Dear Referee #1,

Thank you very much for reviewing our manuscript and for your constructive and valuable comments and suggestions. In the following text, our response to your comments is given in blue, whereas the corresponding revisions in the main text are highlighted in red.

Gao et al present a study of ozone loss near the surface of an outdoor mesocosm sea ice facility in Winnipeg, Canada. The sea ice facility is unique and provides an opportunity to control the formation of the sea ice with complete exposure to the atmosphere, allowing ambient snow accumulation. The comparison of O3 levels during daytime for the UV-transmitting vs UV-blocking tubes is useful. The authors attribute O3 loss at 10 cm above the sea ice surface (observed for the UV-transmitting but not UV-blocking, showing that this is a photochemical process) to reaction with bromine radicals based on their enhancement of seawater Br-, which then migrated into the snow above. My major comment is the lack of discussion of the role of NOx, which is known to be important in O3 and bromine chemistry, and should be particularly important in this urban ambient study (see detailed comments below). This is particularly important because snow photochemical reactions produce NO, which can react with O3, and so disentangling this from reaction with Br is important to consider. Additionally, there is additional published literature, stated below, that is relevant and should be considered in this manuscript.

The role of NOx needs to be discussed in this study, as there is currently no mention of NOx in the paper. NO reacts with O3, and it seems possible that this could be contributing in part to the O3 loss observed over snow (see, for example, Peterson and Honrath 2001, Geophys. Res. Lett., "Observations of rapid photochemical destruction of ozone in snowpack interstitial air"), as NOx is released from the snowpack from snow nitrite and nitrate photolysis. Peterson and Honrath (2001) calculated the fraction of the observed ozone loss rate that could be attributed to NOx (they found it was small for their study and then considered bromine reaction), and this seems important to consider here. Were snow nitrate and nitrite measured? If so, this seems important to report. Further, in the urban environment of this study, NOx is likely elevated due to combustion emissions, especially since the authors discuss O3 formation (involving hydrocarbons and NOx) from vehicle exhaust.

Response: We agree that the role of NO$_x$ should be discussed. Ambient concentrations of NO$_x$ (both NO and NO$_2$) were indeed measured during Experiment #2 from the same gas sample line as the ambient O$_3$ measurement. The concentrations of NO$_x$, O$_3$ as well as O$_3$ loss (%) within the in-tube air (difference between ambient air and UV-transmitting in-tube air) are provided in Figure 1 below. The range for NO$_x$ (NO and NO$_2$) was capped at 100 ppb in Figure 1a, although some extremely high values (up to 300 ppb) were observed due to vehicle activities that were close to the pool. With respect to NO$_x$ influence on ambient O$_3$, the concurrence of NO peaks (Fig 1a) was observed with O$_3$ troughs in ambient air (Fig. 1b), especially when ambient O$_3$ dropped below 10 ppb. On the other hand, NO$_x$ influence on O$_3$ loss (%) within the in-tube air is less consistent. For example, from 11-14 March, NO peaks (20 ppb) were observed on 11 March and 14 March, whereas NO stayed at relative low levels (< 3 ppb) during 12-13 March. Yet, during the same time (11-14 March), O$_3$ loss (%) within the in-tube air reoccurred daily in a diurnal pattern and reached a similar extent regardless of NO concentrations. In the original manuscript, this O$_3$ loss (%) within the in-tube air was attributed to the retardant air mixing rates due to the tube effect or enhanced signals from chemical reactions occurred near ice surface. The observed patterns during 11-14 March suggest a more dominant role of photochemical reactions (e.g., Br chemistry) near ice surface and a lesser influence from ambient NO concentrations.

Both nitrate and nitrite were measured in snow samples by ion chromatography as part of the major ion analysis. Nitrite was always below method of detection limit (MDL) of 4.6 μmol kg^{-1}. Nitrate concentrations in most snow samples were also below MDL of 1.3 μmol kg^{-1}, except for the land snow samples, which were 19 ± 5 μmol kg^{-1}. Nitrate in land snow is likely sourced from atmospheric deposition, which is originally produced from vehicle exhaust, because nitrate was not intentionally added in our artificial seawater. Due to the very low concentrations of nitrate and nitrite found in the snow above sea ice, it is likely that in-situ NO_x production via snowpack photochemistry is limited within the in-tube air mass.

Furthermore, the photochemical O_3 loss we present in the manuscript is obtained by comparing O_3 concentrations between the two different acrylic tubes. This comparison helps to cancel out the O_3 variations in ambient background (caused either by urban signal or NO_x chemistry) since both tubes were open to the same air mass. Thus, we think NO_x, either from ambient air or snowpack photochemistry, has limited influence on the O_3 depletion patterns discussed in this manuscript. In the revised manuscript, we will add NO_x discussion on O_3 dynamics and Figure 1 will be included in the supplement materials.

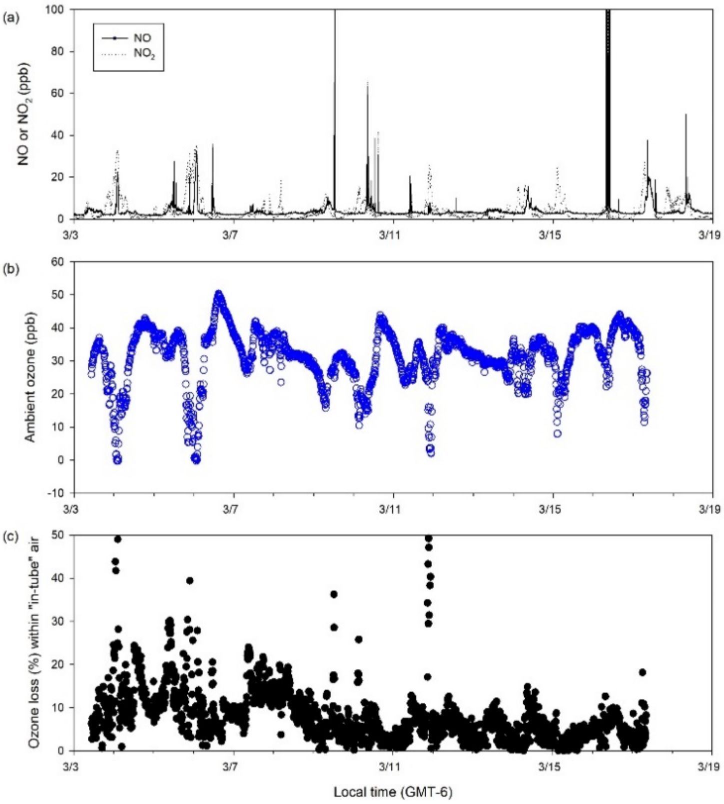

Figure 1. Temporal changes of (a) NO_x (NO and NO_2) in ambient air; (b) ozone in ambient air, and (c) ozone loss (measured as the difference between in-tube air and ambient air) during Experiment #2. (This figure will be added as Figure S3 in the revised manuscript)

Some of the revisions in the main text are provided here: the following changes will be made in Lines 145-150 (Section 2.3): "The recovery and method of detection limit (MDL) were determined from repetitive measurements on a Dionex seven anion standard and a Dionex six cation-II standard, and were 98 % and 1.46 μmol kg^{-1} for bromide, 96 % and 1.96 μmol kg^{-1} for chloride, 99 % and 3.05 μmol kg^{-1} for sulphate, 97 % and 4.59 μmol kg^{-1} for nitrite, 95 % and 1.27 μmol kg^{-1} for nitrate, 107 % and 0.20 μmol kg^{-1} for sodium, 119 % and 0.79 μmol kg^{-1} for magnesium, and 93 % and 0.95 μmol kg–1 for calcium."

Table 1 will also be revised:

Table 1. Major-ion composition of snow, surface ice and surface seawater during Experiment #1

	Concentration (mmol kg^{-1})								Molar ratio					
	Cl^-	Br^-	SO_4^{2-}	NO_2^-	NO_3^-	Na^+	Mg^{2+}	Ca^{2+}	Br^-/Cl^-	Cl^-/Na^+	Br^-/Na^+	SO_4^{2-}/Na^+	Mg^{2+}/Na^+	Ca^{2+}/Na^+
Snow over land (n=8)	1.5 ± 0.8	0.002 ± 0.001	0.01 ± 0.00	< MDL	0.019 ± 0.005	0.4 ± 0.2	0.02 ± 0.02	0.06 ± 0.02	0.001 ± 0.000	4.8 ± 2.6	0.004 ± 0.001	0.04 ± 0.00	0.06 ± 0.03	0.3 ± 0.1
Snow over sea ice (n=11)	290.4 ± 104.5	4.3 ± 2.1	16.5 ± 5.6	< MDL	< MDL	260.8 ± 95.7	19.8 ± 9.8	5.8 ± 2.2	0.02 ± 0.01	1.1 ± 0.0	0.02 ± 0.01	0.07 ± 0.02	0.07 ± 0.03	0.02 ± 0.00
Sea ice (top 3 cm) (n=4)	269.0 ± 23.0	4.9 ± 1.7	17.9 ± 0.8	< MDL	< MDL	251.2 ± 20.2	18.1 ± 3.0	5.0 ± 0.6	0.02 ± 0.01	1.1 ± 0.0	0.02 ± 0.01	0.07 ± 0.00	0.07 ± 0.01	0.02 ± 0.00
Surface seawater (n=3)	532.1 ± 7.7	6.5 ± 1.1	28.4 ± 1.1	< MDL	< MDL	495.1 ± 1.9	33.2 ± 16.6	10.3 ± 0.2	0.01 ± 0.00	1.1 ± 0.0	0.01 ± 0.00	0.06 ± 0.00	0.07 ± 0.03	0.02 ± 0.00

Another aspect for which NOx is important is that BrONO2 production dominates over HOBr at NO2 > ~100 ppt (depending on HO2 as well) (Wang and Pratt 2017, JGR), which is surely the case for this urban study. This should be added to Figure 1 (the role of BrONO2 in molecular halogen production is also discussed by Wang and Pratt (2017)) and included in the introduction at Lines 44-48.

Response: We will modify our original Figure 1 (shown as Figure 2 in this reply) to include $BrONO_2$ cycling as part of Br reactions. In addition, the dark reduction pathways of Hg(II) will be recognized.

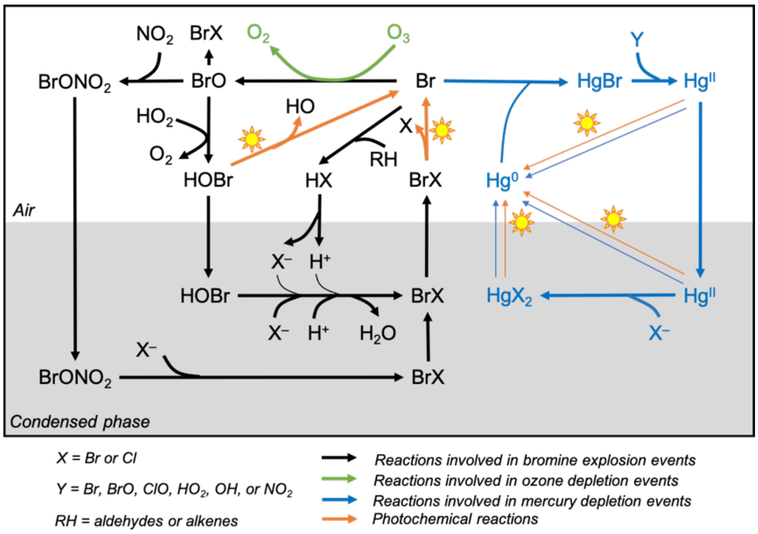

Figure 2. General reaction schemes involved in bromine explosion events, ozone depletion events, and mercury depletion events in the Arctic during polar sunrise: gas-phase reactive bromine species (Br and BrO) produced from multi-phase reactions on the surface of the condensed phase will cause the depletion of ozone and gaseous elemental mercury in the boundary layer air (based on (Abbatt et al., 2012; Saiz-Lopez and von Glasow, 2012; Khiri et al., 2020; Simpson et al., 2015, 2007; Wang et al., 2017; Wang and Pratt, 2017). (This figure will be the revised Figure 1 in our revised manuscript.)

In the main text Lines 40-45 (Introduction), the following changes will be made: "While there is a general consensus on the reaction schemes involved in BEEs, ODEs, and MDEs (Fig. 1), major uncertainties exist with respect to the fundamental cryo-photochemical process causing these events and meteorological conditions that may affect their timing and magnitude. It has been generally assumed that the cycling of reactive Br species is sustained by HOBr and $BrONO_2$ via multi-phase reactions on the surface of a condensed phase during polar sunrise (Abbatt et al., 2012; Simpson et al., 2007, 2015; Wang and Pratt, 2017). ~~For instance, the initiation step is thought to be a multi-phase (mp) oxidation of halide~~

~~by HOBr presumably on the surface of a saline condensed phase (Abbatt et al., 2012; Simpson et al., 2007, 2015):~~

~~$X^- + HOBr + H^+ \xrightarrow{mp} H_2O + BrX$ (R1)~~

~~where X = Br or Cl.~~ Yet the role of HOBr and the nature of the condensed phase remain not well characterized.”

On Lines 114-115, the authors define “boundary layer air” as “the air mass above the sea ice surface inside the tubes, whereas the air outside of the tubes is considered the “ambient air””, and these terms are then used throughout the manuscript, with the comparison between these air samples being critical to the results. While it is helpful that the authors defined this phrasing in the methods section, it was quite confusing and difficult to remember through the Results & Discussion section, as all air within the boundary layer (not just inside the tubes) would be boundary layer air. I suggest that the authors choose different phrasing that is easier to remember – for example “in-tube air” vs “ambient air”.

Response: We agree and the terminology throughout the manuscript will be changed from “boundary layer air” to “in-tube air”, which represents the air mass that is constrained inside the acrylic tubes above the sea ice or seawater surface.

Some clarifications of the study conditions are needed. Please directly state in Section 2.1 that the tubes are open to the overlying air. Also, it would be useful to directly state that the sea ice exposure to the atmosphere results in the deposition of atmospheric trace gases and particles to the sea ice. From the comparison in Table 1, however, it is clear that the snow composition (for the ions reported) above the sea ice is dominated by ions from the sea ice brine, based on the comparison to nearby ‘land snow’; other ions that would be more impacted by the atmosphere and may be important (e.g. nitrate and nitrite for snow NOx production) should be reported if possible. Also, please clarify in the methods when O3 was measured where (heights and which tubes), as Section 2.2 discusses switching between sampling ports at different heights and locations with 5 min resolution, but then Section 3.2 and Figure 4 seem to show O3 measurements at different heights only occurring on different days. This needs to be very clear if vertical profiles of O3 were not measured on the same day.

Response: In Lines 110-115 (Section 2.1), the following revision will be added: “They were placed about 30 cm away from the edge of the pool and were kept vertical by mechanical arms located on the side of the pool (Fig. 2). Both tubes were open to the overlying atmosphere, which allowed direct air-ice interaction and deposition of atmospheric substances into the sea ice or snowpack surface. One of the tubes was made of UV-blocking acrylic material (cut-off wavelength: 370 nm), and the other of UV-transmitting acrylic material (cut-off wavelength: 270 nm) (see Fig. S1).”

As mentioned in previous reply, nitrate and nitrite concentrations will be included in the revised Table 1.

To resolve the confusion regarding the 5 min resolution and the switching mechanism, we will add more clarifications on the switching mechanisms for ozone measurement in Lines 115-125 (Section 2.2): “To allow ozone measurement of the in-tube ~~boundary layer~~ air mass ~~in~~ between different tubes ~~or at different heights above the surface~~, a two-way switch Tekran 1100 dual port module was used to automatically switch between the sampling ports on different tubes at an interval of 5 minutes. For example, during 12 to 23 February, continuous sampling was conducted at the same height on UV-transmitting and UV-blocking tubes for more than 40 hours before moving to another height for sampling. And during the time at one height, ozone sampling switched between different tubes at an interval of 5 minutes. Each ozone data reported herein is averaged over a 5-min integration time. The ozone concentrations in the ambient air near the pool were also measured during the experiments.”

It would be useful on Lines 84-86 and in Table 1 to report Br-/Cl- ratios to place this in the context of previous studies of Arctic snow Br-/Cl- and the potential to produce Br2 (Peterson et al 2019, Elementa (Figure 5 and associated text); Pratt et al 2013, Nat. Geosc.). Also, it would appear that the Br-/Na+ and Cl-/Na+ labels are reversed in Table1; please fix.

Response: The revised Table 1 is provided in this reply. In the revised manuscript, we will add the following revisions to compare our measured results with the previous studies in Lines 210-215 (Section 3.2): "The mesocosm experiment was conducted using bromide-enriched artificial seawater. As expected, considerable amounts of major ions from seawater are retained in sea ice (Table 1). Major ion concentrations are very low in snow collected from nearby land surfaces, whereas considerably (~ 100 times) higher concentrations are found for the thin layer of snow above sea ice, which is consistent with the brine-wetting process in snow overlying sea ice (Barber and Nghiem, 1999). The measured concentrations of bromide and chloride in snow and surface sea ice samples were much higher than previously reported Arctic snow samples over first-year and multi-year sea ice (Krnavek et al., 2012; Peterson et al., 2019). This large difference can be explained by a dominant contribution from sea ice brine in our experiment, and a more prevalent atmospheric source of halides in natural Arctic snowpack (Peterson et al., 2019). Bromide is of particular interest, which was found to be preferentially enriched in sea ice and in the overlying snow, as demonstrated by elevated ~~Br$^-$/Na+~~ Br$^-$/Cl$^-$ molar ratio (0.02) when compared with that in the underlying seawater (0.01). Similar preferential enrichment was not observed for other major ions."

In Lines 290-295 (Section 4.2), the following discussion will be added: "The condensed phase can be either the bare sea ice or the thin layer of snow accumulated on the sea ice surface at the second half of Experiment #1. The observed Br$^-$/Cl$^-$ ratios in saline snow and in surface sea ice samples are found to be in favor of active Br cycling. Pratt et al (2013) suggested an optimal Br$^-$/Cl$^-$mole ratio threshold for Br_2 production of 1:200 (0.005), which is below our observed ratios for the potential condensed phase reactors. However, the highly….."

There are several additional related manuscripts that the authors should consult and incorporate into their manuscript. Nakayama et al. (2015, Tellus, "Ozone depletion in the interstitial air of the seasonal snowpack in northern Japan") is a useful paper for the authors to compare their results to, as they also observed photochemical O3 loss outside of the Arctic. Helmig et al (2012, JGR, "Ozone dynamics and snow-atmosphere exchanges during ozone depletion events at Barrow, Alaska") is also likely useful, particularly to discuss ozone loss near the surface due to deposition (a topic that should be discussed in this manuscript, but so far is not). Additional important laboratory saline ice studies to cite (especially on Line 62 when referring to previous frozen halogen release studies; consider whether these are helpful for interpreting results as well) include: Adams et al (2002, Atmos. Chem. Phys., "Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces between 253 and 233K"), Huff and Abbatt (2000, J. Phys. Chem. A, "Gas-phase Br2 production in heterogeneous reactions of Cl2, HOCl, and BrCl with halideice surfaces"), Wren et al (2013, Atmos. Chem. Phys., "Photochemical chlorine and bromine activation from artificial saline snow"), Halfacre et al (2019, Atmos. Chem. Phys., "pH-dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces").

Response: We compared our O_3 depletion values to Nakayama et al (2015) results, and they are within the similar magnitude. In the original manuscript, we mentioned there was no obvious O_3 deposition on acrylic tubes. This can be supported by the fact that there was no "background" O_3 loss observed at 20 cm and 40 cm above the sea ice surface.

Regarding the O_3 deposition flux calculation into the snow layer or sea ice surface, there is no O_3 measurement available below the surface of the condensed phase. For example, during the entire winter experiment, no substantial natural snow accumulation (> 5 cm) was observed inside acrylic tubes and the relative distance from sampling port to the ice surface was fixed. These conditions do not support O_3 measurement from either snow interstitial air or air trapped within the surface ice sections. Thus, the deposition flux calculation onto the condensed phase (sea ice or snow layer) was not supported in this study.

The following references will be added in the revised manuscript:

Burd, J. A., Peterson, P. K., Nghiem, S. v., Perovich, D. K., and Simpson, W. R.: Snowmelt onset hinders bromine monoxide heterogeneous recycling in the Arctic, 122, https://doi.org/10.1002/2017JD026906, 2017.

Halfacre, J. W., Shepson, P. B., and Pratt, K. A.: PH-dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces, 19, https://doi.org/10.5194/acp-19-4917-2019, 2019.

Huff, A. K. and Abbatt, J. P. D.: Kinetics and product yields in the heterogeneous reactions of HOBr with ice surfaces containing NaBr and NaCl, 106, 5279–5287, https://doi.org/10.1021/jp014296m, 2002.

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, 50, https://doi.org/10.1016/j.atmosenv.2011.11.033, 2012.

Nakayama, M., Zhu, C., Hirokawa, J., Irino, T., and Yoshikawa-Inoue, H.: Ozone depletion in the interstitial air of the seasonal snowpack in northern Japan, 67, https://doi.org/10.3402/tellusb.v67.24934, 2015.

Peterson, P. K., Hartwig, M., May, N. W., Schwartz, E., Rigor, I., Ermold, W., Steele, M., Morison, J. H., Nghiem, S. v., and Pratt, K. A.: Snowpack measurements suggest role for multi-year sea ice regions in Arctic atmospheric bromine and chlorine chemistry, 7, https://doi.org/10.1525/elementa.352, 2019.

Wang, S. and Pratt, K. A.: Molecular Halogens Above the Arctic Snowpack: Emissions, Diurnal Variations, and Recycling Mechanisms, 122, https://doi.org/10.1002/2017JD027175, 2017.

Wren, S. N., Donaldson, D. J., and Abbatt, J. P. D.: Photochemical chlorine and bromine activation from artificial saline snow, 13, 9789–9800, https://doi.org/10.5194/acp-13-9789-2013, 2013.

Additional Comments:

Lines 44-47: Note that Pratt et al (2013, Nat. Geosc.) showed that the initiation step of condensed-phase snowpack photochemical production does not require HOBr. Rather HOBr and BrONO2 participate in the bromine explosion cycle that propagates the bromine chemistry. This should be clarified here, as R1 does not represent an ‘initiation step’ as stated. Dark reaction of O3 with Br- has also been proposed as an initiation step (Artiglia et al. 2017, Nat. Comm.; Simpson et al. 2018, Geophys. Res. Lett.).

Response: The main text will be modified as per our reply above.

Lines 50-52 and 290-291: Note that Pratt et al (2013, Nat. Geosc.) showed directly that Br2 was not produced from sea ice or brine icicles (frost flower proxies) and showed that Br2 production was related to acidity, as supported by lab studies.

Response: We will add more related references to support the statement of acidity requirement in our introduction. The following changes will be made in Lines 50-52: “Yet role of HOBr and the nature of the condensed phase remain not well characterized. Some studies suggested a potential link between the observation of bromine activation with the extent of first-year and multi-year sea ice (Bognar et al., 2020; Simpson et al., 2007) whereas saline snowpack, ~~first-year and multi-year sea ice, frost flowers~~ and sea salt aerosols have ~~all~~ been proposed to provide such a condensed phase for the reactions by both field observations and laboratory studies (Huff and Abbatt, 2002; Pratt et al., 2013; Wren et al., 2013; Wang et al., 2019). ~~However, as Reaction (R1)~~ The cycling of bromine species is favoured under acidic conditions (Pratt et al., 2013; Halfacre et al.,2019) and the surfaces of sea ice and frost flowers, which are highly alkaline (Hare et al., 2013), are unlikely to be effective in ~~initiating~~ sustaining the reactions.”

Lines 52-54: Burd et al. (2017, J. Geophys. Res., “Snowmelt onset hinder bromine monoxide heterogeneous recycling in the Arctic”) would be useful to cite here.

Response: We find this paper very relevant and it will be added in the revised reference list. The following change will be made in Line 54: “… rises to above 0 °C (Bognar et al., 2020; Burd et al., 2017; Steffen et al., 2005).”

Lines 81-84: Did the prepared synthetic seawater contain carbonate/bicarbonate? It appears that it did not. Regardless, this should be stated, as it is important for understanding the pH of the sea ice surface, based on the pH dependence of molecular halogen production and the work of Wren and Donaldson (2012, Atmos. Chem. Phys., “How does deposition of gas phase species affect pH at frozen salty interfaces?”) that showed that the sea ice surface is buffered against pH change.

Response: We did not intentionally add any carbonate or bicarbonate into the artificial seawater. But the pool was left open for equilibrium with the overlying atmosphere for over a month after the artificial seawater was prepared. Total alkalinity and dissolved inorganic carbon were provided in Table 2. Using the temperature measurement from thermocouples, it allowed us to gain a rough estimate of in-situ bulk pH in surface sea ice sections, which is close to the pH measured on snow and sea ice meltwater for most samples. Unfortunately, direct pH measurements at the air-ice interface were not available in this study.

Lines 192-193 and Table 1: Error should be reported with 1 significant figure throughout the manuscript.

Response: Table 1 will be revised as per our reply above.

Lines 199-201: Please state the absolute magnitude of this [O3] difference here in the text and compare to that observed for the ambient vs boundary layer air (Lines 191-193 and Figure 3).

Response: Lines 199-201 (Section 3.2) will be revised as: "The only exception is the measurement conducted closest to the sea ice surface (10 cm) during the ice-covered period in Experiment #1, when the ozone concentration in the UV-transmitting tube was consistently and considerably lower than that in the UV-blocking tube ($p = 0.00$) (Fig. 4c). The averaged ozone difference between two tubes at 10 cm was 4.6 ± 2.3 ppb, whereas the ozone difference between UV-transmitting tube and ambient air was 2.3 ± 1.9 ppb for the entire experiment (when applicable)."

Figure 3: Since snow cover is key in this study, can shading be added to this time series to indicate when snow was present?

Response: Unfortunately, we did not have accurate recordings for the snow thickness. During most times, the snow deposition was attached to the inner side of the tube and no substantial snow layer above the sea ice surface was observed.

Line 228: When was the pH of fresh snow measured, and how/where was this snow obtained?

Response: The fresh snow sample was obtained by scooping untouched surface snow on sea ice within 2 hours after deposition, using 50-mL Falcon tubes. Then, the snow samples were melted at 4 °C in dark until the pH measurement. We will add more details in Section 2.3 regarding the snow and ice sampling for pH measurement in the revised manuscript.