

Atmos. Chem. Phys. Discuss., author comment AC1
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Reply on RC1

William F. Swanson et al.

Author comment on "Comparison of model and ground observations finds snowpack and blowing snow aerosols both contribute to Arctic tropospheric reactive bromine" by William F. Swanson et al., Atmos. Chem. Phys. Discuss.,
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Responses to Reviewer 1

Specific comments:

Does the self-reaction of BrO only produce Br₂ (via R6) in the gas-phase chemical mechanism of GEOS-Chem? Br₂ should rapidly dissociate to Br-atoms by sunlight anyway, but I think a majority of Br-atoms are in fact produced directly via BrO + BrO (see https://iupac-aeris.ipsl.fr/htdocs/datasheets/pdf/iBrOx22_BrO_BrO.pdf). If this is true in the chemical mechanism of GEOS-Chem as well, the authors need to adjust their statement in the second paragraph of introduction, the diagram in Figure 1 and possibly the calculation for R1 presented in Table S1.

Self reaction of BrO also produces two Br atoms in GEOS-Chem (Parrella et al., 2012). The photolysis of Br₂ occurs readily to form two Br atoms, and we have lumped these two rates together for our calculation of R6 in Table S1. We have clarified this in the introduction paragraph and the caption of Figure 1. R6 increases in importance in our model run on the addition of PACK, making BrO self-reactions for those model runs one of the most rapid reactions outside of the reactions involved BrOx cycling.

On Lines 78-79, the authors state: "... bromine nitrate (BrNO₃), which can undergo hydrolysis on a saline surface to form HOBr as in HR3". The reaction of BrNO₃ on the "saline surface" may rather end up in the formation of BrCl and Br₂. It is probably more accurate to say, the hydrolysis of BrNO₃ occurs on aqueous and ice surfaces to form HOBr.

We have updated this sentence to your recommended wording.

In the caption of Figure 1 (Line 84), the authors state: "all gaseous species may undergo wet and dry deposition". Does it mean that even Br and BrO undergo wet and dry deposition in GEOS-Chem?

I have updated this sentence to reflect that all gaseous species can undergo dry deposition. Wet deposition of p-Br is shown in the figure.

Lines 276-277: How are these five particles per snow grain distributed between difference size bins of aerosols? Also, is there not any dependence on ambient relative humidity assumed in the production of SSAs from each snow grain?

The size distribution of the aerosols created by the BLOW mechanism follows a two-parameter gamma distribution following Yang et al. (2008). The value of five particles per snow grain was chosen based both on sensitivity studies and similarity to particle size distributions observed at Utqiagvik (Huang and Jaeglé, 2017). The dependence on ambient RH is encompassed by the threshold requiring relative humidity to be below saturation with respect to ice.

Section 2.5: It is not very clear what is assumed for the role of temperature in the snowpack emissions of molecular bromine. Does the model assume that the Br₂ emissions can occur in the same way as long as temperature is lower than 0 degree Celsius? Also, is the seasonal (summer) snowmelt not assumed to deactivate the capability of the snowpack for producing Br₂ as discussed by Burd et al. (2017)?

We assume in this simplified model that emissions can occur in the same way as long as the temperature is lower than 0 °C. It would be possible to halt all future production of Br₂ from snowpack after temperature rises above 0 °C (assuming instant snowmelt). While Burd et al. (2017) defined the melt onset date as the first time the 3-hour average temperature reached 0 °C. However, there can be a resumption of reactive bromine chemistry following the melt onset date (called a recurrence event in Burd et al. (2017)) and we wanted to include the potential for these events to occur. We also felt that choosing a duration above 0 °C after which all surface snowpack has melted would be arbitrary.

Line 364: Bariteau et al. (2010) estimated the dry deposition velocities of ozone on open oceans from shipboard ozone flux measurements. How has this information been translated to the parameterized dry deposition velocities of ozone on sea ice in GEOSChem?

Pound et al. (2020) updated GEOS-Chem to use a representation of oceanic ozone deposition based on its reaction with sea-surface iodide. This update was included in GEOS-Chem 12.8 and our model runs. However, this update to the ozone deposition scheme does not affect ozone deposition over sea ice within the model.

Line 468-469: It appears to me from Figure 4 that dry deposition velocities are higher (instead of lower) over the ice-covered ocean than over the open ocean in GEOS-Chem. The authors may want to reconsider the argument here and in the subsequent sentence.

I have removed this sentence, as the source does not support this argument. The Toyota 2016 paper only does direct comparisons between bulk Richardson numbers over sea ice and open ocean, finding that the air over sea ice is more likely to be stable. While they do discuss deposition velocities, their discussion is in terms of the sensitivity of ozone deposition velocity over ice to the choice of stability correction algorithm, and does not make any blanket statements about the relative deposition velocities over sea ice and open ocean. Their discussion of deposition velocity calculation is of interest for deposition scheme design but not relevant to this paper.

L538-539: The authors should elaborate on what they believe are the realistic ranges of mixing ratios for "all tropospheric bromine species" based on some observed values reported in the past.

This statement has been removed as we feel that a direct comparison between in-situ sampled observations of BrO mixing ratios and large grid average layer compositions are inappropriate in this context. We believe PHOTOPACK produces a large overestimation of monthly BrY but the bulk of this overestimation comes within the large p-Br mixing ratios near the surface. We have gathered data on BrO mixing ratios at Utqiagvik for five years

and the PHOTOPACK runs predict roughly double the average observed spring Utqiagivik BrO surface mixing ratios, which is an overprediction but is believable given the interannual variability in BrO (Swanson et al., 2020). Our instruments did not gather aerosol bromide content data and we cannot prove that PHOTOPACK p-Br- predictions are outside of a realistic range.

I frequently encountered unclear or inconsistent statements in Section 3.4. I recommend the authors to proofread again. Here are the problems I have noticed: "BASE predicts monthly BrOLTcol on OB10 for two out of three months" – be more specific (Line 551-552),

I have listed the months in which it was most accurate.

"BrO predictions and observations are more active starting on May 10" – clarify what the "more active" means (Lines 557-558),

I have specified that this refers to the increase in predicted BrO variability and higher BrO peaks.

Figure S7 does not seem to be showing the Bry profiles over O-Buoy 10 (Lines 563-564),

I have eliminated this paragraph, which referred to figures originally found in my thesis presentation that are not included in this manuscript.

and "The BLOW+PACK mechanism is skilled in replicating the magnitude and features of a mid-May BrO event on several O-Buoys" – clarify what the "several" indicates (Lines 572-573).

I have specified O-Buoys 10 and 11 here.

Section 4.2: Apparently, even the BASE model under-predicts the background mixing ratios of surface ozone by more than 10 ppb. It is probably worth mentioning the northern hemispheric tropospheric ozone bias in the current generation of GEOS-Chem as indicated in Wang et al. (2021, <https://acp.copernicus.org/articles/21/13973/2021/>).

I have added in a citation of the Wang paper and its finding that tropospheric ozone is underpredicted at high latitudes after the sentence in line 649.

Line 724: The authors should elaborate on what "recurrence events" mean exactly and why they are important or interesting, perhaps in earlier sections.

Burd et al. (2017) defines recurrence events (an increase in BrO after the termination date) in relation to termination date (date at which BrO has been within error of 0 for five days). As we do not have enough continuous May 2015 data on the O-Buoys to define a termination event, we have eliminated this vocabulary and instead noted that GEOS-Chem does a good job predicting BrO events on all O-Buoys in May 2015.

Line 724-725: The authors should discuss the enhancement of aerosol surface areas arising from SSAs in the BLOW mechanism in a quantitative manner (e.g., as compared to the surface areas of more persistent springtime haze aerosol particles), in earlier sections where the difference in model behavior between the PACK and BLOW+PACK cases is discussed.

We have rephrased this sentence to discuss particulate bromide availability. We briefly

discuss the increase in particulate bromide leading to increased BrO in section 3.3. As the particle size distribution produced from BLOW remains constant, any change in surface area is in fact related to the total mass produced, and therefore discussing particulate bromide lends more clarity to our argument.

Figure S6: If I understand correctly, the clear-sky screen is performed by rejecting the instances with the lofted layer degrees of freedom (lofted layer DOF) lower than 0.5, which in general corresponds to cloudy instances with dSCDs of O4 greater than $1.0 \times 10^{43} \text{ molecules}^2 \text{ cm}^{-5}$. However, in the plot shown, I do not see the increase of the lofted layer DOF with decreasing dSCDs of O4 (clearer sky), but actually the increase of the lofted layer DOF with increasing dSCDs of O4 (cloudier sky). Do I misunderstand something here?

While the relationship is complicated by the differential nature of our measurements, clear skies have higher O4 dSCDs than cloudy skies. We mention on line 443 that clear sky conditions have higher dSCD O4. The slant column density of O4 is proportional to the path the incident light travels through the atmosphere. A longer path means more absorption by O4, and clouds and aerosols effectively shorten the path length.

Figure S7: The O3 profiles are not shown for the BASE, BLOW, PACK and BLOW+PACK model results. It will be useful to include them as well.

With multiple small figures, we wanted to retain clarity in each subplot. The X-axis scale on the PHOTOPACK figures was such that we could plot ozone in nmol/mol and Br-eq in pmol/mol without distorting the graph. To add ozone to the other four graphs, we would have to add an additional set of tickmarks on top of an already crowded graph. We have made and examined these graphs and found that ozone is somewhat depleted at the surface but not nearly to the extent that it is depleted in the PHOTOPACK runs. I have attached a test figure showing the vertical extent of ozone depletion in May for the PACK run. While this paper does not focus on the ozone depletion aspect, we realize that there may be readers interested in a more detailed look at ozone depletions. We have prepared animations of the hourly vertical ozone profile at each observation location for May 2015 for each model run and are happy to share them on request.

Test Figure 1 Caption: Average May vertical ozone profile for the PACK run. Ozone in pmol/mol is depicted on horizontal axis, height above ground in km depicted on vertical axis.

Table S1: As indicated in the specific comment #1, I wonder if the self-reaction $\text{BrO} + \text{BrO}$ can directly produce Br-atoms in the GEOS-Chem gas-phase chemical mechanism. If it does, R1 should include its contribution.

This reaction has been lumped into R6, as both involve the reaction of two BrO molecules.

Table S3 contains some important values that should be clearly mentioned and discussed in the text. Comparison between the values of "Emission PACK Br2" and "Emission SSA p-Br-" should be referred to when discussing their respective impacts on the simulated concentrations of gaseous bromine species in the model. I assume that the "Emission SSA p-Br-" include contributions from both bubble bursting on open oceans and the production of SSAs from blowing snow. Please correct if I am wrong. I would also like to confirm that the changes in "Emission SSA p-Br-" are indeed less than 1 millions of moles per hour across the region by switching on the BLOW mechanism in the model.

The emitted SSA p-Br- quantity does include both bubble bursting and SSA production from blowing snow. The change in this quantity from adding blowing snow is an increase

of 390,000 moles per hour on adding BLOW to BASE, but a smaller decrease of 210,000 moles per hour is seen on adding BLOW to PACK. The values in this table are somewhat misleading, as the particulate bromide is not equal to the total particulate mass emitted, nor is it equal to the amount of reactive bromine added to the troposphere. This table provides raw numbers on emission of bromine across a specific region, but we do not feel that a table is the best way to convey this information. We feel that Figure 4 better conveys the spatial differences and patterns in emission. Tables S2 and S3 were included as a reference for other modelers who may be interested in the magnitude of dry deposition terms in our model. Neither are mentioned in the main text and we have decided to eliminate them from the supplement. We have moved table S1 to the main text to provide supporting information for Figure 1 and provide specific details on reaction rates within GEOS-Chem. We are happy to provide these tables and any other bromine budgets to interested colleagues.

Specific notes:

We have made all grammatical and technical changes in accordance with reviewer recommendations.

L444-445: From the sentence, I presume that the authors have computed differential slant column densities of O4 with 3-D meteorological fields of GEOS-Chem (or MERRA-2). Which variables are used in this computation?

We did not compute dSCDs of O4 within GEOS-Chem. We have updated this sentence to reflect that fact that the clear sky screen was only applied to observations, which were then compared to modeled BrO quantities.

Papers cited in responses:

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Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickle, L. J., Miller, B., Evans, M. J., Yang, X., Pyle, J. A., Theys, N. and Van Roozendaal, M.: Tropospheric bromine chemistry: Implications for present and pre-industrial ozone and mercury, *Atmos. Chem. Phys.*, 12(15), 6723–6740, doi:10.5194/acp-12-6723-2012, 2012.

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Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2022-44/acp-2022-44-AC1-supplement.pdf>