Anonymous Referee #1

Summary:

This paper deals with measurements arising from the ARCTAS campaign. A major part of the paper deals with laboratory measurements used to characterise the mist chamber (MC) operating on the NASA DC-8 aircraft. The authors use this characterisation, combined with MC observations of soluble bromide and CIMS observations of BrO, to derive some partitioning of reactive bromine compounds. The final section uses the CIMS BrO data to derive a tropospheric BrO vertical column density which the authors then compare with a trop BrO(VCD) column derived from satellite data. The work falls within the subject area of ACP and should be published once revised.

Specific comments:

i) Methods: please state up front that CIMS suffers an interferent from HOBr conversion, but that is dealt with in your analysis. This just reassures the reader that it's not been ignored. Some mention of this should be included in Section 2.1 (where CIMS is introduced) and 2.1.1 (where CIMS is described) – for the latter, particularly important where estimates are presented of measurement accuracy (line 6).

Agreed - HOBr can be easily converted to Br_2 on the inlet surface for any instrument

P27005 Line 14 column 4: added: In addition, as HOBr can readily convert to Br_2 on surfaces, different inlet setups were used to investigate this issue.

ii) Explain why the soluble bromide detection limit varied with altitude (Section 2.2)

p27009 line 8 column 14 added

The detection limit for the MC is a function of altitude as mass flow through the MC decreases with inlet pressure as a venturi pump is used to maintain the air flow.

iii) The value of this work is that the authors have characterised their MC set up, as used on the NASA-DC8, to be able to derive reactive bromine compounds. However, the key word here is "their" MC set-up. The analysis is very clearly specific to the instrument set-up, critically, the length of the inlet line (upon which HOBr can convert to Br2). There are statements in the text (4 Summary) that this characterisation enables better use of soluble bromide data from previous field missions – this would only be the case if the instrument set-up could be exactly replicated. Throughout the authors need to be more stringent that the results are very specific to their experimental set-up, and do not all represent generalised conversion factors.

Agreed - added to the conclusion - P27017 line 7 column 23 added: As HOBr converts to Br_2 on surfaces, the detection efficiency of HOBr as soluble bromide by MC can vary with inlet length.

iv) Section 3.1.3 Why was BrO only detected in the MC in Setup B..?? Some additional experiments that systematically varied the inlet line length and assessed the BrO detection would seem an obvious thing to try (although clearly not for this paper). Also, please be careful to put statements into the right context – in section 3.1.3, the ratio of BrO to Br- was only found to be 0.4 with setup A, implying that this number depends on additional factors, and is not fixed. Also makes this clear for the equation (1).

We have tried BrO loss in the lab and it is surprisingly not very prone to loss on Teflon tubing. So we have added - P 27013 line 8 column 9 added: BrO was only detected in the MC in setup B because there is no evidence for the conversion of BrO on inlet surfaces in laboratory tests, which is further supported by the excellent agreement between CIMS and LP-DOAS measurements at Barrow, AK [*Liao et al.*, 2011a].
Line 12 column 2 added "in this experiment"

v) Section 3.1.5 Include the major implication also in the Abstract – that a well characterized MC can be used to derive mixing ratios of some reactive Br compounds.

P27001 line 17 column 9 added "A well characterized MC can be used to derive mixing ratios of some reactive bromine compounds."

P27014 line 4,5 changed "This indicates that a MC can be used to examine the areas of active bromine chemistry where BrO and HOBr are enhanced." To "This indicates that a well characterized MC can be used to derive the mixing ratios of some reactive bromine compounds and examine the areas of active bromine chemistry where BrO and HOBr are enhanced."

vi) Section 3.2 the model chemistry scheme was appropriate to conditions where NO2 was less than 5 pptv. But for the case study, unpolluted conditions are described as NO<100 pptv. NO2 will then be higher than 5 pptv – so is the model still appropriate, or ought it to include BrONO2 chemistry?

Agreed this is confusing – NO was in general very low except in pollution plumes so we have restated - P27015 line 10 column 16: added: Except for pollution plumes where high levels of NO (> 100 pmol/mol) were observed, the mixing ratios of NO were less than 10 pmol/mol and NO_2 were near the detection of ~5 pmol/mol.

vii) Figure 4, right panel. Are these data for daytime only so that we don't need to think about Br2? Please clarify in the text and figure caption. Also, in what way is the X-axis the "lower limit" of HOBr + Br2?

The values of "lower limit" of HOBr+Br_2 are the CIMS measurements of Br_2 at mass 160 amu. So only the HOBr converted to Br_2 is observed.

p27029 Figure 4 caption line 6 column 9 added: The x-axis of the right panel is the lower limit of HOBr + Br_2 as only the fraction of HOBr converted to Br_2 in the inlet is observed by the CIMS.

viii) The Summary is basically a repeat of the text. A conclusion would be more helpful, discussing applications and provisos, i.e. the instrument set-up would need to be fully characterised in the lab before a field application, but then it opens some possibilities.

P 27017 line 16 column 6: added "This study also indicates that a fully characterized MC and inlet can be used to derive the mixing ratios of active bromine species.

Typos/minors:
P 27003 line 6: hydrogen bromide should be lower case
P27003 line 6 column 7: changed "Hydrogen bromide" to "hydrogen bromide".

P 27003 line 9: bromine nitrate should be lower case
P 27003 line 9 column 2: changed "Bromine nitrate" to "bromine nitrate".

P27003 line 26: "high latitudes, particularly during boreal spring" – either specify which high latitude (Arctic/Antarctic) or don't mention "boreal" which is obviously specific to the Arctic case
P27003 line 26 column 12: deleted "boreal".

P27005 line 16: don't need the "s" after PAN
P27005 line 16 column 15: changed "nitrate" to "nitrates".

P 27009 line18: reference Bauguitte et al. 2009, given they showed BrONO2 formation was very important for their field conditions

Bauguitte et al. (2009) investigated the impact of halogen on NO_x cycling at Halley Bay, Antarctica. The NO and NO_2 levels at Halley Bay were significantly higher than in the Arctic measured during ARCTAS.

P27014 line 22: please amend to "...BrO and HOBr+Br2 were detected by CIMS".
P27014 line 22 column 8 added "by CIMS".

P27015 line 21: Arctic spelled incorrectly
P27015 line 21 column 5 changed "Artic" to "Arctic".

Caption for Fig 1: "the solid inlet line represents"

P27025 caption for Fig1 line 2: changed "the solid inlet line presents" to "the solid inlet line represents".

R. Sander (Referee)

Liao et al. study the detection efficiency of their mist chambers to several bromine compounds and compare measured to modeled concentrations. CIMS data are also compared to model results. Although the topic of the manuscript would be more suitable for the EGU journal "Atmospheric Measurement Techniques", I think it is still within the scope of ACP. I think that the manuscript could be suitable for publication in ACP after considering my comments described below.

Major comments

- **I am sceptical about your value for the sampling efficiency for HOBr (1.06) compared to that for Br2 (0.9). Since 1.06/0.9 = 1.18, there must be a conversion:**
1 HOBr → 1.18 Br2
In other words, the inlet converts each Br atom in HOBr to 2.36 Br atoms in Br2. How is this possible? Where does the additional bromine come from? If there is bromide in the inlet, why isn't it detected by the mist chamber? If the conversion depends on bromide in the inlet, shouldn't the sampling efficiency change over time? I think these questions should be answered before the manuscript can be published in ACP.

We agree that the ease of which HOBr is converted to Br_2 even in "clean" relatively inert inlets is surprising. However, our lab tests and the work by Neuman (2010) also show that HOBr converts to Br_2 in tubing that nominally contains no bromine.

As there is almost a 25% error bar on the HOBr conversion efficiency alone for the longer inlet so the HOBr/Br_2 ratio is 1.18 +/- 0.30. Therefore, we think this value is 1.0 for a long inlet but it is a difficult measurement due to handling the HOBr. We don't think there is amplification of bromine in the inlet. The HOBr source is more complicated than either the Br_2 or BrO sources as it involves wet chemistry. There may be compounds evolved from the source solution that are not detected by CIMS (i.e. HBr) that give Br^- in the MC. This would lead to over measurement of the HOBr detection efficiency. We have tried to account for this possibility by adding an asymmetrical error bar to the HOBr conversion efficiency in the MC. However, overall we think that conversion of HOBr on inlet surfaces to Br_2 is going to be more the rule than the exception.

Minor comments

- **On p. 27002, l. 2, it is said that "bromine compounds can oxidize gaseous elemental mercury". I think it is more likely that Hg reacts with atomic Br and not with any bromine compounds.**

P27002 line 2 column 3,4 changed "bromine compounds" to "bromine atoms".

- **Reactions (R1) to (R11) are said to be the key reactions as reviewed by Simpson et al. (2007). However, Simpson et al. also mention several important reactions that involve chlorine chemistry (e.g. in their (R10) to (R12)). Why are these neglected here?**

We neglected the chlorine chemistry here because there was no clear evidence for BrCl or Cl_2 during ARCTAS. This is different than our experience in Barrow in a ground based campaign.

- **Page 27005, line 16: Are you talking about PAN only, or about the whole PAN family? It should be either "peroxy acetyl nitrate" or the plural "peroxy acyl nitrates".**

P27005 line 16 column 15: changed "nitrate" to "nitrates".

- **Section 2.1.1 describes how CIMS can detect Br2 and HOBr separately. However, later in the text (p. 27014), it is said that "the CIMS Br2 signal represents the lower limit to the sum Br2 + HOBr." Is there a reason why only the CIMS Br2 signal is used and not the sum of the CIMS Br2 and HOBr signals? Why is it a lower limit? Maybe the answers can be found somewhere in the paper by Neuman et al. (2010) but I think it would be good to add a brief explanation here as well.**

P27014 Line 22 column 9 added: HOBr was not monitored by CIMS during ARCTAS campaign as the reagent ion, SF_6^-, does not selectively react with HOBr (Huey et al., 1995).

• If you use the term "standard liters" (p. 27006, l. 20), please define the temperature and pressure that you use. There are unfortunately many ways to define a "standard", see: http://en.wikipedia.org/wiki/Standard_conditions_for_temperature_and_pressure

p27006 line 21 column 2 changed "(slpm)" to "(slpm, standard temperature = 273 K, standard pressure = 1.01×10^5 Pa)

• On p. 27009, l. 17, a "concentration < 5 pptv" is mentioned. This should be "mixing ratio", not "concentration" (for details, see http://www.mpch-mainz.mpg.de/~sander/res/vol1kg.pdf). Please check all occurences of the word "concentration" in the main text and check if it should read "mixing ratio" instead.

All are corrected.

• On p. 27009, heterogeneous reactions are described as a "loss" for HBr and HOBr. This is not correct (or at least misleading) because reactions like (R10) are an important part of the bromine explosion chain reaction which recycles bromine. Nevertheless, for the model study presented here it is probably okay to neglect multiphase recycling because BrO is prescribed.

P27009 line13 column 13 added: "The model did not include the recycling of HOBr and HBr from aqueous phase to gas phase bromine compounds because the model was constrained by BrO measurements."

• In section 3.1.1, note that Eigen and Kustin not only describe the hydrolysis of Br2 but also the (pH-dependent) back reaction. I think it would be good to check if your calculations are still valid if you consider this back reaction as well.

We agree that the back reaction is very efficient. However, lab experiment founds that no significant Br_2 can be detected after passing through a trap containing deionized water and confirms the nearly complete dissolution of Br_2.

P27012 line 10 column 9: changed "Br_2 is hydrolyzed" to "Br_2 can be hydrolyzed".

• Given the good correlation between predicted and observed soluble bromine in Fig. 4 (left panel), the intercept of -3.5 pmol/mol is probably significantly different from zero. What could be the reason? Why is predicted soluble bromine 3.5 pmol/mol higher than the observed value? Does the MC systematically underestimate soluble bromine?

We agree the offset from zero may be significant. However, we are not sure of the reason. It is possible that the MC would underestimate some components of soluble bromide but this seems more likely to lead to an error on the slope. So we are not comfortable interpreting the intercept of this plot.

• Change Muller to Müller in the Shetter and Müller reference.

Changed

• According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck "Units for use in atmospheric chemistry", Pure & Appl. Chem., 67(8/9), 1377-1406, 1995 http://www.iupac.org/publications/pac/67/8/1377/pdf) the usage of "ppb" and "ppt" is discouraged for several reasons. Instead, "nmol/mol" and "pmol/mol" should be used for gas-phase mole fractions. I suggest to replace the obsolete units.

All are replaced.