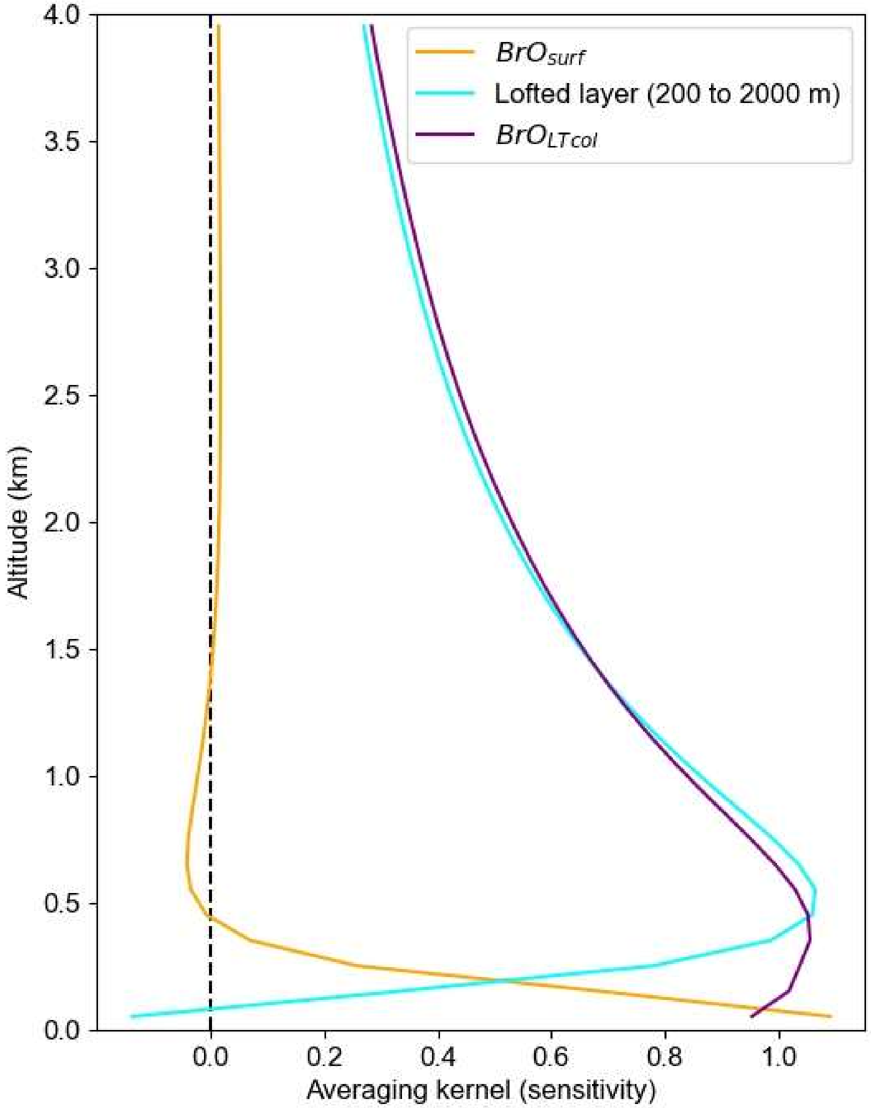

**Figure 3: Averaging kernels showing the sensitivity of retrieved $BrO_{LTcol}$ and retrieved $BrO_{surf}$ to BrO at a range of altitudes.**

Each line represents a row of the averaging kernel matrix. $BrO_{surf}$ is the column from the surface to 200 m and $BrO_{LTcol}$ is the column up to 2000 m.

Although it has been suggested in the literature (von Clarmann and Glatthor, 2019) that averaged averaging kernels can cause problems, we do not report data when there are clouds and thus are only using the more consistent averaging kernels that occur under clear sky conditions. We use other criteria related to vertical visibility to identify clear skies. As described in Peterson et al. (2015), the information content (DOFS) in the lofted layer is nearly linearly related to the aerosol optical depth. We find that the slant column density of the $O_2$-$O_2$ collisional dimer (aka $O_4$) observed at 20° elevation angle is correlated with the lofted DOFS (Supplemental Figure S6). From this correlation we find that clear sky conditions have 20° elevation angle $O_4$ dSCD > $10^{43}$ molecule$^2$cm$^{-5}$ and use this cut to distinguish clear sky versus clouds. To assure that GEOS-Chem results are only compared to the clear-sky observational data, we apply this clear sky screen to the modeled $BrO_{LTcol}$ timeseries. The use of this screen also assists in minimizing variability in the averaging kernels and thus allowing the April averaged partial column averaging kernels (Figure 3) to be applied for clear skies at any time of the year.

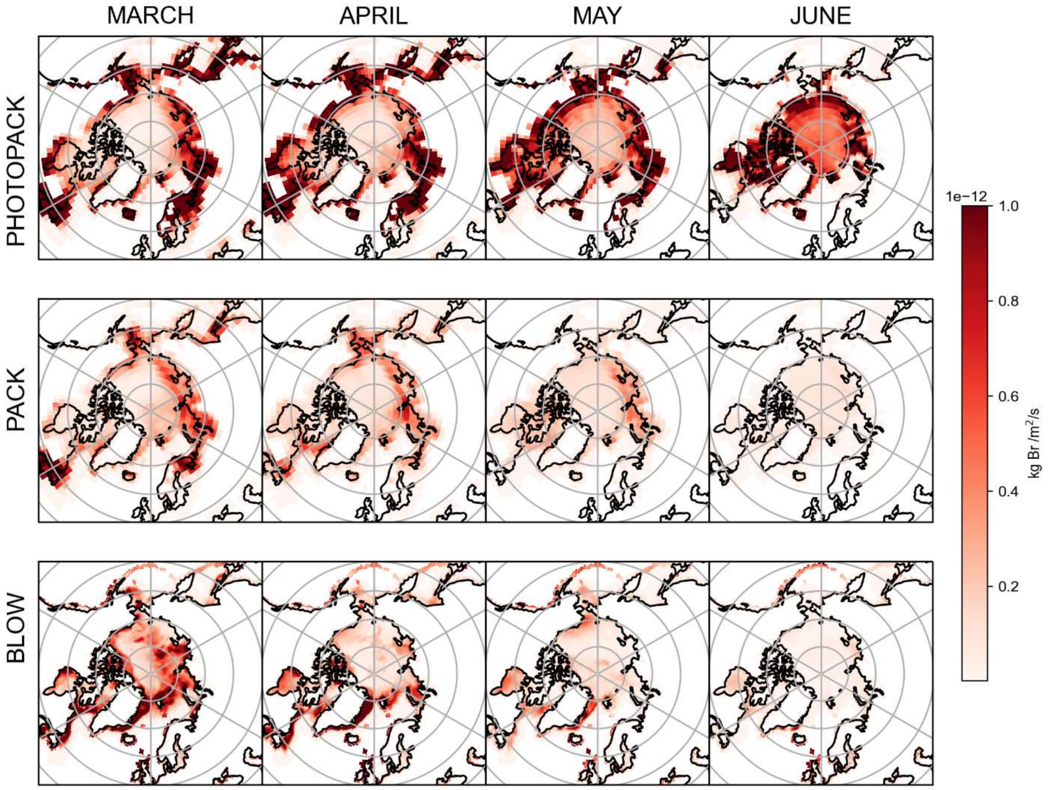

**Figure 4: Mean snowpack $Br_2$ emissions and p-$Br^-$ by month, as simulated by GEOS-Chem.**

The top row shows emissions of $Br_2$ in the PHOTOPACK run, the middle row shows the emissions of $Br_2$ in the PACK run, and the bottom row shows emissions of p-$Br^-$ from adding the BLOW mechanism.

## 3. Examining reactive bromine in the Arctic spring

### 3.1 Snowpack $Br_2$ emissions

The top two rows of Figure 4 shows PHOTOPACK and PACK average snowpack $Br_2$ emissions for each spring month. The emission of $Br_2$ in PHOTOPACK increases over the Arctic Ocean in May and June, when the sun is above the horizon for up to 24 hours per day and ozone deposition yield is almost always at the photo-enhanced level of 7.5%. Notably, $Br_2$ emissions over the Arctic Ocean in the PHOTOPACK and BLOW+PHOTOPACK runs are highest in June when the sun is nearly always five degrees above the horizon and surface temperatures may drop below freezing. The PACK emissions are lower than the PHOTOPACK $Br_2$ emissions by an order of magnitude and shows a seasonal cycle with a high $BrO_{LTcol}$ in April and May with a decrease in May and June. While our ozone deposition velocities (see Supplemental Figure S5) over Arctic sea ice are much higher than previous estimates of an approximate magnitude of 0.01 cm/s (Toyota et al., 2011), the PHOTOPACK run highlights that a 75-fold increase in daytime $Br_2$ yield can lead to predictions of increased $Br_2$ production over the North Pole in June. Monthly satellite observations show that BrO reaches a minimum over the Arctic Ocean in June (Richter et al., 1998).

Coastal land regions within 200 km of the coastline have some of the highest modeled snowpack $Br_2$ emissions (see Figure 4 rows 1 and 2). Dry deposition velocities are lower over ice covered ocean than open ocean due to the higher likelihood of a stable surface boundary layer over the ice-covered ocean (Toyota et al., 2016). This remains true within GEOS-Chem, as deposition rates are greatest over land, less rapid over ice-covered ocean, and lowest over open ocean (see Supplemental Figure S5). Lower dry deposition velocities over the ice-covered Arctic Ocean lead to decreased deposition and conversion to $Br_2$. In GEOS-Chem, ozone mixing ratios and deposition are over three orders of magnitude larger than $BrNO_3$ and HOBr mixing ratios and deposition over the Arctic Ocean, and ozone contributes more than half of total $Br_2$ emitted in the PACK and BLOW+PACK runs. Our snowpack mechanism assumes that all ozone deposited to the surface of a grid cell reacts with the snowpack cover and produces $Br_2$. This assumption is more appropriate in the barren snow-covered coastal tundra but may be less accurate in areas where deposition to vegetation dominates. This nonconservative approach may lead to overestimation of $Br_2$ emissions from snowy vegetated surfaces. Our screens for snowpack emissions described in section 1.3.5 tried to minimize these effects but may not work perfectly due to finite grid cell resolution and other challenges. Increased $Br_2$ emissions observed in Figure 4 in northern Europe may also be partially driven by increased local mixing ratios of ozone and $NO_x$ over industrialized regions such as the Kola Peninsula.

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### 3.2 Blowing Snow pBr$^-$ emissions

The bottom row of Figure 4 shows the total quantity of particulate bromide released by the blowing snow SSA mechanism in the BLOW runs. Emissions over the Arctic Ocean decline each month after the March maximum as rising temperatures increase the windspeed threshold for blowing snow SSA production. Some icy coastal regions with frequently high windspeeds such as the Aleutian Islands south of Alaska and the eastern coast of Greenland continue to emit SSA p-Br$^-$ in April, and the extremely high winds in the Aleutians enable SSA production into May. The location of specific high-wind storm systems in spring 2015 may be evident in the darker red spots over the Arctic Ocean, which are particularly noticeable over the Eurasian and Central Arctic in March. These monthly averages are only accurate for the months in spring 2015 and may not be spatially representative of blowing snow SSA production in other years.

The impact of the blowing snow SSA emissions is minimal on O-Buoys in the Beaufort Gyre, possibly due to the spatial and seasonal variations in SSA p-Br$^-$ emissions. Figure 4 shows that 2015 SSA production was highest in March and April on the Eurasian and Central sector of the Arctic, and thus the O-Buoys deployed as shown in Figure 2 are less exposed to the effects of SSA production than the Arctic as a whole. Particulate bromide must be activated from SSA by heterogeneous reactions as in Figure 1, leading to photochemical cycles that sustain further activation of bromide from SSA. The dearth of sunlight over the Arctic Ocean in early March coincides with the greatest SSA p-Br$^-$ production and means that the increased February SSA p-Br$^-$ emissions may not lead to a direct increase in BrO.

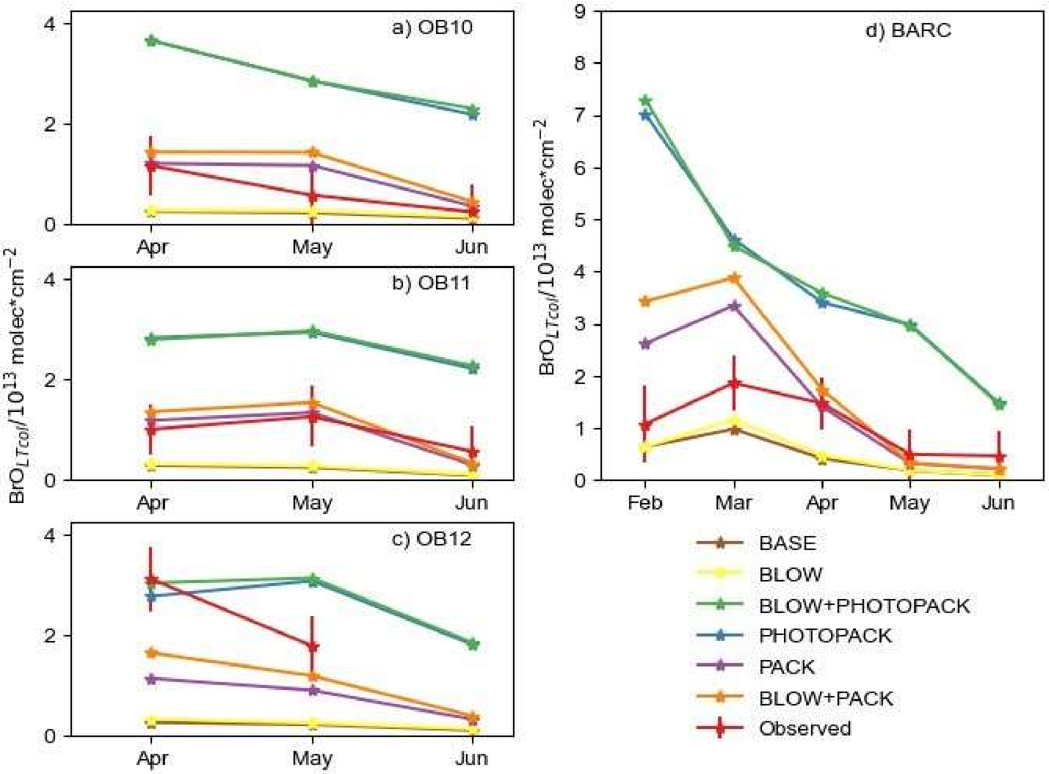

**Figure 5: Monthly average $BrO_{LTcol}$ in observations and model**

Monthly averages of BrO at a) O-Buoy 10, b) O-Buoy 11, c) O-Buoy 12, and d) BARC at Utqiaġvik only using predictions and observations when $dSCDO_4 > 1*10^{43}$ molecules$^2$cm$^{-5}$. Observations with average $1\sigma$ error shown in red. All units in $10^{13}$ molecules/cm$^2$.

### 3.3 Snowpack $Br_2$ emissions have more impact than blowing snow on monthly BrO abundance

Increased levels of bromine have been historically seen at Utqiaġvik during February, March, April and May (Berg et al., 1983). Previous O-Buoy data analysis noted BrO dropping to zero in June (Burd et al., 2017). Figure 5 shows monthly averaged modeled $BrO_{LTcol}$ at Utqiaġvik and on the O-Buoys for each model configuration. The difference in GEOS-Chem modeled monthly averaged $BrO_{LTcol}$ for O-Buoys is minimal between the BASE and BLOW runs, the PHOTOPACK and BLOW+PHOTOPACK runs, and the PACK and BLOW+PACK runs.

Both BASE and BLOW runs predict near-zero $BrO_{LTcol}$ on all O-Buoys and during most months at Utqiaġvik. The exception to this is the slight increases in monthly modeled $BrO_{LTcol}$ to $1*10^{13}$ molecules/cm$^2$ in March and April. This BASE increase in $BrO_{LTcol}$ indicates that oceanic SSA rather than blowing snow SSA can affect modeled BrO at Utqiaġvik due to its closer proximity to open ocean regions

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than the O-Buoys. The PACK and BLOW+PACK runs show the highest skill in reproducing observations, falling within the monthly average of hourly measured $BrO_{LTcol}$ error for 9 of the 13 months plotted in Figure 5. Both PACK and BLOW+PACK replicate the observed monthly pattern on O-Buoy 11 and at Utqiaġvik especially well. The seasonal pattern of maximum modeled $BrO_{LTcol}$ at Utqiaġvik in March followed by a decrease to near-zero modeled $BrO_{LTcol}$ in May is replicated in both runs despite the overprediction of $BrO_{LTcol}$ in February and March. The BLOW+PACK monthly $BrO_{LTcol}$ is between $1*10^{14}$ molecules/cm$^2$ and $1*10^{13}$ molecules/cm$^2$ higher than PACK monthly $BrO_{LTcol}$ due to the addition of blowing snow. This increase is most pronounced in February and March at Utqiaġvik when lower temperatures lead to lower threshold windspeeds and increased SSA production (see Supplemental Figure S4).

The inclusion of increased daytime yield of snowpack $Br_2$ drives monthly average $BrO_{LTcol}$ above $3*10^{13}$ molecules/cm$^2$ in the PHOTOPACK and BLOW+PHOTOPACK runs from February until June, far above peak observed monthly $BrO_{LTcol}$ of $2*10^{13}$ molecules/cm$^2$. The PHOTOPACK and BLOW+PHOTOPACK runs show steady decline in $BrO_{LTcol}$ from February to June at Utqiaġvik. Predictions of PHOTOPACK and BLOW+PHOTOPACK monthly June $BrO_{LTcol}$ above $2*10^{13}$ molecules/cm$^2$ on the O-Buoys is due to increasing photo-assisted local snowpack $Br_2$ emissions over the Arctic Ocean (see Figure 5). The PHOTOPACK mechanism predicts monthly average $BrO_{LTcol}$ within observational error only on O-Buoy 12 in April. Aside from this replication of the sparsely sampled O-Buoy 12 April $BrO_{LTcol}$, the PHOTOPACK mechanism overestimates $BrO_{LTcol}$. This overprediction of $BrO_{LTcol}$ by PHOTOPACK and BLOW+PHOTOPACK extends to prediction of unrealistically high mixing ratios for all tropospheric bromine species (see Supplemental Figure S7). This overprediction is a product of high ozone deposition velocities and daytime conversion rates to $Br_2$.

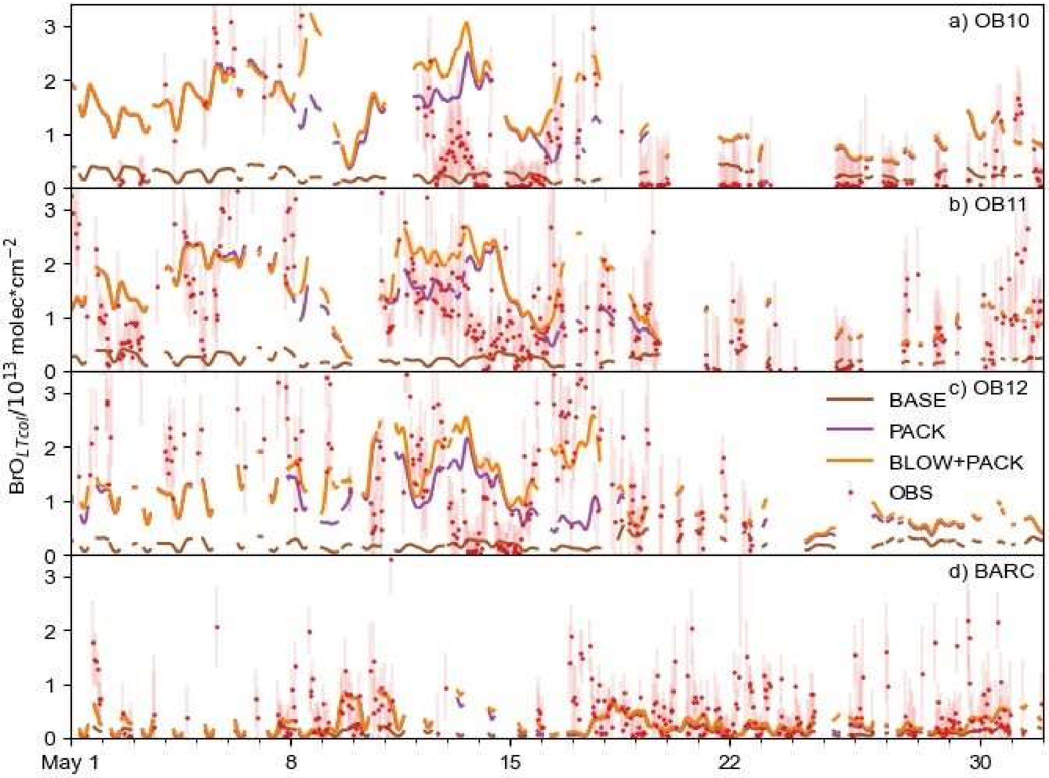

**Figure 6: Hourly $BrO_{LTcol}$ timeseries**

Hourly timeseries of BLOW+PACK, PACK, and BASE $BrO_{LTcol}$ on a) O-Buoy 10, b) O-Buoy 11, c) O-Buoy 12 and d) BARC at Utqiaġvik in the 2015 Arctic Spring. O-Buoy observations and error bars in red, BASE $BrO_{LTcol}$ in brown, PACK $BrO_{LTcol}$ in purple, and BLOW+PACK $BrO_{LTcol}$ in orange. All $BrO_{LTcol}$ plotted continuously except for gaps where $dSCDO_4 > 1*10^{43}$ $molecules^2cm^{-5}$.

### 3.4 BLOW+PACK run best replicates hourly BrO events in mid and late May

The model's hourly predictions of $BrO_{LTcol}$ in May 2015 are shown in Figure 6 for the BASE, PACK, and BLOW+PACK runs. The O-Buoys show fluctuations in observed $BrO_{LTcol}$ during May and show consistent increased columns of $BrO_{LTcol}$ from May 10 to May 20. The BASE run never rises above $10^{13}$ molecules/cm$^2$ and underpredicts most May hourly $BrO_{LTcol}$, although BASE predicts monthly $BrO_{LTcol}$ on OB10 for two out of three months. Both PACK and BLOW+PACK runs show more skill in replicating $BrO_{LTcol}$. The addition of the snowpack mechanism allows us to predict increased $BrO_{LTcol}$ in late May on O-Buoys 10 and 11. This points to the role of surface snowpack in late-season events in agreement with the findings of Burd et al. (2017).

We can identify the role of blowing snow SSA by comparing the PACK and BLOW+PACK runs. Both PACK and BLOW+PACK runs underestimate $BrO_{LTcol}$ during the first ten days of May. BrO

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predictions and observations are more active starting on May 10. The blowing snow mechanism increases BLOW+PACK $BrO_{LTcol}$ on May 12 and 13. PACK is skilled at replicating observed O-Buoy 11 $BrO_{LTcol}$ on both days, and both PACK and BLOW+PACK are within observational $BrO_{LTcol}$ error on May 13.

A BrO event also occurs on May 13 on O-Buoy 10. While the strength of the O-Buoy 10 BrO event is overestimated by PACK and BLOW+PACK, the shape of that event is duplicated in both runs. Examination of the O-Buoy 10 vertical $Br_y$ profile in Supplemental Figure S7 shows surface BrO increasing to 2 pmol/mol in the lowest 200 meters of the troposphere on May 10. BrO is mixed vertically on May 12 and 13 throughout the lower troposphere, with a linear decrease from surface BrO mixing ratios of 3 pmol/mol to 0 pmol/mol at 1200 m altitude. This May 12 $BrO_{LTcol}$ event is also associated with surface ozone depletion to 15 nmol/mol.

Observed $BrO_{LTcol}$ decreases rapidly on all O-Buoys after May 14, and the model is unable to track this sharp decrease. Rapid changes in $BrO_{LTcol}$ may be caused by sharp edges in BrO-enriched airmasses such as those seen by Simpson et al. (2017). GEOS-Chem run at this resolution cannot replicate abrupt changes in BrO, but it does slowly decrease $BrO_{LTcol}$ to reach $BrO_{LTcol}$ to less than $10^{13}$ molecules/cm$^2$ on May 16. The BLOW+PACK mechanism is skilled in replicating the magnitude and features of a mid-May BrO event on several O-Buoys.

Figure 7 shows all Spring 2015 $BrO_{LTcol}$ observations on O-Buoys 10, 11, 12, and BARC plotted against PACK $BrO_{LTcol}$ and BLOW+PACK $BrO_{LTcol}$. The increase in $BrO_{LTcol}$ on adding BLOW leads to fewer underpredictions of observations (see bottom right section of Figure 7b). The Pearson correlation coefficient (r) between PACK $GCBrO_{LTcol}$ and observed $BrO_{LTcol}$ is 0.33, improving to 0.39 on addition of BLOW in the BLOW+PACK run. Other runs show less skill in replicating observations, with a BASE $BrO_{LTcol}$ Pearson correlation to observations of 0.19 and a BLOW $BrO_{LTcol}$ Pearson correlation to observations of 0.23. We also performed a simple linear regression to determine the relationship between predictions and observations for each run. The slope of the line of best fit improves drastically on addition of PACK, changing from 0.06 for BASE and 0.07 for BLOW to 0.33 for PACK and 0.44 for BLOW+PACK. There is a positive synergistic effect on the slope of the line of best fit when using both BLOW and PACK in combination rather than individually. The use of both BLOW and PACK mechanisms implements literature findings on the processes influencing Arctic reactive bromine and increases correlation between GEOS-Chem predictions and observations.

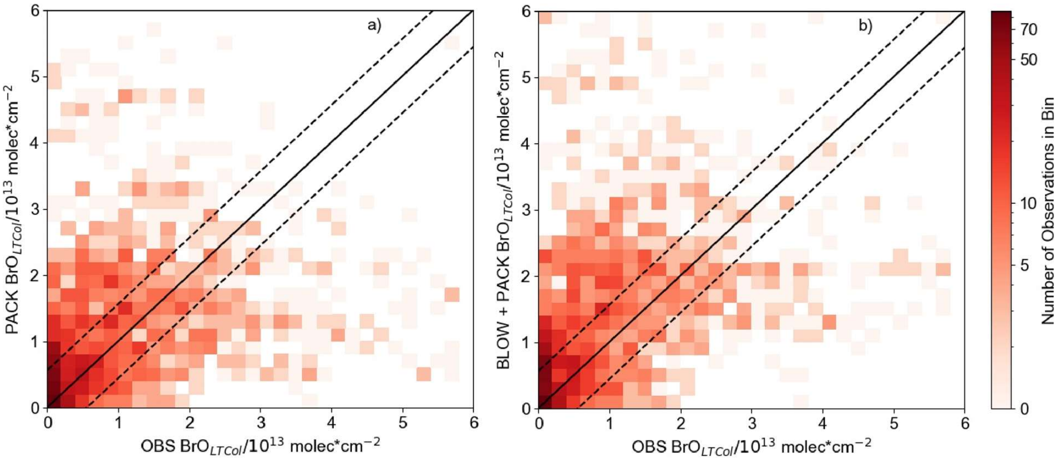

**Figure 7: Hourly modeled BrO$_{LTcol}$ versus BrO$_{LTcol}$ observations**

Two dimensional histograms showing density of GEOS-Chem predicted BrO versus all Spring 2015 hourly Br$_{LTcol}$ , with a) PACK BrO$_{LTcol}$ shown at left sorted into square bins of 0.2 with an Pearson *r* correlation to observations of 0.33 and b) BLOW+PACK BrO$_{LTcol}$ on the bottom sorted into square bins of 0.2 with Pearson *r* correlation to observations to 0.39. All units are in molecules/cm$^2$. 1:1 line drawn in the center in black, with a margin of the average observational error plotted in dashed black lines around the central 1:1 line.

## 4. Arctic Spring reactive bromine modeling discussion

### 4.1 Use of both mechanisms in conjunction leads to best prediction of tropospheric BrO results

Initial implementation of this snowpack mechanism in Toyota et al. (2011) increased the daytime yield of Br$_2$ from ozone depletion to 7.5% to improve agreement between observed and modeled surface ozone mixing ratios. Toyota et al. (2011) also increased the surface resistance of ozone to 10000 s/m, decreased deposition velocities on Arctic snowpack to approximately 0.01 cm/s. Our model using a constant yield of Br from ozone deposition performs best, despite observations that sunlight has an effect on reactive bromine recycling in the snowpack (Pratt et al., 2013; Custard et al., 2017). GEOS-Chem does not explicitly model heterogeneous photochemistry within the snowpack interstitial space but does include heterogeneous bromine chemistry on aerosol particle surfaces after the Br$_2$ is emitted from the snowpack into the lowest model layer. The updates to GEOS-Chem halogen chemistry (Schmidt et al., 2016; Sherwen et al., 2016b; Chen et al., 2017; Wang et al., 2019b) should be mechanistically sufficient to model daytime heterogeneous chemistry of reactive bromine on aerosol surfaces. We note that improvements to GEOS-Chem have increased the explicit modeling of these photochemical recycling and amplification processes, possibly reducing the need for empirical increases to daytime yields.

Our findings differ from recent implementations of the snowpack mechanism in Herrmann et al. (2021) and Marelle et al. (2021). While all snowpack mechanisms are based on Toyota et al. (2011), several large differences in model configuration and mechanism implementation explain these differences. We allow $Br_2$ production from ozone deposition over all snow surfaces, leading to much higher $Br_2$ production over MYI and coastal regions. Land snowpack can produce $Br_2$ on exposure to ozone and sunlight (Pratt et al., 2013; Custard et al., 2017) and Figure 4 shows our coastal snowpack producing large quantities of $Br_2$. Tropospheric reactive bromine chemistry has been observed up to 200 km inland from the coast (Peterson et al., 2018). Marelle et al. (2021) underestimates BrO in late March and overestimates Utqiaġvik BrO in early April. This seasonal pattern may be due to increased daytime ozone yield on first year ice near Utqiaġvik in April. Herrmann et al. (2021) found that HOBr and $BrNO_3$ deposition was more important in driving snowpack $Br_2$ production and that the daytime yield of 7.5% $Br_2$ on ozone deposition underpredicted BrO. We find that ozone contributes slightly more than HOBr and $BrNO_3$ because we allow for $Br_2$ production on ozone deposition over multi-year ice and coastal snowpack regions. The temporal scale of this manuscript spans the entire year, while Herrmann et al. (2021) only spans February, March, and April. Our longer timescale highlights the issue of increased daytime $Br_2$ yield during May and June (see Figure 4 PHOTOPACK) with increased emissions over the Arctic Ocean that are not in agreement with satellite observations of minimal Arctic tropospheric BrO in June (Richter et al., 1998).

### 4.2 Addition of PACK mechanism increases surface ozone predictive skill

The Barrow Arctic Research Center (BARC) in Utqiaġvik has the most comprehensive coverage of surface ozone in Spring 2015. A constant yield of 0.1% $Br_2$ from ozone deposition allows us to approximate the average vertical extent of ozone depletion events at Utqiaġvik in May 2015. The increase in $Br_y$ in the PACK and BLOW+PACK runs is confined to the lowest 1000 m of the atmosphere (see Supplemental Figure S7). Ozone depletions, caused by reactive bromine chemistry, often only occur within the lowest 1000 m of the troposphere (Bottenheim et al., 2002; Salawitch et al., 2010). Previous studies have found evidence of lofted BrO in plumes at altitudes up to 900 m AGL (Peterson et al., 2017). The monthly average Utqiaġvik May surface ozone in BLOW and BLOW+PACK is 22 nmol/mol, matching mean May surface ozone from 1999-2008 (Oltmans et al., 2012). The PHOTOPACK runs generate mean May surface ozone depletion to approximately 5 nmol/mol, far below the May mean. The PACK and BLOW+PACK runs duplicate the approximate vertical extent of elevated bromine levels and the strength of historic May ozone depletion.

Figure 8 shows hourly ozone predictions alongside BARC ozone observations (McClure-Begley, Petropavlovskikh, and Oltmans, 2014). The BASE model fails to replicate variance in ozone measured at BARC in Utqiaġvik, with a Pearson correlation coefficient to observations of 0.35. Adding PACK improves Pearson correlation to 0.47, within rounding error of BLOW+PACK Pearson correlation of

0.47. Both PACK and BLOW+PACK significantly improve model performance in replicating ozone depletions in such as the depletion below 30 nmol/mol from March 20 to March 29 but fail to track the subsequent recovery of ozone to background levels on April 1. Predicted PACK ozone does not recover to backgrounds levels until a height of roughly 1000 m. A similar pattern where our model replicates low ozone but fails to predict the recovery of ozone to background levels occurs on April 5 and 15. Previous modeling of Utqiaġvik spring 2012 ozone in WRF-Chem found a similar linear correlation coefficient of 0.5 to BROMEX observations (Simpson et al., 2017) when using both blowing snow and snowpack mechanisms (Marelle et al., 2021). We are biased low compared to observations, with a root mean square error of 17.0 nmol/mol compared to a root mean square error of 12.9 nmol/mol in Marelle et al. (2021). This may be partially due to limited vertical resolution in GEOS-Chem that may be inadequate to describe shallow surface-based temperature inversions and subsequent recovery. The high bias in ozone deposition velocity over sea ice surfaces may also contribute to low ozone mixing ratios near the surface.

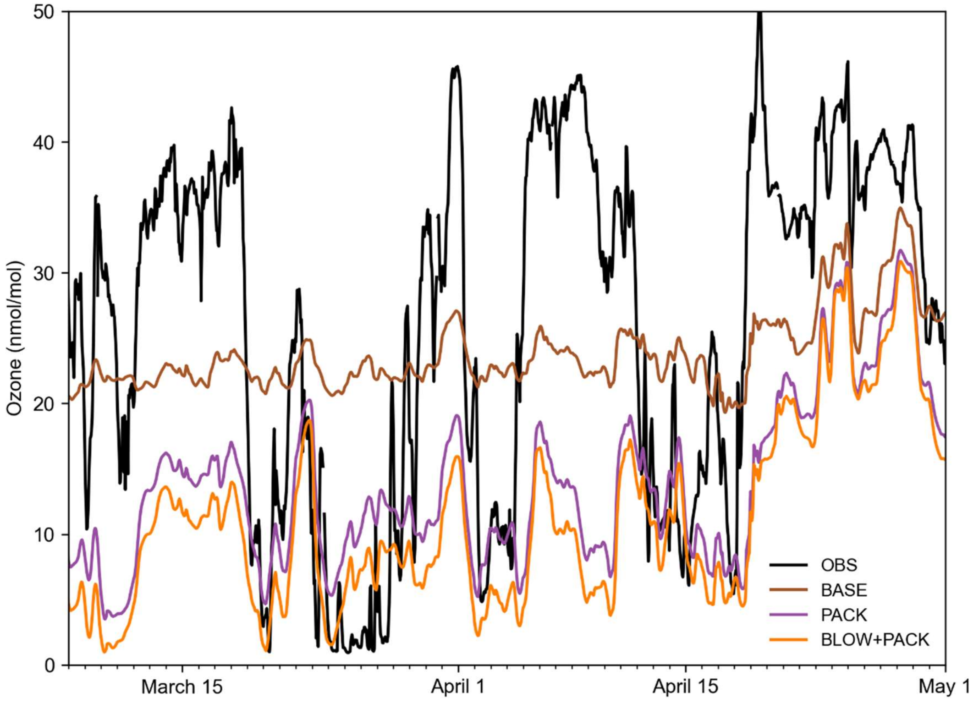

**Figure 8: Hourly Utqiaġvik ozone timeseries**

Hourly timeseries of BLOW+PACK, PACK, and BASE ozone Utqiaġvik in the 2015 Arctic Spring. Ozone observations at BARC in black (McClure-Begley, Petropavlovskikh and Oltmans, 2014), BASE ozone in brown, PACK ozone in purple, and BLOW+PACK ozone in orange. Gaps indicate missing observational data.

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## 5. Examining reactive bromine in the Arctic in September and October

O-Buoys deployed during fall 2015 measured BrO slant column densities characterized by noise around zero (see Supplemental Figures S8 and S9). We do not retrieve vertical column density from these fall slant column densities, because the resulting retrievals would be biased positive due to an algorithm requirement that only positive BrO column densities are allowed in the optimal estimation inversion. These differential slant column densities (dSCDs) can be used qualitatively to determine the presence or absence of BrO above the detection limit. If the dCSDs display noise around zero at all viewing angles, the BrO in the troposphere is below the detection limit of the spectrometer. The pattern of larger BrO dSCDs at near-horizon viewing elevation angles observed at Utqiaġvik during Arctic Spring in 2015 Supplemental Figure S7, indicate the presence of tropospheric BrO above the detection limit, which only occur during Arctic spring. Any BrO present in the Arctic troposphere in September and October falls below detection limits at Utqiaġvik (see Supplemental Figure S8) and on each O-Buoy (see Supplemental Figure S9). The average Arctic Spring 2015 MAX-DOAS $BrO_{LTcol}$ detection limits are 5 x $10^{12}$ molecules/$cm^2$ (Peterson et al., 2015; Simpson et al., 2017; Swanson et al., 2020). Both BLOW and PACK mechanisms lead to prediction of increased fall BrO because the weather and sea ice conditions specified in the emission algorithms occur in fall as well as spring.

Figure 9 shows fall predictions of $BrO_{LTcol}$ filtered for times when solar elevation angle was greater than 5°. BASE and SNOW $BrO_{LTcol}$ remain near zero in September but rise above the MAX-DOAS detection limit of 5 x$10^{12}$ molecules/$cm^2$ $BrO_{LTcol}$ in October. The addition of the blowing snow mechanism propels BLOW $BrO_{LTcol}$ up to 6 x $10^{13}$ molecules/$cm^2$ in October. O-Buoys 13 and 14 have the highest modeled fall $BrO_{LTcol}$ but even Utqiaġvik has several days of $BrO_{LTcol}$ above 5 x$10^{12}$ molecules/$cm^2$ in late October. There is no clear evidence of any BrO above MAX-DOAS detection limits at Utqiaġvik or on any O-Buoy in October, as seen by the dSCDs scattered around zero in Supplemental Figures S8 and S9.

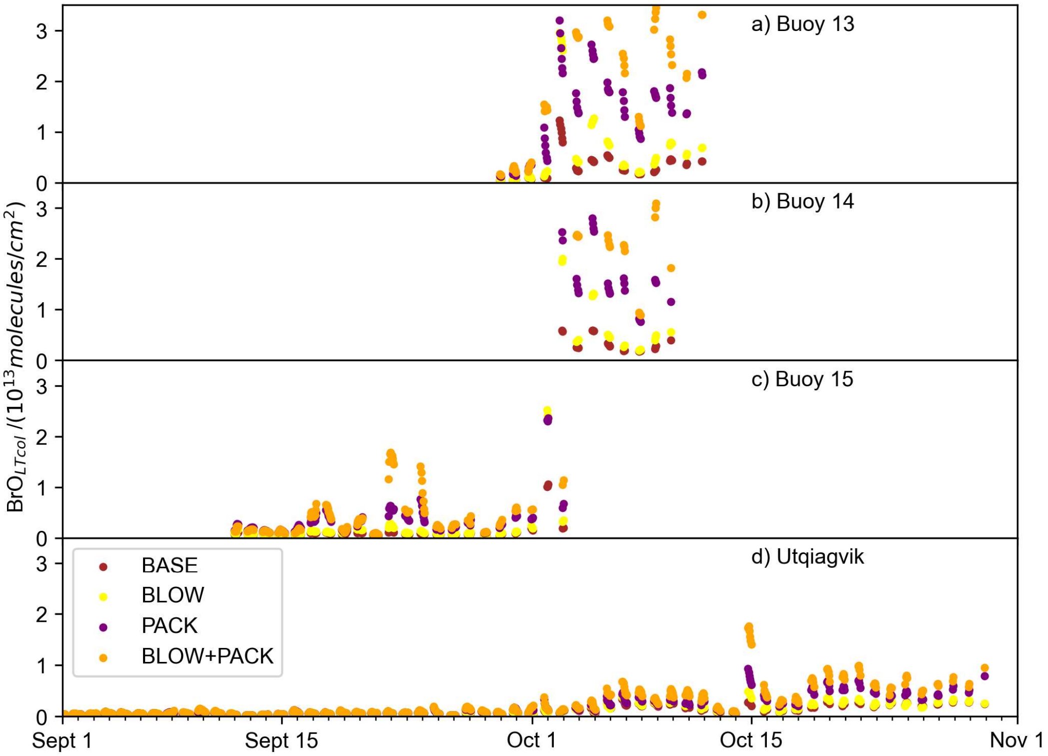

**Figure 9: Fall GEOS-Chem Predicted $BrO_{LTcol}$**

Hourly timeseries of BLOW+PACK, PACK, and BASE $BrO_{LTcol}$ on a) O-Buoy 10, b) O-Buoy 11, c) O-Buoy 12 and d) BARC at Utqiaġvik during September and October 2015 BASE $BrO_{LTcol}$ in brown, PACK $BrO_{LTcol}$ in purple, and BLOW+PACK $BrO_{LTcol}$ in orange. All $BrO_{LTcol}$ plotted continuously except for gaps where solar elevation angle was less than 5˚.

Both mechanisms assume that snowpack and SSA are just as capable of recycling reactive bromine as in the springtime. High fall and winter SSA agrees with observations of peak SSA during polar winter in both Antarctica (Wagenbach et al., 1998) and in the Arctic (Jacobi et al., 2012). The deposition of Arctic haze (Douglas and Sturm, 2004) and SSA (Jacobi et al., 2019) increases snowpack salinity and sulfate content over the course of winter and spring. This seasonal change in snowpack salinity and acidity may enable reactive bromine recycling in the Arctic Spring, but there may not sufficient haze and SSA deposition in fall to decrease snowpack pH and increase snowpack bromide content. Additional observations of fall snowpack over sea ice including ion content could show different snowpack composition in spring and fall. Thus the GEOS-Chem model overestimates fall BrO by assuming the fall snowpack is equally capable of reactive bromine recycling as spring snowpack, possibly due to the assumption of an infinite reservoir of snowpack bromide in all seasons. Most other modeling exercises have focused on spring with unknown predictions in fall, possibly indicating problems in mechanisms or parameterizations being employed, so we suggest that modeling should be done for a full year to improve underlying chemistry and physics.

## 6. Conclusions

We add snowpack $Br_2$ production to GEOS-Chem based on multiple field observations demonstrating molecular bromine production in snowpack interstitial air. We use a mechanistic parameterization of snowpack $Br_2$ production based on Toyota et al. (2011) in which $Br_2$ is emitted from all snowpack of sufficient salinity and depth over land and sea ice upon deposition of the precursor species HOBr, $BrNO_3$, and ozone. Prior work has also added a blowing snow SSA production mechanism that increases aerosol particulate bromide and thus facilitates heterogeneous recycling of reactive bromine on these aerosol particle surfaces. We update the halogen scheme to GEOS-Chem 12.9.3 and performed six model simulations including a BASE run with neither blowing snow nor snowpack emissions, a PACK run assuming constant yield of $Br_2$ on ozone deposition over all snow surfaces, a PHOTOPACK run assuming increased daytime yield of $Br_2$ on ozone deposition (similar in Toyota et al., 2011), a BLOW run using only blowing snow SSA formation and two additional runs combing BLOW and each respective PACK mechanism. The increased daytime yield of $Br_2$ in PHOTOPACK leads to overprediction of BrO in these simulations, but the PACK run (with constant $Br_2$ yield day and night) matches monthly averaged BrO vertical column densities for 9 of 13 cases at O-Buoy and Utqiagvik in springtime months. The PACK and BLOW+PACK runs were successful in replicating observed mid-May BrO events on O-Buoys as well as recurrence events at the end of May. The BLOW mechanism effectively increases aerosol surface available for turnover of reactive bromine. The snowpack mechanism has more impact on modeled BrO mixing ratios than the blowing snow mechanism, but both contribute to tropospheric reactive bromine. We extend our model run to the full year and find that enhanced daytime $Br_2$ yield can lead to increased Arctic Ocean $Br_2$ production in the summer. Examining modeled BrO in fall 2015 reveals prediction of BrO when using these mechanisms that are at odds with observations.

The inclusion of two Arctic reactive bromine production mechanisms based on literature observations of snowpack $Br_2$ emission and blowing snow SSA formation improves model skill in replicating Arctic tropospheric BrO in spring 2015. The snowpack is an important source of reactive bromine, and SSA particles provide an abundant surface for sustained reactive bromine recycling in the troposphere. We find that using both snowpack and blowing snow bromine production mechanisms is necessary for modeling BrO in the Arctic.

*Competing interests:* The authors declare that they have no conflict of interest.

Author contributions. WFS, WRS and CH designed the study. WRS collected and curated MAX-DOAS data. KC, LM, JT, LJ, JH and contributed code for reactive bromine mechanisms. CH, KC, LJ, JH, BA, SZ, QC, XW, and TS contributed model updates. WFS carried out modeling and analysis. WFS wrote the paper with input from all authors.

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