Reply to reviewer #2's comments

We thank the reviewer for the helpful and constructive suggestions regarding how to improve the manuscript. The manuscript was revised carefully after considering the two reviewers' comments. Our responses are provided below in dark blue (and quoted texts added to the revision in italics), with the reviewer's comments included in black.

Reviewer #2:

I find this manuscript confusing and the conclusions over-reaching the actual findings. The authors appear to see a net deposition flux of Br- to snowpack in one year (2019) and a much smaller one in the prior year (2018). The trend of net bromide deposition in 2019 appears to be out of error estimates. Beyond these solid findings, I think that the manuscript does not make clear arguments for how the net deposition flux of Br- is relevant to snowpack emission. Multiple other studies have shown that illuminated snowpack emits reactive halogens, and we know that reactive halogen eventually convert back to halides and deposit to snowpack. If these two processes (emission and deposition) are in balance, then the net deposition to snowpack can be near zero. Their finding of only small net deposition is not in conflict with other studies showing snowpack is a source of reactive bromine, and their finding of small net deposition does not preclude snowpack playing a significant role in reactive halogen production.

Response: We thank you for the constructive comments. To answer your questions raised, we performed further mass balance analysis for bromine in both surface snow and lower troposphere (<4km). As you will find below (a new section 3.7 is added in the revised manuscript) the new analysis still strongly indicates that surface snowpack in Eureka is not a large source of reactive bromine in March. Therefore, our major conclusion made previously remains unchanged.

Error analysis:

Aspects reported in this manuscript seem to be smaller than detection limits. On line 203, it is stated that the limit of detection (LOD) for Br- is 0.2 micromolar. It appears from the slope analysis (main text says it is Table S4, but it appears to be Table S5) that there are enough data points and a long enough time window (about 5-20 March in 2019) to get the slopes to be statistically significant despite this error on Br-.

Response: This is very true; we carefully designed the experiment by collecting daily snow samples over a relatively long period (of 3-4 weeks) with an aim of detecting the possible accumulative change.

Mass balance considerations:

Considering the Br- LOD (0.2 micromole / L) in comparison to the atmospheric column of BrO is instructive. Say the top 1.5cm of snow had density 0.3 g cm^-3 (from Figure S2), then the LOD of Br- (0.2 micromole / L) would be equivalent to: 0.2e-6 mole / 1000 cm^-3 water * 0.3 cm^3 water / 1 cm^3 snow * 1.5cm snow * 6.022e23 molecule / mole = 5e13 molecule cm^-2, which is comparable to the larger BrO partial columns. This calculation just points out that errors on the Br- analysis greatly complicate the interpretation of these data with respect to bromine activation.

Response: You are right, the LOD for bromide analysis is relatively large, almost ten times the average daily change of bromide in surface snow (~0.024 micromolar). A major reason why we performed snow sampling over a period of 3-4 weeks is to derive the possible large long-term trend instead of the small short-term variation.

Tray comparison:

When considering the surface snow, if there was one-way deposition of a species, it would build up in the snowpack and have an increase as is detected for Br- in the top snow, let's say at the 0.024 micromolar / day rate, so 0.024 micromolar is gained every day. It is not clear in the text, but one might assume that the tray samples are swept clean at each (daily) sampling, so there would not be an integration of the Br- over a longer period, but the tray would only have 0.024 micromolar of Br- in it each day. That would seem to say that there should not be a slope of the tray samples, but only a small fixed amount each day.

On the other hand, if there was an increasing flux of atmospheric Br- over this period, which Figure S1 shows to be a period of greatly increasing UV intensity, it might lead to an increasing amount of Br- in the tray deposit samples. One would then expect that the snowpack would be gaining Br- with an accelerating rate (because more Br- is coming down according to the daily tray samples), but that is not observed, possibly because the snowpack is producing reactive halogens that reduce the concentration of Br- in the snow, and we should not consider the deposition to be "one way".

Response: In the revised version, we added one sentence: *"The trays were swept clean daily after sampling using a clean brush"*.

Since the tray at 0PAL was mounted at a height of ~1 m above the ground (at PEARL, it was ~11 m above the ground and ~1.5 m above the building roof), during the ~24 hours period, snow samples collected were unavoidably influenced by surface snow under stronger winds. In section 2.2 we already stated that *"In windy conditions, most of the samples collected by trays consist of blowing snow particles"*. For this reason, we do not treat tray samples completely different from the skin layer snow. Almost same slope values were observed in the first snow layer and in tray samples, see Figures 6&7.

To address your question regarding whether the deposition is "one-way" or "two-way", we added a new section 3.7 (below) for bromine mass balance analysis:

"3.7 Bromine mass balance analysis

For gas-phase bromine (as a family), its concentration C_{air} in the air can be expressed as:

$$\frac{dC_{air}}{dt} = P_{air} - \frac{C_{air}}{\tau_{air}} \qquad\qquad (R7)$$

where P_{air} is the emission flux of reactive bromine from snowpack and τ_{air} is the lifetime of bromine species in the air. The second term $\frac{C_{air}}{\tau_{air}}$ on the right side represents removal of bromine from the air via deposition. At an equilibrium state, concentration C_{air} will reach a stable level($=P_{air} \times \tau_{air}$). However, from Figures 5(c) and 6(c), we see a significant decreasing tend of BrO partial column, indicating the input term P_{air} is much smaller than the loss term $\frac{C_{air}}{\tau_{air}}$. If we take the linear decreasing slope of(-7.21±0.38)×10¹¹ molecules cm^{-2} d^{-1} in 2018,

and $(-3.03\pm0.05)\times10^{11}$ molecules cm^{-2} d^{-1} in 2019 (see below), and apply a 30% partitioning of BrO in total gas bromine species as calculated by models (Legrand et al., 2016), then the loss rate of total bromine species is of $(-2.52\pm0.13)\times10^{7}$ molecules cm^{-2} s^{-1} in 2018 and $(-1.05\pm0.02)\times10^{7}$ molecules cm^{-2} s^{-1} in 2019. The 2019 loss flux is in good agreement with the derived snow bromide deposition flux of $(1.01\pm0.48)\times10^{7}$ molecules cm^{-2} s^{-1}, implying the snow bromide is a deposit of atmospheric gas-phase bromine.

In addition, this linear decreasing trend can be re-expressed by an exponential function, as a mathematical solution of R7. For example, 2018 BrO follows an exponential function of exp(-0.059×t) and the 2019 BrO follows a function of exp (-0.024×t) with very similar R values to the linear regressions (see Figures 5(c) and 6(c)). From this we can derive a lifetime of ~17 days in 2018 and ~42 days in 2019, which are about 2-10 times the model-derived global mean lifetimes of ~10 days (von Glasow et al., 2004) and 4-5 days (Yang et al., 2005).

Similarly, for snow bromide concentration C_{snow}, its time-dependent evolution can be expressed as:

$$\frac{dc_{snow}}{dt} = P_{snow} - \frac{c_{snow}}{\tau_{snow}} \qquad (R8)$$

where P_{snow} is the snow bromide input from the air, which equals the gas-phase bromine loss term $\frac{c_{air}}{\tau_{air}}$ in R7, and τ_{snow} is the lifetime of snow bromide. The second term $\frac{c_{snow}}{\tau_{snow}}$ on the right side represents release of snow bromide (via photochemistry), which equals the input term P_{air} in R7. At a photochemical steady state and under the assumption that snow bromide lifetime τ_{snow} does not change much during the measurement period, a constant $C_{snow}=P_{snow}\times\tau_{snow}$ is expected. However, Figure 6 indicates that C_{snow} increases linearly, suggesting the input term P_{snow} is much larger than the loss term $\frac{c_{snow}}{\tau_{snow}}$, (namely the daytime photochemical release of bromide from the surface snow must be much smaller than the deposited bromide).

If we assume the net increase of bromide in the surface snow layer is roughly balanced by the release of reactive bromine from the whole snow column, then a rough bromine mass balance could be reached. This means the emission flux of reactive bromine from snowpack photochemistry is about the same as the deposited bromide flux of $(1.01\pm0.48)\times10^{7}$ molecules cm^{-2} s^{-1} at sea level. But this emission flux will balance the gas-phase bromine removal flux of $(-1.05\pm0.002)\times10^{7}$ molecules cm^{-2} s^{-1} and should result in a stable atmospheric bromine level rather than a decreased BrO trend as observed, unless the BrO partitioning in total bromine species decreases with time in early spring (March here). Otherwise, we must conclude that deposition of bromide to surface snow is more likely "one-way", namely the photochemical release of reactive bromine from snowpack must be very weak, and much smaller than the derived deposition flux on the order of 1×10^{7} molecules cm^{-2} s^{-1}.
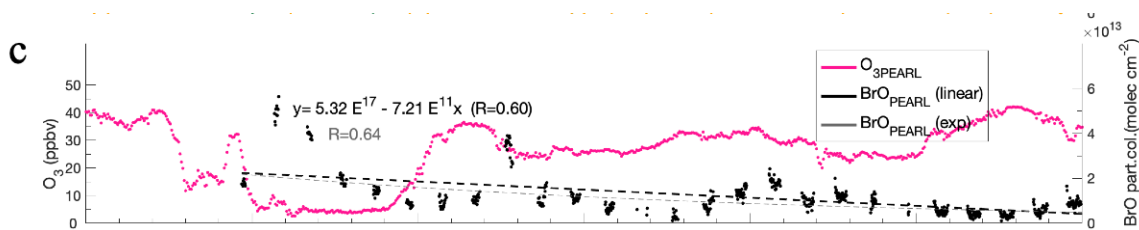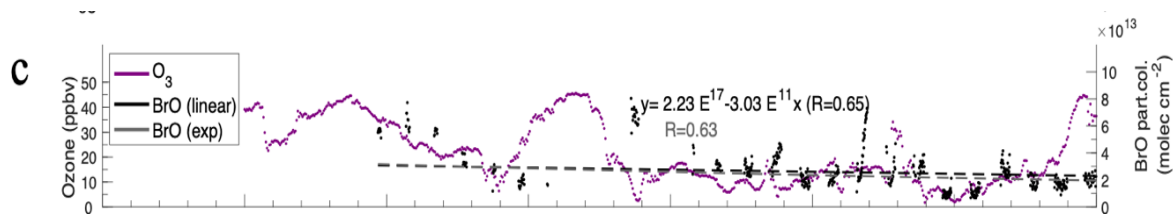
c

$y = 2.23 E^{17} - 3.03 E^{11} x$ (R=0.65)
R=0.63

Morning / afternoon differences:

Lines 463-471 are not very clear to me. They say that "signals are not significant across all sampling sites". From the text, it appears that all of the mentioned differences between morning and afternoon are well below the mutual error of the morning and afternoon samples. For example, on line 464, it says that morning is 0.25+/-0.12 micromolar, and afternoon is 0.23+/-0.21 micromolar. From these error bars, I would say that these numbers are the same. If they want to state that they are different, they would need to give numbers of data points and do careful statistics. Similarly, looking at Figure 8, visually examining the points, it seems 3-4 points on this plot, and the error bars seem to overlap a lot, but I cannot tell which error bar goes with which. I think that the morning/afternoon difference needs a clearer plot and an error analysis to be convincing. This section then concludes by reporting: "Based on the above numbers, a mean daytime bromide loss rate of 0.027 micromolar at sea level was obtained." I don't see how they put these conflicting numbers, all seemingly below error bars to finally result in a number that is about a factor of 7 below their Br- detection limit. Overall, this photochemical difference would need a better explanation to be believable.

Response: Figure 8 is updated and shown below, together with a new Table S6 added (shown below) for updated statistical data for morning and afternoon samples. We agree with you that due to the large error bars it is impossible to detect any signal in statistic confidence of the morning/afternoon difference (for both bromide and nitrate). Therefore, we rewrote section 3.5 and avoided claiming that daytime photochemistry signals were detected. We also deleted the relevant discussion on this in section 4.

New Figure 8. Figure 8. Morning and afternoon nss[Br⁻] and [NO₃⁻] from available snow samples collected between March 3-16, 2019. Note that only the mean values with p<0.1 (in Table S6) are shown and used for the morning-afternoon difference calculation.
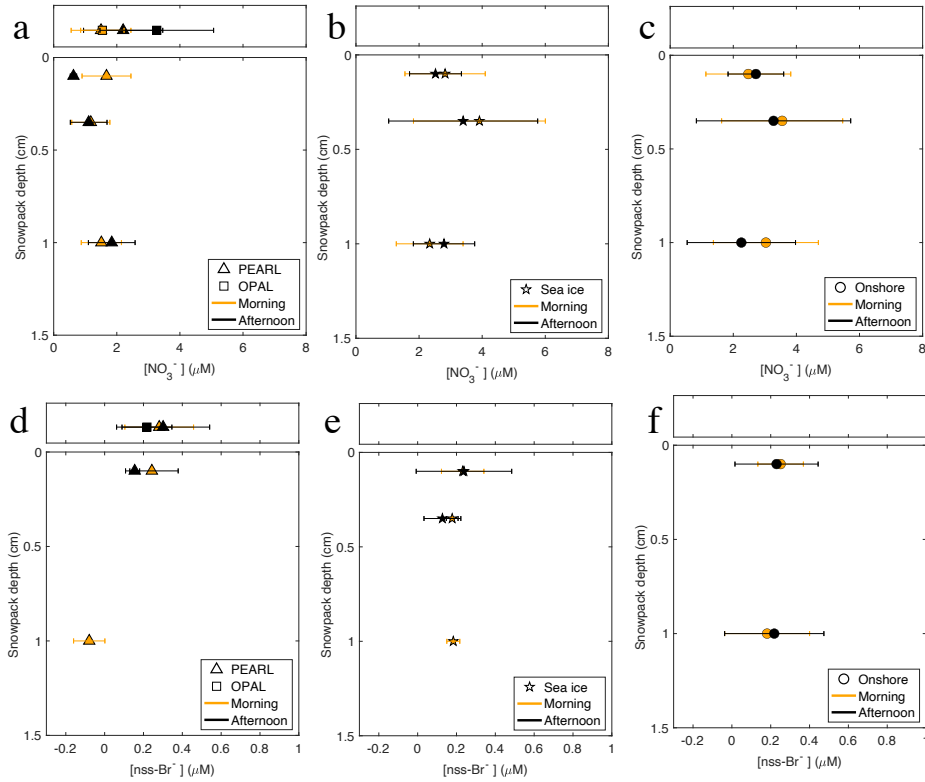
Table S6: Nitrate and bromide analysis between morning and afternoon samples (i.e., mean(μM), one standard deviation(μM), number of observations, and *p*-values) for Figure 8.

			Morning				Afternoon			
			Mean	STD	N	p-value	Mean	STD	N	p-value
[NO₃] (μM)	Tray	PEARL	1.50	0.95	4	0.050	2.20	1.25	9	0.001
		OPAL	1.54	0.69	5	0.007	3.27	1.80	8	0.001
	0-0.2cm	Sea ice	2.83	1.27	14	1.48E-06	2.52	0.82	8	5.43E-05
		Onshore	2.48	1.34	12	5.23E-05	2.72	0.88	8	5.26E-05
		PEARL	1.67	0.77	4	0.023	0.63	0.10	2	0.072
	0.2-0.5cm	Sea ice	3.91	2.09	14	9.27E-06	3.40	2.36	10	0.001
		Onshore	3.55	1.92	14	1.05E-05	3.28	2.45	12	0.001
		PEARL	1.18	0.60	11	7.29E-05	1.11	0.58	5	0.013
	0.5-1.5cm	Sea ice	2.34	1.06	16	2.49E-07	2.79	0.97	10	7.90E-06
		Onshore	3.03	1.66	13	2.63E-05	2.26	1.72	14	2.82E-04
		PEARL	1.51	0.64	17	3.72E-08	1.84	0.74	5	0.005
[nss-Br] (μM)	Tray	PEARL	0.28	0.18	8	0.003	0.30	0.24	9	0.005
		OPAL	0.04	0.09	6	0.340	0.22	0.13	10	4.55E-04
	0-0.2cm	Sea ice	0.23	0.11	13	5.88E-06	0.24	0.25	8	0.029
		Onshore	0.25	0.12	12	1.31E-05	0.23	0.21	8	0.019
		PEARL	0.24	0.14	12	6.56E-05	0.15	0.03	4	0.001
	0.2-0.5cm	Sea ice	0.18	0.03	10	1.73E-08	0.13	0.09	6	0.022
		Onshore	0.01	0.27	14	0.852	0.06	0.22	11	0.404
		PEARL	0.01	0.13	10	0.783	0.04	0.11	5	0.400
	0.5-1.5cm	Sea ice	0.18	0.03	4	0.002	NaN	NaN	NaN	NaN
		Onshore	0.18	0.22	16	0.005	0.22	0.26	12	0.013
		PEARL	-0.08	0.08	11	0.008	-0.05	0.11	5	0.329

Tray samples mass balance problems:

On lines 472-479, it is discussed that trays appear to gain Br- and NO3- over the day. If you wanted to try to compare the trays to snowpack, one would need to consider the amount of snow in each reservoir to calculate the mass of Br- in the tray and then compare to the mass of Br- in say the top of the snow pack. If there is not a lot of water mass in the tray, then a

small addition of Br- (mass) could increase its concentration much more than it would affect the larger reservoir of snow pack. If they want to try to make a mass balance consideration of snowpack bromide emission and uptake of atmospheric particles, they need to consider the sizes of the reservoirs.

Response: It is true that the amount of water mass could affect the concentration. In the revised version, we added a new sentence in section 3.5 to highlight this effect:

"The enhancement of tray sample's concentrations is likely due to the small amount of snow water collected by trays; the small addition of bromide deposited could increase its concentration much more than it would affect the large reservoir of surface snow."

Deposition fluxes:

Section 3.5 attempts to calculate the net deposition flux of bromide from the increase in bromide in the top layers of snow. They get a deposition flux at sea level, but don't have an error bar on this number. From the standard deviation of the slopes given in Table S5, this should be possible to be calculated. The slope errors appear to be on the order of 0.009 micromolar Br- / day. If I compare that to the surface snow slope of about 0.02 micromolar Br- / day, that would be a fractional error of 0.009 / 0.02 = 0.45 or 45% relative error. Therefore, my ball park calculation would indicate that the deposition flux is (1.01 +/- 0.45) x 10^7 molecule cm^-2 s^-1. It appears unlikely that PEARL's error would be very different, so I'm not at all convinced that the quoted "At PEARL, the integrated flux is 7.9 x 10^-6 molecule cm^-2 s^-1, which is ~20% lower than at sea level." is actually true outside of mutual errors. They then go on to say that this proves that snowpack at sea level is not a large source of reactive bromine.

Response: In the revised manuscript section 3.6, we added error bars for both bromide and nitrate fluxes. *For nitrate, "According to the statistical analysis results shown in Table S5, we can work out a mean slope error of 0.066 at sea level and 0.019 $\mu M\ d^{-1}$ at PEARL. If we compare that to the average slopes derived of 0.28 $\mu M\ d^{-1}$ at sea level and -0.018 $\mu M\ d^{-1}$, we can work out relative errors of 37% at sea level and 95% at PEARL. Therefore, we have an integrated nitrate deposition flux of $(2.6\pm0.37)\times10^8$ molecules $cm^{-2}\ s^{-1}$ at sea level and $(-1.0\pm1.06)\times10^8$ molecules $cm^{-2}\ s^{-1}$ at PEARL. These results indicate that surface snow at sea level is a net sink of atmospheric nitrate, and at the hilltop it is a source of reactive nitrogen; however, the negative flux derived at PEARL has a large error bar, indicating the flux has a large uncertainty."*

For bromide: "Similarly, from Table S5 we can derive a mean slope error of 0.0096 $\mu M\ d^{-1}$ at sea level and 0.0059 $\mu M\ d^{-1}$ at PEARL (for the top two layers). If we compare that to the average slope of 0.02 $\mu M\ d^{-1}$ at sea level and 0.015 $\mu M\ d^{-1}$ at PEARL, we have relative errors of 48% at sea level and 39% at PEARL. Therefore the integrated bromide flux is $(1.01\pm0.48)\times10^7$ molecules $cm^{-2}\ s^{-1}$ at sea level and $(0.79\pm0.31)\times10^7$ molecules $cm^{-2}\ s^{-1}$ at PEARL."

The small bromide deposition flux difference (<20%) between sea level and the hilltop indicates that these two sites likely underwent very similar bromine influence. If snowpack in the boundary layer is a large direct source of reactive bromine as proposed, then an enhanced gas-phase bromine loading in boundary layer is expected and should result in an enhanced deposition flux of bromide to surface snow at sea level. However, this is seen in the data. For

this reason, we say that local snowpack at sea level is not likely a large source of reactive bromine.

In Section 3.5, discussing (net) deposition flux of Br-, they make the statement "Therefore, if local snowpack on sea ice in the fiord is a large source of reactive bromine, an enhanced deposition flux at sea level should be detected." Other studies have shown that snowpack produces reactive bromine, which of course depletes snowpack of Br-. Therefore, the snowpack at sea level would be expected to be losing Br- by snowpack photochemistry, which they even claim to observe. Some or all of this later re-deposits, and if the net cycle of snowpack production followed by deposition are in balance, then the net trend of Br- in the snowpack would be very small. They show a very small net deposition flux of Br- in the snowpack, which can be perfectly consistent with snowpack production of reactive Br that then does atmospheric chemistry and eventually is converted back to Br- and deposits back to the snowpack. If snowpack 50km offshore produced reactive bromine through snowpack photochemistry, some of that could transport to their study region in a few hours (at 5m/s wind, 50km is traversed in under 3 hours), and then deposit explaining their small net deposition flux.

Response: The transport of air masses from bromine rich area over sea ice to inland does change the mass balance in both the atmosphere and the snowpack. In the revised version section 4 we added a paragraph to discuss it issue:

" It is reasonable to assume that a rough balance of bromine can be reached in both the atmosphere and the snowpack over the sea ice zone. However, once bromine rich air masses transport from sea ice into inland tundra areas, the bromine budget balance breaks down. In particular, air starts to lose gas-phase bromine and snow begins to gain extra bromide from the air, as we observed at Eureka. However, if quick photochemical equilibrium is reached in surface snow, then we should see a stable bromide concentration in snow. The same goes for gas-phase bromine in the air. However, the significant decrease in BrO partial column in the lower troposphere and the increase in surface snow bromide strongly indicate that they do not reach a photochemical equilibrium state in early spring. Moreover, the significant trends show that it is very likely that snow photochemical release of reactive bromine is a very weak process, and the emission flux must be much smaller than the derived removal flux for gas-phase bromine and the snow bromide deposition flux, which is around 1×10^7 molecules cm^{-2} s^{-1}. "

Nitrate -- bromide relationship:

I don't understand what the sentence from line 521-523 means, and they say that the data is not shown. If they want to make some claim, they should show data for it.

Response: A new Figure S7 is added (see below) to the revised manuscript to demonstrate the relationship between surface snow sodium and bromide at Sea ice and Onshore sites. We added new words in section 3.8 to describe it:

"Figure S7 shows that at the Onshore site surface snow sodium and bromide are not significantly correlated apart from in the third layer. At Sea ice, surface snow sodium and bromide are largely correlated but with $[Br^-]/[Na^+]$ ratios larger than the sea water ratio (~0.0065) indicating that surface snow gains bromide from the air at Eureka, which is generally in line with the finding at coastal Alaska (Simpson et al., 2005)."
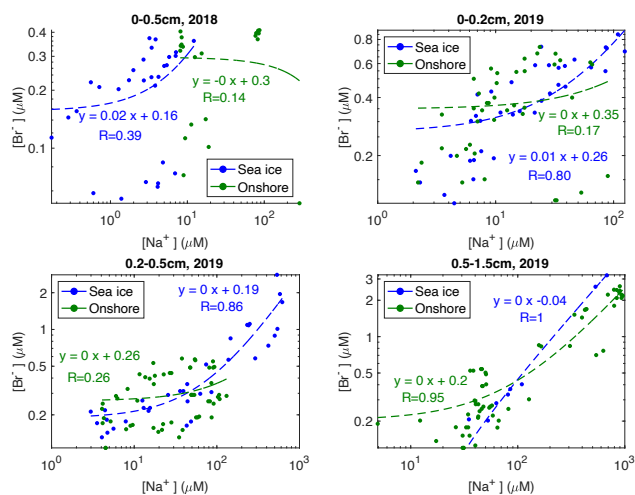
Figure S7: Relationship between surface snow bromide and sodium at Sea ice and Onshore sites: (a) 0-0.5 cm (2018); (b) 0-0.2 cm (2019); (c) 0.2-0.5 cm (2019); and (d) 0.5-1.5 cm (2019).

Similarly, the discussion made later in this section states "the ratio of [NO3-]/[Br-] ranges form 3.5-6.8, indicating that one molecule of bromide deposited to the surface is likely accompanied by 4-7 nitrate molecules." They don't take into account that only the net deposition is being measured in their studies. Given that they don't get at underlying emission and deposition, I don't understand how to make sense of this ratio in terms of gas-phase chemistry (R1 and R2).

Response: In the revised version section 1, we rewrote the relevant paragraph:

"It is well-known that BrO_X can directly react with NO_X via the following reactions R1 and R2:

$$BrO(g) + NO_2(g) \rightarrow BrONO_2(g) \qquad\qquad (R1)$$

$$BrONO_2(g) + H_2O(aq) \rightarrow HNO_3(g) + HOBr(g) \qquad\qquad (R2)$$
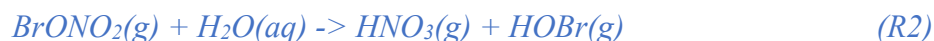
The product HOBr in R2 can photolyze to reform Br atoms (R3) which then react with ozone to form BrO (R4) to further oxidise NO_X in R1.

$$HOBr(g) + h\nu \rightarrow Br(g) + OH(g) \qquad\qquad (R3)$$

$$Br(g) + O_3(g) \rightarrow BrO(g) + O_2(g) \qquad\qquad (R4)$$

Therefore, the net reaction of R1-R4 is:
$$NO_2(g) + O_3(g) + H_2O(aq) + h\nu \rightarrow HNO_3(g) + O_2(g) \qquad\qquad (R5).$$

This means that under sunlight and in the presence of bromine, ozone and NO_X molecules will be consumed effectively via chain reactions. Thus, the presence of BrO_X may accelerate the conversion from NOx to nitrate and influence the atmospheric nitrogen budget."

In revised section 3.8, we added further discussion:

"In early spring, due to the small solar zenith angle, atmospheric OH is very low, and the dominant pathway of oxidising NOx to form nitrate is via the chain reactions R1-R4. From the net reaction in R5 we can see that without net consumption of bromine, NOx and ozone can be effectively consumed, which means more than one NOx molecule can be converted to nitrate per bromine atom. Figure 9 shows that the ratio of $[NO_3^-]/[Br^-]$ ranges from 3.5–6.8, indicating that one molecule of bromide deposited to the surface is likely accompanied by 4–7 nitrate molecules, attributed to the fast recycling of gas-phase bromine species before they deposit to the surface snow."

Two-way fluxes:

Literature has long supported a snowpack source of NOx from nitrate photochemistry. This will cause a flux out of the snowpack. NOx can also convert back to nitrate, which has a fast deposition velocity and will deposit back to snowpack. They don't measure the flux of nitrate being lost from the snowpack photochemically, but only the "net" flux that is the deposition minus the loss. Similarly, for Br-, they only measure the net deposition flux, not either production or loss individually. It is not at all clear that this work has truly quantified the daytime loss of Br- from snowpack, and even if they did measure the net loss during daytime, there could still be faster emission plus some deposition during the day that could make the snowpack production rate faster than their daytime snowpack Br- loss. I think that the discussion in lines 550-578 may be trying to do a calculation to split their net deposition into component true emission and true deposition fluxes, but I cannot follow what they are saying here. In addition to not being able to follow it, the whole discussion seems to be built upon the "daytime loss" of 0.027 micromolar, which had no error analysis and doesn't appear significant from Figure 8. Overall, I think that the discussion in this section is not clear enough that I can even diagnose if their reactive bromine emission flux is realistic or if the range listed is based upon realistic error estimates.

Response: Thank you again for the in-depth thought on this. As discussed previously, due to the large error bars we could not derive robust conclusion regarding the daytime bromide loss, thus relevant text and discussions are modified in the revised manuscript.

The new mass balance analysis (shown above) indicates that photochemical loss of snow bromide is much weaker than we thought, and the emission flux of reactive bromine should be much smaller than the deposition flux of bromine from the air and to the surface snow (which is about 1×10^7 molecules cm^{-2} s^{-1}). Therefore, the deposition of bromide to surface snow is more likely a "one-way" flux, rather than a "two-way".

Overall:

I think that this manuscript would need major revisions with improved error analysis and clearer discussion of how the observed net deposition flux is split into emission and deposition fluxes to be acceptable.

Response: We rewrote the relevant parts according to your suggestions with added new data and analysis, and hopefully they make our points much clear and make sense.