Atmos. Chem. Phys. Discuss., 12, C5469–C5481, 2012
www.atmos-chem-phys-discuss.net/12/C5469/2012/

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.

Z. Buys et al.

zakysa@bas.ac.uk

Received and published: 7 August 2012

We would like to thank the reviewer for his/her comments and feedback. Below are detailed responses to each comment received (marked with a ***).

Referee #2: Reviewer 2 raises a number of issues within the preamble before moving on to specific concerns. We therefore deal with the major issues first, and then the specific ones.

Major Issues:

a) Artifact

*** Clearly when one invests considerable time and effort into making measurements, one would like them to be good quality and correct. It was therefore with great reluctance that we found the need to raise the issue that there could be an artefact in our Br2 and BrCl data, an issue that, at the time we made our measurements, had not been identified. However, equally, when one publishes data, they must be presented within the uncertainties, so it is absolutely necessary to discuss the potential for artefact, especially when the evidence, albeit indirect, suggests that it is likely there. As the reviewer clearly knows, Neuman et al. (2010) first raised the issue that HOBr conversion to Br2 could be an issue for CIMS measurements. They presented results quantifying HOBr conversion to Br2 on a number of surfaces, both coated with NaBr and uncoated, the latter including the Teflon of the instrument inlet, glass, aluminium, stainless steel, PVDF, and several other types of Teflon. Clearly HOBr conversion to Br2 proceeds easily on surfaces, and could therefore be an issue for CIMS measurements. Their results are in line with laboratory studies that have shown the rapid generation of Br2, and to a lesser extent BrCl, on salty surfaces (Abbatt, 1994; Adams et al., 2002; Kirchner et al., 1997). The presence of a CIMS inlet artefact in Br2 has been acknowledged in subsequent field measurements (e.g. Liao et al., 2012a, Liao et al., 2012b). In their paper characterising soluble bromide measurements during ARCTAS, Liao et al. (2012a) state that "Due to the conversion of HOBr on the Teflon inlet, the CIMS Br2 signal represents the lower limit to the sum Br2 + HOBr" and indeed present their observations in this way. The presence of an artefact is not questioned, merely stated as a given and the data appropriately interpreted. In a second 2012 paper reporting observations of HOBr, BrO and Br2 speciation at Barrow, Liao et al. (2012b) state that "Small but detectable levels of daytime Br2 were due to the conversion of HOBr on the Teflon inlet wall and the uncertainty in background signal measurements. The Br2 measurements at night were without interference from HOBr as this species was not observed in the dark." The issue of a potential artefact on CIMS Br2 observations arising from conversion of HOBr on the CIMS inlet, is both in line with laboratory studies and is already accepted within the published CIMS literature. As the instrument used at Halley was

effectively the same as that used in the Liao et al. studies (ours was also built by the Huey group) our instrument will be subject to similar interferent issues as Liao's. As the interference is an inlet artefact, we now provide full description of the instrument inlet, as suggested by the reviewer. The reason that we do not provide HOBr data as support to the claim that we consider the interferent is only likely an issue during daytime is simply because we did not measure HOBr. However, we note from the Liao et al. (2012b) paper, where measurements of HOBr were performed at Barrow, that no significant nighttime concentrations of HOBr were detected. Importantly, this result is in line with our theoretical understanding of HOBr chemistry.

Liao et al. (2012a) "Observations of inorganic bromine (HOBr, BrO, and Br2) speciation at Barrow, Alaska, in spring 2009", J. Geophys. Res., 117, doi:10.1029/2011JD016641. Liao et al. (2012b) "Characterization of soluble bromide measurements and a case study of BrO observations during ARCTAS", Atmos. Chem. Phys., 12, 1327–1338, doi:10.5194/acp-12-1327-2012

b) Section about blowing snow (section 3.2.2)

*** We agree with the reviewer that this section was of insufficient quality to include in the paper, and it has now been removed.

c) Using a 0-D model

*** The paper uses a 0-D model to draw specific conclusions about specific issues in the paper. The first is to explore the HOBr interferent, and whether inclusion of some HOBr conversion can account for specific features in the daytime Br2 and BrCl observations. We believe we have worked within the limitations of the model, by qualitatively looking at the structure of the measured signals, as well as the range of the HOBr conversion. The text in the paper has been altered and now reads: "This approach suggests that the artefact represents a conversion of HOBr to Br2 of the order of several tens of percent, while that for HOBr to BrCl is less but non-negligible." We have also added the following text to justify use of a 0-D model to explore our observations in

the way that we do: "To explore these two hypotheses, we use the 0-D model MISTRA, focussing on two days in September (see Figure 2). The local wind direction throughout this period ($\sim$250o) indicates arrival of air at Halley from over Precious Bay, and wind speeds were constant at $\sim$7 ms-1. Temperatures on these days were at -40oC although rising to -33 oC during the final 12 hours. On both days there is a well-defined boundary layer (at 200 m on Sept 6th and 100 m on Sept 7th), which observations of the temperature profile from an adjacent 30 m mast suggest was well mixed on these days. As the CIMS inlet was roughly 5 m above the snow surface the measurements are likely to be representative of this mixed layer. While the MISTRA runs are not specific to height, given the boundary layer conditions on these days, the output is likely to be reasonably representative." The second is to explore the temperature dependence of the Br2:BrCl ratio. Using MISTRA as a tool to explore the nature of this temperature dependence, we suggest that the chemical thermodynamics in the 0-D MISTRA model give us one possible explanation for the temperature dependence (in line with studies by Sander et al. [2006], Foster et al. [2001] and Adams et al. [2002]). Results from MISTRA are compared, but we state the limitations of this comparison. The third is to explore the potential of long range transport of an ozone depleted air mass. Here we are looking at a specific case, where MISTRA uses a simplified representation of the conditions this air mass may have encountered. The results are used in a qualitative manner to discuss the transport of halogen species, and we state that the ozone depletion at Halley is not reproduced.

d) Paper structure

*** The paper structure and content has been changed considerably in light of the reviewer's comments.

Specific Comments:

1. Lines 61 and 62 - which ones? References?

*** This section of text has now been removed

2. Line 68 - provide references?

*** References have been included: (Gilman et al., 2010; Jacobi et al., 2010)

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

*** Amended text to refer to both high mass and temporal resolution (when relating to other studies).

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.

*** We agree that this information should have been included. This sentence was removed and replaced with the actual inlet geometry and a more in depth description of the setup. Text included reads:

"Ambient air was continually sampled at a high flow rate ($\sim$2400 slpm) by means of a regenerative blower (Ametek BCDC) into a 40 cm long aluminium pipe of 8 cm i.d that protruded 20 cms above the laboratory roof. A smoothed Teflon doughnut-shaped cap was secured to the pipe and positioned roughly 5 metres above the snowpack in the NE corner of the laboratory which allowed the least perturbed flow thereby minimising turbulence as well as shading. To further reduce problems associated with surface adsorption, air was sampled from the centre of the aluminium pipe at a flowrate $\sim$8 slpm which reduced both the residence and possible wall interaction time (t < 0.6 sec). The sampled air was delivered to the CIMS in a heated teflon perfluoroalkoxyalkane (PFA) inlet (i.d.=0.65 cm, length=25 cm) controlled at 40 +/- 2 $^{\circ}$C by a series of thin Kapton heaters."

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.

*** The following text has been included in the manuscript: "The estimated accuracies were obtained from the uncertainties in the flow meter calibrations for the sample and calibration gas obtained with a bubble flow meter before and after each measurement period and was found to be $\sim$ 4%. This also includes the uncertainty in the calibration gas standard which the manufacturer provided (5σ). The precision of the instrument to SO2 was obtained from the scatter (1σ) of the SO2 sensitivity and found to be <2% (at dew point of -24°C)."

*** Table 1 has been updated to include measurement uncertainties for the CIMS halogen data.

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?

*** The amended text: "For our work, MISTRA was modified to be representative of Antarctic conditions. This was achieved by implementing measurements from Halley station, which include: aerosol size distribution and composition (Rankin and Wolff, 2003; Jaenicke, 1988), local meteorology (Anderson and Neff, 2008), and measurements of local chemical composition (NOx, O3, NMHCs, DMS, HCHO, CO) in the model." states what was implemented/ changed in the model.

*** The two consecutive days discussed in the previous Section 3.2.1 were chosen to model using 0-D MISTRA as they have a well defined boundary layer/ mixed layer which, from observations of temperature profiles from an adjacent 30m mast, appear

to be well mixed on these days (winds speeds ∼7 ms-1). As the CIMS inlet was placed 5m from the surface, the measurements are likely more representative of this 'mixed layer' above the surface than of the 'very near surface' layer. All emissions from particles and the surface are strictly resulting from explicit condensed phase chemistry, apart from a prescribed flux of Br2 from the model surface. The only difference (in meteorological terms at least) between the two modelled days are that the mixed layer height is 100m on one day, and 200m on the other. The HYSPLIT trajectories for the two days are near identical so the same prescribed Br2 flux is used in each case. The only parameter changed in the model between these runs was the mixed layer height. We have included text to this effect in the manuscript (section 2.4 and section 3.2)

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.

*** Thank you for pointing this out. It was simply a poor choice of words/ badly phrased. We meant to refer to an area of newly forming sea-ice as a source region, not direct open water. Text has been changed and now reads: "newly forming sea ice" instead of "open water and leads".

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.

*** Text has been reworded.

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

*** This reference is now included.

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.

*** Actually Jones et al., (2009) discussed that ODEs can occur both under conditions of low winds and stable boundary layer, as well as at high wind speeds. However, this section of discussion has been removed from the manuscript, so no reference is needed.

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.

*** Re how we can defend direct comparisons of absolute concentrations of molecular halogens with a 0D model output, please see response to comment 6, above. Equivalent text is now included into the manuscript to address this point.

*** Re making too much of the HOBr interferent, we feel that, unfortunately, we cannot side-step this issue for reasons already outlined in this response. We note also that Reviewer 1 actually asked us to raise the prominence of the interferent discussion, by bringing it into the text earlier. In the manuscript we now refer to Fig 4 of Liao et al. 2012 as a way of linking J(Br2) and [HOBr], and define night and day according to J(Br2), in order to be more specific.

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.

*** This is a good point. Other studies suggested the HOBr interferent would be apparent in our measurements, so that is one of the reasons we pursued this route. However, we did explore several different ideas regarding a surface source of Br2. We looked at a sunlight dependent Br2 flux, a night-time only Br2 flux, a Br2 flux which varies with solar zenith angle, and a persistent Br2 flux. Results did not fit with the data either in magnitude, shape or timing of the maxima and minima we see in the data. To address the reviewer's concern, we now include a full discussion of these flux experiments in the manuscript.

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

*** The following text has been included in the manuscript: "Recent observations of HOBr show that it is above detection limit only when jBr2 (s-1) is greater than zero (Figure 4 of Liao et al., 2012)." Please also see Major Issue a) above.

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??

*** We have addressed the reviewer's concerns over the interference issue as well as fluxes as outline in previous responses above.

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?

*** Please see response to comment no. 12. We do not state that there is definite agreement in the comparison, we simply state that it suggests the presence of an interferent.

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

*** We have amended the text to: "Given the evidence for an interferent in CIMS day time measurements of Br2 and BrCl, all Halley plots are colour coded to differentiate between daytime (JBr2 > 0) and night time (JBr2 < 0) observations of Br2 and BrCl, showing all daytime measurements in black. " Also see responses to major comment a) above.

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

*** Changed text to: "sufficient"

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.

*** Agreed. You're point was raised previously by a co-author, and the section has now been 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.

*** Section has been removed.

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

*** Recent observations of HOBr show that it is above detection limit only when jBr2 (s-1) is greater than zero (Figure 4 of Liao et al., 2012b).

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

*** Given that reduced surface ozone mixing ratios were observed at South Pole, the air mass was clearly influenced by halogen chemistry before transport across the continent. However, in light of the reviewers concern, we have revised the manuscript to read: "A third possibility is that these source regions may have some influence, but most of what we see is the result of chemistry in the near-coastal environment at Halley."

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

*** Text is amended to: "following this possible trajectory" in reference to the previous sentence.

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

*** See response to comment no. 20.

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

*** Agreed, on re-reading this section it has now been removed from the paper. We have, however, amended this section of text to include a comparison with the Liao et al. (2012b) observations.

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?

*** Mixing ratios of BrCl are tiny during these ratio spikes (<1ppt) meaning even small variations/ fluctuations can lead to large changes in the ratio.

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.

*** Text has now been amended to: "Some relationships between Br2 and BrCl appear to hold within certain temperature ranges, for example observed Br2 are clustered at both the coldest temperatures (blue dots) and warmest temperatures (red dots)."

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.

*** Previous statement on open water has been amended.

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 modelling 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.

*** See Major Issues a) - d) above

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.

*** Section removed.

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.

*** Done

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

*** Done

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11035, 2012.