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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Bridging the gap between bromocarbon oceanic emissions and upper air concentrations" *by* S. Tegtmeier et al.

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This paper reports ship-borne observations of emissions of bromoform (CHBr3) and dibromomethane (CH2Br2) from a cruise that went from Japan to Australia during Oct 2009. The observations of ocean to air flux of CHBr3 and CH2Br2 are analyzed using the FLEXPART model. Modeled abundances of CHBr3 and CH2Br2 are compared to observations of these gases in the TTL (tropical tropopause layer) gleaned apparently from Chapter 1 of the 2010 WMO/UNEP Ozone Assessment Report. The ozone depletion potential of CHBr3 and CH2Br2 is calculated, along with estimates of SGI (source gas injection) and PGI (product gas injection) of Bry (inorganic bromine) from these two VSL (very short lived) bromocarbons. The authors conclude that oceanic emission of CH2Br2 and CHBr3 constitute supply of Bry to the stratosphere, from both SGI and

PGI, of 0.4 ppt on average. The maximum value reported is 2.3 ppt.

The paper has a few glaring shortcomings that prevent publication in anything close to its present form.

I have decided to sign this review, in case the authors choose to discuss what is stated below off line, even though by signing such a harsh review, I realize I will likely not be endearing myself to the authors. I hope future exchange can focus on the science which I believe is not well done in the submitted paper.

There are two glaring shortcomings, one of which can be addressed in a straightforward manner (albeit, with some hard work) but the other of which undercuts the central conclusion of the paper. The more easily addressed problem is a number of recent papers on this topic, including one I have led, are not recognized. These papers include atmospheric measurements that are not represented in the paper, yet are crucial to the analysis. The other, more difficult problem is the apparent omission, from the model, of heterogeneous chemical reactions involving inorganic bromine species. If I am interpreting the paper correctly, the calculations assume a certain solubility for each inorganic bromine species, leading to wet deposition. But, as has been shown in the laboratory and discussed extensively in WMO/UNEP as well as numerous papers (key ones not cited!), heterogeneous chemical reactions of HBr and HOBr will release Br back to the gas phase, short circuiting wet deposition. The calculations in the submitted paper of PGI therefore lower limits to the actual, atmospheric PGI yet they are not presented as lower limits.

I will provide more detail below.

Major Points:

1. The submitted paper does not reflect the measurements of bromocarbons obtained in the TTL during TC4. These data are described by Brinckmann et al., ACP, 2012 and Salawitch et al., GRL, 2010. Specifically, Figure S03 of Salawitch et al. establishes

that CH2Br2 carries about 2 ppt of Bry across the tropopause as SGI and that little else makes it across the tropical tropopause as SGI. There is a puzzling suggestion of SGI occurring outside the tropics. The bulge in CBry at the region of convection outflow in the tropics, shown in this same figure, establishes the potential upper limit for much larger contributions to stratospheric Bry from PGI. We state:

The excess content of organic bromine observed in the region of convective outflow relative to the UT (highest altitudes shown) suggests that PGI could be as high as 5 to 7 ppt, or much larger if the influence of decomposition products of highly elevated CBry in the tropical marine boundary layer (MBL) is also considered.

The submitted paper seems to rely on data from tables in the 2010 Ozone Assessment Report, which did not reflect TC4. The Salawitch et al. paper was under review at the time Chapter 1 was being written; this paper was accepted prior to finalization of the Chapter, hence it is cited, but the data from this paper were never incorporated into the tables. Ashfold et al. (ACPD, 2012) present observations of bromocarbons in the tropical TTL from CR-AVE and TC4 and Brinckmann et al. (ACP, 2011) present observations from a balloon flight over Teresina, Brazil as well as the TransBrom cruise. The data shown in these three paper are publically available and should be considered together with the surface measurements from TransBrom.

2. As far as I can tell, the model used does not consider heterogeneous chemical reactions of inorganic bromine species. HBr and HOBr are soluble and likely to be absorbed by aerosol or cloud particles. Depending on the local microphysical environment, sedimentation of these particles could represent an efficient sink for Bry, preventing the decomposition products of biogenic bromocarbons from reaching the lower stratosphere (Sinnhuber and Folkins, ACP 2006) or global troposphere (Yang et al., JGR, 2005). However, the efficiency of aerosol/cloud washout of Bry is likely altered by heterogeneous reactions that release bromine to the gas phase (Iraci et al., ACP, 2005; Salawitch, Nature, 2006; Sinnhuber and Folkins, ACP, 2006). This process is discussed at length in Sections 2.3.4.2 and 2.5.1.3 of the 2006 WMO/UNEP Ozone

Assessment Report, and illustrated by Figure 2-7 (from Sinnhuber and Folkins, ACP, 2006) of this report. The important of production of labile bromine by het chem seems to have been overlooked in the submitted paper (of the papers in this paragraph, only Yang et al. is cited). If the het chem reactions described by the lab study of Iraci et al. have been neglected, then the estimates of PGI in the submitted paper are severe lower limits to reality.

Due to the neglect of recent measurements of bromocarbons in the tropical TTL and the apparent oversight of not including het chem reactions that can release dissolved bromine back to the gas phase, the submitted paper does not provide any insight into how VSL bromocarbons might supply inorganic bromine to the stratosphere.

If het chem reactions involving HBr and HOBr have indeed been included, despite no mention of these reactions and no reference to papers such as those by Iraci, by Abbatt, etc and no mention of the importance of this process, then I suggest the paper be allowed to be revised.

END OF REVIEW

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4477, 2012.