RESPONSES TO REFEREE 1

Lines 10-12: In abstract, the authors concluded 'this suggests that replenishment of bromide in the snowpack occurs faster than bromine activation in mid-strength wind condition'. However, in the discussion section (page 11994, lines 15-17), they texted 'the lack of recorded bromine depletion in the surface snow may indicate that either surface snow bromide concentration is quickly replenished or that blowing snow represents only a small portion of the surface snowpack.' I do not understand why the authors throw the second possibility away? Which I think it could be very possible if that area is lack of strong winds.

We thank Referee $^{\#}$1 for catching this omission. The sentence has been edited to now read:

This suggests that replenishment of bromide in the snowpack occurs faster than bromine activation in mid-strength wind conditions (approximately $10\,m\,s^{-1}$) or that blowing snow represents only a small portion of the surface snowpack.

It would be very helpful if more meteorological information could be supplied for the 24-25 October case from nearby McMurdo station. They include wind speed, relative humidity (RH), temperature, and/or radiation. They may help us estimate the magnitude of the blowing snow event, and sublimation flux related.

In addition to the given wind speeds, we have now added temperature and relative humidity recorded from nearby McMurdo Station. The third paragraph of Section 2 now reads:

Winds during the field campaign were generally mild, only surpassing $10\,m\,s^{-1}$ on a few occasions. Site visits were not feasible during stormy weather, and much of the blowing snow captured during those periods sublimated in the baskets prior to collection as observed by a webcam. Thus, only on 25 October were blowing snow samples collected at both sites and all four heights. The collected snow was the result of approximately $10\,m\,s^{-1}$ southerly winds on 24 October. Visibility at McMurdo station during this blowing snow event dropped below 0.5 miles for about 4 hours. Temperatures ranged from $-20.5\,°C$ to $-11.5\,°C$ with an average relative humidity of 69%

on 24 October and $-17.5\ ^\circ C$ to $-13.5\ ^\circ C$ with an average relative humidity of 61% on 25 October. These temperatures were a couple of degrees warmer than the average for the rest of the field campaign.

Any further information, such as visibilities, that can be derived from webcam image during the BS event? What interested me is that the observation in fig3 shows a significant bromide depletion when height > 2m. Then why is that? Is 2m roughly the top of the blowing snow under a moderate wind speed? Can webcam image give us more information?

The webcam at Butter Point Site recorded a still image approximately every 15 minutes with a field of view limited from the ice surface to about 2 m. Unfortunately, both the reduced visibility of the blowing snow event and the resolution of the still images does not allow direct observation of blowing snow. Reference to the reduced visibility has been added to the manuscript (see above). The webcam images do show that the three lower baskets are blowing in the wind and have collected snow. However, the top basket is not visible in the image.

Have you checked satellite BrO images around 24 October? Any elevated BrO spot occurring around the Ross Sea?

Satellite BrO images collected by the Global Ozone Monitoring Experiment-2 (GOME-2) were analyzed over the duration of the field campaign. There was no discernible BrO concentration spike over the Ross Sea around 24 October. This suggests that the recorded bromine release was a small-scale event that did not directly leaded to a greatly enhanced BrO spot. Since the lack of a dramatic BrO spike does not nullify the occurrence of bromine release, this analysis was not included in the revised manuscript.

Could you get snow samples (lofted and on surface) salinities? As salinity is another key factor that determine sea salt production.

Although we agree that it would be helpful to have both lofted and surface snow salinities, measured values for many of the samples would be less than the 0.1 g/m^3 detection limit of our YSI Pro30 conductivity/salinity instrument. The bulk of each sample was diluted further for ion chromatography. At this point, even with a different instrument that had a lower detection

limit, there would be concern of lost of ions to the walls of the container over the last 2.5 years. We feel that anion concentrations provide more detail than a bulk salinity. We have provided the raw data of anion concentrations as a supplement to the manuscript.

Regarding to the bromine depletion profiles in fig.3, I suggest you thinking about plotting out profiles of depletion factors (DFs). DFs, rather than Cl-/Br- mass ratios, are very useful in modelling. You can use the formula shown below for DF calculation.

$$\text{DF} = \frac{\frac{Br}{Cl}(\text{in sea water}) - \frac{Br}{Cl}(\text{in sample})}{\frac{Br}{Cl}(\text{in sea water})}$$

At DF=0, it means no bromine depletion in particles, while DF=1.0 indicates a complete bromide depletion.

We thank Referee #1 for this recommendation. Since the readership of ACP includes both field scientists and modelers, we have decided to include both mass ratios and depletion factors in the revised manuscript. The suggested figure would show the same trend as existing Fig. 3 and it would be repetitive to have both plots. In the revised manuscript we have kept Fig. 3 with mass ratios on the x-axis as it is a more familiar metric. Depletion factor calculations have been added to a new second paragraph of Section 4, which now reads:

A depletion factor (DF) was defined such that DF= 1 signifies no bromine depletion in particles and DF= 0 signifies complete depletion. 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. These values are consistent with previously reported values and currently used in some models (Sander et al., 2003). 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 also correspond to a decrease in chlorine release. It has been shown that BrCl plays a critical role in chlorine production, and BrCl

release is reliant upon the existence of HOBr from prior bromine activation (Wren et al., 2013).

RESPONSES TO REFEREE 2

General Comments:

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.

We thank Referee #2 for recognizing the need to also present the raw anion concentrations in addition to the mass ratios. We have added a supplement to the revised manuscript that has tables reporting the chloride, bromide, sulfate, and nitrate concentrations for all 83 samples. As can be seen in the data, there is not a trend between anion concentrations and height. In addition, even replicate samples collected from the same basket

had drastically different anion concentrations, suggesting that the snow originated from a variety of locations. We feel that the small sample size is not sufficient to estimate the total mass of bromide lost as a function of height and therefore did not include this estimate in the revised manuscript. We find the hypothesis of greater Br^- mass loss at lower heights interesting but unlikely, as very saline samples were collected from the upper baskets. The following three tables have been included as a supplement to the revised manuscript:

Table 1: Raw anion concentrations of blowing snow samples collected on 25 October, 2012, and measured using a Dionex-600 IC system.

Site	Height (m)	Cl^- (g/m^3)	Br^- (g/m^3)	SO_4^{2-} (g/m^3)	NO_3^- (g/m^3)
Butter Pt	0.3	400	1.3	26	0.4
Butter Pt	0.3	460	1.6	28	0.4
Butter Pt	2.0	23	0.1	1	0.3
Butter Pt	2.0	62	0.2	4	0.4
Butter Pt	2.0	63	0.2	4	0.5
Butter Pt	3.0	4,500	9.5	160	20
Butter Pt	3.0	670	1.3	18	4.3
Butter Pt	5.5	1,400	1.4	47	9.9
Butter Pt	5.5	4,900	6.0	210	30
Iceberg	0.3	150	0.5	14	0.2
Iceberg	0.3	280	1.3	59	0.4
Iceberg	2.0	6,700	18.5	240	13
Iceberg	3.0	2,600	6.0	100	8.3
Iceberg	5.5	3,900	4.9	150	23

Table 2: Raw anion concentrations of surface snow samples collected in October – November, 2012, and measured using a Dionex-600 IC system. All nitrate samples marked BQL were below the quantification limit of 0.1 g/m^3.

Site	Date	Cl$^-$ (g/m^3)	Br$^-$ (g/m^3)	SO$_4^{2-}$ (g/m^3)	NO$_3^-$ (g/m^3)
Butter Pt	10/15	3,400	13	1,600	0.3
Butter Pt	10/15	2,400	8.0	350	0.3
Butter Pt	10/15	950	3.7	150	BQL
Butter Pt	10/17	940	3.0	120	0.5
Butter Pt	10/25	780	2.8	78	BQL
Butter Pt	10/25	1,800	6.9	210	BQL
Butter Pt	10/25	2,700	9.5	210	BQL
Butter Pt	10/25	420	1.5	29	BQL
Butter Pt	10/25	920	3.7	120	BQL
Butter Pt	10/25	1,300	4.9	250	BQL
Butter Pt	10/26	330	1.2	20	0.5
Butter Pt	10/29	350	1.2	50	BQL
Butter Pt	10/31	470	2.0	77	BQL
Butter Pt	11/02	2,200	7.8	210	BQL
Butter Pt	11/06	3,700	13	590	1.2
Iceberg	10/11	1,400	4.4	87	0.3
Iceberg	10/15	4,600	15	1,200	0.9
Iceberg	10/15	550	2.1	160	0.1
Iceberg	10/15	440	1.7	34	BQL
Iceberg	10/17	3,700	13	1,100	0.5
Iceberg	10/19	1,100	4.7	1,600	BQL
Iceberg	10/25	2,100	7.3	140	BQL
Iceberg	10/25	1,100	4.4	58	BQL
Iceberg	10/25	3,700	13	1,600	BQL
Iceberg	10/25	2,300	8.2	2,300	BQL
Iceberg	10/26	370	1.2	100	0.5
Iceberg	10/29	1700	5.1	480	BQL
Iceberg	10/31	150	0.5	74	0.2
Iceberg	11/02	2,000	6.5	160	BQL
Iceberg	11/06	1,400	5.2	540	BQL
Iceberg	11/08	2,300	7.8	240	BQL

Table 3: Raw anion concentrations of sub-samples taken every 10-cm for the length of two ice cores collected at Butter Point Site and Iceberg Site, respectively, and measured using a Dionex-600 IC system. All nitrate measurements in the two ice cores were below the quantification limit of 0.1 g/m^3.

Site	Depth (m)	Cl^- (g/m^3)	Br^- (g/m^3)	SO_4^{2-} (g/m^3)
Butter Pt	0	7,600	25	1,800
Butter Pt	10	5,500	19	1,300
Butter Pt	20	5,200	17	1,900
Butter Pt	30	3,500	11	670
Butter Pt	40	3,800	11	1,400
Butter Pt	50	3,200	11	490
Butter Pt	60	2,900	9.7	570
Butter Pt	70	3,800	13	470
Butter Pt	80	2,500	8.0	420
Butter Pt	90	3,600	12	330
Butter Pt	100	2,900	9.8	680
Butter Pt	110	2,600	8.7	480
Butter Pt	120	2,800	8.9	590
Butter Pt	130	1,900	5.6	440
Butter Pt	140	2,100	6.2	410
Butter Pt	150	2,200	8.6	440
Butter Pt	160	3,300	11	610
Butter Pt	170	3,200	11	690
Iceberg	0	8,000	30	3,100
Iceberg	10	6,000	21	1,200
Iceberg	20	3,200	13	520
Iceberg	30	3,700	13	450
Iceberg	40	3,300	12	1,600
Iceberg	50	2,900	9.7	230
Iceberg	60	3,000	8.9	840
Iceberg	70	2,800	9.8	270
Iceberg	80	3,100	11	490
Iceberg	90	3,100	12	390
Iceberg	100	2,600	9.5	370
Iceberg	110	3,400	12	690
Iceberg	120	2,500	8.2	480
Iceberg	130	3,200	11	560
Iceberg	140	2,700	8.7	460
Iceberg	150	2,300	7.4	440
Iceberg	160	2,200	8.0	420
Iceberg	170	3,000	11	480
Iceberg	180	3,500	13	460
Iceberg	190	9,100	34	1,400

2a) 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.

Referee #2 raises a good observation regarding the design of the experiment and potential source of error. We do note that an improved future design should try to eliminate any exposure to ambient air of collected snow in the basket. However, the current post-collection exposure is small enough that it does not significantly affect the main conclusions of the manuscript. We have added more field observations that should help alleviate some of these concerns. Section 4 of the revised manuscript has been revised to reflect these changes and now reads:

Previously, bromine activation and ODEs were observed in both low (< 5 m/s) and high (> 12 m/s) winds (Jones et al., 2009). Here, the blowing snow event occurred during moderate winds of approximately 10 m/s. Since the wind was from the south and there was no new precipitation, it is safe to assume that the snow originated from the surface of first-year sea ice. It is noted that the blowing snow event lasted approximately $4 - 6$ hours, and that snow samples from the baskets were not collected until $10 - 12$ hours later. During this time, wind speeds dropped to less than 5 m/s, and it is possible that the collected snow was exposed to further wind scouring. However, all baskets would have experienced a similar degree of scouring in these minimal winds and the effect would be minor over the short time period prior to collection. Further, the collected snow was mostly windpacked, suggesting it was unlikely the wind penetrated both the 150 μm nylon monofilament mesh

of the basket and the interior bulk of the snow. Future studies, however, may attempt to better seal off collected blown snow.

2b)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.

The observations raised by Referee #2 have been further explored in the discussion. The first paragraph of Section 4 has been revised and 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 help overcome some these diffusion limitations (Nemoto et al., 2004).

Specific Comments:

Abstract, p11986 line 11. It is not clear what mechanism causes "replenishment" of bromide in the snow. I dont 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.

The two points alluded to here have both been addressed elsewhere in the revised manuscript. Raw anion concentrations have now been included as a supplement to the revised manuscript. The paragraph addressing replenishment of bromide has been rewritten.

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

The change referred to in this sentence is the large Antarctic seasonal change from winter to summer. Antarctic winter sea ice extent is roughly 19 million km^2, while summer extent is roughly between $3 - 4$ million km^2.

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.

This is indeed a helpful observation. However, for clarity, the introductory clause to this sentence was removed. The beginning of Section 1 now reads:

The polar springtime is a season of change, most notably in temperature, sea ice coverage, and weather, but it also signals the onset of many photochemically driven atmospheric chemical reactions, such as tropospheric ozone depletion events (ODEs) (e.g., Barrie et al., 1988). Boundary layer ozone in polar regions has been observed to fall dramatically periodically in the spring in both the Arctic (Barrie et al., 1988) and Antarctic (Kreher et al., 1997; Wessel et al., 1998). These tropospheric ODEs are initiated by increased concentrations of reactive bromine gases (BrO and Br) resulting in

a catalytic removal of ozone

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.

The sentence has been revised to read as:

Specific salts precipitate out of solution when solubility limits are reached below $-2\,^\circ C$ (Light et al., 2003), producing brine with different ion ratios than those found in seawater.

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

We thank Referee [#2] for catching this typo. The word has been corrected to *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 nonblowing snow events.

We did not measure for ozone while in the field. Satellite BrO and O_3 images collected by the Global Ozone Monitoring Experiment-2 (GOME-2) were analyzed over the duration of the field campaign. There was no discernible BrO concentration spike and ODE over the Ross Sea around 24 October. As mentioned above in the response to Referee [#1], this suggests that the recorded bromine release was a small-scale event that did not directly leaded to a greatly enhanced BrO spot. Further, there was no strong ODE over the 2-month long campaign. As was mentioned, the relationship between ozone depletion and halogen activation is complex, and since the lack of a dramatic BrO spike does not nullify the occurrence of bromine release, this analysis was not included in the revised manuscript.

p11991, line 17 missing an "and" somewhere?

We thank Referee #2 for catching this typo. The final paragraph of Section 2 now begins:

Anion chromatography was completed using a Dionex-600 IC system, equipped with a LC 25 chromatogram oven set at 30 °C, GD 50 gradient pump, CD 25 conductivity detector, AS15 anion column with a AG15 guard column, and an auto-sampler.

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.

We thank Referee #2 for catching this inconsistency. All concentrations are now in g m^{-3}. Additionally, anion concentrations for all samples are given in a supplement to the revised manuscript.

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

The first paragraph of the discussion has been reword and 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. We define a depletion factor (DF) such that DF= 1 signifies no bromine depletion in particles and DF= 0 signifies complete depletion. 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, we have DF= $-0.08, 0.20, 0.33$, and 0.64, respectively. 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 also correspond to a decrease in chlorine release. It has been shown that BrCl plays a critical role in chlorine production, and BrCl release is reliant upon the existence of HOBr from prior bromine activation (Wren et al., 2013).

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.

The wording in the original manuscript was not clear in highlighting the potential sources of bromide replenishment. The relevant paragraph of Section 4 has been rewritten and now reads:

The surface snow Br^-/Cl^- mass ratios at both sites showed little variation and no observed trend with date or meteorology over the month-long campaign. If there was a significant amount of lofted snow being depleted in bromide and then falling back to the snow surface, one might expect to detect a signal in the surface snow chemistry. The lack of recorded bromide depletion in the surface snow may indicate that either surface snow bromide concentration is quickly replenished or that blowing snow represents only a small portion of the surface snowpack. Surface snow will be replenished in bromide through interaction with saline brine (Oldridge et al., 2011), deposition of HOBr as a byproduct of the reaction between BrO and HO_2, deposition of HBr, and deposition of aerosol-phase bromine. In cold ambient environments, frost flowers, surface snow, and the sea ice surface have been shown to be bromide enriched sources, likely due to the precipitation of NaCl (Kalnajs et al., 2006; Morin et al., 2008). Additionally, recycling of deposited bromine plays a critical role with as much as 75% of deposited bromine being re-emitted into the gas phase as Br_2 or BrCl (Piot et al., 2008). In future

work, it would be informative to collect both surface and blowing snow during stronger wind events.

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.**

The first sentence of Section 5 has been reworded and now reads:

In summary, this work examined the mass ratio of Br^-/Cl^- in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation.

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.**

We thank Referee #2 for this recommendation. The ratio has been flipped throughout the entire revised manuscript to be Br^-/Cl^- and this should remove any confusion.

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.**

As mentioned above, a supplement containing the raw anion concentra-

tions has been added to the revised manuscript to help address the mass balance considerations. In addition, the conclusion has been revised and now reads as:

In summary, this work examined the mass ratio of Br^-/Cl^- in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation. It was found that while Br^-/Cl^- mass ratios remained relatively constant for sea ice and surface snow, bromide becomes strongly depleted relative to chloride in lofted snow. Thus, we conclude the blowing snow particles provide a very viable surface for the initial heterogeneous reactions initializing ODEs to occur. The findings of this study are consistent with previous modeling results (Yang et al., 2010), suggesting that blowing snow has the capacity to explain the occurrence of ODEs in the polar springtime.

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 sublimate 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 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 $200 - -5,000$ g/m^3 chloride, 1.0–16 g/m^3 bromide, $20 - -2300$ g/m^3 sulfate, and $0 - -1.2$ 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 sastrugi, 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 $500 - -1,600$ g/m^3 chloride and $1.5 - -6$ g/m^3 bromide. Sulfate

concentrations ranged from $30 - -50 \ g/m^3$, 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 $50 - -6800 \ g/m^3$ chloride, $0.2 - -18.5 \ g/m^3$ bromide, $3 - -240 \ g/m^3$ sulfate, and $0.4 - -23 \ g/m^3$ 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, r² 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 (Wrenet 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. 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). 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 bro-

mide 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 (Wrenet 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.

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. Simp-

son, 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 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, 10,961110,974, 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, 351356, 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 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).*

The role of blowing snow in the activation of bromine over first-year Antarctic sea ice

R. M. Lieb-Lappen and R. W. Obbard

14 Engineering Drive, Thayer School of Engineering, Dartmouth College, Hanover, NH, USA

Correspondence to: R. M. Lieb-Lappen (ross.lieb-lappen@dartmouth.edu)

Abstract

It is well known that during polar springtime halide sea salt ions, in particular Br⁻, are photochemically activated into reactive halogen species (e.g. Br and BrO), where they break down tropospheric ozone. This research investigated the role of blowing snow in transporting salts from the sea ice/snow surface into reactive bromine species in the air. At two different locations over first-year ice in the Ross Sea, Antarctica, collection baskets captured blowing snow at different heights. In addition, sea ice cores and surface snow samples were collected throughout the month-long campaign. Over this time, sea ice and surface snow ~~Cl⁻/Br⁻~~ Br⁻/Cl⁻ mass ratios remained constant and equivalent to seawater, and only in lofted snow did bromide become depleted relative to chloride. This suggests that replenishment of bromide in the snowpack occurs faster than bromine activation in mid-strength wind conditions (approximately $10\,\mathrm{m\,s^{-1}}$) or that blowing snow represents only a small portion of the surface snowpack. Additionally, lofted snow was found to be depleted in sulfate and enriched in nitrate relative to surface snow.

1 Introduction

The polar springtime is a season of change, most notably in temperature, sea ice coverage, and weather, but it also signals the onset of many photochemically driven atmospheric chemical reactions, such as tropospheric ozone depletion events (ODEs) (e.g., Barrie et al., 1988). ~~The oxidizing potential of the lower atmosphere is dominated by ozone availability, but boundary~~ Boundary layer ozone in polar regions has been observed to fall dramatically periodically in the spring in both the Arctic (Barrie et al., 1988) and Antarctic (Kreher et al., 1997; Wessel et al., 1998). These tropospheric ODEs are initiated by increased concentrations of reactive bromine gases (BrO and Br) resulting in a catalytic removal of ozone (Fan and Jacob, 1992; McConnell et al., 1992; Frieß et al., 2004), however the mechanism by which Br enters the atmosphere is not well understood (Abbatt et al., 2012). The heterogeneous reaction producing bromine gas and hypothesized to explain the "bromine explosion"

is given by Fan and Jacob (1992):

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{1}$$

Proposed surfaces on which this reaction may occur have included sea spray Sander et al. (2003), frost flowers (Rankin et al., 2000; Kaleschke et al., 2004), surface snow (Simpson et al., 2005), aerosols (Vogt et al., 1996; Frießet al., 2004), and blowing snow (Yang et al., 2008).

Although some bromide may arrive via sea spray produced aerosol (Sander et al., 2003), this mechanism is relatively less efficient and does not produce aerosol with the observed sulfate depletion (Wagenbach et al., 1998). As seawater freezes, salt rejection leads to an increasingly saline brine (Thomas and Dieckmann, 2009). Specific salts precipitate out of solution when solubility limits are reached below $-2\,^\circ$C (Light et al., 2003), producing ~~fractionation different from that~~ brine with different ion ratios than those found in seawater. The brine is expelled to the ice/snow or ice/atmosphere surface, where it forms a fractionated surface skim and slush (Rankin et al., 2002). This reservoir of bromide and other sea salts can be incorporated into frost flowers by wicking, or into the snow lying on sea ice by upward migration through capillary forces (Perovich and Richter-Menge, 1994). It may be transported by the lofting of snow from sea ice with subsequent sublimation and return of the aerosol to the snowpack (Yang et al., 2008; Jones et al., 2009). However, the physical surface at which bromide activation occurs remains a subject of some debate.

It has been shown that brine is wicked upward by frost flowers that form on fresh sea ice, yielding a highly saline surface with the aforementioned sulfate depletion, and that the dendritic nature of frost flowers magnifies the surface area available for atmospheric interactions (Rankin et al., 2002). However, studies have shown that frost flowers do not significantly increase the surface area available for heterogeneous reactions (Domine et al., 2005; Obbard et al., 2009) and that frost flowers are not easily broken and lofted (Obbard et al., 2009). Instead, they accumulate snow on their windward side in strong winds and when broken, fall where they are (Obbard et al., 2009). Laboratory studies of frost flowers have also shown that frost flowers are quite stable in winds up to $12\,\mathrm{m\,s}^{-1}$, and aerosol

3

production is not observed under these conditions (Roscoe et al., 2011). Further, Simpson et al. (2005) and ~~Obbard et al. (2009)~~ Obbard et al. (2009) found that frost flowers are not depleted in bromide relative to sodium and chloride, indicating they are not the immediate source of bromine-depleted snow nor the location of the heterogeneous reactions activating bromine. It has also been shown that first-year sea ice contact better correlates to increased BrO concentrations than does contact with potential frost flower regions (Simpson et al., 2007a).

In Simpson et al. (2005) however, the snowpack did have Br^-/Na^+ ratio fluctuations by two orders of magnitude with bromide depletions of up to 90%, suggesting bromine was released in the aerosol phase or in the snowpack itself. Sea-salts can migrate upwards through the snowpack as high as $17\,cm$, even in cold conditions where slush is not present (Massom et al., 2001; Domine et al., 2004). However, in thicker snowpacks, the surface snow is more readily acidified and influenced by atmospheric processes, and thus, more likely to play a role in halogen activation. Bromine activation is more efficient in acidic conditions and in environments with a lower ~~Cl^-/Br^-~~ Br^-/Cl^- ratio (Pratt et al., 2013). Pratt et al. (2013) further hypothesized that the snowpack interstitial air is the primary location for the heterogeneous reactions, with wind pumping providing a vehicle to release the bromine into the boundary layer.

Yang et al. (2008) proposed a fourth mechanism for bromine activation that involves the lofting of snow from sea ice with subsequent sublimation and either direct bromine release or return of the aerosol to the snowpack. In the model, lofted snow particles were allowed to sublimate to a particle size of $< 10\,\mu m$, whereby the particles instantaneously released bromine or were potentially scoured by more blowing snow particles. Snow salinity was found to have a nonlinear relationship with bromine production, and the reaction rate varied with dry aerosol particle size. It was shown that $1.3\,\mu m$ particles yielded the most efficient release of bromine since the smaller aerosol could be lofted further and longer (Yang et al., 2008). Further work showed that snow in the sea ice zone may contain enough salt when lofted by wind to produce the necessary aerosol to explain the observed Antarctic ODEs (Yang et al., 2010). While it may be difficult for saturated snow lying on surface skim to

become lofted, snow in the upper layers could wick up salts yet remain mobile, providing enormous capacity for transporting bromide into the boundary layer. Yang et al. (2008) provides the theoretical framework and model-based data for the physical measurements observed and presented in this manuscript.

ODEs have been found to occur at a range of wind speeds, something that has made agreement upon a mechanism difficult. Some have observed that ODEs require low winds, a stable boundary layer, and a relatively clear sky, or the movement of air masses from such regions (Simpson et al., 2007b). Using measurements and modeling, Albert et al. (2002) found rapid ozone depletion in the top $10\,\mathrm{cm}$ of the snowpack due to diffusion and ventilation in moderate winds. More recently, ODEs have been recorded during high winds ($> 12\,\mathrm{m\,s^{-1}}$), which increase the snow surface area exposed via blowing snow, and thus, the probability of contact between the gaseous and condensed phases required to initiate bromine release (Jones et al., 2009). During the 2009 OASIS campaign in Barrow, AK, high winds were observed to correspond with increased BrO concentrations (Frießet al., 2011). This was accompanied by decreased HOBr, suggesting that blowing snow likely provided additional surfaces for heterogeneous HOBr loss (Liao et al., 2012). These high wind halogen activation events may have a more widespread role when considering the impact of ODEs on regional tropospheric chemistry (Jones et al., 2010). Additionally, higher winds may enhance the availability of radical bromine precursors in the snowpack, accelerating bromine activation (Toyota et al., 2011). On the contrary, others (e.g. Helmig et al., 2012; Halfacre et al., 2014) have found no correlation between ODEs and wind speed. However, the lack of low ozone observations at high wind speed may be a result of enhanced mixing (Helmig et al., 2012). Although the chemistry of snow has been well studied (Massom et al., 2001; Domine et al., 2004; Grannas et al., 2007), there has been no attempt ~~unto~~ until now at segregating snow capable of wind transport or snow actually blown by wind.

It is noted that both Cl_2 and BrCl play a role in halide boundary layer chemistry and ODEs (Abbatt et al., 2012), but the focus of this work is on bromine because it is a far more efficient catalyst of ozone loss. As the main constituents of seawater, both chloride and sodium have been used as sea salt tracers, and thus chloride was used here to both determine snow

5

and ice salinity and relative activity of other anions. Previous work has shown that sulfate is influenced both by mirabilite precipitation and atmospheric interactions, while nitrate is uncorrelated with sea salt and is deposited as a byproduct of other reactions (Krnavek et al., 2012).

2 Methods

Two field sites on first-year sea ice in the Ross Sea, Antarctica, were chosen, based upon prevailing wind direction, to maximize contact of the blowing snow with the first-year sea ice. Their locations are shown in Fig. 1. Butter Point Site was located 6.5 km from the open ocean and 35 km north of the Ross Ice Shelf. Iceberg Site was located 55 km northwest of Butter Point, and since the ice edge located to the east follows the shore, the distance to open water here was also 5 km. Iceberg Site was chosen based upon the presence of a 740 m long and 35 m high iceberg located 250 m to the west that would block winds sourced over land, maximizing blowing snow collection from over sea ice. At each site, a 5.5 m blowing snow collection tower was erected for the time period of 11 October–8 November 2012. Collection baskets made out of 150 μm nylon monofilament mesh and 7" diameter by 14" long (Midwest Filter Corporation, Lake Forest, IL) were placed at four different heights: 0.3, 2.0, 3.0, and 5.5 m above the snow surface.

The sites were visited approximately every other day, and collection baskets were switched even if no snow was collected. Baskets were triple rinsed with DI water between uses. Surface snow samples were collected each of the 12 days the sites were visited. In addition, 1.78 and 1.89 m ice cores were extracted from Butter Point and Iceberg sites, respectively. Snow samples and sea ice cores were transported at a constant temperature of $-20\,^{\circ}$C back to Thayer School of Engineering's Ice Research Laboratory at Dartmouth College and stored in a $-33\,^{\circ}$C cold room.

Winds during the field campaign were generally mild, only surpassing $10\,\mathrm{m\,s^{-1}}$ on a few occasions. Site visits were not feasible during stormy weather, and much of the blowing snow captured during those periods sublimated in the baskets prior to collection as ob-

served by a webcam. Thus, only on 25 October were blowing snow samples collected at both sites and all four heights. The collected snow was the result of approximately $10\,\mathrm{m\,s^{-1}}$ southerly winds on 24 October. Visibility at McMurdo station during this blowing snow event dropped below 0.5 miles for about 4 hours. Temperatures ranged from $-20.5\,^{\circ}\mathrm{C}$ to $-11.5\,^{\circ}\mathrm{C}$ with an average relative humidity of 69% on 24 October and $-17.5\,^{\circ}\mathrm{C}$ to $-13.5\,^{\circ}\mathrm{C}$ with an average relative humidity of 61% on 25 October. These temperatures were a couple of degrees warmer than the average for the rest of the field campaign.

All surface snow and blowing snow samples were melted into acid-rinsed HDPE vials, and diluted by a factor of 5 with DI water. Those samples falling outside of the calibration standard concentrations were further diluted to fall within the desired range. Each ice core was sub-sampled every $10\,\mathrm{cm}$, melted, and diluted by a factor of 50, except for the bottom-most sample that was diluted by a factor of 100. A $0.5\,\mathrm{mL}$ aliquot of each diluted snow and ice sample was then analyzed for anion concentrations.

Anion chromatography was completed using a Dionex-600 IC system, equipped with a LC 25 chromatogram oven set at $30\,^{\circ}\mathrm{C}$, GD 50 gradient pump, CD 25 conductivity detector, AS15 anion column with a AG15 guard column, and an auto-sampler. A $38\,\mathrm{mM}$ NaOH eluent was used at a flow rate of $1.2\,\mathrm{mL\,min^{-1}}$ and the SRS current was set to $100\,\mathrm{\mu A}$. Pressure in the column was 1600 psi and the signal noise was approximately $0.003\,\mathrm{\mu S}$. Peak analysis was performed using Chromeleon 6.8 software with a 5 point standard calibration curve. IC detection limits were 0.6, 0.1, 0.04, and $0.03\,\mathrm{g\,m^{-3}}$, yielding limits of quantification of 2, 0.3, 0.1, and $0.1\,\mathrm{g\,m^{-3}}$ for chloride, sulfate, bromide, and nitrate, respectively.

3 Results

Raw anion concentrations for sea ice, surface snow, and blowing snow samples are provided in a supplement to this manuscript. Sea ice anion concentrations had nearly identical profiles for Butter Point and Iceberg cores, with both showing the expected C-shape profile (see Fig. 2) (Eicken, 1992). Note that the deepest sample for Iceberg site was directly at the base of the core, while the deepest sample for Butter Point was $8\,\mathrm{cm}$ above the base,

due to a mushy, poorly defined basal layer, and thus missed the saltiest portion. Chloride concentrations ranged from ~~2–8~~2,000–8,000 g m^{-3}, while bromide concentrations ranged from 5–35 g m^{-3}. Sulfate concentrations ranged from 2–3000 g m^{-3}, with increased variation observed over the top 40 cm of both cores. Nitrate concentrations were below detection limits for all sea ice core samples.

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 ~~0.2~~200 –5,~~0~~000 g m^{-3} chloride, 1.0–16 g m^{-3} bromide, 20–2300 g m^{-3} sulfate, and 0–1.2 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 sastrugi, 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 ~~0.5–1.6~~500–1,600 g m^{-3} chloride and 1.5–6 g m^{-3} bromide. Sulfate concentrations ranged from 30–50 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 g m^{-3} chloride, 0.2–18.5 g m^{-3} bromide, 3–240 g m^{-3} sulfate, and 0.4–23 g m^{-3} nitrate. ~~There was no noticeable trend for~~ 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 ~~in~~ for nitrate where concentrations increased with height above the snow surface.

Anion concentrations can provide a general understanding of the overall salinity of the snow and ice, but in order to understand chemical reaction activity, it is instructive to calculate anion concentration ratios. The ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratio has long been used as a metric for analyzing both frozen and liquid saline water samples, and comparing measured values to the well established ~~$290 : 1$~~ $1 : 290$ ratio observed in seawater (Morris and Riley, 1966). This ratio is plotted in Fig. 3 for all samples at both sites. ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratios were relatively constant for all sea ice samples (~~281 ± 24~~ $1 : 281 \pm 24$) and all surface snow samples (~~296 ± 22~~ $1 : 296 \pm 22$). However, there was a linear correlation between ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratios for blowing snow relative to height at both Butter Point ($r^2 = 0.89$) and Iceberg Site ($r^2 = 0.93$). Sulfate mass ratios in sea ice, surface snow, and blowing snow did not show as clear a trend (Fig. 4). In sea ice, the ~~Cl^-/SO_4^{2-}~~ SO_4^{2-}/Cl^- mass ratio was roughly ~~$7 : 1$~~ $1 : 7$ in the bottom half of the cores, consistent with what is generally observed in seawater (Morris and Riley, 1966), but varied from approximately ~~$2 : 1$ to $12 : 1$~~ $1 : 2$ to $1 : 12$ in the upper halves of the cores. Surface snow mass ratios also were quite variable ranging from $1 : 1$ to ~~$19 : 1$~~ $1 : 19$ with no clear correlations. Collected lofted snow was quite depleted in sulfate with mass ratios reaching ~~$20 : 1$ to $40 : 1$~~ $1 : 20$ to $1 : 40$, but did not show the linear trend with height observed with bromide.

4 Discussion

Observation of bromide depletion relative to other salts is an indication of heterogeneous atmospheric chemical reactions and bromine activation (Adams et al., 2002; Huff and Abbatt, 2002; Simpson et al., 2005). Although there was some variability in ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratios for sea ice and surface snow, these ratios were remarkably constant, just ~~under 300 : 1~~ 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 ~~$1000 : 1$~~ $1 : 1000$ at heights of 5.5 m. ~~An increased Cl^-/Br^- mass ratio~~ This is consistent

with aerosol observations by Duce and Woodcock (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 and Nishimura, 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 and Brun, 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 help overcome some these diffusion limitations (Nemoto and Nishimura, 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.

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 ~~later~~ latter hypothesis were true, one would expect to observe increased chloride concentrations in higher baskets. ~~At elevated Cl^-/Br^- ratios, chlorine release actually decreases due to required HOBr involvement (Wren et al., 2013) .~~ The lack of an observed chloride trend with height leads to our interpretation that the ~~increased~~ 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) .

Previously, bromine activation and ODEs were observed in both low ($< 5\,m\,s^{-1}$) and high ($> 12\,m\,s^{-1}$) winds (Jones et al., 2009). Here, the ~~depletion of bromide in lofted snow was observed at moderate wind speeds, suggesting that bromine activation also occurs in these meteorological conditions~~ blowing snow event occurred during moderate winds of approximately $10\,m\,s^{-1}$. Since the wind was from the south and there was no new precipitation, it is safe to assume that the snow originated from the surface of first-year sea ice. It is noted that the blowing snow event lasted approximately $4 - 6$ hours, and that snow samples from the baskets were not collected until $10 - 12$ hours later. During this time, wind speeds dropped to less than $5\,m\,s^{-1}$, and it is possible that the collected snow was exposed to further wind scouring. However, all baskets would have experienced a similar degree of scouring in these minimal winds and the effect would be minor over the short time period prior to collection. Further, the collected snow was mostly windpacked, suggesting it was unlikely the wind penetrated both the $150\,\mu m$ nylon monofilament mesh of the basket and the interior bulk of the snow. Future studies, however, may attempt to better seal off collected blown snow.

The surface snow ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratios at both sites showed little variation and no observed trend with date or meteorology over the month-long campaign. If there was a significant amount of lofted snow being depleted in bromide and then falling back

11

to the snow surface, one might expect to detect a signal in the surface snow chemistry. The lack of recorded bromide depletion in the surface snow may indicate that either surface snow bromide concentration is quickly replenished or that blowing snow represents only a ~~small~~ small portion of the surface snowpack. Surface snow will be replenished in bromide through interaction with saline brine (Oldridge and Abbatt, 2011), deposition of HOBr ~~from the termination step of the radical Br and BrO reactions~~ as a byproduct of the reaction between BrO and HO_2, deposition of HBr, and deposition of ~~aerosol phase~~ aerosol-phase bromine. In cold ambient environments, frost flowers, surface snow, and the sea ice surface have been shown to be bromide enriched sources, likely due to the precipitation of NaCl (Kalnajs and Avallone, 2006; Morin et al., 2008). Additionally, recycling of deposited bromine plays a critical role with as much as 75% of deposited bromine being re-emitted into the gas phase as Br_2 or BrCl (Piot and von Glasow, 2008). In future work, it would be informative to collect both surface and blowing snow during stronger wind events.

The sulfate depletion observed in lofted snow is consistent with the observations of others, most likely a product of mirabilite precipitation occurring at temperatures below $-8\,^\circ$C (Rankin et al., 2000). The range of ~~Cl^-/SO_4^{2-}~~ SO_4^{2-}/Cl^- mass ratios measured in surface snow and the upper halves of the ice cores is also likely due to similar interactions. Sulfate depletion can result from a wide variety of processes involving brine and mirabilite formation as brine constantly moves through sea ice and is also wicked up by surface snow (Krnavek et al., 2012). In addition, non-sea salt sourced sulfate may provide additional sulfate to the surface snowpack (Rankin and Wolff, 2003; Krnavek et al., 2012).

Nitrate concentration in seawater is highly dependent upon phytoplankton blooms, and therefore varies greatly from single digit $g\,m^{-3}$ to less than one $g\,m^{-3}$ (e.g., Gordon et al., 2000; Arrigo et al., 1997). Thus, it was not surprising that sea ice samples were below the quantification limit for nitrate. Surface snow samples also were generally below nitrate detection limits, and those with quantifiable concentrations showed no noticeable trend. Nitrate snow photochemistry is quite complex, with many processes both adding and subtracting nitrate from the snowpack (Grannas et al., 2007; Krnavek et al., 2012). Nitrate sources include biomass burning, lightning production, soil exhalation, and anthropogenic pollutants

that can be carried long distances through atmospheric transport (Galloway et al., 2004; Krnavek et al., 2012). The increase in nitrate concentration observed with basket height may be attributed to increased atmospheric interactions higher above the snowpack. Additionally, basket nitrate concentration may also be influenced by interactions occurring while the snow was sitting in the basket but prior to collection, as cycling of different nitrogen-containing compounds is relatively fast and can vary greatly during a day (Grannas et al., 2007). Considering the number of competing reactions, more data points would be needed to make conclusive statements regarding the cycling of nitrate in the polar boundary layer.

5 Conclusions

In summary, this work ~~primarily examined the role of blowing snow in bromide activation under~~ examined the mass ratio of Br^-/Cl^- in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation. It was found that while ~~Cl^-/Br^-~~ Br^-/Cl^- mass ratios remained relatively constant for sea ice and surface snow, bromide becomes strongly depleted relative to chloride in lofted snow. Thus, we conclude the blowing snow particles provide ~~an ideal~~ a very viable surface for the initial heterogeneous reactions initializing ODEs ~~may~~ to occur. The findings of this study are consistent with previous modeling results (Yang et al., 2010), suggesting that blowing snow has the capacity to explain the occurrence of ODEs in the polar springtime.

References

Abbatt, ~~J.~~ J. P. D., Thomas, J. L., Abrahamsson, K., Boxe, C., Granfors, A., Jones, A. E., King, M. D., Saiz-Lopez, A., Shepson, P. B., Sodeau, J., Toohey, D. W., Toubin, C., von ~~Glasow,~~

Glasow, R., Wren, S. N., and Yang, X.: Halogen Activation Via Interactions With Environemntal Ice and Snow in the Polar Lower Troposphere and Other Regions, Atmos. Chem. Phys., 12, 6237–6271, doi:10.5194/acp-12-6237-2012, 2012.

Adams, J. W., Holmes, N. S., and Crowley, J. N.: Uptake and Reactions of HOBr on Frozen and Dry NaCl/NaBr Surface Between 253 and 233 K, Atmos. Chem. Phys., 2, 79–91, 2002.

Albert, M. R., Grannas, A. M., Bottenheim, J., Shepson, P. B., and Perron, F. E.: Processes and Properties of Snow-Air Transfer in the High Arctic with Application to Interstitial Ozone at Alert, Canada, Atmos. Environ., 36, 2779–2787, 2002.

Arrigo, K. R., Worthen, D. L., Lizotte, M. P., Dixon, P., and Dieckmann, G.: Primary Production in Antarctic Sea Ice, Science, 276, 394–397, doi:10.1126/science.276.5311.394, 1997.

Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone Destruction and Photochemical-Reactions at Polar Sunrise in the Lower Arctic Atmosphere, Nature, 334, 138–141, 1988.

Domine, F., Sparapani, R., Ianniello, A., and Beine, H. J.: The Origin of Sea Salt in Snow on Arctic Sea Ice and in Coastal Regions, Atmos. Chem. Phys., 4, 2259–2271, 2004.

Domine, F., Taillandier, A. S., Simpson, W. R., and Severin, K.: Specific Surface Area, Density and Microstructure of Frost Flowers, Geophys. Res. Lett., 32, L13502, doi:10.1029/2005GL023245, 2005.

Duce, R. A. and Woodcock, A. H.: Difference in Chemical Composition of Atmospheric Sea Salt Particles Produced in the Surf Zone and on the Open Sea in Hawaii, Tellus, 23, 427–435, 1971.

Eicken, H.: Salinity Profiles of Antarctic Sea Ice: Field Data and Model Results, J. Geophys. Res., 97, 15,545–15,557, 1992.

Fan, S.-M. and Jacob, D. J.: Surface Ozone Depletion in Arctic Spring Sustained by Bromine Reacions on Aerosols, Nature, 359, 522–524, 1992.

Frieß,

Frieß, U., Hollwedel, ~~J.~~, Konig-Langlo, ~~G.~~, Wagner, ~~T.~~, and Platt, ~~U.~~: Dynamics and ~~chemistry of tropospheric bromine explosion events~~ Chemistry of Tropospheric Bromine Explosion Events in the Antarctic ~~coastal region,~~ Coastal Region, J. Geophys. Res., 109, D06305, ~~doi:~~doi:10.1029/2003JD004133, 2004.

~~Frieß,~~

Frieß, U., Sihler, ~~H.~~, Sander, ~~R.~~, Pohler, ~~D.~~, Yilmaz, ~~S.~~, and Platt, ~~U.~~: The ~~vertical distribution~~ Vertical Distribution of BrO and ~~aerosols~~ Aerosols in the Arctic: ~~measurements by active and passive differential optical absorption spectroscopy,~~ Measurements by Active and Passive Differential Optical Absorption Spectroscopy, J. Geophys. Res., 116, D00R04, ~~doi:~~doi:10.1029/2011JD015938, 2011.

Galloway, ~~J. N.~~, Dentener, ~~F. J.~~, Capone, ~~D. G.~~, Boyer, ~~E. W.~~, Howarth, ~~R. W.~~, Seitzinger, ~~S. P.~~, Asner, ~~G. P.~~, Cleveland, ~~C. C.~~, Green, ~~P. A.~~, Holland, ~~E. A.~~, Karl, ~~D. M.~~, Michaels, ~~A. F.~~, Porter, ~~J. H.~~, Townsend, ~~A. R.~~, and Vorosmarty, ~~C. J.~~: Nitrogen ~~cycles: past, present, and future~~Cycles: Past, Present, and Future, Biogeochemistry, 70, 153–226, ~~doi:~~doi:10.1007/s10533-004-0370-0, 2004.

Gordon, ~~L. I.~~, Codispoti, ~~L. A.~~, Jr., ~~J. C.~~~~Jennings Jr~~ J., Millero, ~~F. J.~~, Morrison, ~~J. M.~~, and Sweeney, ~~C.~~: Seasonal ~~evolution of hydrographic properties~~ Evolution of Hydrographic Properties in the Ross Sea, Antarctica, ~~1996–1997~~1996-1997, Deep-Sea ~~Res.~~ Research II, 47, 3095–3117, 2000.

Grannas, ~~A. M.~~, Jones, ~~A. E.~~, Dibb, ~~J.~~, Ammann, ~~M.~~, Anastasio, ~~C.~~, Beine, ~~H. J.~~, Bergin, ~~M.~~, Bottenheim, ~~J.~~, Boxe, ~~C. S.~~, Carver, ~~G.~~, Chen, ~~G.~~, Crawford, ~~J. H.~~, ~~Domin,~~ Domine, F., Frey, ~~M. M.~~, ~~Guzmn,~~ Guzman, M. I., Heard, ~~D. E.~~, Helmig, ~~D.~~, Hoffmann, ~~M. R.~~, Honrath, ~~R. E.~~, Huey, ~~L. G.~~, Hutterli, ~~M.~~, Jacobi, ~~H. W.~~, ~~Kln,~~ Klan, P., Lefer, ~~B.~~, McConnell, ~~J.~~, Plane, ~~J.~~, Sander, ~~R.~~, Savarino, ~~J.~~, Shepson, ~~P. B.~~, Simpson, ~~W. R.~~, Sodeau, ~~J. R.~~, von ~~Glasow,~~ Glasow, R., Weller, ~~R.~~, Wolff, ~~E. W.~~, and Zhu, ~~T.~~: An ~~overview of snow photochemistry: evidence, mechanisms and impacts~~Overview of Snow Photochemistry: Evidence, Mechanisms, and Impacts, Atmos. Chem. Phys., 7, 4329–4373, ~~doi:,~~ 2007.

Halfacre, ~~J. W.~~, Knepp, ~~T. N.~~, Shepson, ~~P. B.~~, Thompson, ~~C. R.~~, Pratt, ~~K. A.~~, Li, ~~B.~~, Peterson, ~~P. K.~~, Walsh, ~~S. J.~~, Simpson, ~~W. R.~~, Matrai, ~~P. A.~~, Bottenheim, ~~J. W.~~, Netcheva, ~~S.~~, Perovich, ~~D. K.~~, and Richter, ~~A.~~: Temporal and ~~spatial characteristics of ozone depletion events from measurements~~ Spatial Characteristics of Ozone Depletion Events from Measurements in the Arctic, Atmos. Chem. Phys~~.~~, 14, 4875–4894, ~~doi:~~doi:10.5194/acp-14-4875-2014, 2014.

~~Helmig,~~

Helmig, D., Boylan, P., Johnson, B., Oltmans, S., Fairall, C., Staebler, R., Weinheimer, A., Orlando, J., Knapp, D. J., Montzka, D. D., Flocke, F., Frieß, U., Sihler, H., and Shepson, P. B.: Ozone ~~dynamics and snow–atmosphere exchanges during ozone depletion events~~ Dynamics and Snow-Atmosphere Exchanges During Ozone Depletion Events at Barrow, Alaska, J. Geophys. Res., 117, D20303, ~~doi:~~doi:10.1029/2012JD017531, 2012.

Huff, A. K. and Abbatt, ~~J.~~ J. P. D.: Kinetics and ~~product yields in the heterogeneous reactions~~ Product Yields in the Heterogeneous Reactions of HOBr with ~~simulated sea–ice surfaces,~~ Simulated Sea-Ice Surfaces, J. Phys. Chem. ~~A~~A., 106, 5279–5287, 2002.

Jacobi, H. W., Voisin, D., Jaffrezo, J. L., Cozic, J., and Douglas, T. A.: Chemical Composition of the Snowpack During the OASIS Spring Campaign 2009 at Barrow, Alaska, J. Geophys. Res., 117, 2012.

Jones, A. E., Anderson, P. S., Begoin, M., Brough, N., Hutterli, M. A., Marshall, G. J., Richter, A., Roscoe, H. K., and Wolff, E. W.: BrO, ~~blizzards, and drivers of polar tropospheric ozone depletion events~~Blizzards, and Drivers of Polar Tropospheric Ozone Depletion Events, Atmos. Chem. Phys., 9, 4639–4652, ~~doi:,~~ 2009.

Jones, A. E., Anderson, P. S., Wolff, E. W., Roscoe, H. K., Marshall, G. J., Richter, A., Brough, N., and Colwell, S. R.: Vertical ~~structure of Antarctic tropospheric ozone depletion events: characteristics and broader implications~~Structure of Antarctic Tropospheric Ozone Depletion Events: Characteristics and Broader Implications, Atmos. Chem. Phys., 10, 7775–7794, ~~doi:~~doi:10.5194/acp-10-7775-2010, 2010.

Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A. M., Roscoe, H. K., Hollwedel, J., Wagner, T., and Jacobi, H.-W.: Frost ~~flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry~~Flowers on Sea Ice as a Source of Sea Salt and Their Influence on Tropospheric Halogen Chemistry, Geophys. Res. Lett., 31, L16114, ~~doi:~~doi:10.1029/2004GL020655, 2004.

Kalnajs, L. E. and Avallone, L. M.: Frost Flower Influence on Springtime Boundary-Layer Ozone Depletion Events and Atmospheric Bromine Levels, Geophys. Res. Lett., 33, L10810, doi:10.1029/2006GL025809, 2006.

Kreher, K., Johnston, P. V., Wood, S. W., Nardi, B., and Platt, U.: ~~Ground-based measurements of tropospheric and stratospheric~~ Ground-Based Measurements of Tropospheric and Stratospheric BrO at Arrival Heights, Antarctica, Geophys. Res. Lett., 24, 3021–3024, 1997.

Krnavek, L., Simpson, W. R., Carlson, D., Domine, F., Douglas, T. A., and Sturm, M.: The ~~chemical composition of surface snow~~ Chemical Composition of Surface Snow in the Arctic: ~~examining~~

16

marine, terrestrial, and atmospheric influences Examining Marine, Terrestrial, and Atmospheric Influences, Atmos. Environ., 50, 349–359, 2012.

Liao, J., Huey, L. G., Tanner, D. J., Flocke, F. M., Orlando, J. J., Neuman, J. A., Nowak, J. B., Weinheimer, A. J., Hall, S. R., Smith, J. N., Fried, A., Staebler, R. M., Wang, Y., Koo, J.-H., Cantrell, C. A., Weibring, P., Walega, J., Knapp, D. J., Shepson, P. B., and Stephens, C. R.: Observations of inorganic bromine Inorganic Bromine (HOBr, BrO, and) speciation Br_2) Speciation at Barrow, Alaska, in spring Spring 2009, J. Geophys. Res., 117, D00R16, doi:doi:10.1029/2011JD016641, 2012.

Light, B., Maykut, G. A., and Grenfell, T. C.: Effects of temperature on the microstructure of first-year Arctic sea ice, Temperature on the Microstructure of First-Year Arctic Sea Ice, J. Geophs. Res., 108, p. 3051, doi:doi:10.1029/2001JC000887, 2003.

Massom, R. A., Eicken, H., Haas, C., Jeffries, M. O., Drinkwater, M. R., Sturm, M., Worby, A. P., Wu, X., Lytle, V. I., Ushio, S., Morris, K., Reid, P. A., and Allison, S. G. S. G. W. I.: Snow on Antarctic sea ice Sea Ice, Rev. Geophys., 39, 413–445, 2001.

McConnell, J. C., Henderson, G. S., Barrie, L. A., Bottenheim, J. W., Niki, H., Langford, C. H., and Templeton, E. E. M. J.: Photochemical bromine production implicated in Arctic boundary-layer ozone depletion Bromine Production Implicated in Arctic Boundary-Layer Oone Depletion, Nature, 355, 150–152, doi:doi:10.1038/355150a0, 1992.

Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., and Savarino, J.: Precipitation of Salts in Freezing Seawater and Ozone Depletion Events: A Status Report, Atmos. Chem. Phys., 8, 7317–7324, 2008.

Morris, A. W. and Riley, J. P.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, Deep-Sea Rese. Oceanogr. Research and Oceanographic Abstracts, 13, 699–705, doi:doi:10.1016/0011-7471(66)90601-2, 1966.

Nemoto, M. and Nishimura, K.: Numerical Simulation of Snow Saltation and Suspension in a Turbulent Boundary Layer, J. Geophys. Res., 109, D18206, doi:10.1029/2004JD004657, 2004.

Obbard, R. W., Roscoe, H. K., Wolff, E. W., and Atkinson, H. M.: Frost flower surface area and chemistry as a function of salinity and temperature, Flower Surface Area and Chemistry as a Function of Salinity and Temperature, J. Geophys. Res., 114, D20305, doi:doi:10.1029/2009JD012481, 2009.

Oldridge, N. W. and Abbatt, J. P. D.: Formation of Gas-Phase Bromine from Interaction of Ozone with Frozen and Liquid NaCl/Br Solutions: Quantitative Separation of Surficial Chemistry from Bulk-Phase Reaction, J. Phys. Chem. A, 115, 2590–2598, doi:10.1021/jp200074u, 2011.

Perovich, D. K. and Richter-Menge, J. A.: Surface Characteristics of Lead Ice, J. Geophys. Res., 99, 16,341–16,350, 1994.

Piot, M. and von Glasow, R.: The Potential Importance of Frost Flowers, Recycling on Snow, and Open Leads for Ozone Depletion Events, Atmos. Chem. Phys., 8, 2437–2467, 2008.

Pomeroy, J. W. and Brun, E.: Physical Properties of Snow, Snow Ecology, pp. 45–126, 2001.

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.

Rankin, A. M. and Wolff, E. W.: A Year-Long Record of Size-Segregated Aerosol Composition at Halley, Antarctica, J. Geophys. Res., 108, 4775, doi:10.1029/2003JD003993, 2003.

Rankin, A. M., Auld, V., and Wolff, E. W.: Frost Flowers as a Source of Fractionated Sea Salt Aerosol in the Polar Regions, Geophys. Res. Lett., 27, 3469–3472, 2000.

Rankin, A. M., Wolff, E. W., and Martin, S.: Frost Flowers: Implications for Tropospheric Chemistry and Ice Core Interpretation, J. Geophys. Res., 107, 4683, doi:10.1029/2002JD002492, 2002.

Roscoe, H. K., Brooks, B., Jackson, A. V., Smith, M. H., Walker, S. J., Obbard, R. W., and Wolff, E. W.: Frost Flowers in the Laboratory: Growth, Characteristics, Aerosol, and the Underlying Sea Ice, J. Geophys. Res., 116, D12301, doi:10.1029/2010JD015144, 2011.

Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Honninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C., and Dingenen, R. V.: Inorganic Bromine in the Marine Boundary Layer: A Critical Review, Atmos. Chem. Phys., 3, 1301–1336, 2003.

Simpson, W. R., Alvarez-Alviles, L., Douglas, T. A., Sturm, M., and Domine, F.: Halogens in the Coastal Snow Pack Near Barrow, Alaska: evidence for active bromine

air-snow chemistry during springtimeEvidence for Active Bromine Air-Snow Chemistry During Springtime, Geophys. Res. Lett., 32, L04811, doi:doi:10.1029/2004GL021748, 2005.

Simpson, W. R., Carlson, D., Hnninger, Honninger, G., Douglas, T. A., Sturm, M., Perovich, D., and Platt, U.: First-year sea-ice contact predicts bromine monoxide First-Year Sea-Ice Contact Predicts Bromine Monoxide (BrO) levels Levels at Barrow, Alaska better than potential frost flower contactBetter Than Potential Frost Flower Contact, Atmos. Chem. Phys., 7, 621–627, doi:, 2007a. Simpson,

Simpson, W. R., von Glasow, Glasow, R., Riedel, K., Anderson, P, Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Frieß, Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletionTheir Role in Polar Boundary-Layer Ozone Depletion, Atmos. Chem. Phys., 7, 4375–4418, doi:, 2007b.

Thomas, D. N. and Dieckmann, G. S.: Sea Iceice, John Wiley & Sons, 2009.

Toyota, K., McConnell, J. C., Lupu, A., Neary, L., McLinden, C. A., Richter, A., Kwok, R., Semeniuk, K., Kaminski, J. W., Gong, S.-L., Jarosz, J., Chipperfield, M. P., and Sioris, C. E.: Analysis of reactive bromine production and ozone depletion Reactive Bromine Production and Ozone Depletion in the Arctic boundary layer using Boundary Layer Using 3-D simulations Simulations with GEM-AQ: inference from synoptic-scale patternsInference From Synoptic-Scale Patterns, Atmos. Chem. Phys., 11, 3949–3979, doi:doi:10.5194/acp-11-3949-2011, 2011.

Vogt, R., Crutzen, P. J., and Sander, R.: A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layerMechanism for Halogen Release From Sea-Salt Aerosol in the Remote Marine Boundary Layer, Nature, 383, 327–330, 1996.

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, Sea-Salt Aerosol in Coastal Antarctic Regions, J. Geophys. Res., 103, 10961–1097410,961–10,974, 1998.

Wessel, S., Aoki, A., Winkler, P., Weller, R., Herber, A., Gernandt, H., and Schrems, O.: Tropospheric ozone depltion in polar regions: a comparison of observations Ozone Depltion in Polar Regions: A Comparison of Observations in the Arctic and Antarctic, Tellus B, 50, 34–50, 1998.

Wren, S. N., Donaldson, D. J., and Abbatt, J. J. P. D.: Photochemical chlorine and bromine activation from artificial saline snowChlorine and Bromine Activation from Artificial Saline Snow, Atmos. Chem. Phys., 13, 9789–9800, doi:doi:10.5194/acp-13-9789-2013, 2013.

19

Yang,

Yang, X., ~~Pyle~~Cox, R. A., Warwick, N. J., Pyle, J. A., Carver, G. D., O'Connor, F. M., and Savage, N. H.: Tropospheric Bromine Chemistry and its Impacts on Ozone: A Model Study, J. Geophys. Res., 110, 2005.

Yang, X., Pyle, J. A., and Cox, R. A.: Sea ~~salt aerosol production and bromine release: role of snow on sea ice~~Salt Aerosol Production and Bromine Release: Role of Snow on Sea Ice, Geophys. Res. Lett., 35, L16815, ~~doi:~~doi:10.1029/2008GL034536, 2008.

Yang, X., Pyle, J. A., Cox, R. A., Theys, N., and ~~Van Roozendael, M.: Snow-sourced bromine and its implications for polar tropospheric ozone~~Roozendael, M. V.: Snow-Sourced Bromine and Its Implications for Polar Tropospheric Ozone, Atmos. Chem. Phys., 10, 7763–7773, ~~doi:~~doi:10.5194/acp-10-7763-2010, 2010.
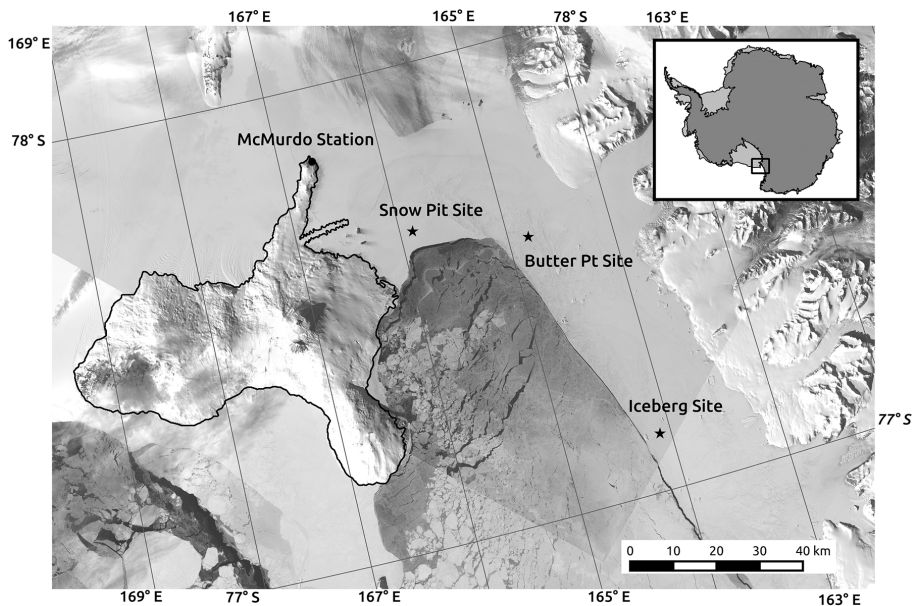
Figure 1. Map of the Ross Sea region showing the two field sites Butter Point and Iceberg. Basemap is Landsat image.
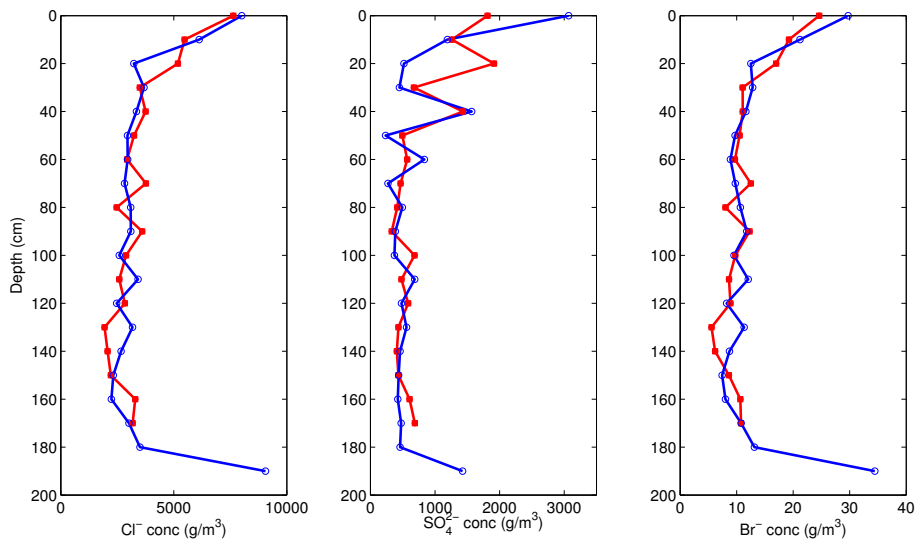
Figure 2. Anion concentrations for sea ice cores. Butter Point Site samples are shown in red filled-in squares and red lines, while Iceberg Site samples are shown in blue open circles and blue lines.
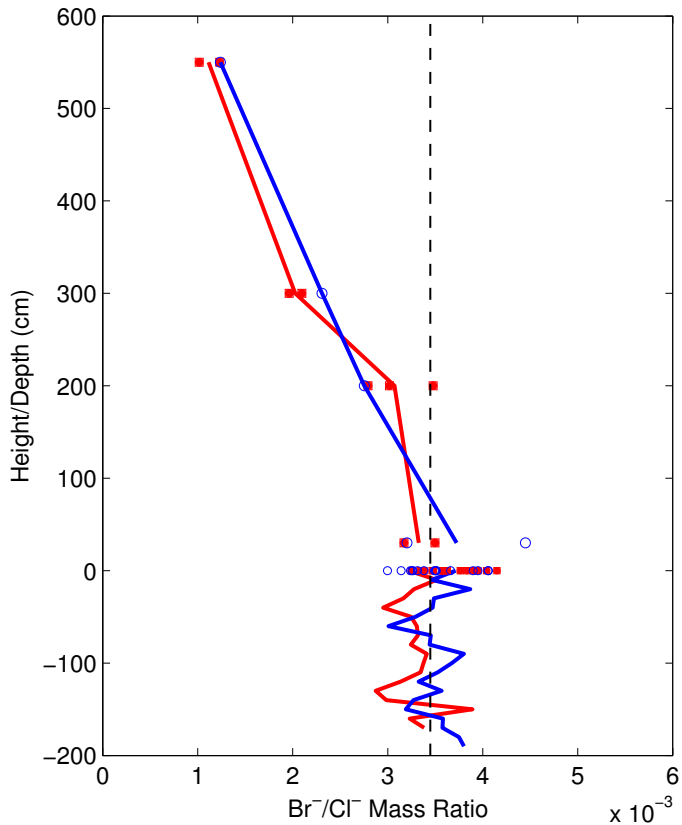
Figure 3. ~~Cl⁻/Br⁻~~ Br^-/Cl^- mass ratios for sea ice (negative heights), surface snow (height of 0), and blowing snow (height above snow surface). Blowing snow lines connect averages for each basket height. Butter Point Site samples are shown in red filled-in squares and red lines, while Iceberg Site samples are shown in blue open circles and blue lines. The standard ocean ~~Cl⁻/Br⁻~~ Br^-/Cl^- mass ratio is shown as a black dashed line (Morris and Riley, 1966).
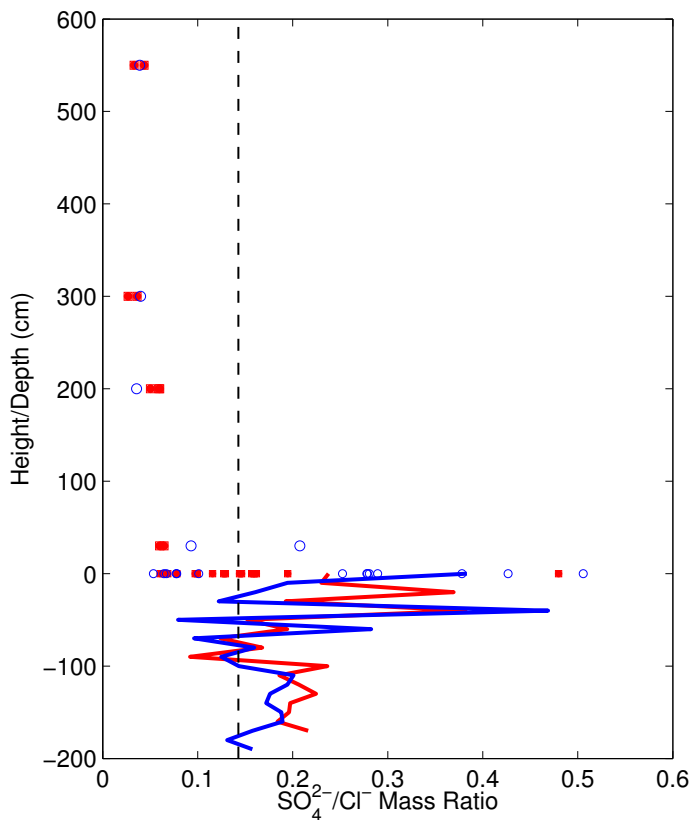
Figure 4. ~~Cl⁻/SO₄²⁻~~ SO_4^{2-}/Cl^- mass ratios for sea ice (negative heights), surface snow (height of 0), and blowing snow (height above snow surface). Butter Point Site samples are shown in red filled-in squares (snow samples) and a red line (sea ice), while Iceberg Site samples are shown in blue open circles (snow samples) and a blue line (sea ice). The standard ocean ~~Cl⁻/SO₄²⁻~~ SO_4^{2-}/Cl^- mass ratio is shown as a black dashed line (Morris and Riley, 1966).

The role of blowing snow in the activation of bromine over first-year Antarctic sea ice

R. M. Lieb-Lappen and R. W. Obbard

14 Engineering Drive, Thayer School of Engineering, Dartmouth College, Hanover, NH, USA

Correspondence to: R. M. Lieb-Lappen (ross.lieb-lappen@dartmouth.edu)

Abstract

It is well known that during polar springtime halide sea salt ions, in particular Br⁻, are photochemically activated into reactive halogen species (e.g. Br and BrO), where they break down tropospheric ozone. This research investigated the role of blowing snow in transporting salts from the sea ice/snow surface into reactive bromine species in the air. At two different locations over first-year ice in the Ross Sea, Antarctica, collection baskets captured blowing snow at different heights. In addition, sea ice cores and surface snow samples were collected throughout the month-long campaign. Over this time, sea ice and surface snow Br⁻/Cl⁻ mass ratios remained constant and equivalent to seawater, and only in lofted snow did bromide become depleted relative to chloride. This suggests that replenishment of bromide in the snowpack occurs faster than bromine activation in mid-strength wind conditions (approximately $10\,\mathrm{m\,s^{-1}}$) or that blowing snow represents only a small portion of the surface snowpack. Additionally, lofted snow was found to be depleted in sulfate and enriched in nitrate relative to surface snow.

1 Introduction

The polar springtime is a season of change, most notably in temperature, sea ice coverage, and weather, but it also signals the onset of many photochemically driven atmospheric chemical reactions, such as tropospheric ozone depletion events (ODEs) (e.g., Barrie et al., 1988). Boundary layer ozone in polar regions has been observed to fall dramatically periodically in the spring in both the Arctic (Barrie et al., 1988) and Antarctic (Kreher et al., 1997; Wessel et al., 1998). These tropospheric ODEs are initiated by increased concentrations of reactive bromine gases (BrO and Br) resulting in a catalytic removal of ozone (Fan and Jacob, 1992; McConnell et al., 1992; Frießet al., 2004), however the mechanism by which Br enters the atmosphere is not well understood (Abbatt et al., 2012). The heterogeneous reaction producing bromine gas and hypothesized to explain the "bromine explosion" is given

by Fan and Jacob (1992):

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \tag{1}$$

Proposed surfaces on which this reaction may occur have included sea spray Sander et al. (2003), frost flowers (Rankin et al., 2000; Kaleschke et al., 2004), surface snow (Simpson et al., 2005), aerosols (Vogt et al., 1996; Frießet al., 2004), and blowing snow (Yang et al., 2008).

Although some bromide may arrive via sea spray produced aerosol (Sander et al., 2003), this mechanism is relatively less efficient and does not produce aerosol with the observed sulfate depletion (Wagenbach et al., 1998). As seawater freezes, salt rejection leads to an increasingly saline brine (Thomas and Dieckmann, 2009). Specific salts precipitate out of solution when solubility limits are reached below $-2\,^\circ C$ (Light et al., 2003), producing brine with different ion ratios than those found in seawater. The brine is expelled to the ice/snow or ice/atmosphere surface, where it forms a fractionated surface skim and slush (Rankin et al., 2002). This reservoir of bromide and other sea salts can be incorporated into frost flowers by wicking, or into the snow lying on sea ice by upward migration through capillary forces (Perovich and Richter-Menge, 1994). It may be transported by the lofting of snow from sea ice with subsequent sublimation and return of the aerosol to the snowpack (Yang et al., 2008; Jones et al., 2009). However, the physical surface at which bromide activation occurs remains a subject of some debate.

It has been shown that brine is wicked upward by frost flowers that form on fresh sea ice, yielding a highly saline surface with the aforementioned sulfate depletion, and that the dendritic nature of frost flowers magnifies the surface area available for atmospheric interactions (Rankin et al., 2002). However, studies have shown that frost flowers do not significantly increase the surface area available for heterogeneous reactions (Domine et al., 2005; Obbard et al., 2009) and that frost flowers are not easily broken and lofted (Obbard et al., 2009). Instead, they accumulate snow on their windward side in strong winds and when broken, fall where they are (Obbard et al., 2009). Laboratory studies of frost flowers have also shown that frost flowers are quite stable in winds up to $12\,\mathrm{m\,s^{-1}}$, and aerosol produc-

3

tion is not observed under these conditions (Roscoe et al., 2011). Further, Simpson et al. (2005) and Obbard et al. (2009) found that frost flowers are not depleted in bromide relative to sodium and chloride, indicating they are not the immediate source of bromine-depleted snow nor the location of the heterogeneous reactions activating bromine. It has also been shown that first-year sea ice contact better correlates to increased BrO concentrations than does contact with potential frost flower regions (Simpson et al., 2007a).

In Simpson et al. (2005) however, the snowpack did have Br^-/Na^+ ratio fluctuations by two orders of magnitude with bromide depletions of up to 90 %, suggesting bromine was released in the aerosol phase or in the snowpack itself. Sea-salts can migrate upwards through the snowpack as high as 17 cm, even in cold conditions where slush is not present (Massom et al., 2001; Domine et al., 2004). However, in thicker snowpacks, the surface snow is more readily acidified and influenced by atmospheric processes, and thus, more likely to play a role in halogen activation. Bromine activation is more efficient in acidic conditions and in environments with a lower Br^-/Cl^- ratio (Pratt et al., 2013). Pratt et al. (2013) further hypothesized that the snowpack interstitial air is the primary location for the heterogeneous reactions, with wind pumping providing a vehicle to release the bromine into the boundary layer.

Yang et al. (2008) proposed a fourth mechanism for bromine activation that involves the lofting of snow from sea ice with subsequent sublimation and either direct bromine release or return of the aerosol to the snowpack. In the model, lofted snow particles were allowed to sublimate to a particle size of $< 10\,\mu m$, whereby the particles instantaneously released bromine or were potentially scoured by more blowing snow particles. Snow salinity was found to have a nonlinear relationship with bromine production, and the reaction rate varied with dry aerosol particle size. It was shown that $1.3\,\mu m$ particles yielded the most efficient release of bromine since the smaller aerosol could be lofted further and longer (Yang et al., 2008). Further work showed that snow in the sea ice zone may contain enough salt when lofted by wind to produce the necessary aerosol to explain the observed Antarctic ODEs (Yang et al., 2010). While it may be difficult for saturated snow lying on surface skim to become lofted, snow in the upper layers could wick up salts yet remain mobile, providing

4

enormous capacity for transporting bromide into the boundary layer. Yang et al. (2008) provides the theoretical framework and model-based data for the physical measurements observed and presented in this manuscript.

ODEs have been found to occur at a range of wind speeds, something that has made agreement upon a mechanism difficult. Some have observed that ODEs require low winds, a stable boundary layer, and a relatively clear sky, or the movement of air masses from such regions (Simpson et al., 2007b). Using measurements and modeling, Albert et al. (2002) found rapid ozone depletion in the top 10 cm of the snowpack due to diffusion and ventilation in moderate winds. More recently, ODEs have been recorded during high winds ($> 12\,\mathrm{m\,s^{-1}}$), which increase the snow surface area exposed via blowing snow, and thus, the probability of contact between the gaseous and condensed phases required to initiate bromine release (Jones et al., 2009). During the 2009 OASIS campaign in Barrow, AK, high winds were observed to correspond with increased BrO concentrations (Frieß et al., 2011). This was accompanied by decreased HOBr, suggesting that blowing snow likely provided additional surfaces for heterogeneous HOBr loss (Liao et al., 2012). These high wind halogen activation events may have a more widespread role when considering the impact of ODEs on regional tropospheric chemistry (Jones et al., 2010). Additionally, higher winds may enhance the availability of radical bromine precursors in the snowpack, accelerating bromine activation (Toyota et al., 2011). On the contrary, others (e.g. Helmig et al., 2012; Halfacre et al., 2014) have found no correlation between ODEs and wind speed. However, the lack of low ozone observations at high wind speed may be a result of enhanced mixing (Helmig et al., 2012). Although the chemistry of snow has been well studied (Massom et al., 2001; Domine et al., 2004; Grannas et al., 2007), there has been no attempt until now at segregating snow capable of wind transport or snow actually blown by wind.

It is noted that both Cl_2 and BrCl play a role in halide boundary layer chemistry and ODEs (Abbatt et al., 2012), but the focus of this work is on bromine because it is a far more efficient catalyst of ozone loss. As the main constituents of seawater, both chloride and sodium have been used as sea salt tracers, and thus chloride was used here to both determine snow and ice salinity and relative activity of other anions. Previous work has shown that sulfate

is influenced both by mirabilite precipitation and atmospheric interactions, while nitrate is uncorrelated with sea salt and is deposited as a byproduct of other reactions (Krnavek et al., 2012).

2 Methods

Two field sites on first-year sea ice in the Ross Sea, Antarctica, were chosen, based upon prevailing wind direction, to maximize contact of the blowing snow with the first-year sea ice. Their locations are shown in Fig. 1. Butter Point Site was located 6.5 km from the open ocean and 35 km north of the Ross Ice Shelf. Iceberg Site was located 55 km north-west of Butter Point, and since the ice edge located to the east follows the shore, the distance to open water here was also 5 km. Iceberg Site was chosen based upon the presence of a 740 m long and 35 m high iceberg located 250 m to the west that would block winds sourced over land, maximizing blowing snow collection from over sea ice. At each site, a 5.5 m blowing snow collection tower was erected for the time period of 11 October–8 November 2012. Collection baskets made out of 150 μm nylon monofilament mesh and 7" diameter by 14" long (Midwest Filter Corporation, Lake Forest, IL) were placed at four different heights: 0.3, 2.0, 3.0, and 5.5 m above the snow surface.

The sites were visited approximately every other day, and collection baskets were switched even if no snow was collected. Baskets were triple rinsed with DI water between uses. Surface snow samples were collected each of the 12 days the sites were visited. In addition, 1.78 and 1.89 m ice cores were extracted from Butter Point and Iceberg sites, respectively. Snow samples and sea ice cores were transported at a constant temperature of $-20\,^{\circ}\text{C}$ back to Thayer School of Engineering's Ice Research Laboratory at Dartmouth College and stored in a $-33\,^{\circ}\text{C}$ cold room.

Winds during the field campaign were generally mild, only surpassing $10\,\text{m s}^{-1}$ on a few occasions. Site visits were not feasible during stormy weather, and much of the blowing snow captured during those periods sublimated in the baskets prior to collection as observed by a webcam. Thus, only on 25 October were blowing snow samples collected at

both sites and all four heights. The collected snow was the result of approximately $10\,\mathrm{m\,s^{-1}}$ southerly winds on 24 October. Visibility at McMurdo station during this blowing snow event dropped below 0.5 miles for about 4 hours. Temperatures ranged from $-20.5\,^{\circ}\mathrm{C}$ to $-11.5\,^{\circ}\mathrm{C}$ with an average relative humidity of 69% on 24 October and $-17.5\,^{\circ}\mathrm{C}$ to $-13.5\,^{\circ}\mathrm{C}$ with an average relative humidity of 61% on 25 October. These temperatures were a couple of degrees warmer than the average for the rest of the field campaign.

All surface snow and blowing snow samples were melted into acid-rinsed HDPE vials, and diluted by a factor of 5 with DI water. Those samples falling outside of the calibration standard concentrations were further diluted to fall within the desired range. Each ice core was sub-sampled every $10\,\mathrm{cm}$, melted, and diluted by a factor of 50, except for the bottom-most sample that was diluted by a factor of 100. A $0.5\,\mathrm{mL}$ aliquot of each diluted snow and ice sample was then analyzed for anion concentrations.

Anion chromatography was completed using a Dionex-600 IC system, equipped with a LC 25 chromatogram oven set at $30\,^{\circ}\mathrm{C}$, GD 50 gradient pump, CD 25 conductivity detector, AS15 anion column with a AG15 guard column, and an auto-sampler. A $38\,\mathrm{mM}$ NaOH eluent was used at a flow rate of $1.2\,\mathrm{mL\,min^{-1}}$ and the SRS current was set to $100\,\mu\mathrm{A}$. Pressure in the column was 1600 psi and the signal noise was approximately $0.003\,\mu\mathrm{S}$. Peak analysis was performed using Chromeleon 6.8 software with a 5 point standard calibration curve. IC detection limits were 0.6, 0.1, 0.04, and $0.03\,\mathrm{g\,m^{-3}}$, yielding limits of quantification of 2, 0.3, 0.1, and $0.1\,\mathrm{g\,m^{-3}}$ for chloride, sulfate, bromide, and nitrate, respectively.

3 Results

Raw anion concentrations for sea ice, surface snow, and blowing snow samples are provided in a supplement to this manuscript. Sea ice anion concentrations had nearly identical profiles for Butter Point and Iceberg cores, with both showing the expected C-shape profile (see Fig. 2) (Eicken, 1992). Note that the deepest sample for Iceberg site was directly at the base of the core, while the deepest sample for Butter Point was $8\,\mathrm{cm}$ above the base, due to a mushy, poorly defined basal layer, and thus missed the saltiest portion. Chloride

concentrations ranged from 2,000–8,000 g m^{-3}, while bromide concentrations ranged from 5–35 g m^{-3}. Sulfate concentrations ranged from 2–3000 g m^{-3}, with increased variation observed over the top 40 cm of both cores. Nitrate concentrations were below detection limits for all sea ice core samples.

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 g m^{-3} chloride, 1.0–16 g m^{-3} bromide, 20–2300 g m^{-3} sulfate, and 0–1.2 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 sastrugi, 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 g m^{-3} chloride and 1.5–6 g m^{-3} bromide. Sulfate concentrations ranged from 30–50 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 g m^{-3} chloride, 0.2–18.5 g m^{-3} bromide, 3–240 g m^{-3} sulfate, and 0.4–23 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.

Anion concentrations can provide a general understanding of the overall salinity of the snow and ice, but in order to understand chemical reaction activity, it is instructive to calculate anion concentration ratios. The Br^-/Cl^- mass ratio has long been used as a metric for analyzing both frozen and liquid saline water samples, and comparing measured values to the well established $1:290$ ratio observed in seawater (Morris and Riley, 1966). This ratio is plotted in Fig. 3 for all samples at both sites. Br^-/Cl^- mass ratios were relatively constant for all sea ice samples ($1:281\pm24$) and all surface snow samples ($1:296\pm22$). However, there was a linear correlation between Br^-/Cl^- mass ratios for blowing snow relative to height at both Butter Point ($r^2 = 0.89$) and Iceberg Site ($r^2 = 0.93$). Sulfate mass ratios in sea ice, surface snow, and blowing snow did not show as clear a trend (Fig. 4). In sea ice, the SO_4^{2-}/Cl^- mass ratio was roughly $1:7$ in the bottom half of the cores, consistent with what is generally observed in seawater (Morris and Riley, 1966), but varied from approximately $1:2$ to $1:12$ in the upper halves of the cores. Surface snow mass ratios also were quite variable ranging from $1:1$ to $1:19$ with no clear correlations. Collected lofted snow was quite depleted in sulfate with mass ratios reaching $1:20$ to $1:40$, but did not show the linear trend with height observed with bromide.

4 Discussion

Observation of bromide depletion relative to other salts is an indication of heterogeneous atmospheric chemical reactions and bromine activation (Adams et al., 2002; Huff and Abbatt, 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 and Woodcock (1971) that measured increased bromide depletion with height, albeit at tropical latitudes. They noted a strong par-

ticle 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 and Nishimura, 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 and Brun, 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 help overcome some these diffusion limitations (Nemoto and Nishimura, 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.

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).

Previously, bromine activation and ODEs were observed in both low ($< 5\,\mathrm{m\,s^{-1}}$) and high ($> 12\,\mathrm{m\,s^{-1}}$) winds (Jones et al., 2009). Here, the blowing snow event occurred during moderate winds of approximately $10\,\mathrm{m\,s^{-1}}$. Since the wind was from the south and there was no new precipitation, it is safe to assume that the snow originated from the surface of first-year sea ice. It is noted that the blowing snow event lasted approximately $4 - 6$ hours, and that snow samples from the baskets were not collected until $10 - 12$ hours later. During this time, wind speeds dropped to less than $5\,\mathrm{m\,s^{-1}}$, and it is possible that the collected snow was exposed to further wind scouring. However, all baskets would have experienced a similar degree of scouring in these minimal winds and the effect would be minor over the short time period prior to collection. Further, the collected snow was mostly windpacked, suggesting it was unlikely the wind penetrated both the $150\,\mu\mathrm{m}$ nylon monofilament mesh of the basket and the interior bulk of the snow. Future studies, however, may attempt to better seal off collected blown snow.

The surface snow Br^-/Cl^- mass ratios at both sites showed little variation and no observed trend with date or meteorology over the month-long campaign. If there was a significant amount of lofted snow being depleted in bromide and then falling back to the snow surface, one might expect to detect a signal in the surface snow chemistry. The lack of recorded bromide depletion in the surface snow may indicate that either surface snow bromide concentration is quickly replenished or that blowing snow represents only a small portion of the surface snowpack. Surface snow will be replenished in bromide through interaction with saline brine (Oldridge and Abbatt, 2011), deposition of HOBr as a byproduct

11

of the reaction between BrO and HO_2, deposition of HBr, and deposition of aerosol-phase bromine. In cold ambient environments, frost flowers, surface snow, and the sea ice surface have been shown to be bromide enriched sources, likely due to the precipitation of NaCl (Kalnajs and Avallone, 2006; Morin et al., 2008). Additionally, recycling of deposited bromine plays a critical role with as much as 75% of deposited bromine being re-emitted into the gas phase as Br_2 or BrCl (Piot and von Glasow, 2008). In future work, it would be informative to collect both surface and blowing snow during stronger wind events.

The sulfate depletion observed in lofted snow is consistent with the observations of others, most likely a product of mirabilite precipitation occurring at temperatures below $-8\,^{\circ}C$ (Rankin et al., 2000). The range of SO_4^{2-}/Cl^- mass ratios measured in surface snow and the upper halves of the ice cores is also likely due to similar interactions. Sulfate depletion can result from a wide variety of processes involving brine and mirabilite formation as brine constantly moves through sea ice and is also wicked up by surface snow (Krnavek et al., 2012). In addition, non-sea salt sourced sulfate may provide additional sulfate to the surface snowpack (Rankin and Wolff, 2003; Krnavek et al., 2012).

Nitrate concentration in seawater is highly dependent upon phytoplankton blooms, and therefore varies greatly from single digit $g\,m^{-3}$ to less than one $g\,m^{-3}$ (e.g., Gordon et al., 2000; Arrigo et al., 1997). Thus, it was not surprising that sea ice samples were below the quantification limit for nitrate. Surface snow samples also were generally below nitrate detection limits, and those with quantifiable concentrations showed no noticeable trend. Nitrate snow photochemistry is quite complex, with many processes both adding and subtracting nitrate from the snowpack (Grannas et al., 2007; Krnavek et al., 2012). Nitrate sources include biomass burning, lightning production, soil exhalation, and anthropogenic pollutants that can be carried long distances through atmospheric transport (Galloway et al., 2004; Krnavek et al., 2012). The increase in nitrate concentration observed with basket height may be attributed to increased atmospheric interactions higher above the snowpack. Additionally, basket nitrate concentration may also be influenced by interactions occurring while the snow was sitting in the basket but prior to collection, as cycling of different nitrogen-containing compounds is relatively fast and can vary greatly during a day (Grannas et al.,

2007). Considering the number of competing reactions, more data points would be needed to make conclusive statements regarding the cycling of nitrate in the polar boundary layer.

5 Conclusions

In summary, this work examined the mass ratio of Br^-/Cl^- in blowing snow during mid-strength winds to better understand mechanisms leading to bromine activation. It was found that while Br^-/Cl^- mass ratios remained relatively constant for sea ice and surface snow, bromide becomes strongly depleted relative to chloride in lofted snow. Thus, we conclude the blowing snow particles provide a very viable surface for the initial heterogeneous reactions initializing ODEs to occur. The findings of this study are consistent with previous modeling results (Yang et al., 2010), suggesting that blowing snow has the capacity to explain the occurrence of ODEs in the polar springtime.

References

Abbatt, J. P. D., Thomas, J. L., Abrahamsson, K., Boxe, C., Granfors, A., Jones, A. E., King, M. D., Saiz-Lopez, A., Shepson, P. B., Sodeau, J., Toohey, D. W., Toubin, C., von Glasow, R., Wren, S. N., and Yang, X.: Halogen Activation Via Interactions With Environemntal Ice and Snow in the Polar Lower Troposphere and Other Regions, Atmos. Chem. Phys., 12, 6237–6271, doi:10.5194/acp-12-6237-2012, 2012.

Adams, J. W., Holmes, N. S., and Crowley, J. N.: Uptake and Reactions of HOBr on Frozen and Dry NaCl/NaBr Surface Between 253 and 233 K, Atmos. Chem. Phys., 2, 79–91, 2002.

Albert, M. R., Grannas, A. M., Bottenheim, J., Shepson, P. B., and Perron, F. E.: Processes and Properties of Snow-Air Transfer in the High Arctic with Application to Interstitial Ozone at Alert, Canada, Atmos. Environ, 36, 2779–2787, 2002.

Arrigo, K. R., Worthen, D. L., Lizotte, M. P., Dixon, P., and Dieckmann, G.: Primary Production in Antarctic Sea Ice, Science, 276, 394–397, doi:10.1126/science.276.5311.394, 1997.

Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone Destruction and Photochemical-Reactions at Polar Sunrise in the Lower Arctic Atmosphere, Nature, 334, 138–141, 1988.

Domine, F., Sparapani, R., Ianniello, A., and Beine, H. J.: The Origin of Sea Salt in Snow on Arctic Sea Ice and in Coastal Regions, Atmos. Chem. Phys., 4, 2259–2271, 2004.

Domine, F., Taillandier, A. S., Simpson, W. R., and Severin, K.: Specific Surface Area, Density and Microstructure of Frost Flowers, Geophys. Res. Lett., 32, L13502, doi:10.1029/2005GL023245, 2005.

Duce, R. A. and Woodcock, A. H.: Difference in Chemical Composition of Atmospheric Sea Salt Particles Produced in the Surf Zone and on the Open Sea in Hawaii, Tellus, 23, 427–435, 1971.

Eicken, H.: Salinity Profiles of Antarctic Sea Ice: Field Data and Model Results, J. Geophys. Res., 97, 15,545–15,557, 1992.

Fan, S.-M. and Jacob, D. J.: Surface Ozone Depletion in Arctic Spring Sustained by Bromine Reacions on Aerosols, Nature, 359, 522–524, 1992.

Frieß, U., Hollwedel, J., Konig-Langlo, G., Wagner, T., and Platt, U.: Dynamics and Chemistry of Tropospheric Bromine Explosion Events in the Antarctic Coastal Region, J. Geophys. Res., 109, D06305, doi:10.1029/2003JD004133, 2004.

Frieß, U., Sihler, H., Sander, R., Pohler, D., Yilmaz, S., and Platt, U.: The Vertical Distribution of BrO and Aerosols in the Arctic: Measurements by Active and Passive Differential Optical Absorption Spectroscopy, J. Geophys. Res., 116, D00R04, doi:10.1029/2011JD015938, 2011.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vorosmarty, C. J.: Nitrogen Cycles: Past, Present, and Future, Biogeochemistry, 70, 153–226, doi:10.1007/s10533-004-0370-0, 2004.

Gordon, L. I., Codispoti, L. A., Jr., J. C. J., Millero, F. J., Morrison, J. M., and Sweeney, C.: Seasonal Evolution of Hydrographic Properties in the Ross Sea, Antarctica, 1996-1997, Deep-Sea Research II, 47, 3095–3117, 2000.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Domine, F., Frey, M. M., Guzman, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klan, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simp-

son, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An Overview of Snow Photochemistry: Evidence, Mechanisms, and Impacts, Atmos. Chem. Phys., 7, 4329–4373, 2007.

Halfacre, J. W., Knepp, T. N., Shepson, P. B., Thompson, C. R., Pratt, K. A., Li, B., Peterson, P. K., Walsh, S. J., Simpson, W. R., Matrai, P. A., Bottenheim, J. W., Netcheva, S., Perovich, D. K., and Richter, A.: Temporal and Spatial Characteristics of Ozone Depletion Events from Measurements in the Arctic, Atmos. Chem. Phys, 14, 4875–4894, doi:10.5194/acp-14-4875-2014, 2014.

Helmig, D., Boylan, P., Johnson, B., Oltmans, S., Fairall, C., Staebler, R., Weinheimer, A., Orlando, J., Knapp, D. J., Montzka, D. D., Flocke, F., Frieß, U., Sihler, H., and Shepson, P. B.: Ozone Dynamics and Snow-Atmosphere Exchanges During Ozone Depletion Events at Barrow, Alaska, J. Geophys. Res., 117, D20303, doi:10.1029/2012JD017531, 2012.

Huff, A. K. and Abbatt, J. P. D.: Kinetics and Product Yields in the Heterogeneous Reactions of HOBr with Simulated Sea-Ice Surfaces, J. Phys. Chem. A., 106, 5279–5287, 2002.

Jacobi, H. W., Voisin, D., Jaffrezo, J. L., Cozic, J., and Douglas, T. A.: Chemical Composition of the Snowpack During the OASIS Spring Campaign 2009 at Barrow, Alaska, J. Geophys. Res., 117, 2012.

Jones, A. E., Anderson, P. S., Begoin, M., Brough, N., Hutterli, M. A., Marshall, G. J., Richter, A., Roscoe, H. K., and Wolff, E. W.: BrO, Blizzards, and Drivers of Polar Tropospheric Ozone Depletion Events, Atmos. Chem. Phys., 9, 4639–4652, 2009.

Jones, A. E., Anderson, P. S., Wolff, E. W., Roscoe, H. K., Marshall, G. J., Richter, A., Brough, N., and Colwell, S. R.: Vertical Structure of Antarctic Tropospheric Ozone Depletion Events: Characteristics and Broader Implications, Atmos. Chem. Phys., 10, 7775–7794, doi:10.5194/acp-10-7775-2010, 2010.

Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A. M., Roscoe, H. K., Hollwedel, J., Wagner, T., and Jacobi, H.-W.: Frost Flowers on Sea Ice as a Source of Sea Salt and Their Influence on Tropospheric Halogen Chemistry, Geophys. Res. Lett., 31, L16114, doi:10.1029/2004GL020655, 2004.

Kalnajs, L. E. and Avallone, L. M.: Frost Flower Influence on Springtime Boundary-Layer Ozone Depletion Events and Atmospheric Bromine Levels, Geophys. Res. Lett., 33, L10810, doi:10.1029/2006GL025809, 2006.

Kreher, K., Johnston, P. V., Wood, S. W., Nardi, B., and Platt, U.: Ground-Based Measurements of Tropospheric and Stratospheric BrO at Arrival Heights, Antarctica, Geophys. Res. Lett., 24, 3021–3024, 1997.

Krnavek, L., Simpson, W. R., Carlson, D., Domine, F., Douglas, T. A., and Sturm, M.: The Chemical Composition of Surface Snow in the Arctic: Examining Marine, Terrestrial, and Atmospheric Influences, Atmos. Environ., 50, 349–359, 2012.

Liao, J., Huey, L. G., Tanner, D. J., Flocke, F. M., Orlando, J. J., Neuman, J. A., Nowak, J. B., Weinheimer, A. J., Hall, S. R., Smith, J. N., Fried, A., Staebler, R. M., Wang, Y., Koo, J.-H., Cantrell, C. A., Weibring, P., Walega, J., Knapp, D. J., Shepson, P. B., and Stephens, C. R.: Observations of Inorganic Bromine (HOBr, BrO, and Br_2) Speciation at Barrow, Alaska, in Spring 2009, J. Geophys. Res., 117, D00R16, doi:10.1029/2011JD016641, 2012.

Light, B., Maykut, G. A., and Grenfell, T. C.: Effects of Temperature on the Microstructure of First-Year Arctic Sea Ice, J. Geophs. Res., 108, 3051, doi:10.1029/2001JC000887, 2003.

Massom, R. A., Eicken, H., Haas, C., Jeffries, M. O., Drinkwater, M. R., Sturm, M., Worby, A. P., Wu, X., Lytle, V. I., Ushio, S., Morris, K., Reid, P. A., and Allison, S. G. W. I.: Snow on Antarctic Sea Ice, Rev. Geophys., 39, 413–445, 2001.

McConnell, J. C., Henderson, G. S., Barrie, L. A., Bottenheim, J. W., Niki, H., Langford, C. H., and Templeton, E. M. J.: Photochemical Bromine Production Implicated in Arctic Boundary-Layer Oone Depletion, Nature, 355, 150–152, doi:10.1038/355150a0, 1992.

Morin, S., Marion, G. M., von Glasow, R., Voisin, D., Bouchez, J., and Savarino, J.: Precipitation of Salts in Freezing Seawater and Ozone Depletion Events: A Status Report, Atmos. Chem. Phys., 8, 7317–7324, 2008.

Morris, A. W. and Riley, J. P.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, Deep-Sea Research and Oceanographic Abstracts, 13, 699–705, doi:10.1016/0011-7471(66)90601-2, 1966.

Nemoto, M. and Nishimura, K.: Numerical Simulation of Snow Saltation and Suspension in a Turbulent Boundary Layer, J. Geophys. Res., 109, D18206, doi:10.1029/2004JD004657, 2004.

Obbard, R. W., Roscoe, H. K., Wolff, E. W., and Atkinson, H. M.: Frost Flower Surface Area and Chemistry as a Function of Salinity and Temperature, J. Geophys. Res., 114, D20305, doi:10.1029/2009JD012481, 2009.

Oldridge, N. W. and Abbatt, J. P. D.: Formation of Gas-Phase Bromine from Interaction of Ozone with Frozen and Liquid NaCl/Br Solutions: Quantitative Separation of Surficial Chemistry from Bulk-Phase Reaction, J. Phys. Chem. A, 115, 2590–2598, doi:10.1021/jp200074u, 2011.

Perovich, D. K. and Richter-Menge, J. A.: Surface Characteristics of Lead Ice, J. Geophys. Res., 99, 16,341–16,350, 1994.

Piot, M. and von Glasow, R.: The Potential Importance of Frost Flowers, Recycling on Snow, and Open Leads for Ozone Depletion Events, Atmos. Chem. Phys., 8, 2437–2467, 2008.

Pomeroy, J. W. and Brun, E.: Physical Properties of Snow, Snow Ecology, pp. 45–126, 2001.

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.

Rankin, A. M. and Wolff, E. W.: A Year-Long Record of Size-Segregated Aerosol Composition at Halley, Antarctica, J. Geophys. Res., 108, 4775, doi:10.1029/2003JD003993, 2003.

Rankin, A. M., Auld, V., and Wolff, E. W.: Frost Flowers as a Source of Fractionated Sea Salt Aerosol in the Polar Regions, Geophys. Res. Lett., 27, 3469–3472, 2000.

Rankin, A. M., Wolff, E. W., and Martin, S.: Frost Flowers: Implications for Tropospheric Chemistry and Ice Core Interpretation, J. Geophys. Res., 107, 4683, doi:10.1029/2002JD002492, 2002.

Roscoe, H. K., Brooks, B., Jackson, A. V., Smith, M. H., Walker, S. J., Obbard, R. W., and Wolff, E. W.: Frost Flowers in the Laboratory: Growth, Characteristics, Aerosol, and the Underlying Sea Ice, J. Geophys. Res., 116, D12301, doi:10.1029/2010JD015144, 2011.

Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Honninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C., and Dingenen, R. V.: Inorganic Bromine in the Marine Boundary Layer: A Critical Review, Atmos. Chem. Phys., 3, 1301–1336, 2003.

Simpson, W. R., Alvarez-Alviles, L., Douglas, T. A., Sturm, M., and Domine, F.: Halogens in the Coastal Snow Pack Near Barrow, Alaska: Evidence for Active Bromine Air-Snow Chemistry During Springtime, Geophys. Res. Lett., 32, L04811, doi:10.1029/2004GL021748, 2005.

Simpson, W. R., Carlson, D., Honninger, G., Douglas, T. A., Sturm, M., Perovich, D., and Platt, U.: First-Year Sea-Ice Contact Predicts Bromine Monoxide (BrO) Levels at Barrow, Alaska Better Than Potential Frost Flower Contact, Atmos. Chem. Phys., 7, 621–627, 2007a.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and Their Role in Polar Boundary-Layer Ozone Depletion, Atmos. Chem. Phys., 7, 4375–4418, 2007b.

Thomas, D. N. and Dieckmann, G. S.: Sea ice, John Wiley & Sons, 2009.

Toyota, K., McConnell, J. C., Lupu, A., Neary, L., McLinden, C. A., Richter, A., Kwok, R., Seme-niuk, K., Kaminski, J. W., Gong, S.-L., Jarosz, J., Chipperfield, M. P., and Sioris, C. E.: Analysis of Reactive Bromine Production and Ozone Depletion in the Arctic Boundary Layer Using 3-D Simulations with GEM-AQ: Inference From Synoptic-Scale Patterns, Atmos. Chem. Phys., 11, 3949–3979, doi:10.5194/acp-11-3949-2011, 2011.

Vogt, R., Crutzen, P. J., and Sander, R.: A Mechanism for Halogen Release From Sea-Salt Aerosol in the Remote Marine Boundary Layer, Nature, 383, 327–330, 1996.

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.

Wessel, S., Aoki, A., Winkler, P., Weller, R., Herber, A., Gernandt, H., and Schrems, O.: Tropospheric Ozone Depltion in Polar Regions: A Comparison of Observations in the Arctic and Antarctic, Tellus B, 50, 34–50, 1998.

Wren, S. N., Donaldson, D. J., and Abbatt, J. P. D.: Photochemical Chlorine and Bromine Activation from Artificial Saline Snow, Atmos. Chem. Phys., 13, 9789–9800, doi:10.5194/acp-13-9789-2013, 2013.

Yang, X., Cox, R. A., Warwick, N. J., Pyle, J. A., Carver, G. D., O'Connor, F. M., and Savage, N. H.: Tropospheric Bromine Chemistry and its Impacts on Ozone: A Model Study, J. Geophys. Res., 110, 2005.

Yang, X., Pyle, J. A., and Cox, R. A.: Sea Salt Aerosol Production and Bromine Release: Role of Snow on Sea Ice, Geophys. Res. Lett., 35, L16815, doi:10.1029/2008GL034536, 2008.

Yang, X., Pyle, J. A., Cox, R. A., Theys, N., and Roozendael, M. V.: Snow-Sourced Bromine and Its Implications for Polar Tropospheric Ozone, Atmos. Chem. Phys., 10, 7763–7773, doi:10.5194/acp-10-7763-2010, 2010.
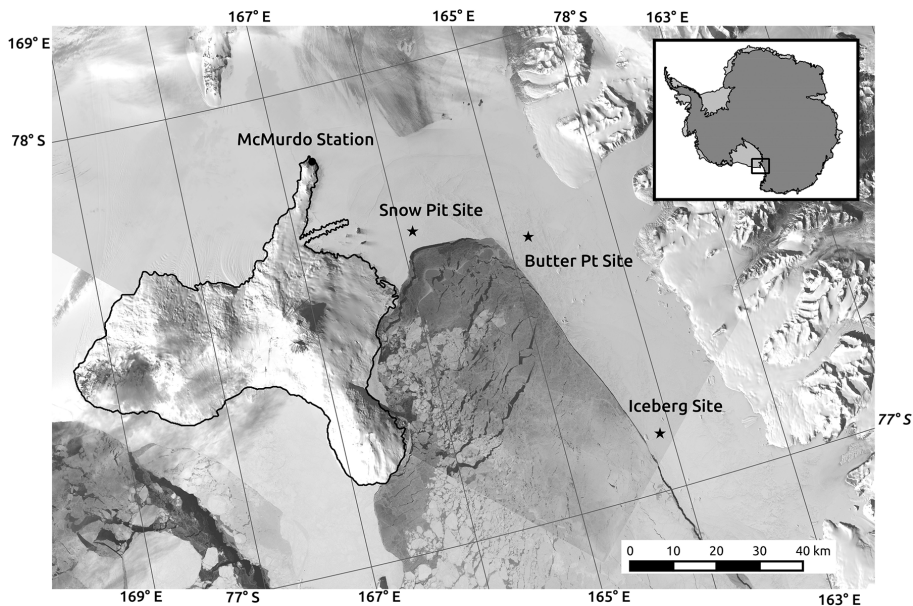
Figure 1. Map of the Ross Sea region showing the two field sites Butter Point and Iceberg. Basemap is Landsat image.
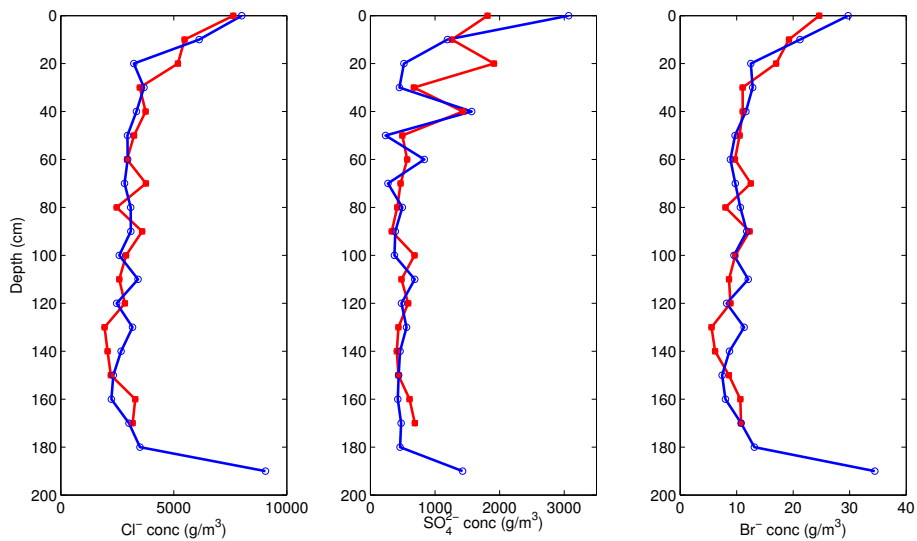
Figure 2. Anion concentrations for sea ice cores. Butter Point Site samples are shown in red filled-in squares and red lines, while Iceberg Site samples are shown in blue open circles and blue lines.
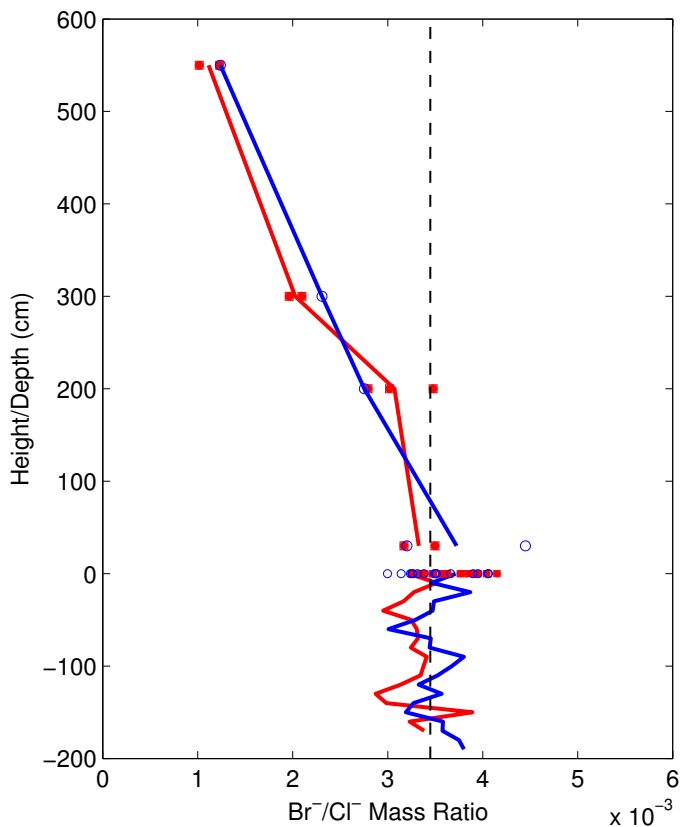
Figure 3. Br^-/Cl^- mass ratios for sea ice (negative heights), surface snow (height of 0), and blowing snow (height above snow surface). Blowing snow lines connect averages for each basket height. Butter Point Site samples are shown in red filled-in squares and red lines, while Iceberg Site samples are shown in blue open circles and blue lines. The standard ocean Br^-/Cl^- mass ratio is shown as a black dashed line (Morris and Riley, 1966).
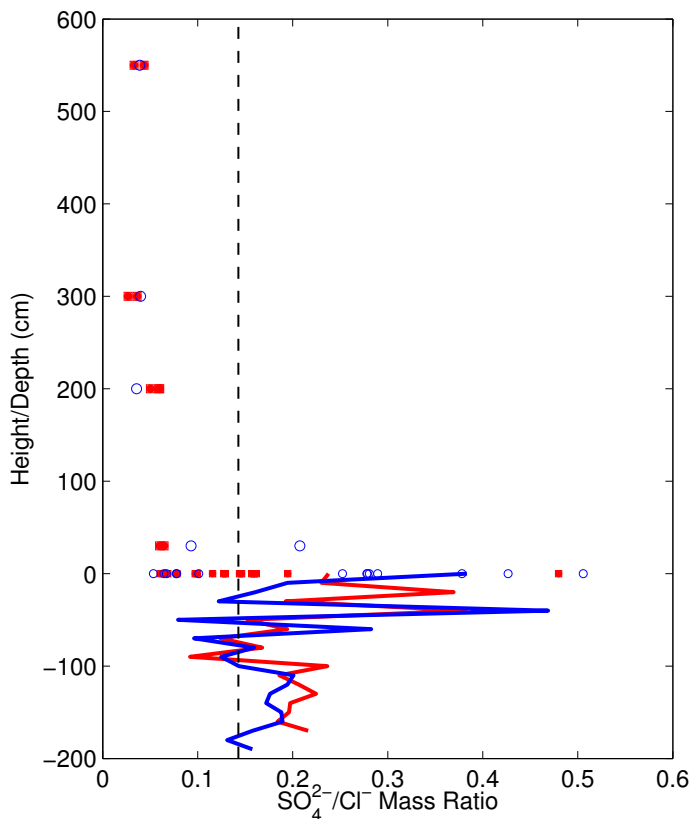
Figure 4. SO_4^{2-}/Cl^- mass ratios for sea ice (negative heights), surface snow (height of 0), and blowing snow (height above snow surface). Butter Point Site samples are shown in red filled-in squares (snow samples) and a red line (sea ice), while Iceberg Site samples are shown in blue open circles (snow samples) and a blue line (sea ice). The standard ocean SO_4^{2-}/Cl^- mass ratio is shown as a black dashed line (Morris and Riley, 1966).

Table 1: Raw anion concentrations of blowing snow samples collected on 25 October, 2012, and measured using a Dionex-600 IC system.

Site	Height (m)	Cl^- (g/m^3)	Br^- (g/m^3)	SO_4^{2-} (g/m^3)	NO_3^- (g/m^3)
Butter Pt	0.3	400	1.3	26	0.4
Butter Pt	0.3	460	1.6	28	0.4
Butter Pt	2.0	23	0.1	1	0.3
Butter Pt	2.0	62	0.2	4	0.4
Butter Pt	2.0	63	0.2	4	0.5
Butter Pt	3.0	4,500	9.5	160	20
Butter Pt	3.0	670	1.3	18	4.3
Butter Pt	5.5	1,400	1.4	47	9.9
Butter Pt	5.5	4,900	6.0	210	30
Iceberg	0.3	150	0.5	14	0.2
Iceberg	0.3	280	1.3	59	0.4
Iceberg	2.0	6,700	18.5	240	13
Iceberg	3.0	2,600	6.0	100	8.3
Iceberg	5.5	3,900	4.9	150	23

Table 2: Raw anion concentrations of surface snow samples collected in October – November, 2012, and measured using a Dionex-600 IC system. All nitrate samples marked BQL were below the quantification limit of 0.1 g/m^3.

Site	Date	Cl$^-$ (g/m^3)	Br$^-$ (g/m^3)	SO$_4^{2-}$ (g/m^3)	NO$_3^-$ (g/m^3)
Butter Pt	10/15	3,400	13	1,600	0.3
Butter Pt	10/15	2,400	8.0	350	0.3
Butter Pt	10/15	950	3.7	150	BQL
Butter Pt	10/17	940	3.0	120	0.5
Butter Pt	10/25	780	2.8	78	BQL
Butter Pt	10/25	1,800	6.9	210	BQL
Butter Pt	10/25	2,700	9.5	210	BQL
Butter Pt	10/25	420	1.5	29	BQL
Butter Pt	10/25	920	3.7	120	BQL
Butter Pt	10/25	1,300	4.9	250	BQL
Butter Pt	10/26	330	1.2	20	0.5
Butter Pt	10/29	350	1.2	50	BQL
Butter Pt	10/31	470	2.0	77	BQL
Butter Pt	11/02	2,200	7.8	210	BQL
Butter Pt	11/06	3,700	13	590	1.2
Iceberg	10/11	1,400	4.4	87	0.3
Iceberg	10/15	4,600	15	1,200	0.9
Iceberg	10/15	550	2.1	160	0.1
Iceberg	10/15	440	1.7	34	BQL
Iceberg	10/17	3,700	13	1,100	0.5
Iceberg	10/19	1,100	4.7	1,600	BQL
Iceberg	10/25	2,100	7.3	140	BQL
Iceberg	10/25	1,100	4.4	58	BQL
Iceberg	10/25	3,700	13	1,600	BQL
Iceberg	10/25	2,300	8.2	2,300	BQL
Iceberg	10/26	370	1.2	100	0.5
Iceberg	10/29	1700	5.1	480	BQL
Iceberg	10/31	150	0.5	74	0.2
Iceberg	11/02	2,000	6.5	160	BQL
Iceberg	11/06	1,400	5.2	540	BQL
Iceberg	11/08	2,300	7.8	240	BQL

Table 3: Raw anion concentrations of sub-samples taken every 10-cm for the length of two ice cores collected at Butter Point Site and Iceberg Site, respectively, and measured using a Dionex-600 IC system. All nitrate measurements in the two ice cores were below the quantification limit of 0.1 g/m^3.

Site	Depth (m)	Cl^- (g/m^3)	Br^- (g/m^3)	SO_4^{2-} (g/m^3)
Butter Pt	0	7,600	25	1,800
Butter Pt	10	5,500	19	1,300
Butter Pt	20	5,200	17	1,900
Butter Pt	30	3,500	11	670
Butter Pt	40	3,800	11	1,400
Butter Pt	50	3,200	11	490
Butter Pt	60	2,900	9.7	570
Butter Pt	70	3,800	13	470
Butter Pt	80	2,500	8.0	420
Butter Pt	90	3,600	12	330
Butter Pt	100	2,900	9.8	680
Butter Pt	110	2,600	8.7	480
Butter Pt	120	2,800	8.9	590
Butter Pt	130	1,900	5.6	440
Butter Pt	140	2,100	6.2	410
Butter Pt	150	2,200	8.6	440
Butter Pt	160	3,300	11	610
Butter Pt	170	3,200	11	690
Iceberg	0	8,000	30	3,100
Iceberg	10	6,000	21	1,200
Iceberg	20	3,200	13	520
Iceberg	30	3,700	13	450
Iceberg	40	3,300	12	1,600
Iceberg	50	2,900	9.7	230
Iceberg	60	3,000	8.9	840
Iceberg	70	2,800	9.8	270
Iceberg	80	3,100	11	490
Iceberg	90	3,100	12	390
Iceberg	100	2,600	9.5	370
Iceberg	110	3,400	12	690
Iceberg	120	2,500	8.2	480
Iceberg	130	3,200	11	560
Iceberg	140	2,700	8.7	460
Iceberg	150	2,300	7.4	440
Iceberg	160	2,200	8.0	420
Iceberg	170	3,000	11	480
Iceberg	180	3,500	13	460
Iceberg	190	9,100	34	1,400