

# ***Interactive comment on “3D simulations of tropospheric ozone depletion events using WRF-Chem” by Maximilian Herrmann et al.***

**Anonymous Referee #2**

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Herrmann et al present regional modeling of ozone and BrO in the Arctic spring troposphere.

The modeling focuses on Feb. – Apr. 2009 with two types of comparisons to observational data: 1) Arctic-wide maps of BrO vertical column densities, and 2) ground-level O<sub>3</sub> at Utqiagvik, AK and Summit, Greenland. The time period was chosen to coincide with the OASIS field campaign at Utqiagvik, AK during which a large suite of ground-level measurements were made “for comparison with the numerical results” (as the authors state on Lines 107-109), but no comparisons are made, even to the authors’ own near-surface BrO data at Utqiagvik, AK (Freiss et al. 2011, JGR). Comparisons to other available observational data, especially the available Br<sub>2</sub>, HOBr, and BrO mole ratios, from the campaign would yield improved understanding of the simulations. For

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example, Figures 4 and 7 currently compare O<sub>3</sub> between two simulations and observations, but only modeled BrO is shown. Since BrO was measured at the same location and time, this lack of comparison is a major weakness of the current paper that was pointed out in the quick review. The authors stated in their response: “It is planned to include the OASIS observations of Freiss et al. (2001) and Liao et al. (2012), but this will be done at the next review stage of the paper. . . We will also investigate further OASIS data, which may be compared to the modeling results.” I consider this to be an essential and critical step for model evaluation. Not only will this make the manuscript much stronger, but it is a huge opportunity, especially given the suite of available data, including the vertically resolved BrO profiles (for the dates and location in Figure 7!) in Freiss et al. However, since this has not yet been completed, I cannot currently evaluate this.

The model is initiated with 0.3 ppt HBr and Br<sub>2</sub> in the lowest 200 m, and CHBr<sub>3</sub> is fixed to 3.5 ppt. Then Br<sub>2</sub> emissions occur via BrONO<sub>2</sub> and HOBr recycling on aerosols (for which the authors are encouraged to cite McConnell et al 1992, Nature (cited elsewhere in this manuscript) & Peterson et al 2017, ACP, “Observations of bromine monoxide transport in the Arctic sustained on aerosol particles” for observational support of this mechanism). The authors then include snow Br<sub>2</sub> emission over sea ice via reaction of O<sub>3</sub> with bromide and then claim “The bromine emission due to bromide oxidation by ozone is found to be important to provide an initial seed for the bromine explosion.” (Abstract, Lines 10-12; also similarly stated on Lines 462-463 and 489-490) However, this is simply because of how the model is set up with this as the initial source, and it is not clear whether this setup and conclusion agrees with observations. Pratt et al. (2013, Nature Geoscience; which includes coauthor U. Platt) did not observe detectable Br<sub>2</sub> production upon ozone reaction with snow bromide in the dark, whereas Br<sub>2</sub> was produced when authentic snow was exposed to sunlight (without O<sub>3</sub>), showing efficient condensed phase formation of Br<sub>2</sub>. Addition of O<sub>3</sub> initiates the traditional bromine explosion mechanism and further Br<sub>2</sub> production (which is included in the model). The authors do not include condensed-phase Br<sub>2</sub> production from the

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snowpack and do state this in the manuscript as something for future work, but it is important when making conclusions statements that the model set-up and uncertainties be very clear, as this is otherwise misleading.

There is an opportunity presented by this work in Figures 12, 13, and associated discussion to compare the modeled snow Br<sub>2</sub> emission rates to those previously measured by Custard et al (2017, ACS Earth & Space Chem.) during Feb in Utqiagvik and modeled by Wang & Pratt (2017, JGR).

In several locations in the Results & Discussion and Conclusions, the authors make statements that are not supported by the literature and modeling presented, especially when considering how the model is setup. Further the lack of comparison to BrO measurements at Utqiagvik weakens the results presented because the ground-level halogen chemistry at ground level cannot be properly evaluated. It is my hope that the authors will add OASIS measurements of Br<sub>2</sub>, BrO, and HOBr so that the model results can be better evaluated. Discussion that needs to be re-evaluated, in particular, includes:

Lines 287-289 and Lines 342-343: “A possible conclusion is that the bromine explosion mechanism is inefficient to explain ODEs in the Arctic, or the present bromine explosion scheme is incomplete for instance with respect to emissions of bromide containing aerosols due to blowing snow and/or regions of increased B such as frost flowers.” “...the bromine explosion mechanism alone is insufficient to properly predict the bromine production.” I’m guessing that the authors may be referring here to the Br<sub>2</sub> production via O<sub>3</sub> reaction with Br- (R10) as the “bromine explosion mechanism”, but this would not be consistent with the literature, that refers to the bromine explosion as R1 + R5 + R6 + R8 + R9. Further, Wang et al. (2019, PNAS) showed, through simultaneous measurements of Br<sub>2</sub>, HOBr, BrO, Br atoms, and O<sub>3</sub>, that local ODEs could be quantitatively explained by the measured [Br], which would quantitatively show to be produced primarily by snow-phase reactions (condensed phase and heterogeneous). Further, the authors’ statement is not in line with published literature and is further

weakened by the fact that the modeling in the current work is missing what has experimentally been shown as a major source of primary Br<sub>2</sub>. It needs to be acknowledged here that the model does not include sunlit condensed phase snowpack Br<sub>2</sub> production (without O<sub>3</sub>), which Pratt et al (2013, Nat. Geosc.) found to be an efficient Br<sub>2</sub> production mechanism, when Br<sub>2</sub> was not detectable from dark reaction of O<sub>3</sub> with snow, sea ice, or brine icicles (proxy for frost flowers). Sunlit condensed-phase Br<sub>2</sub> production was also not observed for either sea ice or brine icicles, as predicted by Kalnajs and Avallone (2006, GRL), who stated “frost flowers are unlikely to be a direct source of atmospheric bromine.”

Lines 300-302: The authors discuss here the transport of BrO from the Bering Sea to Utqiagvik, but it is important to remember that heterogeneous reactions are required in this scenario given the short lifetime of BrO (e.g., Platt and Honninger, 2003, Chemosphere; McConnell et al. 1992, Nature). Given their previous work, the authors are aware of this, but it needs to be clarified in the main text. Further, it is implied here that the model does not produce Br<sub>2</sub> near Utqiagvik in February, but measurements in Utqiagvik in February 2017 showed local measurable Br<sub>2</sub> snowpack fluxes (Custard et al 2017, ACS Earth & Space Chem). Further, U. Platt is a coauthor on the currently uncited, but highly relevant paper describing Jan.-Feb. BrO at Utqiagvik (Simpson et al. 2018, GRL).

Lines 315-316: The authors discuss here model inaccuracies associated with elevated O<sub>3</sub>, attributing this to haze or pollution. The prior modeling by Walker et al (2012, JGR, “Impacts of midlatitude precursor emissions and local photochemistry on ozone abundances in the Arctic”) is relevant here and should be considered in interpreting the authors’ model results (including the separate statement on lines 355-356). Also, the model here does not spatially resolve leads, the convection from which have been experimentally shown to control O<sub>3</sub> recovery (end of the ODE) due to down-mixing from the free troposphere (Moore et al. 2014, Nature, “Convective forcing of mercury and ozone in the Arctic boundary layer induced by leads in sea ice”). The lack of spatial

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resolution of leads and resulting impacts on meteorology (only briefly mentioned on line 375) and ozone should be considered in the discussion and interpretation of model results.

Lines 410-425 and Lines 483-488: This is good discussion, but it would further strengthen the discussion to incorporate observational literature to supports the interpretation here. For example, the model assumption that snow over land and near coasts have no salt content is inaccurate, as shown by Simpson et al (2005, GRL) and supported by BrO measurements by Peterson et al (2018, ACS Earth & Space Chem) and Pratt et al (2013, Nature Geosci.), which are cited elsewhere in the manuscript. Similarly, the discussion of FY sea ice vs MY sea ice as a source of bromine is presented, with measured snow [Br-] by Peterson et al (2019, Elementa) and includes a section of suggestions to modelers.

#### Additional Comments:

Lines 8-10: I suggest leaving the statements about the reactive surface ratios out of the abstract, as there isn't sufficient context here for the reader to understand what this physically means. It would be better to instead discuss other scientific results of the work, especially since this surface ratio seems to effectively be a model tuning parameter.

Lines 22-23: Note that Br atom reaction with ozone was directly observed by Wang et al. (2019, PNAS), so this can be stated more strongly here by inclusion of this reference.

Lines 32-33: Replace "ice" with "snow" to reflect current knowledge based on more recent direct measurements: Pratt et al. (2013, Nature Geoscience), Custard et al. (2017, ACS Earth & Space Chem.). Further, Pratt et al. (2013, Nature Geoscience) showed through direct measurements that sea ice did not produce detectable Br<sub>2</sub>. Further, while there is still much to be learned about Br<sub>2</sub> production, as reflected in the sentence on lines 33-34, this paragraph primarily cites references from the 1990s and

does not discuss current knowledge gained from the last decade, thereby suggesting that less is known.

Line 40: The authors chose to designate heterogeneous reactions with “aq” above the arrow, but this is not a common notation. It would be clearer in the introduction to simply include the phases of each species as subscripts next to them in the equations so that it is clear to a novice reader which species are in the gas vs aqueous phase.

Line 45: The authors can strengthen this sentence by pointing to Pratt et al. (2013, Nature Geoscience), who directly showed the pH dependence of Br<sub>2</sub> production through field-based experiments.

Line 57: Please clarify what is meant by “the surface layer” here. I believe the authors are discussing the snow grain surface, but this phrasing is also used for the atmosphere. Also, the authors should note, for clarity here, that sunlight is required for condensed-phase OH production.

Lines 61-67: References are needed for these sentences. The work of Thompson et al (2015, ACP, “Interactions of bromine, chlorine, and iodine photochemistry during ozone depletions in Barrow, Alaska”) is highly relevant here, especially since that work focused on the OASIS field campaign.

Lines 75-76: The authors cite a 2007 review here for BrCl production via HOBr + Cl<sub>2</sub>. It is important to note that McNamara et al (2020, ACS Earth & Space Chem), who measured BrCl, showed that the Cl<sub>2</sub> + Br<sup>-</sup> reaction is also a significant source of BrCl in the Arctic spring. However, despite mentioning these sources of Br atoms, Tables S3 and 4 do not include these reactions, suggesting that they are not in the model. Please clarify this in the text, as it is an additional uncertainty associated with the model setup.

Lines 80-81: Note that more recent work by Halfacre et al (2014, ACP) showed ozone measurements from five buoys across the Arctic and “no apparent dependence [of ODEs] on local temperature”.

Line 89: Nasse et al 2019 (Atmos Meas Tech) appears to be the incorrect reference here, as it does not include Arctic ozone data.

Lines 93-94: Please connect this sentence about Thomas et al. (2011) to the halogen chemistry being discussed in this paragraph.

Figure 1: Provide the source of the sea ice data. Also label the latitude rings and especially where 88N is, and state in the caption that FY ice is assumed above this latitude, as stated in the text.

Lines 141-142: Note that iodine atom reaction with ozone has been shown to significantly increase the ozone depletion rate, even at low mole ratios (e.g. Raso et al. 2017, PNAS, showed 0.3 ppt of I<sub>2</sub> to increase the initial rate of ozone depletion by 31% in a case study). Adding iodine chemistry to the model would be a significant task, so I think it is ok currently to not include. However, a greater acknowledgement of uncertainty is required here and should be mentioned again in the discussion and conclusions when comparing ozone levels between measurements and modeling.

Line 170 and Table S3 caption: Change “ice/snow” to “snow” here, since Line 191 states that all ice is assumed to be snow-covered.

Line 193: This is the only place that I saw N<sub>2</sub>O<sub>5</sub> deposition mentioned as a source of Br<sub>2</sub>. This is intriguing and should be discussed in the results. What level of N<sub>2</sub>O<sub>5</sub> is predicted by the model, and what fraction of the Br<sub>2</sub> is predicted to be produced? I’m also confused because I don’t see this heterogeneous reaction in Table S3. McNamara et al. (2019, Environ. Sci. Technol.) measured N<sub>2</sub>O<sub>5</sub> in Utqiagvik during spring, which would provide a comparison point.

Lines 234-245: It is suggested to move this text and Table 2 to the Methods section, as results are not presented here.

Line 281 and Figure 4 caption: It is stated that “Figure 4 shows modeled and observed surface ozone and BrO at Utqiagvik” when measured BrO is not shown, and this is

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misleading. It is my hope that the authors will rectify this by adding measured BrO (from the OASIS study) to Figure 4!

Lines 286, 341-343, and Lines 472-473: “This suggests a strong underestimation of BrO emission without a direct emission of BrO due to ozone.” “. . .a reduced BrO emission due to direct bromide oxidation by ozone. . .” “BrO may be emitted by the extended bromine explosion mechanism and/or oxidation of bromide by ozone directly from the sea ice.” These statements need to be rephrased as BrO is not directly emitted from snow or sea ice.

Table 4: Why is simulation 2 shown here for Summit, instead of simulation 3, which was deemed the best setup for Utqiagvik (since simulation 2 missed half of the ODEs at Utqiagvik)? This should be discussed.

Line 350: Fig. 5 doesn’t show Summit results as stated here.

Figures 9-12, 14: Please make the latitude and land lines more visible to aid interpretation of the plots. Also, clarify in the Figure 9 caption what is meant by “cone”.

Figure 12: Does this include only snow, or snow + aerosols? Please clarify.

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