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Comment

## ***Interactive comment on “Halogen activation via interactions with environmental ice and snow” by J. P. D. Abbatt et al.***

**J. P. D. Abbatt et al.**

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The manuscript reviews the current status of knowledge on halogen activation via interactions with environmental ice and snow. When I was approached for a review I made it clear that I certainly planned to read the text, but do not consider myself an expert at all on this. My interest of course comes from trying to understand what could drive a rather peculiar phenomenon, the sudden rapid disappearance of ozone from the polar boundary layer (PBL) air in the spring (and spring only!), first reported about 25-30 years ago by Sam Oltmans (in JGR, 1981, 1986) from observations at Barrow Alaska, and myself at Alert Nunavut.(in GRL, 1986). Since these early reports it has become clear that active halogens, in particular bromine, originating from sea salt drive the chemistry. However, nagging questions remain, in particular how exactly are halo-

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gens transformed from the rather unreactive ionized into the reactive atomic state. This manuscript was prepared following a workshop organized in 2011 to take stock. It is well written and certainly appropriate for publication in ACP. It also appears pleasingly up-to-date, given the many references to publications in 2012. Not being an expert, my comments are largely of an editorial nature. I have several questions for clarifications that I believe would help improve the text. For easy reference each comment is preceded by the page and line number to which it refers in the ACPD version.

*We thank Dr. Bottenheim for his careful reading and comments on the manuscript.*

General suggestion. The emphasis is clearly on chemistry in the Polar lower troposphere (see 8679/12). I think this should be indicated in the title of the manuscript. Furthermore, I recommend to delete section 7. This section feels like a late addition, to at least not completely ignore halogen activation in the UTL. I am sure there is a lot more to say about this than is done in this section. Also, in complete contrast to almost everything else in the paper it talks exclusively about chlorine chemistry and no other halogens.

*We agree with the reviewer and have changed the title of the paper to:*

*“Halogen activation via interactions with environmental ice and snow in the polar lower troposphere and other regions”*

*We understand how the section on the cirrus cloud chemistry section may have appeared as an “add-on” given that the majority of the paper is focused on polar boundary layer chemistry. However, we consider it important to include this section as an example of how ice chemistry may also proceed in other regions of the troposphere. In particular, while the polar chemistry may be more easily identifiable than elsewhere, we see it as an open question for how important ice-halogen interactions may be in the upper troposphere, cold mid-latitude free troposphere, or snow-covered sub-polar regions. By addressing upper tropospheric chemistry we are illustrating that our knowledge of the multiphase chemistry is transferable from one region to another. Indeed,*

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*the multiphase chemistry section was written in a sufficiently general manner that the chemistry it describes should apply widely.*

*That all being said, we recognize the need to restructure the paper. Consequently, we have now re-titled Section 5 to “Field evidence for halogen activation on ice in the troposphere” wherein we describe both polar boundary layer and upper tropospheric processes. The cirrus cloud chemistry fits nicely in this section because it illustrates the importance that chlorine activation on ice may play. By contrast, at this time there is little in the literature on chlorine activation on ice in the polar boundary layer. We believe that the summary of the cirrus cloud chemistry is complete, with this region of the atmosphere having been poorly observed. Likewise, little has been done on Br and I chemistry in this part of the world, as is now stated.*

Comments/questions: 8685/28: “may increase with temperature”, better to say “correlates negatively with temperature”

*This correction has been made.*

8686/12: is that true? I seem to remember that the PFF approach only worked for the Antarctic

*The connection to the Antarctic has been made.*

8688/5: delete “also”

*This change has been made.*

8690/3: interestingly this correlation was also observed in the atmosphere (Li et al., J. Geophys. Res., 99, D12, doi:10.1029/93JD03343, 1994).

*We have now added this reference (Section 3.1).*

8691/1: for clarity say “austral spring/summer”

*This change has been made.*

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8691/15: This is confusing. Even under non-bromine explosion conditions I doubt that  $\text{CHBr}_3$  is an important source of reactive bromine for the boundary layer since it is not photodecomposed by sunlight. At most it is an important “carrier” of Br in the atmosphere?

*This statement has reworded to indicate that  $\text{CH}_3\text{Br}$  does not photolyze rapidly but may nevertheless be a photolytic source of Br on a longer timescale than is normally associated with bromine explosions (Section 3.2).*

8691/18: undersaturated in sea water or air?

*We now state that it is undersaturated in the seawater.*

8692/20: I find this discussion confusing. First you say that the diffusion is possibly much faster through ice than in water due to transport in gas bubbles, and then the lab studies show that it is very slow through consolidated ice (which apparently pertains to brine channels). If it goes via bubbles, and therefore fast, then the slow diffusion through brine channels would probably be unimportant and there would be little chance for chemical change to occur? Some clarification is required here.

*We now state that if species are slowly diffusing there is more time for reaction (e.g. photochemical decomposition) to occur along the way (Section 3.3).*

8692/22: “are a source”. Given that you earlier seem to downgrade the importance of FF it may be better to say “could be a source”?

*This change has been made.*

8693/3: “photochemical” source? Why photochemical? Seems odd to me.

*“Photochemical” has been removed.*

8693/24: since an ODE in the PBL is effectively also creating an “ozone hole”, I recommend to call it a “stratospheric” ozone hole (as community we have enough trouble to make clear that we study PBL ozone depletion, and that not all ozone holes are

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stratospheric)

*“Stratospheric” has been included.*

8696/18: is there enough SO<sub>2</sub> and NO<sub>2</sub> available in the air to actually arrive at that level (pH=3) or is this purely a theoretical exercise? Please explain.

*These were model calculations using assumed SO<sub>2</sub> and NO<sub>2</sub> mixing ratios, as now stated in the paper.*

8697/2: This keeps confusing me. If I read this correct then the original Sander et al. hypothesis does not work because CaCO<sub>3</sub> precipitation is most likely in the form of ikaite and hence does not reduce the buffering capacity? Please explain more clearly.

*This section has been entirely re-written to make it easier to follow (Section 4.1.4). The point is that ikaite precipitation does indeed reduce the buffering capacity, just not as much as if calcite had formed.*

8697/13: can you be more specific at what temperatures this is? Below 100K (which may be theoretically interesting but not in the real world)?

*This is a good point now made in the paper (Section 4.1.5). The work at non-atmospherically relevant temperatures (where HCl may not dissociate) is provided only as a contrast to the higher temperature, more atmospherically-relevant work, where HCl is thought to dissociate.*

8697/14: delete “that”

*This change has been made.*

8700/9: this seems a key finding. If I understand this correct, then the pH does not matter much as long as we deal with surface chemistry with lots of bromide at that surface? So therefore why would one bother about whether alkalinity can be reduced via CaCO<sub>3</sub>, or the pH of the FF reported by Kalnajs and Avallone (2006)?

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*This point is now emphasized more strongly in the summary to the HOBr activation section (Section 4.2.1), and is also mentioned in the Conclusions and Open Issues (Section 7.2).*

8700/24: for the non-physical chemist it will be useful to devote one sentence here on what a Langmuir-Hinselwood process is all about.

*This addition has been made (Section 4.2.2).*

8703/6: “NO<sub>2</sub>”? or “NO<sub>3</sub>”?

*The earliest studies were indeed with NO<sub>2</sub>. Detailed studies of NO<sub>3</sub> with halide-ice surfaces have not been conducted, as mentioned in the paper.*

8703/23: “to which HCl has been exposed”? I presume “which has been exposed to HCl”

*Yes, the wording has now been changed.*

8704/1: same story as before, Br- first, then Cl-. But does this suggest that ClNO<sub>2</sub> might be produced in Polar regions by this chemistry? Is there any evidence for the occurrence of ClNO<sub>2</sub> in Polar regions?

*To our knowledge ClNO<sub>2</sub> has yet to be observed in polar regions but that may only be because the observational technique that most sensitively detects it, i.e. CIMS with iodide reagent ion, has not as yet been deployed in such regions.*

8705/2: There is a switch here, first you were talking about photochemistry in the snowpack, now in snow grains. But a lot of snowpack chemistry is presumably occurring in the interstitial air of the snowpack, which is something else than the surface of snow grains in the snowpack? Please be more specific about what is meant.

*Thanks for pointing this out. We have now put two sentences in the first paragraph of Section 4.3 to help orient the reader and point out that most of the processes in this section are in the condensed phase.*

8705/10 which organics? Presumably not alkanes and the like? Please add more information on that.

*This is a good question, albeit with a complex answer. The reader is now referred to the companion review article (McNeill et al., Organics in environmental ices: sources, chemistry and impacts, ACPD, 2012) which indicates that the organics present in ice and snow are highly complex, having formed from precipitation scavenging, dry deposition of organic aerosol, and biological processes.*

8705/18 again, what organic compounds are you thinking about?

*The McNeill et al. reference has been added at this point (Section 4.3).*

8705/27: or as OH source?

*The wording has been changed.*

8706/16: sure, interesting, but so is the whole paper An explanation is required why this is interesting. After all, this is not intuitive (to me anyway).

*The wording has been changed removing the word “interesting”.*

8707/3: in the context here, is this spectral shift sufficient to make photodissociation possible by sunlight?

*It is now stated that the atmospheric significance of this spectral shift is as yet unknown (end of Section 4.3).*

8707/5 “slowly” (?)

*This change has been made.*

8708/1: maybe no evaluated but certainly hypothesized (e.g. the now somewhat discredited idea of the importance of frost flowers). Might as well mention this?

*The frost flower connection is somewhat different than potential freeze concentration effects of sea ice, given that the frost flowers form by vapor deposition of water and*

*wicking of brine. Freeze concentration is likely to proceed when sea ice freezes itself. Thus, we have not changed the wording in this section.*

8708/21: section 4 as a whole needs a summary. It is highly detailed (and very interesting, at least to me), but difficult to follow for the non physical chemist. In a summary I would state “what should work” for polar boundary layer (or UTLS) conditions. This can serve then as an introduction to the next section, and be a recommendation for what requires priority for evaluation in further field studies.

*This is a good suggestion and so the reader is now directed to the summary in Section 7.2, which now more completely summarizes the chemistry that is likely most important.*

8709/12-13: this sentence does not run correctly. Make it something like “; they observed that a BrO cloud (seen by satellite) and a concurrent surface-based ODE followed a blowing snow event at that site.”

*This wording has been changed.*

8710/7: Bauguitte et al. is not an “O-buoys” paper. Also, it does not do DOAS, so there will not be BrO data, and presumably no insitu met data? It will give an useful survey but I don’t see how it can answer the question posed. Please correct.

*This wording has been changed (Section 5.1).*

8710/10: please give numbers here so one can compare with the Antarctic data from Buys et al. (2012)

*Numbers from the Liao et al. work have now been added to the paper. (Also, we have added the correct Liao et al., 2012 reference to the paper.) Section 5.1*

8710/16: not “potential the” but “the potential”

*The wording has been changed in this section.*

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8711/1: I do agree entirely, but at the same time we should keep in mind that to keep an ODE going one needs BrO. At high temperatures at the observation site, without BrO formation (formation!) one could expect the ODE to disappear.

*This is clearly complicated – initial bromine activation and bromine recycling may have different mechanisms (for example in an ODE bromine recycling occurs efficiently via  $\text{BrO} + \text{BrO} \rightarrow \text{Br}_2$ ). Therefore, to keep an ODE going the temperature may be different than for the initial activation. We have left the wording as in the original manuscript.*

8711/6: no, they were not the first to show this! There was a previous paper: Kieser, B. N., J.W. Bottenheim, T. Sideris, and H. Niki (1993), “Spring 1989 observations of lower tropospheric chemistry in the Canadian high Arctic”, Atmos. Environ., A27, 2979–2988. However, Jobson et al. is much more convincing.

*We have now added this paper and changed the wording (Section 5.1).*

8711/19: I am sure all authors know about the Cl<sub>2</sub> measurements made at Barrow in 2009 (if memory serves me well it was reported at the AGU FM in 2009; they are also alluded to in the paper by Stephens et al., J. Geophys. Res., 117, doi:10.1029/2011JD016649, 2012). Can you mention something about those, in view of their potentially critical importance?

*The Cl<sub>2</sub> measurements from OASIS, while discussed at meetings, have yet to be formally published. However, we do now make reference to this Stephens et al. publication, indicating that such measurements have been made during OASIS 2009 (Section 5.1).*

8713/24: Since there has been a strong tendency to assume that the well-known BrO hot spots are indicative of boundary layer BrO, the cursory reader is somewhat left in doubt here. A definitive statement is required here such as “user beware, these BrO maps are not tropospheric BrO and there are other explanations for the hot spots”.

*This is a good suggestion. A cautionary statement has now been added to the end of*

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*the first paragraph in Section 5.2.*

8714/3: why surprisingly? This runs ahead of what follows I presume (i.e. it has not been seen in the Arctic)? I think it is more surprising that it has not been seen in the Arctic given the early iodine data from Sturges and Barrie, “Chlorine, Bromine AND Iodine in arctic aerosols”, Atmos Environ 22(6), 1179-1194, 1988. See also below.

*The word surprisingly has been removed and added to the section describing the lack of high levels of iodine in the Arctic! (Section 5.3)*

8714/3: about the secondary peak during autumn. I presume that secondary peak is not seen for BrO? Interestingly, going back to Sturges and Barrie (1988), they reported a secondary autumn peak for iodide but not for bromide in the Arctic.

*There is a much less pronounced peak for BrO in the autumn, as illustrated in Figure 4 of Saiz-Lopez et al., Science, 317, 348-351, 2007.*

8714/25: delete “recently” (it feels odd, since they were observed at almost exactly the same time as the Pohler et al observations).

*This change has been made.*

8714/28: delete “However” (So what “however”, it was observed!)

*The change has been made.*

8715/3: I think it would make sense to have a short subsection 5.4 devoted to ClO<sub>x</sub>. Did one look for it? OCIO? etc. Implications of the Barrow 2009 Cl<sub>2</sub> data?

*With the Cl<sub>2</sub> data from OASIS not published, it is not possible to discuss them in depth. OCIO measurements were mentioned briefly in Section 5.1 As such, we do not see the need for a separate section on ClO<sub>x</sub>, especially without ClO measurements themselves. However, as described above, we now have included the cirrus cloud discussion at this point, as another indication of how heterogeneous chemistry can occur on ice, in this case indeed giving rise to chlorine activation.*

8715/16: Poor sentence. I would say “the dominant origin is assumed to be seawater”.

*This change has been made.*

8716/19: the most important criterion, for simplified chemistry parameterizations in particular, is that the parameterizations should be such that they do not give the right answer for the wrong reasons!

*This is an important point. Simplified chemical schemes will always ignore some of the chemical complexity in the system. However, this is necessary for modeling at regional and global scales. The key in developing these schemes is to use parameterizations that adequately represent the chemistry (influence on oxidation capacity, links to other chemical cycles, etc) and source strength under a variety of different conditions. If this can be developed, then hopefully it will mean we have understood the fundamental processes at a sufficient level to simplify them correctly.*

8717/17: ikaite again. I thought that ikaite precipitation would not help to reduce alkalinity necessary for bulk liquid chemistry to work. I obviously am confused.

*It is hoped that the rewritten section on carbonate precipitation (Section 4.1.4) makes this issue more easily understood. In particular, ikaite precipitation does indeed reduce the alkalinity, just not as much as if calcite were to form.*

8718/10: Morin et al. conclude the same from the perspective of the XO chemistry, based on isotope data.

*We have added: As was expected based on the nitrate oxygen isotope anomaly measured during polar sunrise ODEs (Morin et al., 2007) (Section 6.2). Morin et al., Signature of Arctic surface ozone depletion events in the isotope anomaly ( $\Delta^{17}\text{O}$ ) of atmospheric nitrate, Atmos. Chem. Phys., 7, 1451–1469, 2007*

8719/10: did not Michalowski et al. (2000) come to the same conclusion?

*The study of Michalowski et al. was not a 1D model study. Therefore, we have left a*

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discussion of it out of this section. In addition the focus is on the work conducted since the Simpson et al. 2007 review.

8719/20: “activation of NO<sub>x</sub>”? I presume “production of NO<sub>x</sub>”

*This change has been made.*

8720/11: “Very large iodine precursor fluxes” is teasing and needs some elaboration. Were the required large fluxes sensibly possible? Were they observed? (after all, these precursors probably do not have a long lifetime so they should be somewhere in the neighborhood) What are the implications for the IO observations?

*The iodine precursor fluxes required to sustain these levels of IO are predicted to be 10 times the fluxes to sustain a similar amount of BrO. The reason is both 1) the shorter lifetime of IO compared to that of BrO, and 2) the more efficient heterogeneous recycling of bromine on seasalt aerosols than for iodine. There were no measurements of fluxes or measurements of inorganic iodine precursors. The measurements of iodocarbons showed that the concentrations were too low to explain the observed IO. We have modified the sentence to elaborate of this (end of Section 6.3):*

*In the model, very large iodine precursor fluxes ( $1 \times 10^{10}$  molecule  $\text{cm}^{-2} \text{s}^{-1}$  to sustain IO levels, up to 20 pptv) were required to reproduce measured IO levels, due to the short lifetime of IO and the slower aerosol recycling for iodine (which helps to sustain BrO levels). Future measurements are needed to determine if these large fluxes occur over sea ice.*

8720/15: delete “operating”

*The change has been made.*

8721/2-4:! YES!! And this is something that could use some more attention, as much as the emphasis is really on the chemistry in this paper.

*Given the limited number of 3D model studies, we feel this particular sentence cannot*

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*be further expanded. This is covered in more detail in section 8.3 (now section 7.3).*

8721/13-15: if these very high winds are required, how often do those (blizzard) conditions really occur? Does that match up with the frequency of BrO clouds?

*These are good questions but hard to answer. For example, while high wind speed events occur frequently in polar regions, due to lack of observational data, we almost know nothing about the threshold of the blowing snow (blizzard) on sea ice (which means that the blizzard mechanism on sea ice could be different from that inland). It is true that observed BrO plumes are not always associated with high surface wind speeds, which means that either a different bromine releasing mechanism occurs or that there is transport of already activated air masses from the upwind direction (see Section 7.3).*

8721/22: can you give a hint of these uncertainties?

*The uncertainties arise from the fact that the processes that govern halogen release are yet to be fully understood. We believe the uncertainty in our understanding is adequately discussed in other parts of the paper.*

8726/1: add something like “and the results need to be tested in the actual environment. That is hard work but nowadays quite doable”.

*This is a good suggestion and now has been added to the paper (Section 7.1).*

8726/5: does it? In any case, I feel you should add cross references to the statements in this section - would make it even more valuable as a reference source paper.

*A number of references to specific sections of the paper are now made in this concluding Section, to relate the specific conclusions to the relevant text in the review.*

8728/27: is this true, is this what they find?? Or is it for year round no ice?? I would say that in the spring there will be a lot of first year ice under these summer conditions (it still will be Polar with very low temperatures in the winter and spring). For summer,

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yes, but for spring?

*Yes, the statement in the original version of the paper was incorrect. It is only when spring-time ice was removed that ozone increased substantially in the model. We now state that this is just an example of how atmospheric composition may respond to changing sea ice conditions, but that it is unlikely that all springtime sea ice will disappear (Section 7.4).*

8730/31: chapter number?

*Chapter 18, as now indicated in the paper.*

8759: rather odd, 22 references for a maximum of 16 numbers? Are they all truly relevant references?

*The number of references arises because we have given the ranges of organo-bromine and organo-iodine levels from measurements of a number of halocarbons.*

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8677, 2012.

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