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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of blowing snow in the activation of bromine over first-year Antarctic sea ice" *by* R. M. Lieb-Lappen and R. W. Obbard

Anonymous Referee #2

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Overall Review:

This short manuscript describes observations of ionic content in ice, snowpack, and blowing snow in Antarctica. The data are consistent with halogen activation from blowing snow. However, some aspects of the manuscript should be stated more cautiously given the small amount of data shown, and the indirectness of the measurement. Specifically, questions of mass balance, post-collection sample modification, and diffusion of gases to suspended surfaces need to be addressed. The observations are certainly of interest to the community, and after significant modification to the discussion, this manuscript could be appropriate for publication in Atmospheric Chemistry

and Physics.

General comments:

Halogen activation is the process of creating reactive halogens from halides in snow/ice/aerosols. This manuscript examines loss of halides (e.g. bromide) from snow by using chloride as a tracer for sea-salt halide sources. In that way, the measurements are indirect because "activation of bromine" (e.g. production of reactive halogen species = Br, BrO) was not measured. This brings up two main points:

1) Activation of a certain amount of bromine into the atmosphere can come from a small fraction of activation of a saline (bromide-rich) snow/ice, which would lead to a small enhancement in the Cl-/Br- ratio (choice of ratio as in the text, but not preferred), but a large total amount of reactive Br produced. Alternatively, for the same amount of reactive Br production, a snow/ice sample that happened to have less bromide to start with (e.g. a less saline sample) would show a larger enhancement in the Cl-/Br- ratio. Therefore, the plot shown in Figure 3 does not tell the complete story. Specifically, how much Br- and/or Cl- are present in each of these samples? If the blowing snow at higher altitude (e.g. 550 cm) has much less total salinity, little reactive bromine would have been produced from this sample.

The authors need to include the full measurements of Cl- and Br- in their samples in some manner so that readers could explore other hypotheses. Inclusion of the data as a supplementary data table could be a good solution, and just indicating that the data are on a website, which is not archival, is not sufficient. The discussion of ranges on page 11992 is not sufficient to get a full picture of the data, and the large ranges shown on that page motivation the need for inclusion of more data.

The authors should also explore the total mass of Br- lost from samples as a function of height. Even though the fractional Br- lost is highest at 550cm, the lower portion of the column could be releasing more Br-, if it is more saline.

2) The authors made a good design for collecting blowing snow, but the design still leaves some challenges in interpretation. Specifically, snow in the basket is being exposed to ambient air, which could be leading to depletion of Br- after sampling snow. One could argue that the authors have produced a snowpack that is being held aloft (in baskets) and wind is ventilating this snowpack and causing depletion of halogens in a snowpack-like process. The greater windspeed at higher altitude could then cause the profile observed in Fig. 3. It is not clear if the snow in the baskets is permeable to air. The authors should give a description of what the snow looked like (was a fine dust or a packed windslab that might not be very permeable). That description could possibly help in the interpretation, but I think that both the possibility of depletion of Br- from the blowing snow phase and post-sampling depletion of Br- need to be discussed.

Along the lines of this discussion, blowing snow clearly suspends surface area that presumably contains bromide, but to the extent that the snow moves with the airstream, the relative velocity of air as compared to ice surface decreases as compared to the fixed snowpack situation. Snow blowing at the windspeed has no relative motion compared to the gases, and then gas-phase diffusion to the snowgrain becomes the mass transfer limitation for halogen activation. For large particles (above a few micron diameter), the diffusion limitation dominates the mass transfer of gases to the surface. This point should be discussed more fully in the manuscript. Saltating (bouncing) snowgrains present an intermediate case, where there is some slip velocity between air and particle.

Specific comments:

Abstract, p11986 line 11. It is not clear what mechanism causes "replenishment" of bromide in the snow. I don't think that this sentence in the abstract is well justified in the manuscript. Eliminate from abstract or explain more. Again, the mass balance aspects (point 1 above) of the problem are lost by this ratio-based analysis, and the mass balance needs more discussion.

p11986, line 16 – Does sea ice coverage change a lot in springtime?

p11986, line 19 – In the polar regions, halogens are often the dominant oxidizers. Halogens oxidize hydrocarbons, and that signature is clear in VOC data. This sentence needs modification to indicate that halogens are themselves oxidizers.

p11987, line 12 – The use of "fractionation" is not being used appropriately. Fractionation is a process – the changing of ratios of ions from sea salt ratios to different ratios. This section needs rewording to be consistent.

p11989, line 27 – the word "unto" is not correct. Possibly "until".

p11991, line 3 – Winds were mild is indicated. Was ozone measured? If so, was ozone also not depleted often? While the relationship between ozone depletion and halogen activation is complex, it would be valuable to examine if ozone was depleted during these blowing snow events, and/or if ozone depletion was observed during non-blowing snow events.

p11991, line 17 – missing an "and" somewhere?

p11992, line 9 – the unit of kg m-3 is used here for chloride, but line 25 on the same page has an overlapping range that is instead written as g m-3. Please make consistent. Again, ranges are not sufficient to answer mass balance questions and somewhere this manuscript needs a full data table.

p11994, line 2 – the section "...actually decreases due to required HOBr..." is not very clear. Reword.

p11994, line 16 – How is surface snow bromide "replenished"? An argument is made about "small proportion of surface snowpack", which starts the discussion of a mass balance (point 1 above). This can be made more quantitative through the inclusion of all concentration data instead of only ratios. The production of HOBr is not really much of a termination reaction – HOBr + HBr -> Br2 + H2O on snow is the "bromine explosion" reaction, not a termination. Deposition of "aerosol-phase bromine" only

represents a "replenishment" if the aerosol-phase bromine is enhanced compared to chloride in the particles. Please clarify this mechanism.

p11995, line 19 – This work examined the ratios of Cl- to Br- in snow deposited in baskets, and did not observe bromine activation (e.g. production of Br and/or BrO). Please clarify.

p11995, line 21 – The ratio chosen is Cl-/Br-, but which becomes enhanced in blowing snow. The reason for that enhancement is interpreted as the depletion of the denominator. Therefore, the wording "depletion" in this line is confusing. If the full manuscript were changed to the Br-/Cl- ratio, it would read easier. Presumably Cl- is a relatively conserved sea salt tracer, so having that as the denominator makes sense.

p11995, line 23 – The conclusion is written in a way stronger than the discussion of the manuscript. The observation is depletion of Br-/Cl- in snow in baskets more aloft. The Br- depletion could have happened while the snow was blowing, or could have happened post-catch in the basket but before collection of the basket. Mass balance considerations are absent and not checkable given the data in the manuscript. Diffusion to ice surfaces is not sufficiently discussed, and snow in baskets aloft is probably better ventilated than both snowpack and blowing snow, which moves with the wind. Therefore the statement "...we conclude the blowing snow particles provide an ideal surface for the initial heterogeneous reactions..." is a stretch. Reword to make conclusions from these observations.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 11985, 2015.