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Atmospheric Chemistry and Physics
Discussions

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 #2

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This paper uses a 0D box model with a simplified description of heterogeneous chemistry to study the cycle of bromine during ozone depletion events and non-ozone depletion conditions in Barrow, Alaska. This paper is interesting because it proposes to use the bromine chain length to study the relative importance of gas phase cycling of bromine compared to primary emissions/heterogeneous recycle of bromine, both of which have long been thought to be important for catalytic ozone destruction by bromine in the Arctic boundary layer.

Upon a first look, the paper appears to be well thought out and presented resulting in some interesting conclusions. But, upon deeper scrutiny it is clear there are some major problems with the modeling approach that need to be addressed. In its current form, the paper does not meet the standards for publication in ACP. The paper may eventually be considered for publication, but major modifications to the modeling approach and conclusions are required.

The main problem is that the model in its current state make it impossible to answer the questions proposed by the authors. How can the authors compare chain cycling with primary emissions, when they don’t model either primary emissions or heterogeneous recycling of halogens on aerosols? In their model, Br2 is fixed to the measured concentrations (not formed by processes in the model) therefore, there is a contribution from some unknown source or sink of Br2 (and hence 2Br) at each time step of the model. Another way to think about this is to ask the question – how can the authors distinguish heterogeneous chain propagation to form Br2 from surface emissions of Br2? Using the current model setup, these cannot be distinguished making the analysis of the chain length and comparison to primary emissions rates derived incorrect.

There are further warnings of serious problems for using this modeling approach to understand how BrO + BrO competes with primary emissions of Br2 (or heterogeneous recycling of HOBr to Br2). These include:

1. The measured concentrations of BrO and HOBr are not actually captured by the model (Figure 2, 30 & 31 March). Given this, the regime where BrO + BrO dominates cannot be studied adequately.

2. The model over predicts very high HOBr concentrations (Figure 2, 30 & 31 March), leading to the conclusion that there may be something wrong with their heterogeneous uptake and recycling to Br2 of HOBr. This also limits the ability of the model to compare/contrast Br2 formed in the gas phase with Br2 formed via heterogeneous chemistry.

3. Equation 9 is extremely misleading – attributing all Br2 photolysis to surface emissions. Br2 is also the product of the BrO + BrO self-reaction. Br2 formed from BrO+BrO in the gas phase must also be considered in this equation and throughout the paper

when discussion the Br chain length.

4. There is no mention of the prior work by Toyota et al. (2014, 2011) on the importance of surface recycling for HOBr to sustain ozone depletion events/bromine release. These modeling papers should be referenced and fully discussed. References to other modeling work on this topic is also missing and should be more thoroughly discussed/thought through.

5. There is no discussion of the role of HOBr formation (XO + HO2) and subsequent photolysis in bromine recycling. This is a major problem, given its role in chain propagation.

6. Do the authors propose to separate primary emissions (bromine explosion initiation step) from emissions on snow/aerosols via HOBr recycling?

7. There is no discussion of the role of heterogeneous recycling of BrNO3. The paper cannot be considered for publication without heterogeneous recycling through BrNO3 uptake included in the model.

8. Given the high NOx levels at Barrow, a thorough discussion (including figures that demonstrate that nitrogen oxides are adequately modeled) is needed. The role of chain recycling through NOx must be considered and discussed.

9. Given the nature of surface emissions from snow, which are the main focus of the conclusions, there are likely to be vertical gradients in the concentrations of both nitrogen and bromine containing species. What are the implications of ignoring these vertical gradients on the conclusions regarding the chain length compared to primary surface emissions?

10. Are the model rate constants independent of temperature as suggested by Table 1? If there is no temperature dependence of rate constants included, the model is likely wrong during portions of the day as many of the reaction rates depend on temperature and the surface temperature at Barrow has an important diurnal cycle during

this portion of the year.

The paper cannot be published in the current format. The heterogeneous reactions involved in halogen recycling are not thoroughly discussed/considered in chain propagation. The most recent halogen review papers have more clear discussions of these radical cycles (e.g. Abbatt et al., 2012). There is also a clear discussion of these cycles in earlier reviews, for example Monks et al. (2005).

The authors have done some modeling work that can potentially be extended to answer questions about the relationship between bromine cycling and ozone depletion events. However, with their current model the authors cannot adequately compare the bromine chain length with primary emissions using a 0D chemical box model setup that relies on fixing the essential radial precursors to measurements. The authors should consider a major revision that answers a set of scientific questions that are appropriate for the model they use.

Minor comments:

1. Figure 1 is already found in Thompson 2015 (Figure 1a). Is there a specific reason for it to be included as a separate figure here? The ozone time series can simply be added to what is now Figure 2.

2. The authors should mention in their reaction schemes (equations listed) that HOBr also reacts to OH + Br in the gas phase.

References:

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