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Comment on acp-2021-157

Anonymous Referee #2

Referee comment on "Reproducing Arctic springtime tropospheric ozone and mercury depletion events in an outdoor mesocosm sea ice facility" by Zhiyuan Gao et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-157-RC2>, 2021

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.

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?

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?

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.

Figure 1: Realizing this is meant to be a simplified schematic, reactions reducing Hg^{II} 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.

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 H_2O_2 (Bray and Livingston, 1928).

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?

L119: "at every minute" could the authors clarify what is meant by this? Is O_3 measured as an integration over each minute, or is it a shorter sample taken once each minute.

L171: "isothermal" here should be "isotherm"

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 $p < 0.01$.

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?

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.

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

L249: The one way ANOVA demonstrates that the UV-transmitting cylinder has lower O_3 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.

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

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