

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-157

Anonymous Referee #1

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-RC1>, 2021

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.

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.

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".

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.

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 Table 1; please fix.

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 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").

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.*).

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.

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.

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.

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

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).

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

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