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Atmospheric
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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.

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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 #1: The measurement of reactive halogens with CIMS greatly extends our ability to study the chemistry of such species in polar (and other) environments. Prior to measurements of the type presented in this paper, DOAS-based BrO measurements were pretty much the only thing going for speciated, reactive halogens. And so, there is considerable value to these CIMS results, the first for the Antarctic. Although DOAS was not deployed at this time, the results from this study for BrO are comparable in

order-of-magnitude to what has been measured before, plus there is some information on Br2 and BrCl provided. Data are presented for a roughly month-long period during which considerable variability in the mixing ratios was observed. Three different interesting case scenarios are presented. In addition, there is recognition of a potential inlet artifact in such measurements that has to be recognized and discussed in the literature. Indeed, it may well have affected earlier Arctic measurements (e.g. those of Spicer et al.) Thus, I recommend publication of the paper after the following issues are addressed.

1. The HOBr artifact. A major issue with the measurements is, clearly, the HOBr artifact in the Br2 and BrCl daytime data. It is important that this issue be presented within the scientific literature: there may not be an easy way around it! The artifact is that it is well known from a number of laboratory studies that HOBr will react with Cl-/Br- on surfaces to form BrCl/Br2. As well HOBr can react with itself to form Br2O (plus H2O), and the chemistry of Br2O is not well characterized. BrO is, by contrast, known to be not nearly so surface active, with relatively low propensity to self-react or react with halides. For this reason the BrO measurements are thought to be unperturbed by inlet effects. The authors don’t hide this issue, and do their best to deal with it by highlighting all the data during the day which they think may be impacted.

I have a few suggestions and questions though:

I) It was only when I was well into Section 3.2.1 that I realized how the authors are doing to deal with this issue. Indeed, it is largely by looking at the Case 1 data in comparison to the MISTRA model results that the issue is discussed at length. I propose that they feed the reader through this thought process much earlier, by putting into the Introduction as a summary of what is to come, e.g. a précis of the important issues that are arising. Also, some of the statements are not clear – e.g. page 11043/line 10 it is stated that no daytime data will be discussed, but that is not true. All the BrO data are discussed.

*** We agree that this would be a good course of action. Text has been included at the end of the Introduction to highlight our manner of dealing with these measurements in the rest of the paper.

*** page 11043/line 10: this statement has been changed to emphasise only Br2 and BrCl night time data will be discussed.

II) I also recommend that the authors add references for the source of the artifact chemistry, e.g. the lab studies done with HOBr and BrO on surfaces that show that the former is highly reactive and the latter not (currently the only reference in the paper is from Fickert et al. which is for aqueous surfaces, which do not pertain to inlet surfaces).

*** We agree, and have now included the following text and references in section 3.2.1: "The proposed mechanism is the reaction of HOBr on salty surfaces which has been shown in laboratory studies to rapidly generate Br2, and to a lesser extent BrCl (Abbatt, 1994; Adams et al., 2002; Kirchner et al., 1997)."

III) The inlet geometry (length, diameter), materials (any metal fittings?), flow rates, and the materials in the source region of the CIMS have to all be described in detail. This would more easily allow at some later time a better estimate of the artefact to be made.

*** We agree that this information should have been included. The actual inlet geometry and a more in depth description of the setup are in the new text which 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 °C by a series of thin Kapton heaters."

IV) In Figure 4, with a lot of HOBr included, the MISTRA model results can match experiments. I realize there are huge uncertainties here, but I nevertheless think it is useful to document the amount of atmospheric HOBr that this is consistent (i.e. using the model results) to put alongside the measured values for the other halogenated species that are presented in the paper.

*** The modelled values of HOBr are similar to those observed by Liao et al. (2012) (maxima of $\sim$8-12 pptv on these days) and follow a similar diurnal pattern.

2. BrO Measurements. I was surprised to not find in the paper the manner by which BrO is calibrated. This is a radical and known amounts of BrO have to be generated in order to do the calibration. This would be a non-trivial exercise, and has to be in the paper. Were the calibrations done post or prior to the campaign? Also, in Figure 5, there appears to be nighttime BrO, much higher than the stated detection limit of 0.1 pptv. This is highly surprising. In that context, the paper needs to better describe how the detection limits were calculated, how backgrounds were handled, etc. Are these detection limits that have taken into consideration any chemical backgrounds?

*** BrO calibration - As far as we are aware there is no known direct calibration method for BrO. Therefore, BrO calibration was achieved using a similar method to that described in section 2.2 in Liao et al. (2011a). We use the ratio of the rate constant for Reaction [Br2+SF−6 → Br−2 +SF6] to Reaction [BrO+SF−6 → BrO-+SF6] (determined to be 1.0±25% in the laboratory by Liao et al., 2011a), along with the dew point calculation, to determine the BrO calibration. To determine the sensitivity of the CIMS system, a mass flow controller (MKS 1479A) provided a continuous 8 sccm flow of 0.2% (+/- 5 σ) of a certified standard of our calibration gas (SO2 in nitrogen) (Air

Products, speciality gases) to the insulated inlet system every two hours for a 1 minute period. The sensitivity of the CIMS system was then used as a proxy to track the sensitivity of BrO (Liao et al., 2011a).

*** Detection Limits – Thank you for pointing out the BrO night time measurements above the detection limit. After looking at the method we previously used, there were a few errors which led to an inaccurate final LOD for all compounds. These have now been re-calculated using the method described here, and the measurements lie within the new LOD (as they should). Limits of detection were estimated using 1σ counting precision of the 10 second zero background signal. This approach was assumed to represent the detection limit (Ridley et al., 1994) as there was no suitable invariant ambient data. The standard deviation of the zero data was transformed to pptv using the averaged sensitivity of the instrument to SO2. It can be assumed that when the data is averaged to 10 minutes the LOD would improve by $1/(\sqrt{60})$.

*** Backgrounds – Background or zero measurements were obtained by allowing a teflon plunger in the inlet system to be pneumatically moved into position every 10 minutes. This meant that instead of the ambient air directly entering the CIMS instrument it was first drawn through a 20 cm x 5 cm i.d stainless steel filter tube for a 3 minute period. The filter tube contained activated coarse charcoal and nylon glass wool that had been previously soaked and dried in a concentrated NaHCO3 solution. A similar scrubbing method had previously been successfully employed (Slusher et al., 2004; Liao et al., 2011a) and showed high efficiency for removing HNO4 and other molecules from the sampled air.

*** All of these points are now included in the paper in Section 2.2.

*** Section including figure 5 has been removed.

3. Blowing Snow. There is a flurry (no pun intended) in the community these days about the blowing snow hypothesis giving rise to active bromine. While this may be true, it is also possible that high wind speeds give rise to more snowpack pumping.

I thus recommend that the paper adjust how it describes the case study when high levels of bromine and high wind speeds were observed.

*** This section was questioned previously by a co-author and now by reviewer #2, so has now been removed.

4. Abstract. I found the Abstract to be very choppy and hard to read; I recommend having another go at it. I think the authors should present the artifact earlier in the paragraph, and then go on to explain the main findings from the study with that information in mind.

*** The Abstract has been restructured/ re-written to more easily convey the results of the paper (and bring in the idea of the artefact at an earlier stage in the paragraph, as suggested).

5. Small points. Page 11044/line 5 – change units from ppbv to pptv.

*** Done.

Section 3.1 - I found reading the section that the reader had to take a lot for granted because the data were not shown (e.g. diurnal plots through the full campaign, different shapes of the BrO signal as a function of time of day.)

*** These data are highlighted in figure 1. Plots showing the different diurnal shapes of BrO are shown in Figure 2 and Figure 9. This has also now been highlighted in the text.

Page 11054/line 3 – I wouldn't say that salt crystallization 'drives' the bromine explosion but may 'participate' in it.

*** Agreed, amended text reads: "and thereby participating in..."

Figure 2 – Could the solar zenith angle be plotted on this figure?

*** Yes, this could be included. However, the black part of the Br2 and BrCl data show the hours of sunlight (indication of SZA) so we don't feel the need to include this.

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