Reply to Reviewers' Comments

We thank Editor Dr. Jayan Kuttippurath and two reviewers for their comments on an earlier version of the manuscript. We have carefully considered all the comments and revised the manuscript accordingly.

Below we provide a detailed, point-by-point list of our reply to all the comments. The comments from the reviewers are shown in **bold** text, and our responses in normal text. We also show in blue the revised text as it appears in the revised manuscript. The page and line numbers in the reviewers' comments refer to the previous version, whereas those in this reply refer to the latest revised manuscript.

Reviewer #1:

[No further comments. Recommended the manuscript be accepted as is.]

Reviewer #2:

Gao et al present a revision of their manuscript describing observations of ozone loss above snow in an outdoor mesocosm experiment. The change of phrasing to "in-tube air" and "boundary layer air", in particular, is very helpful in clarifying the discussion and results. The addition of the GEM measurements in Dec 2020 and associated simultaneously observed GEM and O_3 depletion is highly compelling for the role of Br chemistry and a great addition to the manuscript. As discussed below, the manuscript would be further significantly strengthened by quantitative calculations of the contribution of NO titration by O_3 (when NO_x data were available) to indirectly, quantitatively calculate the expected contribution by Br (see below for details). Line numbers below refer to the track changes version of the manuscript.

In response to the reviewer #1 point about likely NO_x influence, the authors added NO and NO_2 ambient observational data, which is excellent, in Figure S3, which also shows ozone in the ambient air (ppb), and ozone loss (%) within in-tube air. NO_x often increased to 30-40 ppb, and sometimes higher, and during these periods O_3 typically declined by 10-30 ppb, as shown in Figure S3. The largest ozone losses (%) within the in-tube air appeared to occur simultaneously with the ambient ozone reductions and NO_x peaks (e.g. Mar 4, 6, 9, 10, 12). The authors state, however, in their response that "we believe NO_x, either from ambient air or snowpack photochemistry, has limited influence on the O_3 depletion patterns discussion in this manuscript." (Similar wording is presented in the new text on Lines 310-317 of the manuscript.) However, no calculations are presented to quantify the O_3 loss due to NO titration in the in-tube air to support this statement, and the data in the Figure S3 do not appear to support the authors' assertion of a lack of temporal correlation between NO_x and O_3 loss. Such calculations are necessary to quantify the loss of ozone by reaction with NO (which is photochemically produced) given the common correlation between O_3 loss and NO_x in the ambient air, as well as the very high [NO_x] levels observed in this work. If a large fraction of the O_3 loss cannot be accounted for by NO titration, this would quantitatively

support the authors' assertion. Examination of the O_3 loss rates for each depletion period would also be helpful for this evaluation and useful for quantifying the role of Br. It would also be helpful for the absolute [O_3] within the in-tube air to be included in Figure S3.

We agree and have made several revisions to clarify the role of NO_x chemistry in the O_3 dynamics. First, the original Fig. S3 has been updated (see Fig. 1 in this reply). The NO_x graph has been changed to have the same resolution (10-minute) as the O_3 loss measurements, instead of the one-minute resolution in the previous version. Absolute O_3 loss (ppbv) has also been provided, which shows a very similar trend as the normalized O_3 loss (%). The use of absolute O_3 loss removes some overestimated O_3 loss (%) points when the ambient O_3 is mostly depleted (< 5 ppbv) (e.g., on March 4, 6 and 11).

For O_3 in the ambient air, ambient O_3 troughs were often observed with NO peaks, most of which were during night (20:00 to 7:00; local time) when O_3 in the ambient air was largely depleted (< 10 ppbv). This observation can be explained by the NO + O_3 reaction and the ambient air dynamics during night. Occasionally, a sharp increase of NO_x in the ambient air and a small scale of O_3 depletion in both the ambient air and in-tube air were observed during daytime, which are most likely caused by the occasional use of vehicles within the SERF facility (e.g., 12:00 on March 6 and 9, see Fig. 2).

In this manuscript, we studied the ozone loss (ΔO_3) by comparing between different locations (the ambient air vs. in-tube air; the UV-transmitting tube vs. UV-blocking tube). For ΔO_3 within the in-tube air (the ambient air vs. in-tube air), the ambient air can be considered as a control group while the in-tube air is the experimental group that examines the influence from sea ice and the acrylic tube. Since the tube was open to the ambient environment, we consider similar air mass for both the ambient air and in-tube air, including NO_x from urban signal that was already present in the background ambient air. This assumption is also supported by overall similar O_3 trends observed between the ambient air and in-tube air (see Fig. 3a in the revised manuscript and Fig. 2 in this reply). In this case, NO titration (mainly produced from urban signals) would equally affect O_3 dynamics in the ambient air and in-tube air, which is an offset process when studying ΔO_3 via the comparison between the ambient air and in-tube air. Thus, such ΔO_3 should not be affected by variations of NO_x in the background ambient air. Since the ΔO_3 within the in-tube air examines the influence from sea ice, NO_x production via snowpack photochemistry may be important, yet this process is considered negligible due to the low concentrations of nitrite and nitrate found in surface ice and saline snow samples as discussed in the manuscript. Then, NO_x that may influence O_3 dynamics is only expected from urban signals (the background ambient air) and should have little influence on the ΔO_3 within the in-tube air. Furthermore, when we compare O_3 between the UV-transmitting and UV-blocking tubes, we consider both in-tube air masses are similar and background NO_x would affect both to a similar extent whereas the only variable being examined is the UV radiation. We thus believe our general assumption that variations of NO_x in the background ambient air do not affect ΔO_3 obtained from comparisons is sound.

The assumption that the air mass between the ambient air and in-tube air was similar is challenged when there was a sudden and rapid disturbance (e.g., occasional use of vehicles within the facility). In this case, the vehicle exhaust signal was readily captured in the ambient air, whereas the in-tube air was less affected due to a lack of rapid air mixing. During daytime, O_3 can be produced from oxidation of hydrocarbons in the vehicle exhaust or NO_2 photochemistry. This increased O_3 signal (within 20 minutes from the vehicle use) could be immediately observed as a lesser extent of O_3 depletion in the ambient air at the beginning of the disturbance, whereas such O_3 increase was not necessarily captured in the in-tube air due to a lack of rapid air mixing. This condition would overestimate ΔO_3 and result in those abnormal high values out of the general ΔO_3 trend observed around 12:00 on March 6 and 9 (shaded areas in Fig. 2). NO produced from on-site use of vehicles could subsequently cause small-scale O_3 depletion in both the ambient air and in-tube air. However, during each day, the ΔO_3 was observed before the sharp increase of NO_x and continued until sunset, indicating that daytime NO_x production due to on-site use of vehicles was not the main driver for ΔO_3 within the in-tube air.

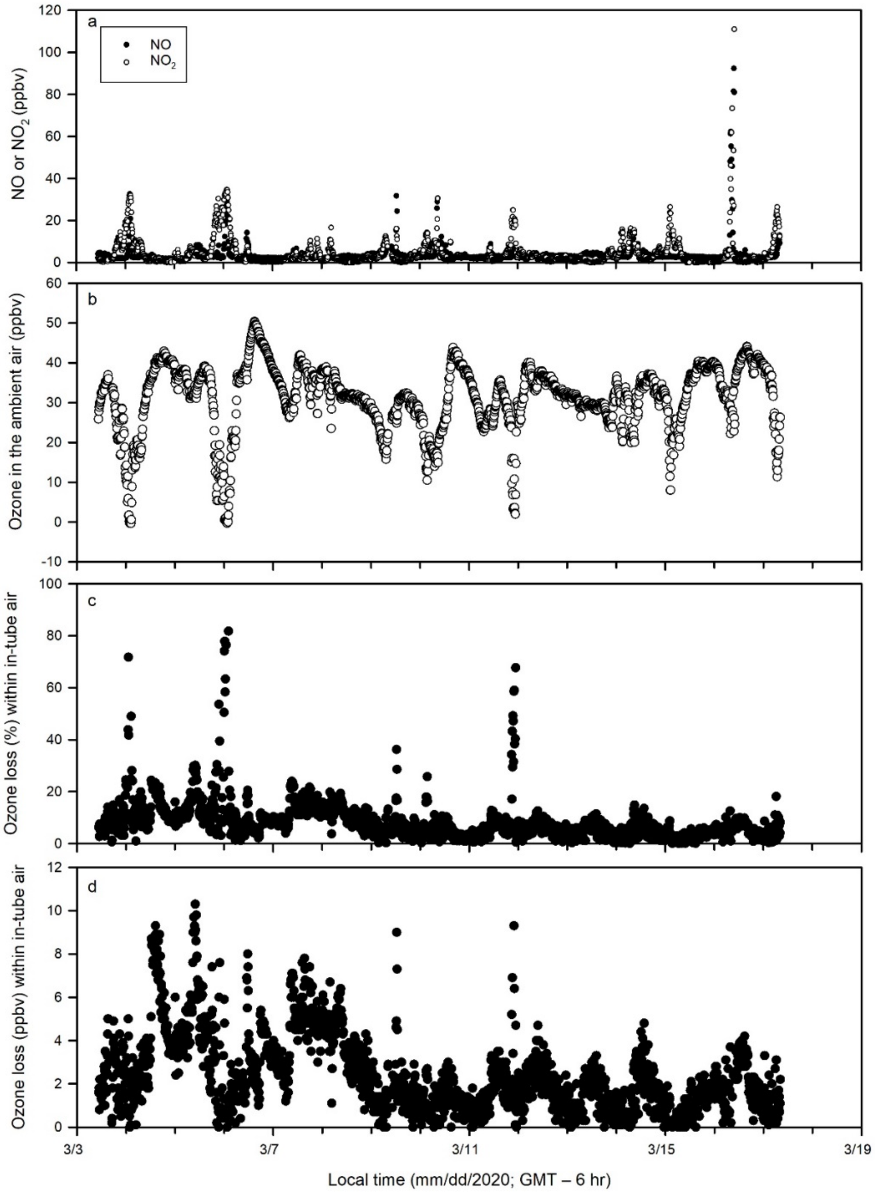

Figure 1. Temporal changes of (a) NO_x ($NO + NO_2$) in the ambient air; (b) ozone in the ambient air; (c) ozone loss (%) and (d) ozone loss (ppbv) (measured as the difference between the ambient air and in-tube air) during Experiment #2. (This figure has been added as Figure S3 in the Supplementary Information)

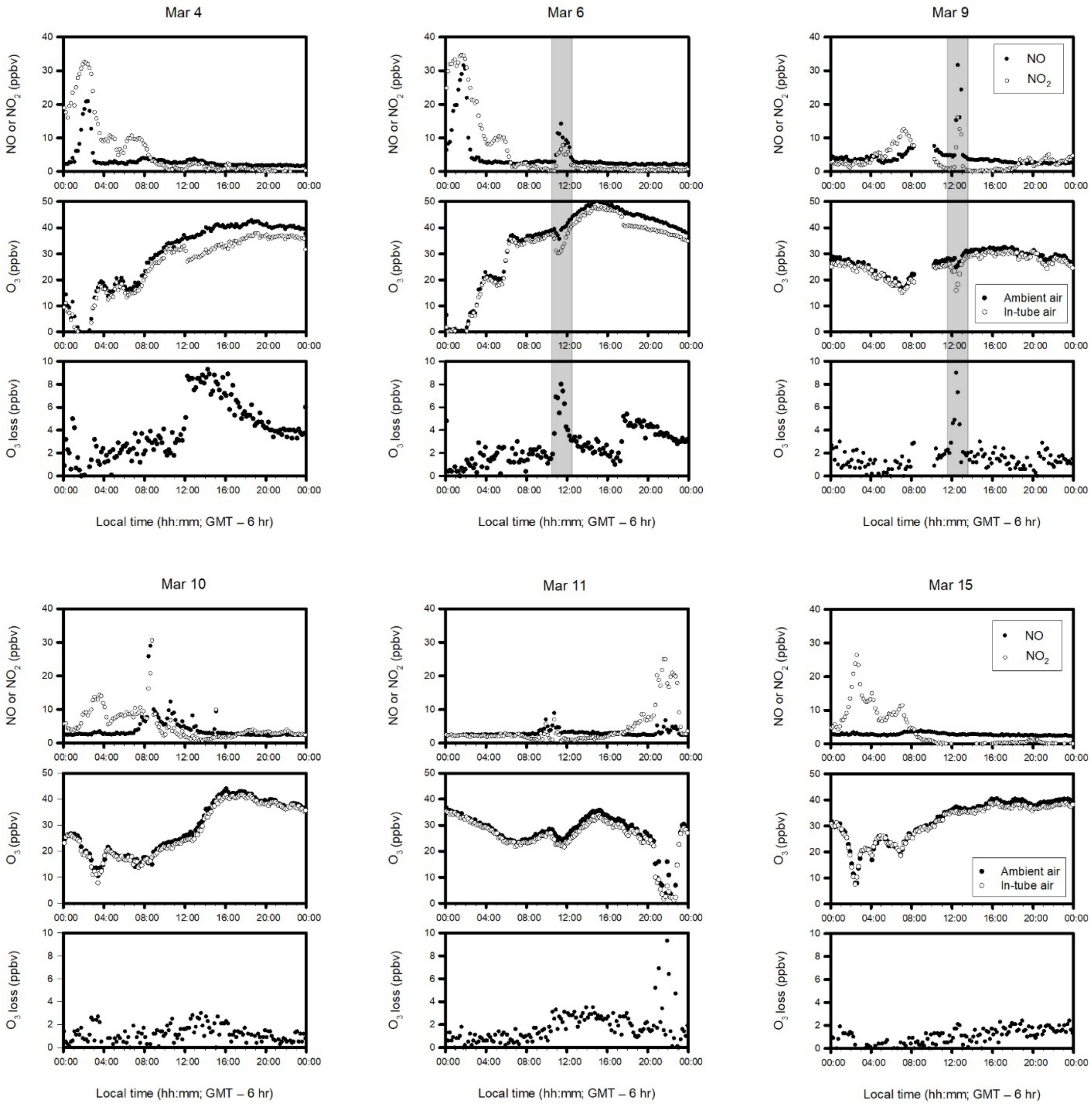

Figure 2. Temporal changes of O_3, NO, NO_2, and O_3 loss within the in-tube air (measured as the difference between the ambient air and in-tube air) during each major ambient O_3 depletion event of Experiment #2. (This figure has been added as Figure S4 in the Supplementary Information)

The reviewer pointed out that the largest ΔO_3 (%) within the in-tube air sometimes coincides with NO peaks and ambient O_3 depletions. After examining each ambient O_3 depletion period (< 20 ppbv, March 4, 6, 9, 10, 11 and 15) thoroughly with absolute ΔO_3 (ppbv), we think such temporal coincidence is not prevalent (Fig. 2). Major ambient O_3 depletions and NO peaks were mostly observed during night except those small scale O_3 depletions during daytime (see discussion above). On the other hand, ΔO_3 showed up during daytime with a diurnal pattern and the duration is generally longer than the occasional daytime NO peaks. Meanwhile, the maximal extent of ΔO_3 (ppbv) from March 9 to 16 was similar regardless of the variations of NO_x in the ambient air. Moreover, the correlation between NO concentrations and ΔO_3 (ppbv) or ΔO_3 (%) is examined and the correlation coefficient (r) is –0.18 and 0.13, respectively, suggesting no strong correlation.

Unfortunately, we currently do not have all the parameters to quantify the NO influence using a model simulation. However, the contribution from NO_x chemistry on depleting ozone can be qualitatively estimated using the NO/NO_2 ratio. When the total amount of NO_x ($NO + NO_2$) remains relative stable and without high concentrations of volatile organic compounds, the NO/NO_2 ratio would decrease if the $NO + O_3$ reaction proceeds to any substantial extent; otherwise, it would increase (Finlayson-Pitts and Pitts, 2000). In Fig. 3, typical daytime patterns are provided, which shows a distinct behavior of NO_x chemistry: the NO/NO_2 ratio increased on March 5 and 14 whereas it decreased on March 11 while NO_x stayed at a relative stable level during the observed ΔO_3 span. Based on our experimental design, ΔO_3 should not be attributed to NO_x in the ambient air, but if we assume NO_x chemistry-driven O_3 depleting process does contribute to ΔO_3 within the in-tube air, a more important contribution from NO_x chemistry would be expected on March 11 and other processes (e.g., Br chemistry) would have contributed to the ΔO_3 on March 5 and 14. Such examinations are carried out on each daytime ΔO_3 period when NO_x measurements were available (March 3 to 16), and the potential NO_x contribution to ΔO_3 (decreasing NO/NO_2 ratio during the observed ΔO_3 span) was only observed on two days (March 3 and 11).

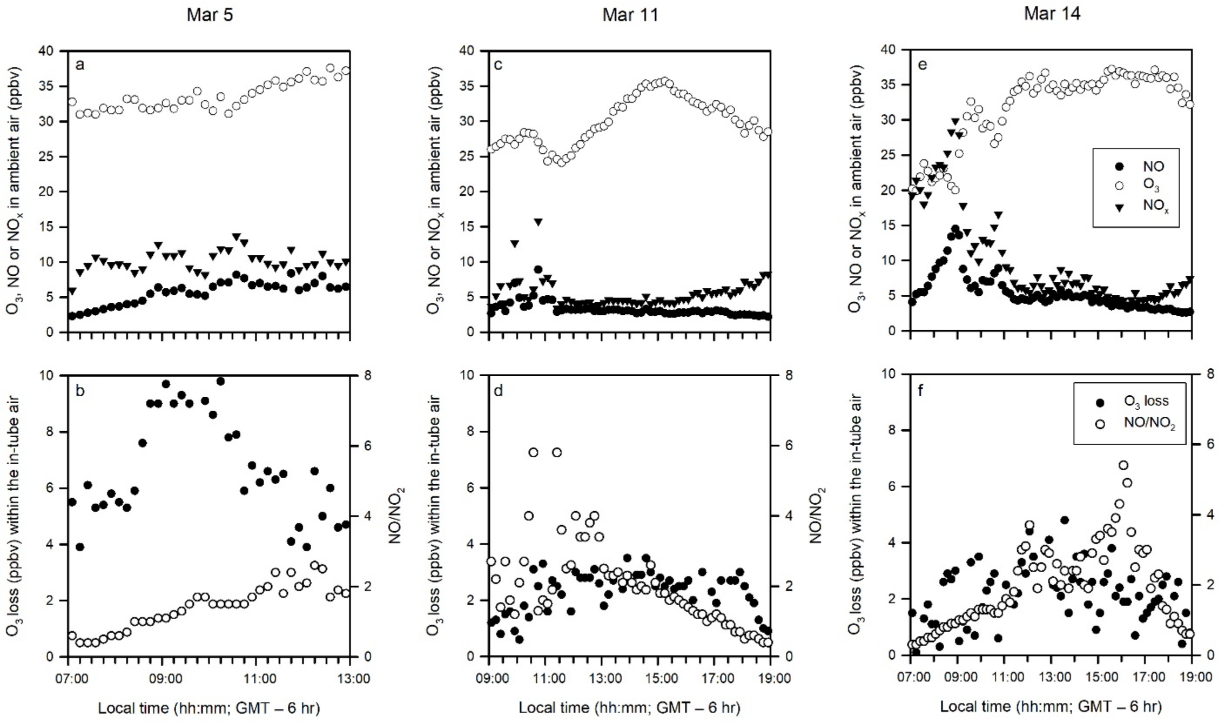

Figure 3. Temporal changes of ambient O_3, NO, NO_x, and O_3 loss within the in-tube air (measured as the difference between the ambient air and in-tube air) and NO/NO_2 ratio during the daytime O_3 loss span on March 5 (a, b), March 11 (c, d) and March 14 (e, f). (This has been added as Figure S5 in the Supplementary Information)

There is a possiblity that the ΔO_3 between the UV-transmitting and UV-blocking tubes can be affected by photochemically active NO_x chemistry, especially intiated by UV radiation. This influence, if possible, is expected to occur throughout the arcylic tube and regardless of the sea ice presence. However, the obervation that no such O_3 loss was observed at 20 cm and 40 cm above the sea ice surface or above open water surface suggests this process has minimal contribution to the cryo-photochemical ozone loss we report in the manuscript.

In conclusion, the ambient O_3 dynamics is associated with NO concentrations, especially during ambient O_3 depletions over night. However, ΔO_3 obtained from comparisons should not be attributed to variations of NO_x in the background ambient air by the experimental design and the in-situ NO_x production via snowpack photochemistry is considered negligible. Thus, NO_x produced either from the urban signal or snowpack photochemistry has limited influence on the ΔO_3 within the in-tube air. Still, if we assume NO_x chemistry does contribute to ΔO_3 within the in-tube air, the potential contribution is only indicated by a decreasing NO/NO_2 ratio on two days during the two-week Experiment #2. Since the general diurnal pattern of ΔO_3 cannot be explained by NO_x chemistry, we believe Br chemistry is most likely the main driver for ΔO_3 reported in this manuscript.

The related discussion has been added in the Supplementary Information.

In lines 309-315, the main text has been revised as: "*Yet, during the same time, ΔO_3 within the in-tube air reoccurred daily in a diurnal pattern and reached a similar extent regardless of NO concentrations. Additional discussion and figures on the potential influence of NO_x chemistry on ΔO_3 within the in-tube air can be found in the Supplementary Information. On the other hand, the in-situ NO_x production via snowpack photochemistry of nitrate and nitrite is considered negligible due to the low amount of both ions (below the detection limit) found in surface sea ice and saline snow samples. Thus, NO_x produced either from urban transportation (in the background ambient air) or snowpack photochemistry had negligible influence on ΔO_3 within the in-tube air (i.e., ozone difference between the ambient air and in-tube air inside the UV-transmitting tube).*"

In lines 336-340, the main text has been revised as: "*The observation that no such ozone loss occurred in the in-tube air when measured farther away (20 cm and 40 cm) from the sea ice surface (Fig. 5a, b) suggests that the ozone loss between two tubes is not associated with NO_x photochemistry or ozone photolysis, which should occur universally throughout the tube. Instead, it is most likely triggered by cryo-photochemical processes that involve the sea ice environment.*"

In lines 350-353, the main text has been revised as: "*Moreover, comparing ozone concentrations between tubes cancels out the variations that exist in the ambient air (e.g., background NO_x produced from urban transportation) since both tubes were open to the same air mass and the ozone dynamics in the ambient air should be equally applied to both tubes.*"

Additional Comments:

Lines 58-59: Kalnajs and Avallone (2006, Geophys. Res. Lett) is an important original reference for the suggestion that the pH of frost flowers is too high to support reactive bromine chemistry.

This paper has been added as a reference in the revised manuscript.

Lines 178-182 and Table 1 caption: Please define what the detection limit is here, since several data points in Table 1 are below the detection limit. Is this the 3*sigma of nanopure water, for example?

The detection limit was determined from 8 repetitive measurements on the least concentrated point of the calibration curve (28 µmol kg^{-1} chloride for anions and 4.3 µmol kg^{-1} sodium for cations, respectively). The detection limit was calculated as 2.998 × standard deviation of the repetitive measurements.

In lines 174-176, the main text has been revised as: *"The recovery and detection limit were determined from repetitive measurements on the least concentrated point of the calibration curve, prepared from a Dionex seven anion standard and a Dionex six cation-II standard respectively"*.

Table 1 title has been revised accordingly: *"**Table 1.** Ion composition of snow, surface ice and surface seawater during Experiment #1. DL: Detection limit calculated as 2.998 times the standard deviation determined from eight repetitive measurements on the least concentrated point of the calibration curve"*.

Figure 1: Note that BrONO2 is also thought to undergo hydrolysis in the condensed phase to produce HOBr, which then reacts to produce BrX (Aguzzi and Rossi 2002, J Phys Chem A). Also, in the caption, did the authors mean to cite Wang et al 2019 (in their reference list) instead of Wang et al 2017 here, since Wang et al 2019 (PNAS) was the first to quantitatively observe O3 and Hg(0) loss via reaction with Br? Likewise, Wang et al 2019 (PNAS) would be useful to cite on Lines 49-51 because that work included measurements of Br, BrO, Br2, and HOBr.

Figure 1 has been modified (see next page). The $BrONO_2$ hydrolysis reaction that produces HOBr on the condensed phase has been added. The reduction pathway of Hg^{II} to Hg^0 in the gas phase has been updated with a recognition of the potential role of Hg^I during the reduction. In the caption, Wang et al. (2017) (Sea Ice Book chapter) is cited as a reference for Hg chemical cycles in the polar environment. The Aguzzi and Rossi paper, Wang et al. 2019 (PNAS) paper and Saiz-Lopez et al. (2018, 2019) papers on Hg^{II} and Hg^I reduction have also been added as additional references.

Figure 8: There appears to be a typo in the caption, as part b is referred to as both ice-covered and open water. Please fix. I am assuming that the authors mean to write "open water (c, d) experiments".

This mistake has been corrected in the revised manuscript.

I am confused by the authors statement on Page 8 of their response that "no substantial snow layer above the sea ice surface was observed" (in response to the request to add shading for when snow cover was present) because the methods section and elsewhere discusses snow composition, and Lines 222-223, for example, state "…up to 4 cm of natural snow accumulation inside the tubes were observed above sea ice…".

Regarding the shading for snow cover presence, we did not record the temporal change of the snow depth and structure; instead, we only measured the depth of the snow right after the precipitation. Thus, we cannot show the exact duration for the presence of the snow cover but only the thickness of the snow cover that was measured at one time.

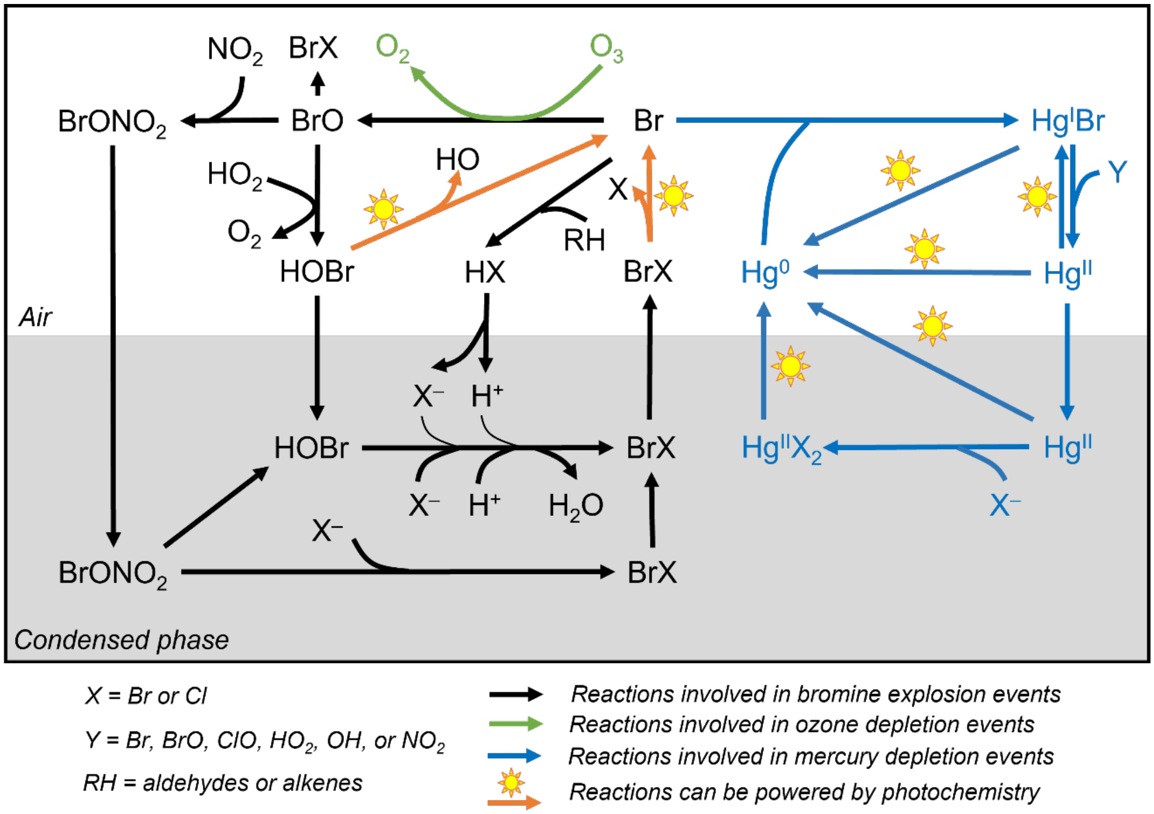

Figure 4. General reaction schemes involved in bromine explosion events, ozone depletion events and mercury depletion events in the Arctic during polar sunrise. The photochemical activation of gas-phase reactive bromine species (Br and BrO) produced from multi-phase reactions on the surface of the condensed phase causes the depletion of ozone and gaseous elemental mercury in the boundary layer air (based on Abbatt et al., 2012; Aguzzi and Rossi, 2002; Khiri et al., 2020; Saiz-Lopez et al., 2018, 2019; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2007b, 2015; F.Wang et al., 2017; S.Wang et al., 2019; Wang and Pratt, 2017). (This figure is the new revised Figure 1 in the revised manuscript)

Lines 371-372: To clarify, consider rephrasing sentence as “Pratt et al. (2013) and Peterson et al. (2019) suggested that snow Br2 production is enhanced above a Br-/Cl- mole ratio of 0.005.”

The text has been revised as suggested to avoid confusion.

In lines 367-368: *“Pratt et al. (2013) and Peterson et al. (2019) suggested Br_2 production from snow is enhanced above a ~~an optimal~~ Br^-/Cl^- mole ratio ~~threshold for Br_2 production~~ of 0.005”.*

Significant Figures in Reported Errors: The authors state in their response that they fixed the reporting of errors to be 1 significant figure throughout the manuscript, but at a quick glance, that does not appear to be the case throughout (e.g., Lines 229-231).

For NO_x and O_3 measurements, the instrument detection limit is 0.4 ppbv, and we report numbers above that and keep accuracy to 1 ppbv. For ion analysis, chloride and sodium results are reported to the first digit for most samples except for "snow over land"; for the rest ions, the results are reported to be first decimal point except for "snow over land".

Additional Revisions

In addition to the reviewer's comments, we have made the following revisions to the manuscript:

1) The unit for O_3 and NO_x data has been changed from ppb to ppbv.

2) Clarifications on the resolution of NO_x and ozone loss measurement have been added in lines 138-139: "*The quantify and normalize the ozone difference inside the UV-transmitting tube relative to other locations, the ozone loss (%) is reported for every 10 minutes and calculated by Eq (1):*"

3) In lines 154-156, the text has been revised as: "*The instrument reports data for every minute with a detection limit of 0.4 ppbv. The NO_x data reported in this study is averaged for every 10 minutes, which is the same resolution as the ozone loss (ΔO_3) measurement.*"