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Interactive comment on “The NO_x dependence of bromine chemistry in the Arctic atmospheric boundary layer” by K. D. Custard et al.

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Comments/Changes from Reviewer 1

The manuscript by Custard et al. reports results of 0-D box model simulations which seek to unravel the manner in which NO_x influences Arctic bromine chemistry. It is certainly an important and interesting topic for investigation, but I have read this manuscript several times, and am still confused as to its main points. I think it would benefit greatly by some restructuring and rewriting in places, to maintain a focus on the key results.

â–Pg 8331 line 13-14: The abstract was reworded to emphasize the main point that elevated NO_x concentrations inhibit the ozone depletion rate.

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To start: the authors constrain the model amounts of halogens to a set of observations, then simulate a 10 day period with imposed high and low NO_x amounts. But surely, since the gas phase halogens are already determined by nature, this will "twist" the chemistry in unrealistic ways in order to "keep up" with the observed Br₂ and Cl₂?

There has never before been a set of Br₂ and Cl₂ measurements in the Arctic. The chemistry of ozone depletion occurs via free radicals, i.e. Br, BrO, Cl, and ClO (along with OH and HO₂). Having the actual Br₂ and Cl₂ radical precursor data ensures that we have the rate of production of the halogen radicals right. This is far better than not having this information, and it is an unprecedented opportunity. It is also the case that the community does not have the fundamental understanding of the condensed phase mechanisms, chemical kinetics, and physics of mass transfer (we don't even know what the phase is (solid or liquid)) to enable any realistic simulations of the condensed phase processes. So, our analysis focuses on the interaction of NO_x with the radicals that do the ozone depletion, as discussed near the top of page 8 of the revision.

We also examine and discuss differences between the NO_x-polluted days and clean days in the observations of products of the condensed-phase chemistry in Figures 7, 8, and S1. The NO_x-dependence of Br₂ production is reflected in Figures 8 and S1.

Perhaps I am missing something ... This problem pops up in a few places in the MS, in discussing times when observational halogen data was absent (pg 8338, lines 19-23; pg 8340, lines 18-20; pg 8341, lines 13-14).

We believe that the chain length for March 25 is large because of the combination of large NO and BrO (numerator) and low HO₂ and aldehydes (denominator) for this day, as now discussed on page 10 of the revised manuscript (pg 8338 line 25). For the cases in which BrO is undersimulated it is quite possible that Br₂ was greater than assumed.

Even accepting this limitation, I was left wondering about several of model results. The

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major result (not clearly stated) seems to be that there is no difference in bromine chain length between the High- and low-NO_x cases. There is a brief discussion of this on pages 8337 and 8338, but I do not really follow the reason for why this is the case.

As we now discuss on page 10 of the revised manuscript, HO₂ is suppressed at high NO_x, so at low NO_x the BrO + HO₂ termination reaction becomes much more important. (pg 8338 line 10-12)

Likewise, it is not clearly explained why the O₃ loss rate behaves the way it does in the two model scenarios (pg 8339).

We now provide improved discussion of this on page 11 of the revision, i.e. BrO_x decreases at high NO_x, largely from reaction 10, Br + NO₂.

Some more minor points: On page 8337 (line14), it is stated that BrONO is not considered to be a sink for BrO_x, yet in Section 3.4 it is considered in just that way.

We revised the Figure 4 caption to note that only the reaction that resulted in BrNO₂ was counted toward the BrO_x sink.

I do not understand how Eqn 2 in obtained.

On page 11 of the revision we provide further explanation for the derivation of Equation 2.

Pg 8340, lines 2-6 about the importance of BrONO₂ in ODEs seems a bit of a nonsequitur. We clarified the point on page 12 of the revision.

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