Review of acp-2013-422, “Modelling the chemistry and transport of bromoform within a sea breeze driven convective system during the SHIVA Campaign” by Hamer et al.

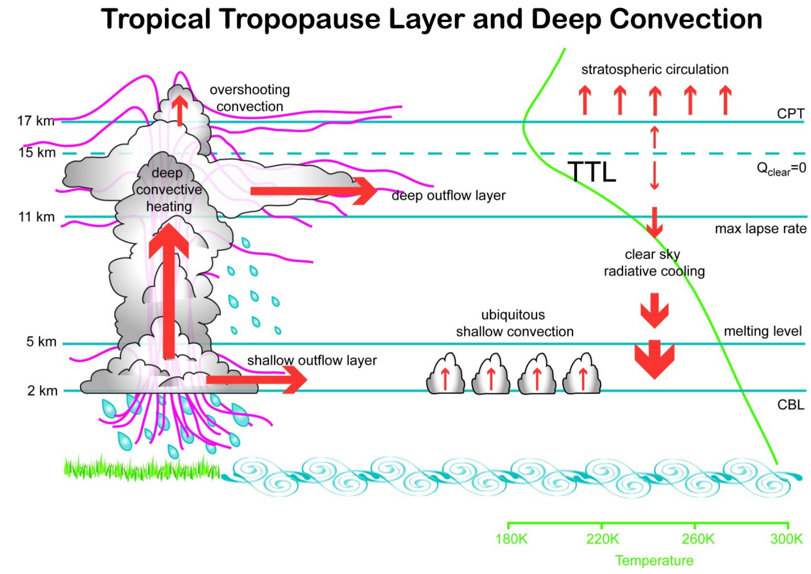
This paper describes measurements and model simulations of bromoform ($CHBr_3$) obtained by airborne, ship-borne, and ground based sensors near Borneo in Nov 2011, as part of the SHIVA campaign. The authors attempt to relate the measurements and model simulations to stratospheric supply of bromine from very short lived (VSL) bromocarbons. They apply a very comprehensive model, with nested grids, resolution of convection, and a very detailed chemical mechanism for bromine species. This is a comprehensive analysis of data from a variety of platforms and for this the team should be applauded.

However: the paper does NOTHING however to advance our understanding of stratospheric supply of bromine from VSL bromocarbons. The measurements from the Falcon airplane were conducted at altitudes too low to be relevant for stratospheric transport. The airplane sampled to a maximum altitude of 12 km: it is well known that ascent to the stratosphere begins above the Q = 0 line (about 15 km altitude in the tropics). Below 15 km altitude, the net tendency for air is descent. Above 15 km, hydro-meteors large enough to precipitate are uncommon. Below 15 km, hydro-meteors that reach the ground are quite common. The results of this paper therefore have essentially NO BEARING whatsoever on the stratospheric supply of bromine from very short lived halocarbons.

I suggest this paper be rejected for ACP and be sent to a more specialized journal, perhaps Atmospheric Environment or Journal of Geophysical Research, where the tropospheric findings could be pursued. The publication of this paper in ACP will unduly complicate our understanding of stratospheric supply of VSL bromine from VSL bromocarbons.

Major comments:

1. As noted above, the sampling is entirely below Q = 0. This is a fatal flaw. The climatology of the sampled airmasses is to descend rather than ascend. I have no idea why the Falcon, with a ceiling of 12 km, was used to sample VSL bromocarbons for a project with an apparent stratospheric focus. The paper makes NO ATTEMPT to describe the fate of the sampled airmasses after the time of measurement. As noted above, if the measurements were obtained below the level of zero heating, these airmasses are headed down and not up. This is an absolute truth, outlined in an iconic figure from SPARC drawn by Diane Pendlebury that I am sure most of the authors know quite well:



So all the words about the stratosphere in the paper have no meaning whatsoever! Unless the authors can address this concern about the fate of the air after encounter, all of the words about the stratosphere should be stricken and the paper should be re-cast to focus on the effect of halogens on tropospheric O_3 which of course means IO and its sources must be considered (i.e., Saiz-Lopez et al., ACP, 2012).

2. This paper has also been frustrating to read because GROSS discrepancies between the model and measurements are swept under the rug. For example, Figure 13 compares measured and modeled $CHBr_3$. Editor, please have a careful look at this figure. The orange line in Panel C shows simulated $CHBr_3$ along the flight track of Flight B, whereas the black line shows observations of $CHBr_3$ obtained by the GHOST instrument. Presumably the dashed line indicates measurement uncertainty. Line 16 of page 20631 states:

> Within the instrumental uncertainty the model reasonably reproduces the magnitude of the observed enhancements in CHBr3 due to convective outflow at 12 km during Flight B, which is one focus of the case study. Therefore, our conclusions regarding the chemistry and transport of the VSLS within the convective outflow from Region 2B are well supported, and we infer too that this is also true for the results within the convective column itself.

Not in my book! Panel C of Figure 13 shows a large difference between modeled and measured $CHBr_3$, approaching a factor of 2 and exceeding the measurements uncertainty by a large amount. It is unfathomable to me how the authors can state this model reasonable reproduces the observations.
The difference between measured and modeled CHBr3 is larger for Panels A & B (both panels show results for Flight A, with the measurements in Panel A being from one instrument and the measurements in Panel B from another instrument.

How in the world the authors could write:

> The simulated transport of bromoform from the boundary layer up to 12 km compares well to aircraft observations to support our conclusions (abstract)
>
> In summary, despite the identified problems, the comparison to the $CHBr_3$ observations supports our conclusions regarding bromine chemistry within the cloud and outflow argued in the following sections, validates the $CHBr_3$ emissions (Pyle et al., 2011) throughout most of the year at Bukit Atur (bottom page 20633)
>
> Although the simulation of $CHBr_3$ within the convective system has been well validated (last PP of paper)

is beyond me! Almost certainly, there is either a problem with the specification of the $CHBr_3$ emissions (a way too long PP that spans all of pages 20633 and 20634, and part of 20632, discusses the fact that the modeled emissions are seasonally invariant (apparently) although perhaps not (i.e., sentence "Thus, the emissions used were adapted for more typical conditions …" on page 20633 that I totally do not understand) or the model's meteorology.

Top of page 20631 states "Having established that the simulation offers a sufficiently realistic representation of the meteorology during the case study …" whereas Figure 7 shows large differences in modeled and measured wind direction, Figure 9 shows a troubling offset between observed and simulated T, and Figure 2 shows the modeled origin of convection (Region 2B) originated over land whereas radar imagery shows the actual convection originated over water (Region 2A). Other than this, the meteorology is realistic. Sorry to be so sarcastic, but this is a long paper, the authors have tackled a challenging problem, they have but together a very comprehensive model … yet they seem incapable of dealing with model deficiencies!

3. Much of the paper, despite the length, is "clear only if known" (COIK). This poses a huge problem.

For instance there is no description of the GHOST instrument. In some places GHOST-MS is used; in other places GHOST GC-MS is used. Is it a MS or a GC-MS? Are other VSL bromocarbons measured? If so do the measurements of the other VSL bromocarbons support the sole focus on $CHBr_3$?

The WASP instrument is also not described. In Table 2 it is called WASP GC-MS, so I assume this is a gas chromatograph / mass spectrometer. As for GHOST, were other bromocarbons measured? Why is the altitude range of WASP limited ? (page 20633 states WASP can not make measurements for altitudes above 6 km).

Other COIK problems: page 20621 states "the model represents microphysical processes using the single-moment bulk parameterization (Walko et al., 1995) whereby rain, cloud, pristine ice, snow, aggregates, graupel and hail are considered." I am astonished to read this given that the highest resolution of the model is 2 x 2 km. There must be some serious parameterizations to represent cloud microphysics at such course resolution. The paper has many references for various model components, but lacks sufficient detail for a reader who is not knowledgeable about these references. If this was a short paper, relying on references in this manner would be fine. But this is a long paper and important aspects of the model should be explained. For instance, there is no discussion about how clouds effect photolysis rates. Much of the $CHBr_3$ loss discussion focuses on OH, but the most likely sink for $CHBr_3$ is photolysis. So, um … how does the model handle impact of clouds on J values ?!?

4. Measurement uncertainties are not described well. Indeed, only info is in caption of Figure 13. Are these numbers 1 sigma or 2 sigma? Text says these are accuracies … what is measurement precision? Also need uncertainty estimate for the met data shown in various figures.

Minor points:

1. Many key papers are not cited. For instance, Saiz-Lopez et al., ACP, 2012 (the paper to which the present work is most closely related) is not cited at all. The companion Ordoñez et al., ACP, 2012 paper is cited, but for some reason does not appear in Table 1. The two VSL Bry estimates of Salawitch et al. (GRL, 2005; GRL, 2010) should certainly be cited in the introductory PP. The Iraci et al. (ACP, 2005) paper on HOBr+HBr is too important to not cite: also, upon revision, there should be comparison of the modeled Henrys Law coefficients and heterogeneous reaction probabilities to the work of Iraci, the work of Abbatt, etc. Finally, the notion of PGI and SGI was first put forth, in an ozone assessment, by Ko and Poluet's Chapter 2 in the 2002 WMO/Ozone Assessment. This chapter should be cited somewhere, perhaps line 7 of page 20616.

2. Line 11, page 20615, states $CHBr_3$ has the shortest atmospheric lifetime of recognised brominated VSLS. This is not true: n-propyl bromide is a recognised brominated VSLS and has about half the lifetime of $CHBr_3$.

3. Line 13 to 15, page 20619, states “Thus, enhancements of up to 15 nmol mol^{-1} are therefore indicative of enhanced vertical transport.”. Presumably authors mean enhancements of CO. If so, to me, such enhancements are indicative of entrainment of polluted air and not enhanced vertical transport!

4. Lines 2 to 5, page 20622, state:

> Finally, chemical species caught within ice particles are considered to be lost via washout and we assume a retention coefficient of 1 for all species. This assumption is valid since ice particles primarily develop into hail and graupel, which sediment rapidly relative to the retention time of chemical species on their surfaces.

These are critically important sentences. This probably explains why the model simulates such strong removal via washout of inorganic bromine species. Large paper, complicated model, and at the end of the day, a key assumption (washout scrubs products) seems to be tied back to a model assumption. Um … to me this assumption is far from valid. Chemical reactions releasing Br_2 to the gas phase can occur rapidly. Much more discussion is needed of the justification of this assumption but, at the end of day, I think the authors need to consider the sensitivity of their results to the value of this retention coefficient. If not, then this seemingly complex model is simply yielding a result dependent on a critical assumption that is not IMHO justified.

5. Line 25, page 20624, states “we allowed the model to resolve clouds and convective processes directly for the finest resolution”. The finest resolution is 2 x 2 km. You resolve clouds at 2 x 2 km? Really ?!? Well, with a retention coefficient of 1 and 2 x 2 km resolution for clouds, no wonder you find efficient washout for inorganic products. Yikes! Most cloud resolving models are much higher spatial resolution.

6. Lines 4 to 12, page 20632: the numbers given in the text differ from the numbers given in Table 4. This makes the paper hard to follow. Also, Table 4 gives observed mean and background numbers for $CHBr_3$, but I did not see in the paper a description of how the observed mean and background are found. OK, I can guess that mean is average of all the values. But how is background found? And shouldn’t the Table be comparing enhancements above background (which are not the mean!) from measurement to enhancements above background from model ?!?

7. Lines 17 to 26, page 20634. First, I doubt the discrepancy could be resolved by OH, but hard to assess without knowledge of impact of clouds on J_{CHBr3}. Second, OH in the region of interest is likely dependent on the accuracy of modeled NO_x, due to HO_2+NO. Unless there is a comparison of measured and modeled NO, I place little weight on the evaluation of the modeled OH described in this section.

8. Appendix gives a list of reactions. Sorry, but need rate constants (or origin of rate constants) for this to be suitably documented. Most importantly for the three Aqueous Phase reactions, need to know reaction probabilities!