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Interactive comment on "Numerical analysis of the chemical kinetic mechanisms of ozone depletion and halogen release in the polar troposphere" *by* L. Cao et al.

Anonymous Referee #3

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The authors present a sensitivity analysis of a box model representation of ozone depletion events in the polar boundary layer. Key reactions are identified via the sensitivity analysis and their effect on ozone and BrO in particular are quantified. Some interesting sensitivity studies regarding boundary layer height, surface conditions and heterogeneous reaction parameters are conducted as well. While I would argue that the reactions, cycles and processes identified as being important are largely already known, the ability to put some quantitative structure to this (via the sensitivity analysis) is worthwhile. I do have some significant questions and concerns, however, (as detailed below) and it is my opinion that some significant modifications are required before publication in ACP can be considered.

The model appears to be running without any diurnal pattern, i.e., with fixed photolysis rates, a situation that I do not think is representative of springtime conditions in the about 70-80 degree North regions where these ozone depletion events are typically investigated. At the very least, the authors need to discuss limitations of this approach, and justify the use of the model in this configuration. How are photolysis rates determined? How are the timescales for depletion altered by this assumption? Can any chemistry occurring in nighttime or low sun conditions play a role (e.g„ through formation of reservoir compounds) that is not captured in the model?

There are now measurements of HBr, HOBr and BrO from Barrow (Liao et al., JGR, 2012) – the authors should compare data from Figure 1 with this literature result.

My understanding of this chemistry is that there is currently no consensus as to whether HOBr activation (R14, R15) occurs on aerosol or on the ice- or snow-covered ground. The results here seem to indicate that both are relevant – some further discussion seems warranted, particularly as a function of BL height since those tests were conducted.

This is somewhat a case of semantics, but reaction (R5) and (R7) are referred to as a cycle, as are (R1) and (R3). However, these reaction pairs are really ‘do-nothing’ cycles, and it is really the difference in the rate of the reactions in each pair that determines whether ozone is destroyed or created. This point comes out to a certain extent, where differences in (R5) and (R7) are pointed out, but I would guess that (R1) and (R3) are nearly identical in rate and one could leave them out of the model entirely without any significant effect. Some further discussion or re-wording might be useful here. Also, I wonder (p. 24184, line 22-23) if it is HOBr formation from the BrO/HO2 reaction that has more effect in driving the difference between the rates of (R5) and (R7) than the formation of Br atoms in the BrO/BrO self-reaction.

With respect to NOx, cycle (N-I), is HO2NO2 in roughly steady-state with HO2 and

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NO2, such there is no net change in NOx? Again, this is a do-nothing cycle, unless other chemistry is affecting things and the rates of (R62) and (R63) are not in balance.

On page 24189, it still seems that HNO3 photolysis on surfaces will be very slow (lifetime of a couple of days even if it is 100X faster than in the gas phase). Thus, it is not clear to me that the reaction cycle (I) is really representative of what is happening.

There is at least one previous discussion in the literature of the effect of NOx on ozone depletion events (e.g., Ridley et al., J. Atmos. Chem., 2003) – the results here should be compared and contrasted with that work. Also, the recent work of Stephens et al. (JGR, 2012) contains new information regarding Cl chemistry in polar regions, and this work could be discussed as well.

I am confused by the concluding paragraph (p. 24194). If the heterogeneous reactions (i.e., HOBr reaction with HBr) are left out of the model during the induction phase, will it not be the case that one will never get to the depletion phase?

p. 24172, line 3 – might read better in the past tense – "…polar regions has been investigated…"

p. 24173, line 19-20 – might read better as follows: "…since the 1990's. Box models…"

p. 24180, line 17 – 'considered' is spelled incorrectly

p. 24182, line 3-4 – might read better as follows: "…which photolyzes very slowly …"

There are a few places in the manuscript where what I would call obvious or repetitive statements are made. For example, the paragraph beginning on p.24185, line 26 could be condensed into a 'tighter' statement. Another place is with respect to PAN (on p.24188, line 11).

p. 24190, line 4 – It would be more accurate to state the following: "Peroxy radicals generated from volatile organic compounds (VOCs) could also replace HO2…"

One detail regarding the mechanism – it seems as though O(3P) and O(1D) atoms are being treated as one species. For example, NO3 photolysis produced O(3P), but in the mechanism these atoms are ‘allowed’ to react with H2O to produce OH, which is not correct. (This probably is only a small effect, but something to perhaps change for future work).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24171, 2013.