

Interactive comment on “The chemistry influencing ODEs in the Polar Boundary Layer in spring: a model study” by M. Piot and R. von Glasow

Anonymous Referee #4

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A box model is used to study the impacts of HCHO, H₂O₂, DMS, Cl₂, C₂H₄, C₂H₆, HONO, NO₂, and RONO₂ on Ozone Depletion Events (ODEs). A large number of sensitivity cases were calculated and representative cases were discussed in the paper. Chemical shifts of BrO_x to HOBr and HBr, which lead to deposition and removal of atmospheric bromine, are analyzed. Overall, this study is well executed. The results will be useful for uninformed readers to understand the halogen chemical cycles of ODEs.

As a journal publication, I feel that this paper lacks new insights of ODEs. Reaction (14) is the known mechanism for rapid production of halogens in the Arctic. Through this mechanism, deposition of HOBr (and not as important, HBr) increases the halogen

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sources and speeds up the halogen cycles. In contrast, the results in this paper are obtained by assuming that this deposition only leads to a loss of atmospheric bromine. The previous paper on ODEs by the authors, in comparison, does not have such an assumption and is more insightful in my opinion. The problem is acknowledged nicely in the discussion section by the authors (I am glad to see that the discussion was added in this submission). Qualitatively, if the halogen sources are decoupled from HOBr deposition, any reactions that shift HOx to HO₂ or BrOx to BrO lead to a faster loss of bromine. Essentially that is what the additions of VOCs (HCHO, H₂O₂, DMS, Cl₂, C₂H₄, and C₂H₆) or NO_x (HONO, NO₂, and RONO₂) do (i.e., counter cycle). The quantitative aspects need model calculations. As noted in the paper, realistic emissions of these species do not make appreciative changes to halogen chemistry. The large effects seen in the model are usually associated with extreme emission levels. While interesting, I wonder how these results contribute to new understanding of ODE chemistry.

This paper is well organized, the supplemental kinetics data compilation is informative, and a lot of work went into it. Yet I find it difficult to recommend the ACP publication of this paper. Listed below are specific comments that can improve the paper, but they cannot solve the main problem noted above.

1. P. 7397, line 22. The model is set for Alert, Canada in early spring. The temperature is very low (~250 K). Can the sea salt production parameterization for open ocean be used here?
2. P. 7399, line 3. With a temperature of 240-250 K and sea surface frozen, is the DMS flux from the tropical Pacific appropriate to use?
3. P. 7400, line 7. How are the deposition rates calculated in the model? The model results shown later are sensitive to the deposition rates.
4. P. 7400, line 25. Is the CLAW hypothesis relevant to this paper?

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5. P. 7406, line 9. I think the emission flux is set in order to either maintain the initial concentration or increase the concentration to x times of the initial value. It will be easier to understand if the target relationship between the end and initial concentrations is given.

6. P. 7407, line 9. The Br⁻ liberation from sea salt aerosols takes < 1 day. It seems too fast to me. How does this rate compare with other studies?

The effect of sea salt Br⁻ depends on the total sea salt amount. The way SSA is simulated in the model is very crude. A steady-state SSA concentration would be more appropriate.

7. P. 7411, section 4.5. With a temperature of 240-250 K and frozen ocean surface at Alert, the probability of finding significant DMS emissions is remote. I suggest removing this section.

8. P. 7419, line 27. What is the fate of deposited BrNO₃? Will it hydrolyze back to gas-phase BrO?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7391, 2008.

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