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Interactive comment on "Pan-Arctic surface ozone: modelling vs measurements" *by* Xin Yang et al.

Anonymous Referee #1

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The authors present results of model simulations of halogen chemistry including Arctic ozone and bromine monoxide (BrO) abundance. These simulation results are compared to observations of the same species. Two different models are used, p-TOMCAT and UKCA, and are compared. A critical part of the modeling effort is the need to model the production of sea-salt derived aerosol particles (SSA), which is done here by including both modeled open ocean (OO) and sea ice (SI) processes based upon a blowing snow model. Overall, I think that the manuscript is not carefully argued and would need major revisions to be considerable for publication in ACP. I come to this decision based upon the following major points. After discussion of the major issues, I note a number of smaller or typographical issues.

A major lack of the manuscript comes from the belief that the process trying to be mod-

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eled is uniquely represented by the model. This belief underlies statements such as in the abstract, where the manuscript states "...reproducing both ODEs and BEEs in the Arctic indicates that the relevant parameterizations implemented in the models work reasonably well, which supports the proposed mechanism of SSA and bromine production from blowing snow on sea ice." It is true that inclusion of this modeled process reduces springtime ozone and thus getting the model results closer to observations. However, to really make this statement (and many others like it in the manuscript), other models of sea-ice-related reactive bromine release would have need to have been considered and shown to be of lower skill than the proposed blowing snow SI-sourced bromine model. Without considering if other sea-ice-related processes could work effectively, the authors have not shown that this process is uniquely the one that is responsible. Other models in the literature could release of reactive bromine from snowpack (e.g. Pratt et al. 2013), production of SSA from wind over open water in sea ice leads between ice floes (e.g. Kirpes et al., 2019). To be devil's advocate, one could make a model of seasonally varying dry deposition of ozone to snowpack, which could be tuned to get agreement with the observed average monthly ozone data. Should the agreement of this model with average ozone observations then be taken as a sign that this process is the actual physical process that is occurring? The authors neither show that their model is unique nor do they present external validation of aspects of their model. The use of Antarctic snow salinity data scaled by what appear to be a number of tuning parameters without Arctic validation does not give confidence in this SSA production model. Specifically, on page 5, line 37, the authors indicate that they have altered parameters of their model. Why? To what end? Why did they change the snow salinity by 3.5 times Antarctic data? The authors indicate on page 10, line 37 that "We lack snow data on Arctic sea ice to constrain the dataset used in this study". There are papers on snow on sea ice in the Arctic (e.g. Pratt et al. 2013, Krnavek et al., 2012, Xu et al., 2016). How do these observations compare with their scaled salinity. The use of these tunings without any justification of what is trying to be obtained gives me caution in believing statements like the one at the start of this paragraph, and particularly with

attribution of ozone losses to processes, such as the abstract, which states: "In April, bromine chemistry can cause a net loss (monthly mean) of 10-20 ppb, with almost half attributable to open-ocean-sourced bromine and the rest to sea-ice-sourced bromine". I find the link between the modeled processes and real processes, which underlies this statement, suspect given the lack of uniqueness and I find that attribution questionable given the apparent tuning of processes to some unknown end.

It is not clear from this study how reactive bromine is produced from the SSA bromide. The section on this topic is 3.1, and also refers to the supplemental table 1. First, it is not clear what the model is doing. Is the model actually considering heterogeneous chemical reactions that would convert SSA bromide (Br-) to gas-phase reactive bromine precursors (e.g. Br2)? I expect that the model is not actually considering these reactions, but instead simply multiplying the DF * SSA to get "lost" Br- from the SSA and making this into Br2. The manuscript should be clear as to what is actually being modeled. If the process is simply taking the bulk DF times SSA bromide, then there are a number of physical and chemical problems with this approach. For example, we know that reactive bromine deactiviates fairly rapidly (e.g. reaction of Br with H2CO to form HBr), which then partitions to the aerosol particle phase, increasing Br- in the SSA (and thus reducing the DF). This recycling of reactive bromine is needed for persistent (e.g. multi-day) BrO events, such as are observed in the large satellite-detected BrO events associated with storms. The DF is a bulk average for the month, but there were very likely periods where the actual DF was larger, only to be reduced by return of bromide following deactiviation. A DF-based model would also not properly deal with mass transport limitations to aerosol particles that limit gas-surface reactions for supermicron aerosol particles. Thus, there would be a size dependence to aerosol reactivity that is not modeled by a simple DF-based approach. Lastly, it seems likely that there is a limit to how much reactive bromine can be produced, where the limit is likely related to the availability of radicals. This apparent limit is observed in the fact that few manuscripts report BrO mixing ratios more then ∼30-40 pptv. Presumably any such limit would affect the Antarctic DF data that are the basis for the seasonal DF model

being applied in this manuscript. If a DF-based scheme from the Antarctic were used and then the snow salinity (thus SSA mass concentration) is scaled by 3.5x, it would give 3.5x as much production of reactive bromine, but that may then exceed the ability to actually produce reactive bromine precursors from this SSA. The text also says that "... we could not justify this seasonal DF pattern, which demands further systematic measurements in the Arctic. As used in previous modeling studies, a non-seasonal (size dependent) DF scheme for the NH is used for comparison." I think the authors are saying that the process that they are using in this manuscript is not justifiable; if so, why did they describe the seasonal DF mechanism, and it seems they used it for most of the modeling.

The abstract (and text) read as if the "result" of attribution of bromine is a result of this study or that model simulations were modified to agree with some aspect of the observations, which doesn't appear to be the case. The model seems to turn on and off processes that are prescribed to get this attribution and no clear "inverse modeling" was carried out to get this reported attribution. This wording should be clearer. In lines 27-29, the implication is made that blowing snow is the source of ODEs, but as described above, they have not uniquely shown that other sea-ice processes (e.g. snowpack chemistry, SSA production from open leads) cannot also be a source of ODEs. Therefore, this wording is misleading. I don't mean to differ with the idea that some ODEs may arise from blowing snow; I think they do, but the wording here discounts other literature-supported ideas for reactive halogen production by not testing them and also by believing that their parameterization is uniquely identified with they process they are trying to model. On lines 34-37, the abstract again tries to uniquely connect the improvement of agreement with observations with the process they intended to model (e.g. blowing snow). I expect that addition of other reactive halogen production models (e.g. snowpack and SSA from open leads) could also result in a model that "works reasonably well", so they have not shown that their improvement requires blowing snow.

Other issues:

The manuscript's writing is not precise and lacks significant details. The terms "bromine" is used very often, but in some cases they seem to be referring to reactive bromine (e.g. bromine radical species), total inorganic bromine (which is sometimes described as BrY, but often it is not clear), or sometimes seeming to include SSA bromide (Br-). The manuscript should chose a language for these species and use them consistently as opposed to the current confusing approach.

p2, line 15. VMR is not defined.

P2, line 26. The inclusion of "stratospheric BrO intrusions" is misleading here. Salawitch et al. 2010 discusses BrO total column enhancement due to stratospheric BrO intrusions, while this section is talking about release of reactive halogens in the lower troposphere. This should be clarified.

p2, line 34. "cruise data" – clarify. Note that this is Antarctic data.

p2, line 43. The text says "bromine depletion", when I think they mean "bromide depletion". This is one of many instances of inaccurate use of bromine-related terms. I am not pointing them all out, but they happen dozens of times throughout the text. Please chose terms, define them early and use them accurately.

p3, line 15. Specify "Pallas, Finland"

p3, line 24. What is an "integration"? Please explain.

p3, line 26. Is "validate" the right term here? Neither SSA production nor reactive bromine release is actually validated in this study – the effect of these modeled processes on ozone depletion and BrO are explored.

p4, line 7. The sentence "During the period..." is quite hard to read. I think "All" on line 8 maybe should not be capitalized?

p4, line 29. Cut "that" at the end of the line. Next line says "surface spectral reflectance

of 0.9" and is confusing. I think a non-spectral (e.g. not a function of wavelength) albedo of 0.9 is used in the spectral band of the retrieval (a band in the UV). If a spectrally varying albedo is used, please give more details describing this function.

p5, line 4. "...to the surface." is not well defined here. Earlier, the manuscript indicates that for VCD trop correction, BrO is assumed to be well mixed and below 400m. Thus this station (610m AGL) is above the BrO layer and looks up, so it has little sensitivity below it. Please clarify what is meant by "surface" in this context.

p5, line 15. 10 hPa is a pressure not an altitude, please be clearer.

p5, line 22. Has this model actually been validated in terms of vertical transport under stable Arctic conditions? I went to check these citations and found that "Ruti et al. 2011" is not in the citations, so I could not check. In another place, the text seems to indicate that the validation in Russo et al. 2011 is for tropical conditions. On page 6, it says "A detailed comparison of model characteristics in vertical mixing and transport of tropical boundary layer tracers was performed by Russo et al. (2011)". Please indicate if the model has been validated for the Arctic.

p5, line 26. Ozone deposition has been studied by Helmig, Bocquet, and others working in that group. Please include this work.

p6, line 38. How is "a full distribution of surface snow salinity" used in the model? Please clarify. Generally, details on how this model works are lacking.

p7, lines 1-5, also bottom of prior page. Why were these changes made? It appears that the model was being tuned in some way, but to what end? I believe that the Huang and Jaegle work has tuned the model in multiple ways so as to agree with various truth metrics (e.g. aerosol extinction from satellite, SSA observations, etc.). Please put your modifications into the context of other tunings and give a description of why this was done (e.g. what truth metric were you trying to match when you chose say N=20?).

p7, line 15. It is discussed that this approach "may introduce bias". Please describe

the model here, possibly pointing to a future "discussion" of this point.

p6, line 21. The language seems to often be in jargon of the field. What is a "dynamical core"?

p6, line 25. What does "but has since developed differently and now..." mean?

p6, line 28. I think it points to lack of detail on what the models are doing, but I don't understand what "tagged and tracked for online calculation of heterogenous reaction rates." means. Does the UKCA model not consider heterogenous reactions?

p6, line 36. Is there no heterogenous reaction of HOBr with aerosol bromide? If that process is considered, is the Br2 produced by it put in the grid cell (vertically) where it happened or is it placed at the surface?

p7, line 10. "model responses"? Maybe "model results"? This confusion continues onto line 11, where I think the species compared are bromine mixing ratio (or partial column) and ozone mixing ratio.

p7, line 12. maybe "model configuration" instead of "set-ups"?

p7, line 16. Many acronyms in this line. Can the point be made with words?

p7, line 27. I think the "minimum monthly-average VMRs" are being discussed. These are not the "minimum VMRs", which are clearly lower than the monthly average.

p7, line 32. I would say "further south".

p7, line 25. Again the use of imprecise language on bromine species is evident. I don't think they mean "Br" atoms on this line.

p7, line 37. I think they mean to say "OO-sourced bromine does not alter..."

p7, line 40. "maximum ozone loss" is confusing in this context. Maybe the peak of the annual ozone loss amount is meant?

p8, line 5. This finally defines BrY. Please move the definition much earlier and clarify

your bromine terms. I think the formula should say 2 times Br2. The X is confusing.

p8, line 29. 0.5 ppt of BrY is discussed here, which makes me wonder if BrY is the surface BrY, or includes BrY at higher altitudes? Please clarify what is being measured and how VSLS bromocarbons contribute to it.

p9, top. The manuscript does a good job describing the distributions of ozone observed and as calculated by the model, but the discussion of this point is lacking. The observed ozone distributions are sometimes bimodal, and are generally much flatter, while the modeled distributions are mono-modal and simply shifted to lower values. However, the general metric used for skill of the model is the monthly mean (e.g. Fig. 2). Even if the mean were correct, a differing distribution function indicates that the modeling is having problems reproducing the processes.

p9, line 27. The statement "In general, boundary layer ozone is influenced by column BrO...." I am not sure I understand if this is a result of the current study or an idea from the literature that is being cited (without reference) as a partial explanation of this study. Please clarify this section of the text.

p10, line 33. Please add "modeled" to make the text read "that affect modeled bromine emissions".

p10, line 37. Please consider Arctic snow data as discussed above.

p11, lines 1-4. This sentence is long and not clear. I'm not sure what is being discussed with respect to a "cut-off size". If there were actual heterogeneous processes being modeled, then the size distribution would matter a lot. Submicron aerosol particles tend to have little mass transport limitations for gas-surface reactions, but super-micron particles suffer transport limitations, so the same mass loading of SSA would have drastically different heterogeneous reactivity if it were all sub-micron or all super-micron. Please clarify and discuss.

p11, lines 10-14. In the presence of heterogenous reactions that release Br- from

aerosol particles and also formation of HBr that then sticks back to particles, the DF will be highly variable. Snowpack bromide observations (e.g. Krnavek et al., 2012) indicate that some snow is enhanced and some is depleted, and that varies in time. Thus, the use of a monthly DF seems unrealistic in the presence of gas-surface exchange of bromine species.

p11, lines 22-32. Again, other models of sea-ice-related production of reactive bromine (e.g. snowpack, SSA from open water leads) may be able to also explain the springtime ODEs and tropospheric BrO – this manuscript just did not test them. Thus, I agree that there is some sea-ice-related mechanism, but not necessarily only the blowing snow mechanism. The manuscript disregards other potential processes and thus may be misrepresenting the actual underlying physical process (or more likely multiple processes).

References:

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