

Interactive comment on “Bromine atom production and chain propagation during springtime Arctic ozone depletion events in Barrow, Alaska” by Chelsea R. Thompson et al.

Anonymous Referee #1

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[Summary]

If my guess is right, a majority of modelers who have put their hands on the development of a model of tropospheric bromine chemistry know, sort of heuristically, that the partitioning of inorganic bromine in the troposphere is highly sensitive to heterogeneous recycling (e.g., $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$) in/on the aerosols (see, for example, Yang et al., 2005). So I wasn't surprised too much while reading the present paper by Thompson and co-workers despite the tone of its message. In my opinion, the main value of the present paper is the use of the “radical chain length” as an objective measure. I find it very interesting. That being said, I feel that the authors should revise their discussions and, possibly, even redo their model calculations as detailed below. One of

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my major concerns is that the authors seem to have precluded much too easily a possibility for the under-representation of heterogeneous reactions in/on the aerosols while discussing the missing source of Br_2 in their model calculations. I would recommend the publication of this work in ACP with major revisions.

[Specific comments]

1. For the analysis of the same dataset obtained at Barrow in the spring 2009, Liao et al. (2012) apparently used aerosol physical parameters from in-situ measurements for estimating the rate of HOBr uptake onto aerosols. On the other hand, I cannot find a description of how the present study deals with the aerosol volume and surface area and their temporal variability to constrain the rate of reactions involving aerosols. This aspect needs to be discussed thoroughly before concluding the predominant contribution of the surface snowpack in explaining the levels of Br_2 measured in the field.

2. Observational data for Br_2 are apparently missing for the majority of period between March 29-30 (Figure 2A; see also, Liao et al., 2012). Among the entire period of March 25-31 studied here, the period of March 29-30 is quite distinct in that ozone is recovered to near-background levels at 20-30 ppbv, which I understand is important for examining a contrast between ODE and non-ODE conditions. I suggest the authors to comment on the unavailability of Br_2 data between March 29-30, how they have managed to fill in this data gap and what it means to the completeness of their model-assisted analysis. I also feel that the time series in Figures 2, 3, 5, 6, 7, 8A and 9 should be marked to indicate that the Br_2 measurements were missing during March 29-30.

3. Any explanation for apparently much higher short-term variability in simulated BrO (black line) than in-situ measurements (red dots), especially during March 29-31, in Figure 2B? Although not necessarily relevant, it is during this period of time that disagreement between modeled and measured HOBr becomes really bad.

4. Lines 299-318 (Chain lengths defined by Method 1 & Method 2): I believe, “ $\text{J}_{\text{BrONO}_2} * [\text{BrONO}_2]$ ” should be taken away from the numerator of the Method 1

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formula. It should also be moved from the numerator to the denominator in the Method 2 formula. According to the authors' definition, BrONO₂ is the product of a termination reaction (hence $k \cdot [\text{BrO}] \cdot [\text{NO}_2]$ is in the denominator of the Method 1 formula). If these are not simple typographic errors, the authors should recalculate the chain lengths with corrected formulae.

5. Line 346-348: If the authors rationalize the exclusion of the photolysis of organobromine compounds from the chain initiation term (denominator) in Equation (6), there's not much point for including the OH-attack on CH₃Br and CHBr₃ instead. I would have liked the formula better if the authors had included all the following terms in the denominator of Equation (6): $J_{\text{BrONO}_2} \cdot [\text{BrONO}_2]$, $J_{\text{BrNO}_2} \cdot [\text{BrNO}_2]$, $J_{\text{CHBr}_3} \cdot [\text{CHBr}_3]$ and $k \cdot [\text{HBr}] \cdot [\text{OH}]$.

6. I would like to see plots equivalent to Figures 6-7 for the chain initiation. How dominant is the photolysis of Br₂ in there?

7. The role of BrO + HO₂ followed by the photolysis of HOBr in the net loss of ozone has been already recognized to be relatively important in the context of chemistry in the springtime polar boundary layer (Piot and von Glasow, 2008, see their introduction; Hausmann and Platt, 1994; Sander et al., 1997). In particular, Hausmann and Platt (1994, section 5 and Fig. 8) and Sander et al. (1997, section 3.1 and Fig. 2) conducted some useful calculations that can be compared with the analysis performed in the present study. Therefore, the discussion of the role of BrO + HO₂ should start from Section 3.4 on ozone loss rate (rather than Section 3.5) where Figure 8 could be expanded to include additional lines and dots with contributions from $k \cdot [\text{BrO}] \cdot [\text{HO}_2]$ added to $2 \cdot (k \cdot [\text{BrO}]^2 + k \cdot [\text{BrO}] \cdot [\text{ClO}])$. And the authors should refer to those two earlier studies at first and then explain what is new and perhaps different in the present study. Then, in Section 3.5, the authors must clarify how much of HOBr thus generated ends up in heterogeneous reactions on the aerosol and snow surfaces rather than photolysis in the gas phase. Also, it seems useful to mention the dominance of Br + HCHO as a source of HO₂ (Thompson et al., 2015) under the conditions of the air

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studied here and what it means to the contributions of BrO + HO₂ to the ozone loss and the heterogeneous formation of Br₂ and BrCl in the snow and the aerosols. The role of aerosol uptake in controlling the HOBr mixing ratios has been discussed using the same dataset from Barrow by Liao et al. (2012), which should be referred to and discussed in the context of the present study.

8. Are the aqueous-phase (or surface) reactions of BrNO₂ and BrONO₂ with halide anions in aerosols and snow grains included in the model? I don't see them in Table 1, but they could be rather important at high levels of NO_x such as on March 25.

9. Although I understand it useful to refer to a possible involvement of iodine photochemistry, there is no unequivocal evidence for its strong contributions at Barrow as much as assumed in the "High Iodine" scenario. Since, despite its hypothetical nature, this topic has been addressed once in their earlier paper (Thompson et al., 2015), I suggest the authors not to stress it much too strongly in the present paper. For example, the first paragraph of Section 3.3 may indeed need a brief comment on the hypothetical nature of the "High Iodine" scenario.

10. Line 229: Here, the first-order rate constant of transfer out of the snowpack of emitted species is referred to as the same as the first-order rate constant of transfer of depositing species from the air to the snowpack. But this seems odd, considering a large difference in assumed volumes between the air (the entire boundary layer) and the snowpack.

11. Line 402: Looking at the NO_x data presented in Custard et al. (2015), NO_x appears to have been pretty high on March 26 as well.

12. Lines 468-470: This finding is not new; the authors should read Barrie et al. (1988, page 140), Zeng et al. (2006, equation (2) and paragraph [15]) and Holmes et al. (2010, equation (2)).

13. Lines 496-497: Cite Bottenheim et al. (1990) along with Shepson et al. (1996)

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when referring to the role of CH₃CHO as a sink for Br-atom.

14. Lines 599-601: There are no actual model results presented in this paper regarding the role of snow gain acidity in the Br₂ surface fluxes. This statement should be dropped; otherwise, cite the model study of Toyota et al. (2014), which have demonstrated the role of pH in the snow QLL in the production of Br₂ using a condensed-phase chemical mechanism similar to the one employed in the present study.

[Technical suggestions]

1. Throughout the manuscript, the authors use the nomenclature “mole ratio” when referring to what is normally called “mixing ratio” or “mole fraction” in atmospheric chemistry. I suggest the authors to use either of the latter two.

2. Explain what the J-max is (Line 200) – a theoretical daily maximum under the clear sky? Also, how are the J-values are scaled under cloudy conditions? A sentence or two will do.

3. Line 209: . . . using this mechanism; however, . . .

4. Table 1: It appears that the mass transfer of HCl between gas and condensed phases should be included, as it is probably important for the formation of BrCl in the aerosols.

[References]

Barrie, L. A., et al.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic troposphere, *Nature*, 334, 138-141, 1988.

Bottenheim, J. W., et al.: Depletion of lower tropospheric ozone during Arctic spring: the Polar Sunrise Experiment 1988, *J. Geophys. Res.*, 95, 18555-18568, 1990.

Custard, K. D., et al.: The NO_x dependence of bromine chemistry in the Arctic atmospheric boundary layer, *Atmos. Chem. Phys.*, 15, 10799-10809, doi:10.5194/acp-15-10799-2015, 2015.

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Hausmann, M., and Platt, U.: Spectroscopic measurement of bromine oxide and ozone in the high arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, 99, 25,399-25,413, 1994.

Holmes, C. D., et al.: Global atmospheric model for mercury including oxidation by bromine atoms, *Atmos. Chem. Phys.*, 10, 12037-12057, doi:10.5194/acp-10-12037-2010, 2010.

Liao, J., et al.: Observations of inorganic bromine (HOBr, BrO, and Br₂) speciation at Barrow, Alaska, in spring 2009, *J. Geophys. Res.*, 117, D00R16, doi:10.1029/2011JD016641, 2012.

Piot, M. and von Glasow, R.: The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events, *Atmos. Chem. Phys.*, 8, 2437-2467, doi:10.5194/acp-8-2437-2008, 2008.

Sander, R., et al.: Modeling the chemistry of ozone, halogen compounds and hydrocarbons in the arctic troposphere during spring, *Tellus Ser. B*, 49, 522-532, 1997.

Thompson, C. R., et al.: Interactions of bromine, chlorine, and iodine photochemistry during ozone depletions in Barrow, Alaska, *Atmos. Chem. Phys.*, 15, 9651-9679, doi:10.5194/acp-15-9651-2015, 2015.

Toyota, K., et al.: Air–snowpack exchange of bromine, ozone and mercury in the spring-time 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, doi:10.5194/acp-14-4101-2014, 2014.

Yang, X., et al.: Tropospheric bromine chemistry and its impacts on ozone: A model study, *J. Geophys. Res.*, 110, D23311, doi:10.1029/2005JD006244, 2005.

Zeng, T., et al.: Halogen-driven low-altitude O₃ and hydrocarbon losses in spring at northern high latitudes, *J. Geophys. Res.*, 111, D17313, doi:10.1029/2005JD006706, 2006.

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