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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of soluble bromide measurements and a case study of BrO observations during ARCTAS" *by* J. Liao et al.

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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 Br_2 (0.9). Since 1.06/0.9 = 1.18, there must be a conversion:

  1 HOBr $\rightarrow$ 1.18 Br_2

  In other words, the inlet converts each Br atom in HOBr to 2.36 Br atoms in Br_2. 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.

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.
- 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?
- 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".
- Section 2.1.1 describes how CIMS can detect Br_2 and HOBr separately. However, later in the text (p. 27014), it is said that "the CIMS Br_2 signal represents the lower

ACPD
11, C12260–C12263, 2011

limit to the sum Br_2 + HOBr." Is there a reason why only the CIMS Br_2 signal is used and not the sum of the CIMS Br_2 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.

- 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

- 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.

- 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.

- In section 3.1.1, note that Eigen and Kustin not only describe the hydrolysis of Br_2 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.

- 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 understimate soluble bromine?

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

ACPD
11, C12260–C12263, 2011

- 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 26999, 2011.