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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Very short-lived bromomethanes measured by the CARIBIC observatory over the North Atlantic, Africa and South-East Asia during 2009–2013" *by* A. Wisher et al.

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We would like to thank the reviewer for his/her helpful comments. Reviewer comments are repeated below in bold along with our responses.

Seasonality is mentioned in the text in a couple of places, but it is unclear why this is invoked as a potential means by which differences can be explained as opposed to variations in transport and upwind emission rates. I refer to p. 29957, lines 26-28: is there evidence that suggests seasonal variation in some aspect

of sources or concentrations of these gases? It isn't shown or cited here.

Seasonality is mentioned to highlight that our data do not have the seasonal coverage necessary to determine whether there is any seasonal cycle in these compounds. Furthermore, when comparing data (within the CARIBIC data set or with other data sets) we were cautious to highlight that differences/similarities observed may or may not be influenced by seasonal factors. There are other factors which may be responsible for differences in VSLB mixing ratios. These include variability in transport processes, variability in source emissions and the data coverage limitations of our study. To clarify, the following has been added to the discussion of Central American results:

> "Seasonality has been observed for $CHBr_3$ in the boundary layer (e.g. Carpenter et al., 2005). However, it is uncertain as to whether this seasonal cycle would be present in the upper troposphere or the regions sampled in this study. Due to the limited temporal coverage of CARIBIC, seasonal cycles cannot be identified or ruled out. Transport processes and the high degree of variability in source emissions of VSLB could also account for these differences."

Also on p. 29963 lines 25-28, the message being conveyed from these statements is unclear. (Note I am not talking about the seasonality discussion of Figure 4, which is clear and useful as is).

This has been altered to clarify its meaning and referenced to the caveats stated in the Central American results as follows:

> "This indicates that there is a greater emission of CH_2Br_2 in the South-East Asian Pacific tropics than in either the Western Atlantic or African tropics. Emissions of the other VSLB are more similar. Caveats relating to data limitations, including seasonality, are the same as those discussed in Section 3.1.1."

On relative abundances of VSLSs. P. 29957, line 1-6, is it possible that source variations could contribute some to this anomaly? If so, modify the text.

We agree that source variations cannot be ruled out and he following line has been added:

> "It is possible that source emission variations could also contribute to lower mixing ratios in this region."

In Section 3.3, it is not well described why the high mixing ratio of CH_2Br_2 relative to $CHBr_3$ in the BKK-KUL leg needs such an in depth discussion; inform us why this difference is more interesting than the others.

The interest arises from the high mixing ratio of CH_2Br_2 in the BKK-KUL leg when compared to the other tropical regions covered. The emission ratio of CH_2Br_2 relative to $CHBr_3$ is invoked as a possible explanation for this difference. We have included the following to point out the importance of this region:

> "The tropical West Pacific is considered a potentially important region for transport of VSLB into the stratosphere (e.g. Aschmann et al., 2009). Frequent and intense convection provides an efficient pathway for boundary layer air to be transported to the TTL (e.g. Fueglistaler et al., 2009). Additionally, emissions in the region are poorly sampled, including those of farmed macroalgae species. These could impact on future VSLB emissions due to interest in increasing seaweed aquaculture in the region (Leedham et al., 2013)."

HIPPO-4 data are mentioned here, but the discrepancy in this region is not apparent in that data.

HIPPO-4 data agree with our measurements within the variability given as stated in the paper. However, given that the HIPPO measurements are from further east and

the small number of samples involved (both in HIPPO-1 and HIPPO-4), it is difficult to speculate regarding OH processing or source emission ratios from this data.

Also, local lifetimes in WMO are not representative of any specific atmospheric region and are not likely to be representative of the true loss frequencies in this region of the atmosphere. To make this discussion useful you'll need to consider some realistic values for OH and photolysis in this region.

We agree that local lifetimes in WMO are not representative of the region of the atmosphere that CARIBIC samples in. However, the bromomethanes sampled in this region have been photochemically processed over the course of the transport of air from the surface to cruising altitude. Back trajectories indicate that air reaching the aircraft in this region was recently uplifted from the surface. Therefore, we believe that the "average" OH lifetimes given in WMO are representative enough for the purposes of speculative discussion. Additionally, our discussion of this point revolves around the variability of local lifetimes for these compounds.

On the peak in tropics observed during the South African flights (Figure 7): Given the relatively few samples and the fairly high degree of variability in concentrations, it seems a stretch to conclude that these gases (minus CH_2BrCl) all are higher in the tropics. They give a hint of this, sure, but extratropical NH results do not look very different. Consider some rewording.

An increase in mixing ratios over the tropics might be expected due to uplift around the ITCZ. However, we do not see this clearly enough to claim a definite tropical enhancement. P 29961 L 21 has been changed to the following:

> "However, there is a possible increase in mixing ratios in all except CH_2BrCl in the tropics e.g. $CHBr_3$ is enhanced by up to ~ 0.4 ppt. This increase is small when variability is taken into account with limited sampling. Therefore, these results should be taken as suggesting the possibility of a tropical enhancement over Africa rather than being definitive."

On HIPPO data and its use. Multiple groups reported data for CH_2Br_2 and $CHBr_3$ from the HIPPO campaigns. Did you use only the data from the Univ. of Miami, or the entire set of results? This needs specification in the text, as a subset of results is likely to provide different means than the entire set even with the data being referenced to a common scale. I'm surprised the HIPPO team involved with these mostly unpublished measurements wasn't brought more fully into this analysis; I imagine they could have contributed quite a bit to this paper.

HIPPO data averages were based on a regionally relevant subset of bromomethane data from the entire set of results as made openly available on the HIPPO website (http://hippo.ornl.gov/dataaccess). The data set has been referenced in Table 2 using the citation suggested in the HIPPO documentation. This paper is focused on CARIBIC data and a small subset of the HIPPO data was used for comparison as it is a relatively recent dataset with coverage in similar regions to CARIBIC. In addition, we used data on the same calibration scale to improve compatibility. A detailed study of the HIPPO dataset would be more appropriate for a separate publication. To clarify which HIPPO data were used the following line has been added to P 29957:

> "HIPPO values are based on a regionally relevant subset of all measurements made during the campaign available from the HIPPO data archive (Wofsy et al., 2012)."

and on P 29964:

> "HIPPO values are based on a subset of all measurements made during the campaign available from the HIPPO data archive (Wofsy et al., 2012)."

Details: On figures. Overall the figures do a very nice job of displaying the data and making the points being described in the text. It seemed implied from the text that data displayed in Figures 5 and 6 were only from the extratropical

tropopause layer; if so, please indicate this in the caption. In the Figure 5 caption, the description of the averaging is unclear. Furthermore, the text relating to the delineation of color in Fig 5 could be improved, what"degree of stratospheric influence" is used to separate the colors (p. 29959, l22)? In the Figure 6 caption, indicate if the tropopause is at zO_3=0.

Figure 5 plots are all samples collected along the FRA-CCS/BOG route. This has been clarified in the text and the following line added to point out that all tropical samples are tropospheric due to the nature of the only being able to sample at cruising altitudes.

> "All tropical samples are below the CT due to the restricted altitude range of the aircraft."

Similarly, this has been clarified in the text for the height above thermal tropopause (Figure 6) and the following line added.

> "Due to the limited cruising altitude range of the aircraft, height above the thermal tropopause is only available for extra-tropical samples."

The caption for Figure 5 has been updated to the following:

> "Plots of VSLB and total VSLB-derived bromine (VSLB Σ Br_{org}) for all samples on Central American flights against O_3 with 100 ppb binned means $\pm$ 1 σ error bars representing variability. Error bars on sample data points represent analytical uncertainties. Data points have been separated by colour into tropospheric samples and those with stratospheric influence (see Section 3)."

and the caption for Figure 6 to:

"Plots of VSLB and VSLB-derived total bromine (VSLB Σ Br_{org}) for Central American flights with O_3-derived height above the thermal tropopause (zO_3) as defined by Zahn and Brenninkmeijer, 2003. Error bars represent analytical uncertainties. The tropopause is defined as $zO_3 = 0$."

The WMO reports provide a useful service in compiling and assessing results from the community, so citing them is important. Yet citing them alone leaves out critical information valuable to the reader. Consider describing the results reported in WMO as a compilation of data from multiple sampling mission by many different groups, and possibly also describing (if not also citing) some of the methodologies and results that were compiled in the WMO reports.

To aid the reader in understanding WMO values we have included the following text on P 29957.

"Additionally, CARIBIC results can be compared to WMO 2010 (Montzka and Reimann, 2011). WMO 2010 values referred to in this study are 10–12 km upper tropospheric values from Table 1-7 of WMO 2010. These values are mean values of DC-8 observations made during the TC4, PEM-West A and PEM-West B campaigns (Toon et al., 2010, Hoell et al., 1999, Hoell et al., 1997, Schauffler et al.,1999). The minimum and maximum values given in WMO 2010 are based on the smallest mean minus one standard deviation and the largest mean plus one standard deviation respectively, across all campaigns. Again, note that the differences in calibration scales for these compounds limit this comparison."

Consider also that some of the uncertainty in the Br delivered to the stratosphere from VSLSs arises from kinetic parameters that have uncertainty (p. 29951, lines 1-5).

Regarding kinetic parameters, P 29951 L 1-5 has been updated to the following:

"Uncertainties in this estimate include the high degree of variability in source emissions, limited understanding of transport pathways to the upper tropical tropopause, differences in calibration scales between measurements, limited spatial and temporal data coverage and uncertainties in kinetic parameters used to calculate decomposition rates."

Stratospheric ozone depletion is associated with increased anthropogenic trace gas emissions. Consider clarifying the text on p. 29950, lines 20-23 to avoid the interpretation that VSLS gases might be a significant contributor to this time-dependent problem. We agree that this is misleading. Natural halocarbon emissions do contribute to stratospheric O_3 depletion. However, their current and future impacts differ greatly from those brought about by anthropogenic emissions. The relevant section of the introduction has been modified to the following:

"...cooling water (Quack and Wallace, 2003).

Recent WMO reports (Law and Sturges, 2007; Montzka and Reimann, 2011) indicate that natural halocarbon emissions are associated with significant stratospheric O_3 depletion. Bromine has an ~ 60 times higher efficiency, on average and on a per atom basis, to destroy ozone than chlorine (Sinnhuber et al., 2009). This, combined with the highly variable spatial and temporal distribution of VSLS in the troposphere, indicates that even at low mixing ratios, brominated VSLS species could contribute significantly to stratospheric ozone depletion. Hossaini et al. (2012a) suggest that VSLS source gas injection into the stratosphere is likely to increase in response to future climate change. Furthermore, as levels of anthropogenic halogenated source gases are predicted to decrease (e.g. Montzka and Reimann, 2011), as a result of the Montreal Protocol, biogenic halocarbons including bromomethanes will become proportionally more significant in the future. Additionally, there is a relative paucity of measurements in the

region of the upper troposphere/lower stratosphere (UTLS); an important region when considering the transport of compounds into the stratosphere."

p. 29957, l. 23, value for CH_2Br_2 does not agree with Table 2 entry.

The value for CH_2Br_2 has been corrected in the text.

p. 29959, lines 1-4. I presume you are referring to VSLB in the form of organic Br here, as opposed inorganic Br from the degradation of organic trace gases. This distinction needs to be made for the sentences to be accurate.

This sentence has been modified to:

"Rather, they represent an upper limit on organic bromine derived from VSLB available for transport into the stratospheric overworld. . . ".

Table 1., I agree with the other referee, specify the concentrations for which the stated precision is relevant.

Table 1 and the relevant section of the text has been updated. See response to Referee #1.