

Referee comments are included below in **bold** along with our responses. *Italicised line references* show where the changes have been implemented in the updated manuscript.

Responses to Anonymous Referee #1

- P 29949, L 2:** Short-lived organic brominated compounds make up a significant part ($\sim 20\%$)
5 of the organic bromine budget in the atmosphere. This statement is not so clear. Where in the atmosphere? If I just produce a “count” in the MBL it would be around 16 pt from the long-lived ones (as Br) but about 7 ppt (as Br) for the short-lived ones. These are only rough guesses, but you should say where and on which basis you get to 20 % (or leave it without a number).

- 10 The percentage contribution given has been removed.

Page 1, line 1.

P 29949, L 5: Measurements of five short-lived... If you use VSLB it should be: Measurements of five very short-lived...

- “Measurements of five short-lived...” has been changed to “Measurements of five very short-lived...”.

P 1, line 5.

P 29949, L 15: Either VSLS-derived bromine or VSLB

We agree that this is potentially confusing and have changed VSLS-derived bromine to VSLB-derived bromine.

- 20 *P 1, line 13.*

P 29950, L 19: an ~ 60 to a ~ 60 ...

We believe this is typographically correct and has been confirmed with the publishers.

P 2, line 40.

P 29952, L 12: in situ should be *in-situ*

- 25 The publisher’s author guidelines suggest that in situ is correct for this publication. This has been confirmed with the publishers.

P 3, line 89.

P 29952, L 15: Baker et al. (2011b) should be Baker et al. (2011a) and vice versa

The labelling of these references has been corrected.

- 30 *P 4, line 90 and P 4, line 100.*

P 29953, L 24:(105 m, 320 μm OD... : here the convention is to use: (105 m \times 320 μm OD... : (this is a \times (arithmetic multiplicator, not a letter x).

This has been changed as suggested.

P 4, line 121.

35 P 29956, L 12: You should not use the ppbv, ppb is enough

Agreed. Additionally, following a comment from the editor, the statement regarding units on Page 29956 Lines 3-4 has now been updated and moved to the end of the paragraph where we explain the drying of samples.

“CARIBIC measurements of VSLB are reported as dry-air mole fractions, pmol mol⁻¹ (dry air), abbreviated here to ppt (parts per trillion).”

Additionally, the description of ozone measurements has been updated to include the following:

“Ozone mixing ratios are reported in this study as wet-air mole fractions, nmol mol⁻¹ (air), abbreviated here to ppb (parts per billion).”

P 5, line 127–128 and P 5, line 140–141.

45 P 29964, L 28: The number of 26 days is not consistent with the 24 days lifetime mentioned at L 2, P 29957. Furthermore, the T(OH) should be 76 days and not 26 days

The local lifetime of CHBr₃ on P 29964, L 28 has been corrected to 24 days and the OH lifetime for CHBr₃ on P 29964, L 29 has been corrected to 76 days.

P 13, line 414 and P 13, line 415.

50 P 29973: The precision in % is misleading. You should also indicate the concentration where this has been measured (near the detection limit this must be higher)

The table of precisions (P 29973, Table 1) has been updated to include the mixing ratios at which the precision was calculated. The relevant text (P 29954, L 1-5) has been updated to refer to this.
Table 1 on P 20 and P 5, line 129–133.

55 P 29974: Although it is implicitly clear you should mention in which region of the atmosphere this has been measured (10-12 km?).

The table caption has been amended to: “Summary of tropospheric tropical and extra-tropical 10–12.3 km mid-upper tropospheric means and medians...”. This is reiterated in the table footnotes.
Table 2 on P 20.

60 P 29977: It should be mentioned that this was in the Northern hemisphere

The figure caption has been amended to “Northern-hemispheric latitudinal distributions...”.
Figure 3 on P 22.

Responses to Anonymous Referee #2

65 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.

70 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.

75 To clarify, the following has been added to the discussion of Central American results:

80 "Seasonality has been observed for CHBr₃ 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."

P 8, line 228–232.

85 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:

90 "This indicates that there is a greater emission of CH₂Br₂ 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."

P 12, line 386–389.

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

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

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

P 7, line 197–198.

100 In Section 3.3, it is not well described why the high mixing ratio of CH₂Br₂ relative to CHBr₃ in the BKK-KUL leg needs such an in depth discussion; inform us why this difference is more interesting than the others.

105 The interest arises from the high mixing ratio of CH₂Br₂ in the BKK-KUL leg when compared to the other tropical regions covered. The emission ratio of CH₂Br₂ relative to CHBr₃ is invoked as a possible explanation for this difference. We have included the following to point out the importance of this region:

110 “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).”

P 11, line 349–354.

115 **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.

120 **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 youll need to consider some realistic values for OH and photolysis in this region.**

125 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 130 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 CH₂BrCl) 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.

135 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:

140 “However, there is a possible increase in mixing ratios in all except CH₂BrCl in the tropics e.g. CHBr₃ 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.“

P 10, line 325–328.

145 **On HIPPO data and its use.** Multiple groups reported data for CH₂Br₂ and CHBr₃ 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.

150 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 155 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).”

160 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).”

P 7, line 204–206 and P 12, line 392–393.

165 **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, 170 indicate if the tropopause is at zO₃=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.

175 “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.”

180 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 O₃ with 100 ppb binned means $\pm 1\sigma$ 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:

190 “Plots of VSLB and VSLB-derived total bromine (VSLB Σ Br_{org}) for Central American flights with O₃-derived height above the thermal tropopause (zO₃) as defined by Zahn and Brenninkmeijer, 2003. Error bars represent analytical uncertainties. The tropopause is defined as zO₃= 0.”

P 9, line 284-285; Figure 5 on P 24 and Figure 6 on P 25.

195 **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.

200 “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.”

P 7, line 208–215.

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).

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

215 “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.”

P 2, line 53–56.

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.

220 We agree that this is misleading. Natural halocarbon emissions do contribute to stratospheric O₃ 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).

225 Recent WMO reports (Law and Sturges, 2007; Montzka and Reimann, 2011) indicate that natural halocarbon emissions are associated with significant stratospheric O₃ 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

230 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 de-
crease (e.g. Montzka and Reimann, 2011), as a result of the Montreal Protocol, biogenic
halocarbons including bromomethanes will become proportionally more significant in
235 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 2, line 38–49.

p. 29957, l. 23, value for CH₂Br₂ does not agree with Table 2 entry.

240 The value for CH₂Br₂ has been corrected in the text.

P 7, line 221.

**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.**

245 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...”.

P 8, line 256–259.

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

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