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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

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RESPONSES TO SHORT COMMENT BY H.-W. JACOBI

1. The authors base their analysis on chloride-to-bromide ratios to determine processes related to bromine. However, it is well known that chloride concentrations in snow can also be modified. This may be negligible for high chloride concentrations, but it can become important at concentrations below 1 kg m^3 [e.g. Simpson, W. R., L. Alvarez-Aviles, T. A. Douglas, M. Sturm, and F. Domine, Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active

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bromine air-snow chemistry during springtime, Geophys. Res. Lett. 32, L04811, doi: 10.1029/2004GL021748, 2005 or Jacobi, H.-W., D. Voisin, J.-L. Jaffrezo, J. Cozic, and T. A. Douglas, Chemical composition of the snowpack during the OASIS spring campaign 20009 at Barrow, AK, J. Geophys. Res. 117, D00R13, doi: 10.1029/2011JD016654, 2012]. A more conservative tracer is sodium. Why don't the authors use chloride-to-sodium and bromide-to-sodium ratios to remove the possible role of processes acting upon chloride?

We recognize that both sodium and chloride are used commonly in the literature as sea-salt tracers when considering halide ratios. There is nearly a perfect linear correlation between sodium and chloride in snow samples as was observed in the two papers referenced above (Simpson et al., 2005 and Jacobi et al., 2012) for Cl concentrations greater than $1,000$ μg/L. As the blowing snow samples in this study were quite saline, often with Cl concentrations greater than 1g/L, we feel that we are well above this threshold. Even the less saline samples in this study generally had Cl concentrations of hundreds of mg/L. We recognize that other processes can alter both the chloride and sodium concentrations of blowing snow and in the snowpack itself. Wagenbach et al. [Wagenbach, D., Ducroz, F., Mulvaney, R., Keck, L., Minikin, A., Legrand, M., Hall, J. S., and Wolff, E. W. Sea-Salt Aerosol in Coastal Antarctic Regions, J. Geophys. Res., 103, 10,961–10,974, 1998] discusses the challenges of using sodium as a sea-salt tracer due to the precipitation of mirabilite. The study estimates that errors of up to 10% can result if one uses sodium as the reference ion. Further, recent studies such as Pratt et al. [Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pohler, D., General, S., Zielcke, J., Simpson, W. R., Platt, U., Tanner, D. J., Huey, L. G., Carlsen, M., and Stirm, B. H. Photochemical Production of Molecular Bromine in Arctic Surface Snowpacks, Nat. Geosci., 6, 351–356, doi:10.1038/NGEO1779, 2013] have used chloride as the reference anion. In keeping with the convention of these studies, we have chosen to use chloride as the reference ion here. We also feel that chloride as the reference ion is a conservative estimate for this study. If other processes have resulted in lower measured concentrations of Cl in our samples, bromide depletion due to bromine release would be even greater than suggested here.

In contrast to the comment of referee $\#1$, we already reported the chemical composition of mobile blowing snow in the Arctic, which we classified as "Fresh blowing snow" [Jacobi, H.-W., D. Voisin, J.-L. Jaffrezo, J. Cozic, and T. A. Douglas, Chemical composition of the snowpack during the OASIS spring campaign 20009 at Barrow, AK, J. Geophys. Res. 117, D00R13, doi: 10.1029/2011JD016654, 2012]. The samples were collected directly into the sampling bottles very close to the snow surface (less than 5 cm). The advantage of this technique is that samples can be collected within minutes reducing a potential modification after collection. It is allows studying the temporal evolution of the composition of the blowing snow during the blowing snow events. For example, we found that during the event described in Jacobi et al. the depletion in bromide became only detectable after a period of several hours, while at the beginning of the blowing snow event the snow was enriched in bromide. In contrast, the samples collected by Lieb-Lappen and Obbard represent samples integrating over one blowing snow event possibly masking depletions and enrichments occurring during different phases of the event.

We thank Dr. Jacobi for referring us to the referenced 2012 manuscript. We feel our study complements the Jacobi et al., 2012 well as we have added information regarding height variability. In Jacobi et al., 2012, anion and cation concentrations were measured for a variety of snow types. Pertinent to this study, at multiple times during a blowing snow event, they collected mobile snow 5 cm above the surface, representing a mixture of snow mobilized by suspension, saltation, and creep. The focus of our study was to determine how the chemical composition of blowing snow varies with height. Since our collection was a conglomerate of snow from the $4-6$ hr blowing snow event, the depletion we observed is consistent with the depletion measured by Jacobi et al., 2012, although it adds additional information regarding the location of bromine release. The second paragraph of the discussion has been edited as follows

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to include reference to Jacobi et al., 2012.

A depletion factor (DF) was defined such that DF$= 0$ *signifies no bromine depletion in particles and DF*$= 1$ *signifies complete depletion (Yang et al., 2005). We note that a negative value for DF indicates bromine enrichment. Averaging the* Br^-/Cl^- *mass ratios at each height for Butter Point yields DF*$= 0.04, 0.11, 0.41,$ *and* 0.68 *for heights of* $0.3, 2.0, 3.0,$ *and* 5.5 *m, respectively. At Iceberg Site, DF*$= -0.08, 0.20, 0.33,$ *and* 0.64 *for the four heights, respectively. Depletion factors were relatively small for both surface snow and ice core samples, with values ranging from* -0.20 *to* 0.13 *and* -0.13 *to* 0.17*, respectively. These values are consistent with previously reported values and currently used in some models (Sander et al., 2003; Yang et al., 2005). Previously, Simpson et al. (2005) observed up to* 90% *bromide depletion in surface snow, while Jacobi et al. (2012) observed up to* 70% *depletion in snow mobilized* 5 *cm above the surface. The latter study also noted that during a blowing snow event, there was first bromide enrichment in the snow during the initial part of the storm followed by later bromide depletion (Jacobi et al., 2012). An increased depletion factor can either signify bromide depletion due to bromine release or chloride enrichment from, for example, gaseous HCL uptake. If the latter hypothesis were true, one would expect to observe increased chloride concentrations in higher baskets. The lack of an observed chloride trend with height leads to our interpretation that the decreased mass ratio is a clear indicator of bromine activation. Interestingly, lower* Br^-/Cl^- *ratios have also been found to correspond with a decrease in chlorine release (Wren et al., 2013). This is due to the fact that BrCl plays a critical role in chlorine production. BrCl is initially formed from the reaction between HOBr and* Cl^-*, and then upon later photolysis, can lead to chlorine release (Wren et al., 2013).*

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