

SECOND RESPONSES TO REFEREE 1

Bromide depletion: Based on new meteorology data given, it is clear that the blowing snow event on 24 October near McMurdo Station was under a mid-strength wind and a relatively dry condition with mean relative humidity (RH) of 69%. Under this unsaturated condition, blowing snow particles would sublime and shrink, especially in aloft layer. We know, during blowing snow, RH near snow surface or within saltation layer is saturated and then reduces with increasing heights. This means there is more water vapour loss at a greater height than at a lower height, indicating an enhanced ion concentration condensation at a higher layer. The new Table 1 dataset clearly matches this prediction. The raw data in Table 1 shows that averaged Cl⁻ concentrations at 5.5 m (based on all samples in both Iceberg and Butter Point) is 10 times of that at 0.3 m. This means, assuming a spheric shape of suspended snow particles in blowing snow layer, the particle size (radius) at 5.5 m is less than half of that at 0.3 m. Although the reduction in particle size does not necessary mean an enhancement of photochemical reaction rate, it does prolong the airborne time of particles and eventually result in more bromine release (this is what Yang et al. (2008)'s mechanism about). Thus, the potential effect of sublimation process on reducing snow particle size as well as on bromine release should be mentioned in the revised version.

We thank Referee #1 for his comments regarding particle size and sublimation. We agree that the manuscript would benefit from adding a comment regarding sublimation and the increased airborne time for more bromine release. However, we do not feel that there is sufficient data to make a definitive statement on particle size. The lack of a statistically significant trend in Cl⁻ concentrations (see second and third responses below) means that there is not enough data to suggest a clear trend in particle size with height. However, we have edited the first paragraph of the discussion to include this recommendation and it now reads:

Observation of bromide depletion relative to other salts is an indication of heterogeneous atmospheric chemical reactions and bromine activation (Adams et al., 2002; Huff et al., 2002; Simpson et al., 2005). Although there

was some variability in Br^-/Cl^- mass ratios for sea ice and surface snow, these ratios were remarkably constant, just over 1 : 300. As shown in Fig. 3, signs of bromide depletion occur above the snowpack, with greater depletion occurring at greater heights, reaching mass ratios of nearly 1 : 1000 at heights of 5.5 m. This is consistent with aerosol observations by Duce et al. (1971) that measured increased bromide depletion with height, albeit at tropical latitudes. They noted a strong particle size dependence with increased bromide depletion corresponding to mid-sized aerosol particles. Further studies have shown that particle size influences the mode of transport and it may not be realistic to differentiate snow saltation and suspension based solely on wind speed and height (Nemoto et al., 2004). Nevertheless, both processes greatly increase the snow surface area exposed for gas-phase reactions by as much as 3,000 times that of surface snow (Pomeroy et al., 2001). It is noted that snow blowing at the windspeed will have no relative motion compared to the gases and gas-phase diffusion becomes an important consideration, especially for large grain particles. Local turbulence however, will help overcome some these diffusion limitations (Nemoto et al., 2004). We also note that sublimation of blowing snow particles likely has a strong effect on anion concentrations. Consistent with the mechanism suggested by Yang et al. (2008), lighter particles would remain airborne for longer periods of time, leading to suspension at greater heights and more time for photochemical reactions. However, since particle sizes were not measured in this study, we solely mention the potential sublimation may have on increasing bromine release through this pathway.

About salinity: in my first round comment I suggested authors deriving snow salinity from their data, instead of giving snow salinity, they supplied anions concentrations (in response to reviewer #2 request). Obviously, these anions data are quite useful and contain more detailed information, but snow salinity is still a quite useful parameter in many studies in both oceanic and atmospheric chemistry. Here I tried to work out some. Based on dominant anion Cl^- concentrations, I derived an averaged blowing snow salinity of 0.25 PSU at 0.3 m, while at 5.5 m, it is 2.6 PSU (these data are quite useful for estimating/quantifying saline amount lifted and sea salt production from blowing snow). Thus, I again suggest authors thinking about deriving salinity from your raw data (including surface snow salinity).

We thank Referee #1 for the suggestion to include salinity data. We first note our comment in our original response that measured values for many of the samples were less than the 0.1 g/m^3 detection limit of our YSI Pro30 conductivity/salinity instrument. Thus, to achieve salinity values, we needed to estimate them based upon chloride concentrations. We have done so and edited the second and third paragraphs of the Results section accordingly. Those two paragraphs now read:

Surface snow anion concentrations varied greatly, but were of similar magnitude at the two sites and showed no noticeable trend with time over the field campaign. Concentrations ranged from $200 - 5,000 \text{ g/m}^3$ chloride, $1.0 - 16 \text{ g/m}^3$ bromide, $20 - 2300 \text{ g/m}^3$ sulfate, and $0 - 1.2 \text{ g/m}^3$ nitrate, though the majority of samples were below detection limits in nitrate. If we assume Cl concentrations to be a good proxy to estimate salinity using sea water ion ratios, this corresponds to a mean surface snow salinity of 3 PSU, with a range of $0.4 - 9$ PSU. There was little snow cover at Butter Point with the surface varying from completely wind scoured to several cm of snow. Iceberg Site had a more variable snowpack, with prevalent rafted ice and sstrugi, resulting in snow depths varying from tens of cm to over 1 m. A 21 cm snow pit was dug 15 km from Butter Point Site to study a more consistent snowpack that is representative of the greater first-year sea ice of the region. In this snow pit, both chloride and bromide concentrations increased steadily from the snow surface to the snow/ice interface, with concentrations ranging from $500 - 1,600 \text{ g/m}^3$ chloride and $1.5 - 6 \text{ g/m}^3$ bromide. Sulfate concentrations ranged from $30 - 50 \text{ g/m}^3$, but showed a C-shaped profile with highest concentrations found near the top and bottom of the snow pit. A second snow pit located slightly closer to the open ocean showed similar trends.

Anion concentrations from the blowing snow samples collected on 25 October in both towers varied greatly, including separate samples from the same collection baskets, indicating that blown snow can be quite varied in its salt concentration. Concentrations ranged from $50 - 6800 \text{ g/m}^3$ chloride, $0.2 - 18.5 \text{ g/m}^3$ bromide, $3 - 240 \text{ g/m}^3$ sulfate, and $0.4 - 23 \text{ g/m}^3$ nitrate. Using chloride concentrations to derive an estimate of salinity, blowing snow samples ranged from 0.1 PSU to 12 PSU. Comparing the 0.3 m and 5.5 m baskets at both sites suggests a 10-fold increase in salinity from 0.6 PSU to 6 PSU. However, when all blowing snow samples are considered, there is not

a statistically significant trend of increasing salt concentration with basket height, except for nitrate where concentrations increased with height above the snow surface.

About Chlorine: In your reply, you said 'the lack of an observed chlorine trend with height ...' (see 4th-5th pages from bottom in reply to reviewer #2). In contrast, I actually saw a clear increase trend of Cl⁻ (and for other ions) with height. As I mentioned above, the increase in Cl⁻ is very likely due to loss of water via sublimation processes, but others. Also in the same paragraph, you said 'Interestingly, lower Br⁻/Cl⁻ ratios also correspond to a decrease in chlorine release'. Do you want to address the effect of chlorine activation on the Br⁻/Cl⁻ ratio? I do not feel you have enough data to support this exploration, and moreover in a clean polar regions, the effect of BrCl release (via HOBr uptake) on Cl⁻ should not be important before complete bromide depletion in particles (which is not the case). Thus I suggest re-written of this paragraph.

Although some of the less saline samples were from the lowest basket, the data does not show a clear linear trend of increasing salinity with height. In fact, samples from the 2 m basket at Iceberg site had the greatest salinity by a large margin, while that same height basket had the least saline samples at Butter Point. At Butter Point, there was not much difference in anion concentrations between baskets at 3 m and 5.5 m. We have addressed the comment regarding sublimation in the first response, but considering the sample size, r^2 values for a correlation between height and salinity are below the critical threshold for statistical significance. We have edited the results section (see response above) to comment on this trend. In regards to the comment on chlorine activation, we agree that our data does not warrant a full exploration on chlorine release. However, considering that Wren et al., 2013 found decreased chlorine release to coincide with bromide depletion, we feel that it is important to note the implications of our finding of bromine depletion. We have rewritten the final sentences of the paragraph to make it clear that we are referring to the work of Wren et al., 2013 in this instance. Those sentences now read:

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).

New figure 4 (about DF): 1) it would be useful to include surface snow DF and ice core DF in same DF plot.

We thank Referee #1 for this recommendation. For the reasons mentioned in our first response, we have limited our figures to be mass ratios rather than depletion factors. However, we have added DF values for surface snow and ice core samples in text. The second paragraph of Section 4 now reads:

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).

Definition of DF. I think your explanation of DF is not correct. As I mentioned in the previous comment, DF=1 means complete bromine depletion (all bromide in particle go into air); while DF=0 means no bromine depletion. For a negative DF, it signifies a net bromine uptake by particle, or bromine 'enrichment'. Note, DF was firstly introduced by Yang et al. 2005 (doi: 10.1029/2005JD006244), which is quite different from the 'bromine enrichment' factor introduced by Sander et al. (2003) in expressing bromine depletion in aerosols. I noticed that you cite Sander et al. 2003 paper for DF, which was not a proper one. Also, given a formula of DF maybe a good idea to avoid further confusion.

We thank Referee #1 for catching this mistake in our response and we apologize for the error. The DF values given were calculated correctly, but the wording of the first sentence in the paragraph was accidentally switched. Additionally, the correct reference to Yang et al., 2005 has been added. In the revised manuscript, the paragraph reads as in our response above.