Atmos. Chem. Phys. Discuss., 12, C3953–C3956, 2012
www.atmos-chem-phys-discuss.net/12/C3953/2012/

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.

Anonymous Referee #1

Received and published: 22 June 2012

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 poten-

tial 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. 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). 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 artifact to be made. 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.

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?

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.

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.

5. Small points. Page 11044/line 5 – change units from ppbv to pptv. 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.) Page 11054/line 3 – I wouldn't say that

salt crystallization 'drives' the bromine explosion but may 'participate' in it. Figure 2 – Could the solar zenith angle be plotted on this figure?

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