Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2022-44-RC1, 2022

Comment on acp-2022-44

Anonymous Referee #1

Referee 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., https://doi.org/10.5194/acp-2022-44-RC1, 2022

[General comments]

In this study, the authors incorporate parameterizations in the GEOS-Chem model for two mechanisms believed to play pivotal roles as a source of gaseous reactive bromine in the springtime Arctic lower troposphere. The first mechanism considered is the production of sea-salt aerosols (SSAs) from the saltation and sublimation of blowing snow. These SSAs are assumed to contain a trace amount of bromide anion, which is then converted to gaseous Br_2 via heterogeneous chemical reactions on the aerosol surface explicitly modeled in GEOS-Chem. This whole process representation is called "BLOW". The model also simulates the production of SSAs from bubble bursting on open oceans and the subsequent production of gaseous Br_2 in the same manner, included in the "BASE" case. The second mechanism considered in this study is the emissions of gaseous Br_2 from the snowpack. The representation of this process is based on the assumption that bromide contained in the snowpack on sea ice and coastal land surfaces is oxidized to Br_2 via dry deposition of ozone, HOBr and $BrNO_3$. Following original and more recent modeling studies that adopted this parameterization, the depositional loss of ozone is empirically associated with the production of Br_2 at the molar yield of 0.1%, with an option to increase this molar yield to 7.5% under the influence of sunlight. These process representations with and without the sunlight-related enhancement are called "PHOTOPACK" and "PACK", respectively. One of the major differences from the previous modeling studies in the implementation of "PACK" and "PHOTOPACK" is the assumption that the land snowpack within 200 km from coastlines contain the inexhaustible amount of bromide that can be released to the atmosphere as Br_2.

Even with some exploratory quantification attempts available in the literature, the physical and chemical processes representations related to "BLOW", "PACK" and "PHOTOPACK" inevitably bear high degrees of uncertainty in one way or another if we aim at their numerical modeling. As stated in the introduction by the authors, one of the lingering debates in the community of Arctic halogen chemistry is the relative importance of blowing snow and snowpack as a source of high concentrations of reactive bromine observed in the springtime polar (Arctic and Antarctic) boundary layer. A recent study by

Marelle et al. (2021) was the first attempt at simulating the effects of both blowing snow and snowpack in a single 3-D chemical-transport modeling framework using WRF-Chem. The present study employs the same approach but using GEOS-Chem with some changes in the implementation details. Both the Marelle study and the present study indicate that the source strength of bromine from SSAs associated with blowing snow is not large enough to account for the observed high concentrations of reactive bromine in the springtime Arctic troposphere in most cases but can be notable in some cases. We must note, however, that the parameterizations for "PACK" and "PHOTOPACK" have been adjusted more empirically than that for "BLOW" to match up with observed BrO enhancement and ozone depletions in the springtime Arctic boundary layer, calling for further research efforts in the community to evaluate the realism of these adjusted parameters and to sophisticate the formalism of process representations.

This study has some novelty in its methodology and scope. For the evaluation of model results, the authors mostly rely on the lower tropospheric vertical column densities of BrO (BrO LTVCDs) retrieved from several MAX-DOAS instruments at a coastal site in UtqiaÄivik, Alaska and at O-Buoy platforms floating with sea ice. They delve into the consistent application of averaging kernels between simulated and observed BrO vertical profiles and the screening of cloudy instances (rejected in the MAX-DOAS data processing) from the model output. This approach allows for more stringent apples-to-apples comparison than previously employed in the evaluation of model results for Arctic tropospheric BrO against the MAX-DOAS data. Another novelty of the present study is the simulation of Arctic bromine chemistry extended into summer and autumn seasons. The empirically defined "PHOTOPACK" algorithm is apparently at odds with the decreased source strength of reactive bromine from the snowpack in the summertime Arctic. In addition, the "BLOW" and "PACK" algorithms both produce relatively strong source strengths of reactive bromine in autumn, in obvious contraction with lower than detection limits of BrO LTVCDs measured from MAX-DOAS instruments. This finding calls for a better understanding of what causes the difference between spring and autumn in the source strengths of reactive bromine from blowing snow (or SSAs produced from it) and snowpack.

Overall, this study will be a useful addition to the literature. The manuscript could be accepted for final publication once the authors have addressed the following points adequately.

[Specific comments]

- Does the self-reaction of BrO only produce Br_2 (via R6) in the gas-phase chemical mechanism of GEOS-Chem? Br_2 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.
- On Lines 78-79, the authors state: "… bromine nitrate ($BrNO_3$), which can undergo hydrolysis on a saline surface to form HOBr as in HR3". The reaction of $BrNO_3$ on the

"saline surface" may rather end up in the formation of BrCl and Br_2. It is probably more accurate to say, the hydrolysis of $BrNO_3$ occurs on aqueous and ice surfaces to form HOBr.

- 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?
- 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?
- 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 Br_2 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 Br_2 as discussed by Burd et al. (2017)?
- 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 GEOS-Chem?
- 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.
- 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.
- 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 BrO_{LTcol} on OB10 for two out of three months" – be more specific (Line 551-552), "BrO predictions and observations are more active starting on May 10" – clarify what the "more active" means (Lines 557-558), Figure S7 does not seem to be showing the Bry profiles over O-Buoy 10 (Lines 563-564), 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).
- 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/).
- Line 724: The authors should elaborate on what "recurrence events" mean exactly and why they are important or interesting, perhaps in earlier sections.
- 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.
- 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 O_4 greater than $1.0x10^{43}$ molecules^2 cm^{-5}. However, in the plot shown, I do not see the increase of the lofted layer DOF with decreasing dSCDs of O_4 (clearer sky), but actually the increase of the lofted layer DOF with increasing dSCDs of O_4 (cloudier sky). Do I misunderstand something here?
- Figure S7: The O_3 profiles are not shown for the BASE, BLOW, PACK and BLOW+PACK model results. It will be useful to include them as well.
- Table S1: As indicated in the specific comment #1, I wonder if the self-reaction BrO +

BrO can directly produce Br-atoms in the GEOS-Chem gas-phase chemical mechanism. If it does, R1 should include its contribution.

- Table S3 contains some important values that should be clearly mentioned and discussed in the text. Comparison between the values of "Emission PACK Br_2" 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.

[Technical suggestions]

L20: "models" -> "modeling"

L36 and other lines: "windspeeds" -> "wind speeds" and "windspeed" -> "wind speed"

L65-66: "P1" -> "P2" (occurring twice)

L73: "bromine radical" -> "bromine atom"

L116: as well AS

L126-127 & 1057-1059: The reference to Toyota et al. (2014) appears to be inaccurate. From the context of the sentence, the authors may instead want to cite this article: Toyota, K., McConnell, J. C., Staebler, R. M., and Dastoor, A. P.: Air–snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS – Part 1: In-snow bromine activation and its impact on ozone, Atmos. Chem. Phys., 14, 4101–4133, https://doi.org/10.5194/acp-14-4101-2014, 2014. This Toyota et al. (2014) article may also be more appropriate than Thomas et al. (2011) for citation regarding Arctic surface ozone depletion associated with snowpack reactive bromine production.

L191: I see the MODIS imagery shown in the main map rather than in the inset map.

L224-225: The main sentence does not seem be completed with a verb.

L237 and other lines: “ten-meter” -> “10-m”

L241: C^o -> ^oC

L326: “no mention of” -> “no strong indication for”

L366: THE deposition VELOCITY OF O_3

L389: multiphase reactions INVOLVING CLOUD DROPLETS (?) and INTER-HALOGEN reactions between bromine, chlorine and iodine species

L444-445: From the sentence, I presume that the authors have computed differential slant column densities of O_4 with 3-D meteorological fields of GEOS-Chem (or MERRA-2). Which variables are used in this computation?

L525: “$1*10^{14}$ molecules/cm^2” -> “$1*10^{12}$ molecules/cm^2” (?)

L552: “more skill” -> “better skill”

L562: “duplicated” -> “reproduced”

L577: “PACK $GCBrO_{LTcol}$” -> “PACK BrO_{LTcol}”

L598: “ozone depletion” -> “ozone deposition”

L599: “10000 s/m” -> “10^4 s/m, which”

L640: “historic” -> “typical”

L648: “backgrounds levels until a height of” -> “background levels up to the height of”

L669: “dCSDs” -> “dSCDs”

L670-673: Consider rephrasing; “during Arctic Spring” is said twice.

Figure 9: Model results from “BLOW” (in yellow) are shown in the time series but they are not referred to in the caption.

Figures S8 and S9: Perhaps, the Y-axis title should be corrected from “BrO_{LTcol}” to “BrO SCD” or “BrO dSCD”.