Atmos. Chem. Phys. Discuss., 15, C4602–C4606, 2015
www.atmos-chem-phys-discuss.net/15/C4602/2015/

Atmospheric Chemistry and Physics
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Discussions

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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Received and published: 8 July 2015

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 (“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. âĂć 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 NOx-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 NOx-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 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-

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out, averaged mixing ratios of NOx 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 NOx levels in the model. This appears to be a weakness of the present study. âĂć We are in fact using as the two NOx scenarios, the average diurnal profile from days that are NOx-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 NOx 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 NOx, 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 NOx levels may have enhanced or suppressed bromine chemistry as observed. âĂć 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 NOx. 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 NOx” rather 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. âĂć 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 NOx, within the range of the NOx 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? âĂć 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 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. âĂć 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. âĂć 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 know/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). âĂć 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. âĂć 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). âĂć We added a note in the supplementary information about C3H6O; C4H8O is not in the model.

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