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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimating the contribution of bromoform to stratospheric bromine and its relation to dehydration in the tropical tropopause layer" *by* B.-M. Sinnhuber and I. Folkins

Anonymous Referee #3

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Review of Sinnhuber and Folkins, Estimating the contribution of bromoform to stratospheric bromine and its relation to dehydration in the tropical tropopause layer, ACPD-2005-0372

This is a well written paper on a timely subject that nicely documents the key factors affecting the transport of bromine to the stratosphere from a very short lived bromocarbon. I like the modeling approach: it is a nice complement to more sophisticated and complicated approaches that are not nearly as transparent as the one dimensional, hueristic description of the atmosphere that is used here.

I believe the data model comparison is fine, and was surprised to see criticism of this in the other reviews. Basically, bromoform is under sampled in all important regions: the marine boundary layer, the free troposphere, the tropical tropopause layer, and the lowermost stratosphere. To me, the model describes rather well the available observations, albeit, some of which are obtained at different latitudes than the model.

I especially liked discussion in the paper regarding how the ˜0.5 ppt "Source Gas" injection of bromine from bromoform could be checked by measurements of bromoform in the TTL (lines 170-174) and how "this situation constitutes only an upper limit ... if it is assumed detrained air does not contain Bry (lines 178-180)". For the first of these, the paper would be stronger if the nomenclature of Source Gas Injection and Product Gas Injection were adopted throughout (e.g., use the nomenclature defined in Chapter 2 of WMO 2003). For the second of these key points, I am afraid this point (which is alluded to earlier in the paper) is buried in the middle of a long paragraph. I suggest devoting a single paragraph to this point (e.g., break up the long PP from lines 174 to 188 into several shorted PPs).

In my opinion, two important aspects of CHBr3 and Bry chemistry are missing from the paper, and should be mentioned upon revision. First, it is assumed that once CHBr3 is lost by either photolysis or reaction with OH, Bry is immediately formed. Of course, in reality, OH+CHBr3 probably leads to C(O)Br2+Br, and hv+CHBr3 probably leads to C(O)HBr+Br+Br (see Fig 2-6 of WMO, 2003). There are little or no kinetics studies of C(O)Br2 and C(O)HBr: while they are probably shorter lived than CHBr3, I don't know if this is certain. Nonetheless, some comment about the intermediates is warranted. For a discussion of CHBr3 photochemistry, see R. Weller et al., Berichte der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics, 96, 409, 1992. This study probably should be cited (a resourceful postdoc found this paper and pointed it out to me several months ago!).

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5, S5281–S5283, 2005

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The second item that, if mentioned, would strengthen the paper, is the possibility that heterogeneous recycling of Bry species could lead to higher values of tau_washout. This is discussed in general terms by Platt and Hoenninger, Chemosphere, 52, 325, 2003 and in specific terms by the laboratory study of Iraci et al. (ACP, 5, 1577, 2005). I think both of these studies should be cited, and discussion should be added to state how tau_washout might be modified by the heterogeneous recycling of Bry species that are produced following decomposition of CHBr3.

A few very minor points:

line 35, perhaps "have been observed" rather than "were observed"

line 38: delete comma after "indicated"

line 127, 227: should be "soluble" rather than "soluable"

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I'm signing here, because I could not figure out how to get the COSIS website to have this be a "signed review". The authors should feel free to contact me if they have any questions about this review.

Sincerely,

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12939, 2005.