Dear Referee #2,

Thank you very much for reviewing our manuscript. We appreciate 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. 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.

Response: 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 (Figure 1). These co-variations between GEM and ozone further demonstrate the capacity of the mesocosm approach in studying photochemical phenomena in the polar troposphere. We will include the data (GEM and ozone) from the follow-up experiment (2020 to 2021) in the revised manuscript.

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

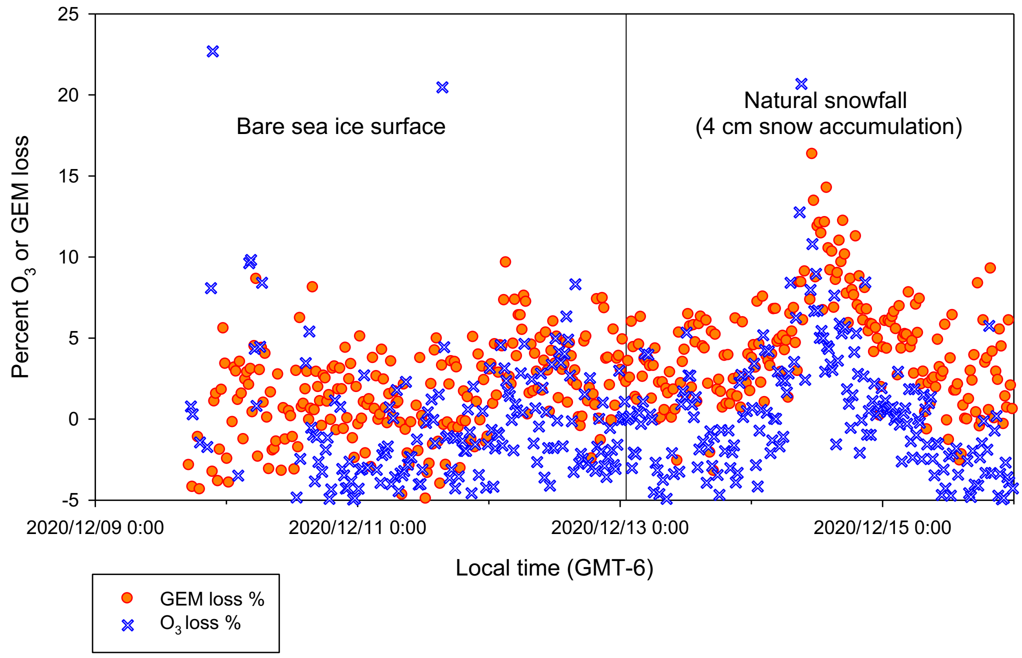

Figure 1. Temporal changes of gaseous elemental mercury (GEM) and ozone difference that is calculated between UV-transmitting and UV-blocking tubes during December 2020. (This figure will be added in the revised manuscript)

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?

Response: 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 will clarify this in the revised manuscript.

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?

Response: 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 (1.12×10^{-6} g CL^{-1} h^{-1} and 0.008 µg L^{-1}, respectively) (Gelifus et al., 2016; Rysgaard et al., 2014). We will clarify this in the revised manuscript.

In terms of the role of ice-nucleating particles, it was not explicitly addressed in the original manuscript, but we will add our perspectives in the revised manuscript. 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.

Response: We agree. In the revised manuscript we will change "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.

Response: We agree. The original Figure 1 will be updated accordingly in the revised manuscript (see below).

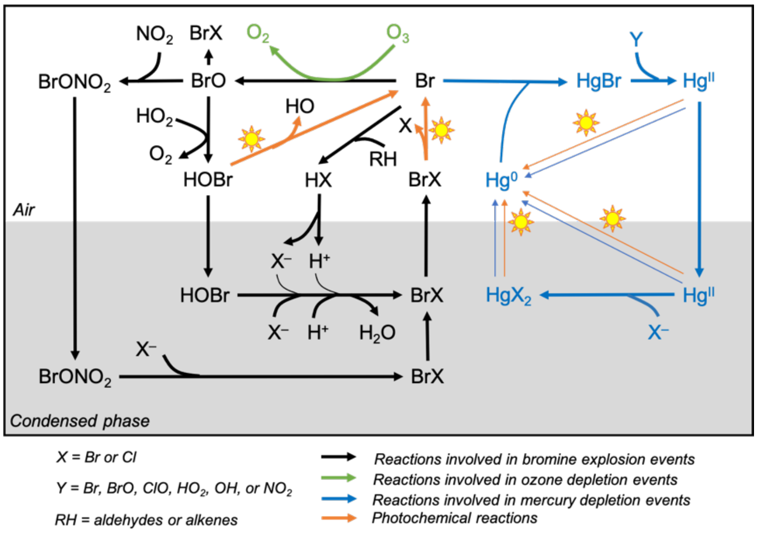

Figure 2. General reaction schemes involved in bromine explosion events, ozone depletion events, and mercury depletion events in the Arctic during polar sunrise: gas-phase reactive bromine species (Br and BrO) produced from multi-phase reactions on the surface of the condensed phase will cause the depletion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

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).

Response: 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. The main text will be rephrased to avoid the confusion and original Figure 1 will be updated.

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."

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?

Response: 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.

Response: 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 will be clarified in the revised manuscript.

L171: "isothermal" here should be "isotherm"

Response: Agreed and it will be 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 $p<0.01$.

Response: 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 will change 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?

Response: 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. 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 will mention this in the revised manuscript.

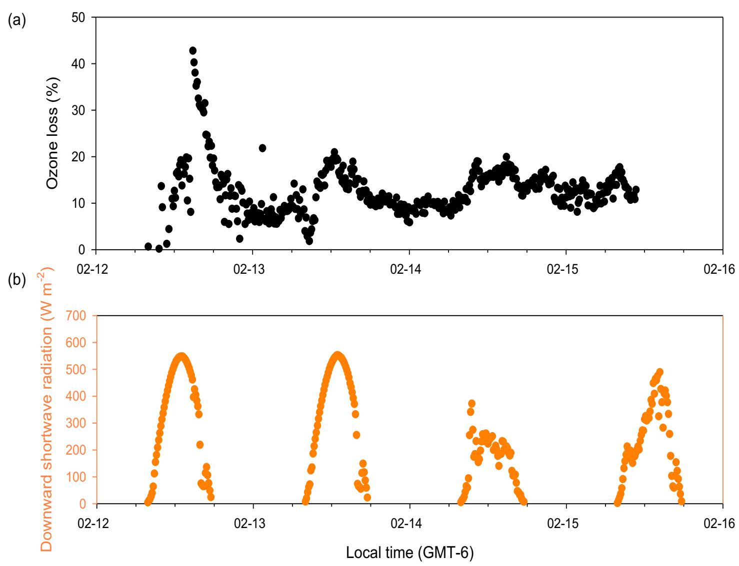

Figure 3. Temporal changes of (a) ozone loss (%) between UV-transmitting and UV-blocking tubes; and (b) downward shortwave radiation during 12-15 February 2020. (This figure will be added as supplementary materials in the revised manuscript)

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 pKa of HOBr is 8.59 and HOBr concentrations would change significantly for the pH conditions in this plot.

Response: 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 will include this in the discussion section of the revised manuscript.

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

Response: The mistake will be corrected, and the revised Table 1 is provided.

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

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.

Response: We agree that "consistently" is not appropriate to be used here. In the revised manuscript, we will rephrase the text.

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

Response: The mistake will be corrected in the revised manuscript.