

Reply to Reviewers' Comments (acp-2021-157; Gao et al.)

We thank two reviewers for their very insightful and constructive comments and suggestions. We have carefully considered all of them and revised the manuscript (ms) accordingly. The revisions are detailed in the track-changes file.

Below we provide a point-by-point response to the reviewers' comments and highlight where changes have been made. The comments from the reviewers are shown in black and **bolded**. Our response is given in the regular font, whereas the corresponding revisions are highlighted in blue. The line numbers in the comments refer to the original manuscript, whereas those in our reply refer to the revised manuscript.

Reviewer #1

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 NO_x, 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 NO_x needs to be discussed in this study, as there is currently no mention of NO_x 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 NO_x 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 NO_x (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, NO_x is likely elevated due to combustion emissions, especially since the authors discuss O₃ formation (involving hydrocarbons and NO_x) from vehicle exhaust.

We agree that the role of NO_x should be discussed. Ambient concentrations of NO_x (both NO and NO₂) were indeed measured during Experiment #2 from the same gas sample line as the ambient O₃ measurement. The concentrations of NO_x, O₃ as well as O₃ loss (%) within the in-tube air (difference between the ambient air and the in-tube air inside the UV-transmitting tube) are provided in [Figure S3](#) in the revised manuscript (see below also). The range for NO_x (NO and NO₂) is capped at 100 ppb in [Figure S3a](#), 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 O₃, the concurrence of NO peaks ([Fig S3a](#)) was observed with O₃ troughs in the ambient air ([Fig. S3b](#)), especially when ambient O₃ dropped below 10 ppb. On the other hand, NO_x influence on O₃ 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), O₃ 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 O₃ 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 the detection limit (DL) of 4.6 $\mu\text{mol kg}^{-1}$. Nitrate concentrations in most snow samples were also below DL of 1.3 $\mu\text{mol kg}^{-1}$, except for the land snow samples, which were $19 \pm 5 \mu\text{mol kg}^{-1}$. 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 O₃ loss we present in the manuscript is obtained by comparing O₃ concentrations between the two different acrylic tubes. This comparison helps to cancel out the O₃ 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 believe NO_x, either from ambient air or snowpack photochemistry, has limited influence on the O₃ depletion patterns discussed in this manuscript.

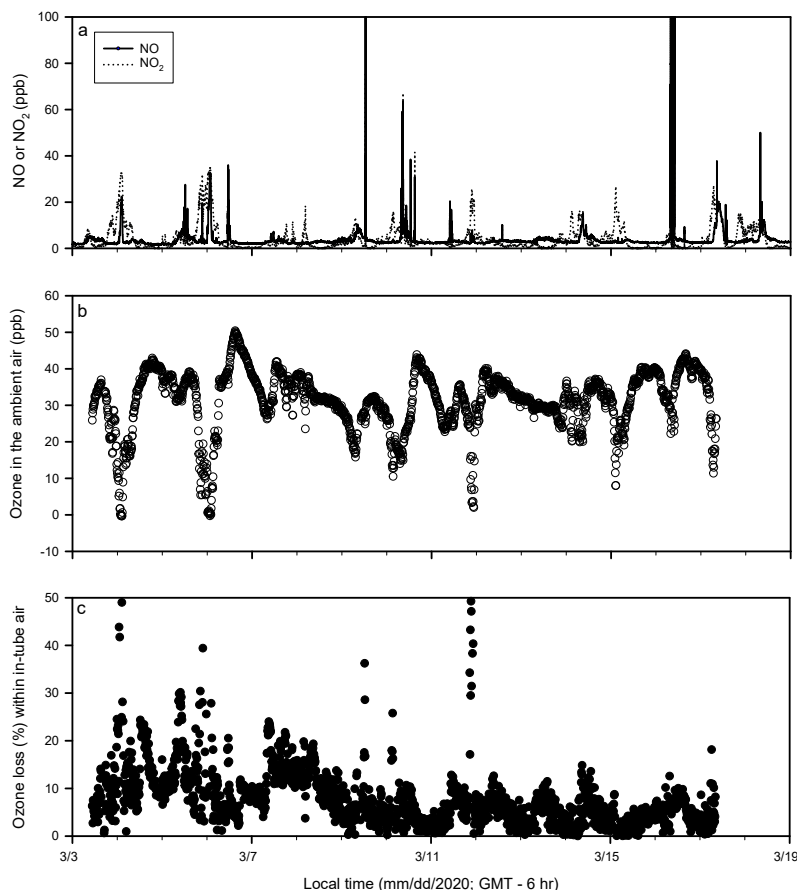


Figure S3. Temporal changes of (a) NO_x (NO and NO₂) in ambient air; (b) ozone in ambient air, and (c) ozone loss (measured as the difference between in-tube air and ambient air) during Experiment #2.

In addition to the new Figure S3, other revisions are provided below.

Lines 150–153: “In addition to ozone and GEM, nitrogen oxides (NO, NO₂ and their sum NO_x) concentrations in the ambient air were measured using a Teledyne T200 NO/NO₂/NO_x analyzer near the pool during Experiment #2. The instrument reports data for every minute with a detection limit of 0.4 ppb.”

Lines 171-175: “The recovery and detection limit were determined from repetitive measurements on a Dionex seven anion standard and a Dionex six cation-II standard, and were 98 % and 1.5 μmol kg⁻¹ for bromide, 96 % and 2.0 μmol kg⁻¹ for chloride, 99 % and 3.0 μmol kg⁻¹ for sulphate, 97 % and 4.6 μmol kg⁻¹ for nitrite, 95 % and 1.3 μmol kg⁻¹ for nitrate, 107 % and 0.20 μmol kg⁻¹ for sodium, 119 % and 0.8 μmol kg⁻¹ for magnesium, and 93 % and 1.0 μmol kg⁻¹ for calcium.”

Lines 289–315: “In addition, the presence of NO_x would also affect ambient ozone dynamics (Fig. S3) as occasional ozone troughs (near 0 ppb) in the ambient air were observed with NO peaks (Fig. S3a). Similar diurnal patterns of the ozone concentrations are evident in the ambient air and the in-tube air inside the UV-transmitting tube even at 10 cm above the sea ice surface (Fig. 3a and Fig. 7a), suggesting that the ozone concentration in the in-tube air is largely controlled by the urban signal (i.e., the ambient air). However, ozone concentrations in the ambient air are considerably higher than that inside the UV-transmitting tube during sun-lit, daytime (Fig. 7a). This could be indicative of limited mixing of the ambient air inside the tube due to the wall effect, influence on ozone dynamics from NO_x chemistry, and/or loss of ozone inside the tube due to the presence of the experimental sea ice.

To address which of these processes is primarily responsible for the observed ozone difference, we investigate the influence of NO_x chemistry and compare the ozone concentrations measured inside the UV-blocking and UV-transmitting tubes. The temporal pattern of the ozone difference between the in-tube air inside the UV-transmitting tube and the ambient air (Fig. S3c) shows the influence of NO_x on the ozone loss (ΔO₃) within the in-tube air is limited. For example, from 11 to 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 to 13 March. Yet, during the same time, ΔO₃ within the in-tube air reoccurred daily in a diurnal pattern and reached a similar extent regardless of NO concentrations. In addition, 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 automobile exhaust or snowpack photochemistry had negligible influence on ΔO₃ within the in-tube air.”

Line 352–355: “The other known tropospheric ozone depletion mechanisms include direct photolysis (Wu et al., 2007), NO_x chemistry (Nakayama et al., 2015), and ozone deposition on the tube walls, which are negligible at the study site as demonstrated by a lack of ozone loss during the early fall (Fig. 8c).”

Table 1 has been revised as:

Table 1. Ion composition of snow, surface ice and surface seawater during Experiment #1. DL: Detection limit.

	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	< DL	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	< DL	< DL	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	< DL	< DL	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	< DL	< DL	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 NO_x 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.

We have modified our original Figure 1 (shown below) to include BrONO₂ cycling as part of Br reactions.

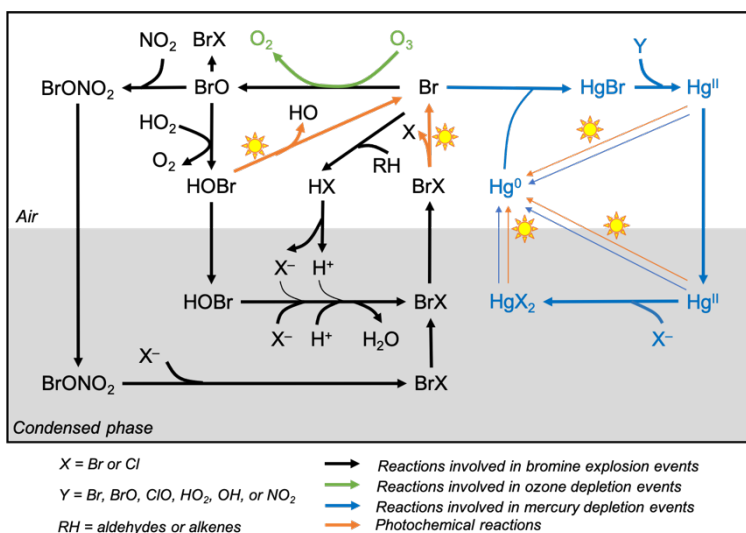


Figure 1. General reaction schemes involved in bromine explosion events, ozone depletion events and mercury depletion events in the Arctic during polar sunrise. The photochemical activation of gas-phase reactive bromine species (Br and BrO) produced from multi-phase reactions on the surface of the condensed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

Lines 36–41: the following changes have been 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 bromine species is sustained by HOBr and BrONO₂ 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):~~



~~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”.

We agree and the terminology throughout the manuscript has been 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 NO_x 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.

In Lines 105-115, the following revision has been made: “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 have been included in the revised Table 1.

To resolve the confusion regarding the 5 min resolution and the switching mechanism, we have added more clarifications on the switching mechanisms for ozone measurement in Lines 125-135: “To allow ozone measurement of the **in-tube boundary layer** air **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 one height on both UV-transmitting and UV-blocking tubes for more than 40 hr before moving to another height for sampling. During data collection at each height, ozone sampling switched between different tubes at an interval of five minutes. Thus, each ozone data reported herein is averaged over a 5-min integration time (five measurements).** 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.

The revised Table 1 is provided in this reply. In the revised manuscript, we have revised the text to compare our measured results with the previous studies in Lines 252–263: “**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 saline snow and surface sea ice samples were much higher than the values previously reported for 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 mesocosm 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^- mole 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 357–361, the following discussion has been 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 and during Experiment #4. The observed Br^-/Cl^- ratios in saline snow and in surface sea ice samples are found to be in favor of active cycling of bromine species. Pratt et al (2013) suggested an optimal Br^-/Cl^- mole ratio threshold for Br_2 production of 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 O_3 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 Br_2 production in heterogeneous reactions of Cl_2 , HOCl, and BrCl with halide ice 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”).

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 have been 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, *J. Geophys. Res. Atmos.*, 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, *Atmos. Chem. Phys.*, 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, *J. Phys. Chem. A*, <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, *Atmos. Environ.*, 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, *Tellus B*, <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, *Elementa*, <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, *Atmos. Chem. Phys.*, 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, *Atmos. Chem. Phys.*, 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 Br₂ has also been proposed as an initiation step (Artiglia et al. 2017, Nat. Comm.; Simpson et al. 2018, Geophys. Res. Lett.).

The text has been revised 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.

We have included more related references to support the statement of acidity requirement in our introduction. The following changes have been made in Lines 40–46: “Yet the role of HOBr and the nature of the condensed phase remain not well characterized. Some studies have suggested a potential link between bromine activation and the extent of first-year and multi-year sea ice (Bognar et al., 2020; Simpson et al., 2007a), whereas field observations and laboratory studies show that saline snowpack and sea salt aerosols are more likely to provide such a condensed phase for the reactions (Huff and Abbatt, 2002; Pratt et al., 2013; Wang et al., 2019; Wren et al., 2013; Xu et al., 2016). The cycling of bromine species is favoured under acidic conditions (Halfacre et al., 2019; Pratt et al., 2013), and the surfaces of sea ice and frost flowers, which are highly alkaline (Hare et al., 2013), are unlikely to be effective in 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.

We find this paper very relevant and it has been added in the revised reference list. The following change has been made in Line 48: “... 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.

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.

The following changes have been made in Lines 89-90: “... a S = 32.8 seawater. [Once prepared, the artificial seawater was left to equilibrate with the atmospheric CO₂ for more than one month.](#)”

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

The manuscript including Table 1 has been revised.

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).

The following sentence has been added (Lines 229–230): “[The averaged ozone difference between the UV-transmitting tube and ambient air was \$2.3 \pm 1.9\$ ppb for the entire experiment when measurements were done.](#)”

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

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?

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 have added more details in Section 2.3 regarding the snow and ice sampling for pH measurement in the revised manuscript (Lines 157–169).

Reviewer #2:

Gao et al. demonstrate that a mesocosm sea-ice facility can be utilized to study bromine explosion events (BEEs) and resultant ozone depletion events (ODEs). The study is to my knowledge an unprecedented demonstration of the utility and potential of mesocosms to study chemistry above sea ice. In particular, the authors are able to compare and contrast bromine and ozone inside two acrylic cylinders one UV-transmitting the other UV-blocking. The authors attribute differences in O₃ at 10 cm above the ice surface to a photochemical process being key. Changes in ice and snow conditions and temperature which are largely naturally driven complement this finding by further demonstrating a likely importance of snow and cold temperatures. Where the work can be most improved is that since the work serves primarily as a demonstration of the mesocosm facility and mesocosm experiments generally, certain limitations of this demonstration are inadequately assessed and discussed. In particular the authors note that mercury depletion events (MDE) which typically accompany BEEs can be studied, but this is not yet demonstrated. Further whether the facility replicates organic chemistry and biology which might be relevant to BEEs is not assessed or discussed. Given that the authors point specifically at using the facility to investigate MDEs in future but have not done so, it would be useful to have some general outline of how such an experiment could be conducted to demonstrate that the mesocosm facility is useful in this regard. This can be very general as much as indicating whether Hg would be a controlled or free variable in such an experiment with some limited detail. Without this limited detail it is difficult to assess if the facility can be used for this purpose as contended.

We thank the referee for recognizing the significance of the novel mesocosm approach we reported here to reproduce Arctic springtime tropospheric chemistry. In this manuscript, the reproduction of ozone depletion events (ODEs) is confirmed by monitoring temporal changes in ozone concentrations above sea ice and relating it to active bromine chemistry (bromine explosion events, BEEs). We expected that the mercury depletion events (MDEs) likely also occurred, but unfortunately, gaseous elemental mercury (GEM) was not measured during the data collection period (2019 to 2020) covered in the original manuscript. In a follow-up experiment conducted during December 2020, both GEM and ozone were measured from the same gas sample line. As expected, MDEs were indeed observed along with ODEs in the same pattern that is consistent with bromine photochemistry (new [Figure 4](#) in the revised manuscript; see below also). These co-variations between GEM and ozone further demonstrate the capacity of the mesocosm approach in studying photochemical phenomena in the polar troposphere. We have included the data (GEM and ozone) from the follow-up experiment (December 2020) in the revised manuscript, and thus changed the title and related sections accordingly.

Our response to the comments on organic chemistry and biology can be found below.

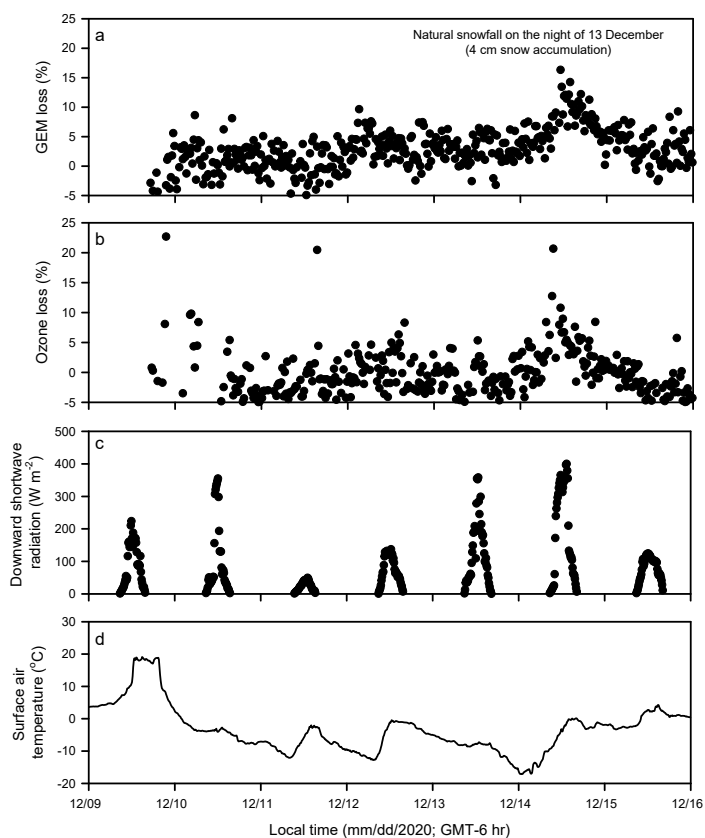


Figure 4. Temporal changes of (a) gaseous elemental mercury (GEM) loss and (b) ozone loss (measured as the difference between the UV-transmitting and UV-blocking tubes), (c) downward shortwave radiation, and (d) surface air temperature during Experiment #4.

There are additional variables which might be relevant to BEE which is it unclear if the facility has replicated or can replicate. One is organic carbon content and composition, especially organic carbon present at the surface. Studies have found that the presence of organics can have complex effects on bromide oxidation (Edebeli et al., 2019). In addition, a dark process leading to significant organic bromine from ice and snow in the Antarctic appears to operate under conditions similar to those investigated (Abrahamsson et al., 2018). Can the authors comment on any constraint on the possible effects of organic carbon and whether these are variables the facility can control?

In the mesocosm design, no organic materials were introduced intentionally into the SERF artificial seawater which was prepared freshly from groundwater with NaCl brine and inorganic salts two months before the freezing started. It is possible that traces of organic matter could have entered the outdoor pool (e.g., from dust deposition), but the algal and microbial community growth were minimal due to the cold temperature. As such, we do not think there were any meaningful concentrations of bromocarbons in the experimental seawater/sea ice. Now that we have shown the mesocosm approach is successful, our future research will investigate other processes, including those involving bromocarbons, that may be involved in the occurrence of BEEs/ODEs/MDEs.

We have added the following discussion in the revised manuscript (Line 377–383): “Several improvements can be made for future studies. Even though organic matter and biota were not intentionally introduced into the mesocosm, some of them could have made into the system; to which extent they could have influenced the cryo-photochemical processes (e.g., via the production of bromocarbons) warrants

further exploration. Another aspect is related to ice-nucleating particles which are likely to affect the roughness of the sea ice surface and assist in frost formation on the tube walls during mornings, which could potentially act as a temporary condensed phase for bromine activation just after sunrise. Time-series measurements of pH at the air-ice/snow interface could also be explored to probe the availability of protons and the efficiency of HOBr dissociation on the surface of sea ice or snow layer.”

A further potential contributing factor are biota. In particular these are likely contributors to ice-nucleation (Irish et al., 2017; Ickes et al., 2020) which can be relevant to the freezing of the simulated sea-water and potentially to the formation of ice particles above the simulated sea or sea-ice surface. Given the identified importance of snow the latter would appear to be especially relevant. Can the authors comment on the microbiome of the microcosm and the capability of the facility to simulate the sea in this regard?

We agree that biota play an important part in the natural cryospheric environment. However, as per our response above, the contribution of biota in the SERF experiments we reported in this manuscript is considered as negligible, since neither biota nor organic matter were added intentionally to the water. This was confirmed in earlier experiments that employed similarly formulated SERF seawater, where the maximal bulk ice microbial activity and algal chl *a* at the SERF pool were measured to be extremely low ($1.12 \times 10^{-6} \text{ g CL}^{-1} \text{ h}^{-1}$ and $0.008 \mu\text{g L}^{-1}$, respectively) (Geilfus et al., 2016; Rysgaard et al., 2014).

In terms of the role of ice-nucleating particles, it was not explicitly addressed in the original manuscript, but we have added our perspectives in the revised manuscript (see our reply above). We think their potential importance could arise from two processes. First, ice-nucleating particles may affect the roughness of the sea ice surface, which will influence the availability of bromide substrates at the air-ice interface. Second, ice-nucleating particles can assist the formation of frost inside the tube walls, which was observed in early mornings. The frost may serve as a temporary condensed phase medium for the reactions to occur. To which extent these processes can be reproduced at SERF remains uncertain, as both are likely to play a bigger role in a more dynamic ocean environment which is difficult to reproduce in mesocosm experiments. Instead, we think the main advantage of the mesocosm approach is in studying fundamental chemistry and sea ice dynamics.

**Regarding this latter point,
I have the following specific comments:**

L14: First encountered here but found throughout. I would not use the term “mesocosm scale” or “mesocosm-scale”. I am not an expert in mesocosm experiments but I understand them to span several decades of scale (perhaps more) and do not associate them with any inherent scale. In most if not all instances the word “mesocosm” as a noun or adjective would communicate the authors’ intent as far as I can tell.

We agree. In the revised manuscript we have changed “mesocosm scale” or “mesocosm-scale” to “mesocosm” accordingly.

Figure 1: Realizing this is meant to be a simplified schematic, reactions reducing HgII are not necessarily limited to photolyses, e.g. modeling indicates reduction of HgBrO by CO may be significant (Khiri et al., 2020). Consider adding dashed lines similar to the current photolyses.

We agree and Figure 1 has been updated accordingly in the revised manuscript (see our reply to Reviewer #1 above).

L45-47: It is very likely that Br- oxidation is the source of volatilized bromine in BEE, however, the central role of HOBr is less certain. In particular, some plausible alternative oxidants include HOCl (Kumar and Margerum, 1987), HOI (Holmes et al., 2001), and H2O2 (Bray and Livingston, 1928).

We agree that many oxidants can be involved in BEEs and we realized that the HOBr reaction originally present in the manuscript may not be the best representation for the entire reaction series of BEEs. We have made the following revisions (Lines 36–41): the following changes have been 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 bromine species is sustained by HOBr and BrONO₂ 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):



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

L84-86: The authors note that they have increased the bromide content of the simulated sea water by a factor of roughly eight to enhance the resulting effects and signals. To paraphrase, one function of the mesocosm is to elucidate fundamental processes. It is not known whether BEE are linear with respect to sea water bromide or have some other relation. As such the ability to vary bromide across different mesocosm experiments or even over the course of one experiment would be valuable. The total mass of bromide required, mixing time of the pool, and/or replacement time for the simulated sea water would be helpful in this regard. Can the authors provide this information or point to a relevant reference?

The referee raised a very intriguing question regarding the relationship between BEEs and seawater bromide concentrations, which we do not think has been addressed in the literature. Our mesocosm approach is potentially helpful to carry out such studies in the future.

For the experiments reported in this manuscript, the artificial seawater was prepared by mixing groundwater with NaCl brine and other inorganic salts two months before the start of the winter experiment. During the preparation of artificial water, the dissolution of salts and the mixing of brine were achieved gradually, and no visual observation of solids was confirmed after the preparation of the artificial seawater. In addition, similar salinity measurements were found for waters sampled at different depths in the pool, suggesting a homogeneous distribution of the artificial seawater (no halocline) was reached before the experiment.

Other related SERF experiments are published in the following papers:

- Geilfus, N. X., Galley, R. J., Else, B. G. T., Campbell, K., Papakyriakou, T., Crabeck, O., Lemes, M., Delille, B. and Rysgaard, S.: Estimates of ikaite export from sea ice to the underlying seawater in a sea ice-seawater mesocosm, *Cryosphere*, 10(5), 2173–2189, doi:10.5194/tc-10-2173-2016, 2016.
- Hare, A. A., Wang, F., Barber, D., Geilfus, N. X., Galley, R. J. and Rysgaard, S.: PH evolution in sea ice grown at an outdoor experimental facility, *Mar. Chem.*, 154, 46–54, doi:10.1016/j.marchem.2013.04.007, 2013.
- Rysgaard, S., Wang, F., Galley, R. J., Grimm, R., Notz, D., Lemes, M., Geilfus, N. X., Chaulk, A., Hare, A. A., Crabeck, O., Else, B. G. T., Campbell, K., Sørensen, L. L., Sievers, J. and Papakyriakou, T.:

Temporal dynamics of ikaite in experimental sea ice, *Cryosphere*, 8(4), 1469–1478, doi:10.5194/tc-8-1469-2014, 2014.

Xu, W., Tenuta, M. and Wang, F.: Bromide and chloride distribution across the snow-sea ice-ocean interface: A comparative study between an Arctic coastal marine site and an experimental sea ice mesocosm, *J. Geophys. Res. Ocean.*, 121(8), 5535–5548, doi:10.1002/2015JC011409, 2016.

L119: “at every minute” could the authors clarify what is meant by this? Is O₃ measured as an integration over each minute, or is it a shorter sample taken once each minute.

The response time of the ozone instrument (Teledyne T400) is less than 30 s to reach 95 %. The raw ozone file obtained from the instrument was an average over each minute. Since a two-way switch port was used in our gas sample line and the sampling path was switched every 5 minutes between different tubes, each ozone data point discussed throughout the manuscript is an average over five measurements (5 minutes) reported by the instrument from the same sampling port.

This has been clarified in the revised manuscript (Line 128–134): “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 one height on both UV-transmitting and UV-blocking tubes for more than 40 hr before moving to another height for sampling. During data collection at each height, ozone sampling switched between different tubes at an interval of five 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.”

L171: “isothermal” here should be “isotherm”

Agreed and it has been corrected in the revised manuscript.

L193: This is the first instance but more follow. Significances for the one-way ANOVA should not be reported as 0.00. They should be reported with the determined significance at higher precision or else as $p < 0.01$.

In section 2.4, we mentioned that the significant level for the statistical test conducted in this manuscript was set at 0.05, but this is not emphasized in the later text. In the revised manuscript, we have changed the expression to either “ $p > 0.05$ ” or “ $p < 0.05$ ”.

Fig. 4 c: Certain periods on 2/13 and 2/15 appear to show less difference between the acrylic cylinders, from Fig. 3 these appear to have less shortwave radiation as well. This would seem to be a significant supporting argument for the importance of UV which is not commented on. Could the authors comment?

We agree that there should be a link between shortwave radiation and the photochemical ozone loss we observed between the two acrylic tubes. Yet this link requires further exploration. At this point, the temporal trend shown in Figure 3 does not support the potential link pointed out by the reviewer, as shown in a new Figure S4 in the revised manuscript (see below also). More evidence is required to support that higher shortwave radiation will lead to more photochemical ozone loss. Several other factors may affect this process, including the amount of shortwave radiation (ultraviolet and visible range in particular), the presence of condensed phase reactors (frost, flurries etc), and air temperatures. Thus, more comprehensive mesocosm experiments should be designed to study BEEs.

We have included this discussion in the revised manuscript (Line 343–348): “It should also be noted that the relationship between the intensity of downward shortwave radiation and the extent of the cryo-photochemical ozone loss is yet to be validated (Fig. 4 and Fig. S4). The lack of correlation may be explained by the fact that the downward shortwave radiation reported in this study covers wavelength from 300 nm to 2800 nm, whereas UV radiation (< 400 nm) has been generally considered the most effective range causing photochemical ozone loss. Other factors, such as the presence of various condensed phase, the availability of Br⁻ substrates and air temperatures would also affect the extent of the cryo-photochemical ozone loss.”

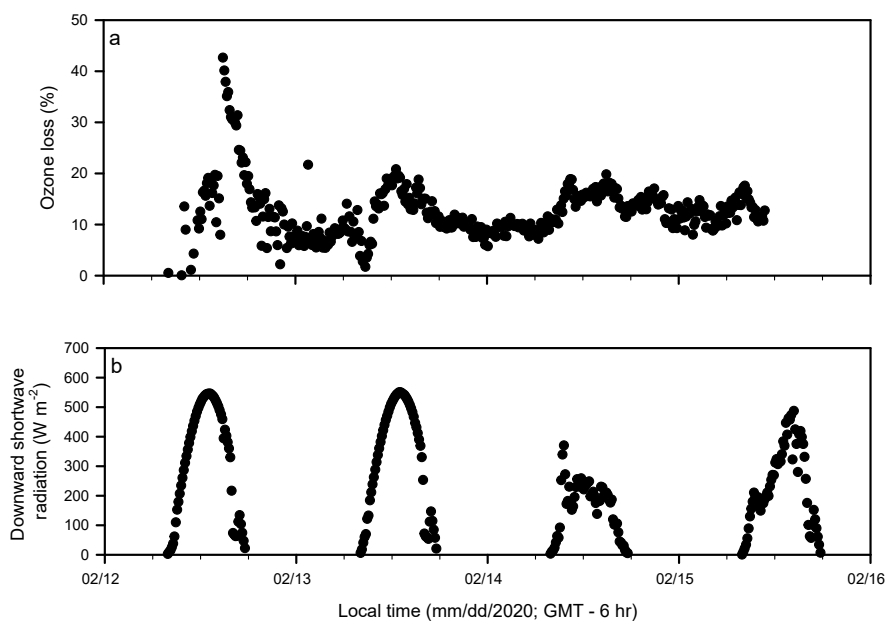


Figure S4. Temporal changes of (a) ozone loss (%) between the UV-transmitting and UV-blocking tubes; and (b) downward shortwave radiation during Experiment #4.

Fig. 5 and discussion: The authors comment primarily on pH, however they should also consider the effects of pH on the availability to relevant oxidants and the redox reaction. For instance the pK_a of HOBr is 8.59 and HOBr concentrations would change significantly for the pH conditions in this plot.

The discussion on pH was aimed to provide support for protons that are required in the cycling of reactive bromine species as indicated in the original Figure 1. We agree that the influence of pH on HOBr dissociation is also an important factor that should be considered. However, one important thing that needs to be clarified is that pH reported in this manuscript is measured on meltwater of bulk snow and sea ice samples, instead of direct pH measurements at the air-ice interface. The dissociation of HOBr will be greatly determined by the pH at the interface, which is not readily available in this study. We have included this in the revised manuscript (Lines 382–383): “Time-series measurements of pH at the air-ice/snow interface could also be explored to probe the availability of protons and the efficiency of HOBr dissociation on the surface of sea ice or snow layer.”

Table 1: The columns for Br⁻/Na⁺ and Cl⁻/Na⁺ appear to be reversed.

The mistake has been corrected; see the revised Table 1 in our response to Reviewer #1 above.

L249: The one way ANOVA demonstrates that the UV-transmitting cylinder has lower O₃ on average, but not that it is consistently so. See the comment on Fig. 4 on how the consistency is not clear at certain times.

We agree that “consistently” is not appropriate to be used here. In the revised manuscript, we have rephrased the text in Lines 307-310: “The overall temporal patterns between the two tubes were similar during Experiment #1 (Fig. 5). Generally, the ozone concentration in the boundary layer air immediately (10 cm) above the sea ice in the UV-transmitting tube were considerably lower than those in the UV-blocking tube (Fig. 5c).”

L261: I believe this refers to Fig. 4c not Fig. 6c

The mistake has been corrected in the revised manuscript.