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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Br_2, BrCl, BrO and surface ozone in coastal Antarctica: a meteorological and chemical analysis" *by* Z. Buys et al.

Anonymous Referee #2

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The paper by Buys et al. reports on the first measurements of molecular halogens (Br2 and BrCl), as well as BrO measurements, at Halley Bay, Antarctica. These are difficult measurements in a challenging environment, and such measurements are badly needed for the Antarctic troposphere. I would very much like to see the data published as soon as possible. There is no question that the data set could form the basis for a very nice paper. The measurement data may be good quality, but the authors spend considerable time trying to convince the reader that there is an artifact for Br2, caused by HOBr reaction on the inlet, but do not provide HOBr data, to enable assessment of the claim that this interference is only important in the daytime, nor do they provide any specific proof that this is in fact happening for their inlet. They refer to Neuman et al.

regarding this interference, but it is an inlet artifact, and the paper does not describe the inlet except to say that it was Teflon. Given the importance of this to the paper, this is quite odd. Then, the paper continues to discuss the Br2 data, including some daytime data, which has already been discredited in the paper. The paper indicates that there is "evidence for blowing snow as a source of reactive bromine" when in fact there is no evidence of any kind, other than there were higher winds; but having winds does not indicate evidence of blowing snow as the source. Why can't winds = wind pumping and increased emissions of halogen precursors out of the snowpack? The paper uses a 0d model to draw conclusions without any meaningful description of how the model was initialized, whether there were non-simulated prescribed 0D fluxes, what the effective mixing height is, etc. To use a 0D model (that instantaneously mixes in the vertical direction) in a quantitative sense to compare to absolute concentration measurements in a highly stratified stable environment is difficult to defend. The paper does not recognize or consider that molecular halogens, as an example, are likely not present at a concentration that is constant with altitude, and yet they draw specific conclusions through comparison of measurements (at an unspecified height above the surface) with the model. There are so many omissions, and inappropriately justified conclusions in this paper that it really should not be published in anything like its present form, until these issues are straightened out. This is quite important to do, since, as the authors point out, these measurements are, so far, one-of-a-kind for Antarctica. It is also important to note that the subject and scientific questions for the paper seem to randomly move around, discussing three cases studies, chosen for reasons that don't derive from any particular question, other than addressing variability. When the paper is rewritten, the authors should carefully consider, and address, their carefully articulated question or questions for the paper. Below, I discuss issues and recommendations for a rewrite, in the order the issues arose in the paper.

1. Lines 61 and 62 - which ones? References?
2. Line 68 - provide references?

3. Line 114 you mean high mass resolution, or temporally high resolution?

4. Line 123 - It is critically important that you describe the inlet in detail - what kind of Teflon, what diameter, what length, is it filtered? Heated? How does it compare to the inlet used in Neuman et al? The sentence that contains "…this larger sample inlet to the smaller flow tube." is not understandable.

5. Text around lines 128 - 130 - since you quantitatively compare the measurements to 0D model output (a highly challenging approach for a stable surface layer!) you really should provide estimates of the uncertainty for all measurement data. Refer in the text to Table 1 for the limits of detection. Regarding Table 1, I note that a sensitivity is not a particularly useful quantity for the reader, compared to an uncertainty.

6. Line 168 - what does "representative of Antarctic conditions" mean? Just temperature? How do you deal in a 0D model with the fact that the surface layer is very poorly mixed, and that what you measure at the surface might be strictly representative of only the very near-surface layer? Do you have any separately prescribed fluxes, or are all emissions from particles and the surface strictly resulting from explicit condensed phase chemistry? Do the fluxes mix into an effective boundary layer height? How would your conclusions change if you used a different boundary layer height?

7. Lines 183 - 184 - this last sentence worries me a great deal. It presupposes that "areas of open water and leads" are "the halogen source region". Aren't you trying to determine/study the nature of the halogen source region? Aren't open water and leads at relatively high pH? Based on the literature, couldn't one reasonably hypothesize that regions of open water and leads are NOT the halogen source region? Line 187 - there is no justification presented for the assumption that Br2 is derived from open water. I am not aware of any measurements that indicate that Br2 is derived from open water. This should be discussed in more detail and justfied.

8. Line 199 - "it is now acknowledged…" should be reworded. It is only acknowledged that there is an interference for the Neuman et al. data. There is no real evidence

provided in this paper for the interference, for your measurements and inlet. It is simply stated, and the Neuman et al. paper is cited.

9. Line 217 - it is apparent in Figure 4 of Liao et al., 2012.

10. Line 247 - it just seems odd that the reference would be Jones et al., when Jones et al., including in this paper, are proponents of the idea that it isn't stability that you need for an ODE, but blowing snow. Given that this paper claims to provide evidence that blowing snow is important to ODEs, I think you should find a different citation for the importance of low winds speeds and a stable boundary layer.

11. Lines 259 - 266. Please explain how you can defend direct comparisons of absolute concentrations of molecular halogens with a 0D model output. There are so very many reasons for differences, starting with the vertical mixing issue. But also the chemistry. For example - it is known that N2O5 reaction with sea salt can make Br2. Do you have snowpack N2O5 chemistry, that makes Br2? If so, is the snowpack NOx and O3 concentration simulated properly? These of course are tough/unfair questions, but they point out that you should be openly circumspect about direct comparisons of the absolute concentrations from a 0D model and the measurements at one fixed height above the surface. You could just say that they are different, and there are a multitude of possible reasons, and list and discuss them. In my view, way too much is made of the HOBr interference, e.g. in Figures 4c and d; and if you are convinced of this, you shouldn't be discussing Br2 for any period, e.g. "end of the day" (line 263) for which there could be HOBr present.

12. Line 268 - maybe there is a large and persistent Br2 and BrCl flux! On what basis do you rule this out? There have no previous measurements of this kind in Antarctica.

13. Line 277 - is the MISTRA model correct regarding "an absence at night"? How do you know?

14. Line 278 - this sentence should be removed. You don't show this at all. The

only evidence you have provided for this is the Neuman et al. reference. It could be the case, but isn't it also possible that you are throwing away information previously unknown, about a strong surface source of Br2? I note that the flux number needed effectively assumes a vertical mixing rate, which you have not discussed at all. Perhaps your model mixes too fast, and the surface layer in which the measurements are made is very stable, leading to high surface layer concentrations??

15. Line 283 - 284 - but this doesn't mean it is right. As you know, you can get agreement for the wrong reasons. You could have improved the agreement by adding a sunlight-dependent surface source of Br2 to your model. In that model case, would it show that there is a sunlight-dependent surface source of Br2?

16. Line 287 - the actual "evidence" presented here is mostly just the citation.

17. Line 299 - you mean "finite", or "sufficient", rather than "increased".

18. Line 303, and following text - "some evidence of ozone depletion". Really? How do you define that. It looks to me like just pure continental background with an impressively small amount of variability. This really is a stretch. You also discuss low levels of daytime Br2, which you have already discredited. The evidence does not suggest anything about blowing snow. What you have is some high winds, which suggests only high winds, and some questionable Br2 data, and no ozone depletion. What you actually have is literature suggestion that blowing snow is important. But there is no evidence presented in this paper for this, and this section should be removed.

19. Line 315 - do you really think HYSPLIT is so good (for Antarctica) that you can distinguish between back trajectories 1 and 2, e.g., with respect to sea ice contact? I really don't think so.

20. Line 328 - there is HOBr near sun set?

21. Line 336 - or, most of what you see is the result of chemistry occurring in the near-coastal environment at Halley Bay?

22. Line 344 - "passing at height" should be repaired.

23. Line 380 - again, you should explain why there is no HOBr at night. At sunset and sunrise what is the lifetime of HOBr?

24. Lines 390-395 - this section seems out of place and/or unnecessary.

25. Top of page 16 - I note that MISTRA never simulates Br2/BrCl as high as the $\sim$50-60 observed, as shown in Figure 11. Why do you think this is the case?

26. Lines 444-445 - I see clustered data at the lowest temperature and at the highest temperatures, so, what you are saying here isn't readily apparent.

27. I note that the discussion of the temperature dependence of the Br2/BrCl ratio and the behavior of sea ice contradicts the earlier discussion of Br2 emission from open water.

28. A main result of the paper is presented on line 471, and lines 508 and 509. Perhaps the latter should be more a focus of the revised paper? Your modeling results do not do what is stated on line 476 in any way that is defensible. Obviously, model and measured Br2 could differ for a wide variety of reasons. There is actually no evidence presented in this paper for inlet line conversion of HOBr to Br2. I believe that it is likely happening, but there is no proof presented in this paper.

29. Line 493 - you have no evidence of blowing snow whatsoever, and any discussion of it should only be in passing, as something that can indeed happen when winds are high. This is all you know for sure.

30. The Figure 1 x-axis could use more tick labels; you don't really need any of the 2007s on the labels, as that is in the caption.

31. Figures 13a and b should have consistent temperature units.

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