

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.

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

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 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 is 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.

Comments/Changes from Reviewer 2

Custard et al. attempt to quantify the impact of NO_x emissions from a large oil field in Prudhoe Bay and perhaps the town of Barrow on bromine chemistry as observed at/near Point Barrow during the OASIS field campaign in March-April 2009. This is done by constraining a photochemical box model partially with in-situ measurements of key compounds (O₃, Br₂, VOCs, etc.) during the OASIS. To complement the argument, the authors also show aircraft MAX-DOAS measurements of BrO and NO₂ column densities near Prudhoe Bay, which were conducted during a different field campaign, BROMEX, in a different year (2012). This latter case was not attempted to be simulated by the photochemical box model. The subject of this study is important and relevant to ACP. The authors extract two “representative” diurnal variations in the NO_x mixing ratios (“high NO_x”, 700-1600 pptv and “low NO_x”, 50-100 pptv) and use them perpetually to simulate the 10 day period between March 24 and April 3, 2009 at Barrow where intensive field observations (OASIS) were conducted and available for their photochemical box model constraint. As such, the paper represents more or less a hypothetical scenario study discussing the potential impacts of local combustion emissions of NO_x on arctic bromine chemistry. At the same time, by constraining the Br₂ and Cl₂ mixing ratios as observed

in the field, the model configuration limits the capacity of assessing what the increased local sources of NO_x would bring about, such as increased nitrate content in the surface snow (thereby increasing OH radical in the liquid layer of the snow and resultant bromine release to the ambient air) and possibilities of enhanced bromine release from the snow via uptake of BrONO₂ and N₂O₅.

- This is, as the paper states, not at all the case, because the community does not have the ability to simulate the condensed phase chemistry. We don't have the rate constants for the condensed phase reactions, we don't know where in the snow grains the chemistry occurs, and we don't quantitatively understand the mass transfer. Indeed, we don't really even know how to properly describe the phase in which the chemistry occurs in the snowpack, and, e.g. what is the viscosity and thus diffusion rates, what is the ionic strength, what is the pH, etc. However, the availability of the Br₂ and Cl₂ data, which are in fact, together quite unprecedented, represents a fantastic opportunity to simulate the NO_x-dependence of the gas phase photochemistry, where in this case, given properly calculated J-values, we accurately know the rate of production of bromine radicals. As discussed above, we do observe the NO_x-dependence of Br₂ production, e.g. as discussed for Figure 8 and S1.

On March 25, the bromine release was apparently enhanced as a result of local NO_x pollution, despite the main message the authors try to convey from this study, namely, the impedance of arctic bromine chemistry via increased local emissions of NO_x. After all, instead of assessing what may be happening during the photochemical evolution of air masses after the initial release of NO_x perhaps along with other pollutant VOCs, the authors use smeared-out, averaged mixing ratios of NO_x in a hypothetical fashion and the time-varying Br₂ source strength from the snow surface (although constrained by insitu observations at Barrow) in a manner not directly linked to the NO_x levels in the model. This appears to be a weakness of the present study.

- We are in fact using as the two NO_x scenarios, the average diurnal profile from days that are NO_x-polluted, and those when the wind direction is from the clean air sector, i.e. the Northeast. It is obvious that ambient Br₂ is not directly dependent on NO_x only, but dependent on a variety of factors, including radiation, atmospheric stability, and a number of characteristics that we cannot constrain and simulate, e.g. the rate of OH radical production in the compartment of the snow grains where OH precursors (H₂O₂ or NO₃⁻?) sit (the QLL?), and diffusion rates out of the snow grains and out of the snowpack, while photolytic loss is occurring. Thus we focus here on the gas phase halogen radical chemistry and how that is impacted by NO_x, as explained at the top of page 8 of the revised manuscript.

As it stands, the paper reads a bit like a series of intriguing anecdotes compiled from field data, to which model runs do not necessarily answer why. The paper would read much better if the authors could demonstrate and categorize, aided by the photochemical box modeling,

circumstances where higher NO_x levels may have enhanced or suppressed bromine chemistry as observed.

- This is clearly shown in Figures 6 and 8, and with the model, throughout the paper. Having instrumented the aircraft for BrO measurements, and flown the flights over Deadhorse ourselves, it is hard for us to regard the data shown in Figure 8 as "anecdotal". To us, this is very real, and very unusual (there is nothing else like it in the literature) data, that directly shows that BrO is inversely correlated with NO₂. The model shows this, and Figure S1 clearly shows that Br₂ is enhanced only at low NO_x. There is similarly nothing else like this in the literature. It is clearly incremental new understanding, and data.

Here are some specific comments that I hope help the revision of the paper.

1. Observed BrO and HOBr time series from OASIS during the polluted period (gray shaded in Figure 7a-b) often agree better with a model run with the "low NO_x" rather than the "high NO_x", in apparent contradiction with the authors' main message from the present paper. I suggest the authors to conduct additional model runs that better reproduce the observed temporal variability of BrO and HOBr during the "polluted period" if at all possible for really making a case of how local NO_x sources influence bromine chemistry.

- It is important to stress that it is very difficult to accurately simulate absolute concentrations in this environment, and, for halogen species, this has never been done. This is partly, as we have explained for the snowpack-derived species, due to the fact that we don't quantitatively understand the production processes and kinetics (or even in what compartments the chemistry occurs). For the gas phase, the above-snowpack air is highly stratified due to the extreme static stability. Parameterizing the turbulence with average eddy diffusivities is difficult/problematic because turbulence in this environment is episodic (Boylan et al., 2014). With the extreme static stability and episodic vertical mixing in a stratified environment, getting fine details "right" is not realistic. But, the objective here, e.g. as shown in Figures 7a and 7b, is to examine the sensitivity of these species to ambient NO_x, within the range of the NO_x variability. Clearly, these figures do that very well indeed.

2. The authors barely refer to BrCl as a source of gaseous bromine in the model runs as well as in the actual arctic air (e.g., Foster et al., 2001). Is there experimental evidence for negligible BrCl occurrence during the OASIS? Also, is BrCl negligible (or not) compared to Br₂ as a source of reactive bromine in the model runs?

- Liao et al. 2014 (supplementary information) don't report BrCl concentrations but state that BrCl was often below the LOD of 0.5 to 2.0 ppt. They also say that BrCl was only observed in the presence of Cl₂ and believe it was being formed through chlorine

chemistry. It does not appear that BrCl is an important source of Br atoms, compared to Br₂.

3. It is stated that, on the basis of Villena et al. (2011), the CO mixing ratio is used to classify the air between polluted (“high NO_x”) and non-polluted (“low NO_x”) conditions during the OASIS (Section 2). It is useful to state more explicitly as to a threshold CO mixing ratio or whatever criteria employed for this air-mass classification. Furthermore, it would be helpful to show some statistics for other relevant species (HCHO, CH₃CHO, BrO, HOBr, etc.) than NO_x in a table for polluted and non-polluted conditions. Figure 4 would speak better then.

- The 160 ppb threshold is now referenced on page 7 of the revised manuscript.

[Technical comments]

1. The nomenclature “mole ratio” is used throughout the paper to mean “mixing ratio” or “mole fraction”. Is it really appropriate? I asked this question during the quick review process and the authors already answered “yes”. Apologies for bothering by repeated queries, but I just wish to confirm again.

- We do not prefer the term "mixing ratio" as its meaning is unknown outside the atmospheric science community, and the implied units can vary, e.g. meteorologists use g/kg for the water vapor "mixing ratio", which is not the same as the number or mole ratio. It is also noteworthy that the origin/source of the term "mixing ratio" is generally not known/understood within the atmospheric science community. When one uses the term "mole ratio" or "mole fraction" there is no doubt what is meant. We will not insist on this point, if the reviewer would like to insist on "mixing ratio"?

2. Page 8334, Line 26: “CH₃OCH₃” seems to be a typo for “CH₃COCH₃” (check with Table S5).

- This typo has been corrected, on page 6 of the revised manuscript.

3. Page 8337, Eq. (1): “k[BrO][C₃H₆]” in the denominator seems to be a typo for “k[BrO][C₃H₆O]” (check with Table S1). Also, it would be nice to number all the k coefficients in this equation based on Table S1.

- The typo in Eq. 1 has been corrected. We prefer to not add complexity to Eq. 1 with the numbers.

4. It would be helpful to clearly state that “C₃H₆O” and “C₄H₈O” mean propanal and n-butanal, respectively, somewhere in the supplement table(s).

- We added a note in the supplementary information about C₃H₆O; C₄H₈O is not in the model.

Comments/Changes from Reviewer 3.

In this manuscript the authors present an analysis of gas-phase chemistry in the Arctic troposphere. The focus is on the impact of elevated NO_x levels on bromine chemistry. They demonstrate using a simple 0-D model, constrained by ambient observations, that elevated NO_x can lead to decreased BrO levels by tying Br and other radical species up in nitrogen-containing reservoir species. The study is well-designed and provides insight into Arctic atmospheric chemistry. I have a few technical questions or comments which should be addressed before publication.

- Snow chemistry may have a major impact on photochemistry in the Arctic (and specifically Br and NO_x chemistry), but the representation of mass transfer to snow and snow chemistry is very simplified in the model used in this study. While many simplifications could be pointed out, for one thing, there appear to be no snowpack photolysis re-actions, and these may have a significant impact on gas phase photochemistry. The authors should justify in the revised manuscript the use of such a simplified model and comment on the possible contributions of snowpack processes to discrepancies observed between modeled and measured data, e.g. Fig 5 and Fig 7.

- As discussed on page 8 of the revision, and in response to Reviewers 1 and 2 above, constraining to observations for Cl₂ and Br₂ reflects the impact of snowpack photochemistry, reflected in these molecular halogen concentrations, and thus we are assured of accurately simulating the ensuing radical chemistry. However, that relevant snowpack chemistry and physics is not quantitatively understood well enough to enable accurate simulation of those processes and the upward fluxes.

- I agree with Reviewer 1 that the apparent lack of impact of NO_x levels on the Br chain length demands more discussion.

- This is now discussed on page 10 of the revision, in reference to the impact of NO_x on HO₂, HO₂ being an important BrO_x sink.

- Figure 7 is too small to be legible.

- Each panel of Figure 7 is a separate Figure and can be appropriately sized for readability by the Journal. We will request this.

- Some explanation is needed for the values in Table S4. How have the authors arrived at the different aqueous rate constants? I assume "actual" means the measured aqueous reaction rate constant, but how are the different values for "particle" and "snow" obtained?

- We have expanded the explanation for the numbers in Table S4 in the Table caption in the revision.