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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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Custard et al. attempt to quantify the impact of NOx 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 Mach-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 NOx mixing ratios

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("high NOx", 700-1600 pptv and "low NOx", 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 NOx 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 NOx 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. On March 25, the bromine release was apparently enhanced as a result of local NOx 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 NOx. After all, instead of assessing what may be happening during the photochemical evolution of air masses after the initial release of NOx perhaps along with other pollutant VOCs, the authors use smeared-out, averaged mixing ratios of NOx in a hypothetical fashion and the time-varying Br2 source strength from the snow surface (although constrained by in-situ observations at Barrow) in a manner not directly linked to the NOx levels in the model. This appears to be a weakness of the present study.

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 NOx levels may have enhanced or suppressed bromine chemistry as observed.

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 NOx" rather

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than the “high NOx”, 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 NOx sources influence bromine chemistry.

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?

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 NOx”) and non-polluted (“low NOx”) 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 NOx in a table for polluted and non-polluted conditions. Figure 4 would speak better then.

[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.

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

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.

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

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 8329, 2015.