Atmos. Chem. Phys. Discuss., 12, C3107–C3114, 2012
www.atmos-chem-phys-discuss.net/12/C3107/2012/

Atmospheric
Chemistry
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Discussions

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

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Received and published: 30 May 2012

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 halogens 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 APCD version.

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 UTLS. 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.

Comments/questions:

8685/28: "may increase with temperature", better to say "correlates negatively with temperature"

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

8688/5: delete "also"

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

8691/1: for clarity say "austral spring/summer"

8691/15: This is confusing. Even under non-bromine explosion conditions I doubt that CHBr3 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?

8691/18: undersaturized in sea water or air?

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.

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"?

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

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 stratospheric)

8696/18: is there enough SO2 and NO2 available in the air to actually arrive at that level (pH=3) or is this purely a theoretical exercise? Please explain.

8697/2: This keeps confusing me. If I read this correct then the original Sander et al. hypothesis does not work because CaCO3 precipitation is most likely in the form of ikaite and hence does not reduce the buffering capacity? Please explain more clearly.

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)?

8697/14: delete "that"

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 $CaCO_3$, or the pH of the FF reported by Kalnajs and Avallone (2006)?

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.

8703/6: "NO_2"? or "NO_3"?

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

8704/1: same story as before, Br^- first, then Cl^-. But does this suggest that $ClNO_2$ might be produced in Polar regions by this chemistry? Is there any evidence for the occurrence of $ClNO_2$ in Polar 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.

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

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

8705/27: or as OH source?

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).

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

8707/5 "slowly" (?)

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?

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.

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."

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.

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

8710/16: not "potential the" but "the potential"

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.

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.

8711/19: I am sure all authors know about the Cl2 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 my 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?

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".

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.

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.

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

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

8715/3: I think it would make sense to have a short subsection 5.4 devoted to ClOx. Did one look for it? OClO? etc. Implications of the Barrow 2009 Cl2 data?

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

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!

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.

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

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based on isotope data.

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

8719/20: "activation of NOx"?? I presume "production of NOx"

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?

8720/15: delete "operating"

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.

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?

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

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

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.

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, yes, but for spring?

8730/31: chapter number?

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

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