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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics – a case study" *by* J. C. Laube et al.

Anonymous Referee #2

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General comments: This work represents data from a high altitude balloon flight regarding the sum of chlorinated and brominated gases measurable from flasks. Because of the issues related to the contribution of non-regulated and short-lived halogenated gases to ozone-depleting Cl and Br in the stratosphere, this work has a place in the literature. This is perhaps especially true because a wider suite of gases has been measured than in past studies, though the significance of the contribution from these additional gases is not clear.

Despite this, I would urge the authors to consider making changes to the manuscript to improve its message and readability. In places the writing could be improved to make it

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more precise and clear. Some important details and considerations are not discussed. Furthermore, information on methods is interspersed throughout the discussion section, and this makes for a difficult read. For example, most of section 3.1 and a good deal of 3.2 could go into the experimental section. As is, the paper is unclear in places and does only a fair job at getting its main points across.

Specific comments (examples of issues raised in general comments section): p. 6, I appreciate the effort to provide a comment on the accuracy of results, but the comparisons to global mean surface data are potentially of limited use. It is unclear how 3% agreement with global mean surface mixing ratios suggests "little influence from local convection" especially when vertical gradients in this region of the globe for most of the compounds listed are likely insignificant. The more important gradients for many of the compounds listed are across latitudes, but these are not considered and likely play a role. For example, Khalil et al., show that mixing ratios of this gas are notably elevated in the tropics at the surface. One could assume that this would be true at tropical high altitudes too. For HCFCs and CH3Br the hemispheric gradients are large enough so that it would be difficult to sample air having the global mean mixing ratio! How can one assess the comparison given this situation? In section 3.2 you "do not claim global significance" for the sample you are making comments concerning accuracy (what does this mean, exactly?). How should the reader consider/reconcile these statements? Also, what is meant by the comment regarding the 16.4 km sample that "should be representative for the inner tropics"–at all longitudes??

p. 6, Trajectories are interesting but I did not find them that useful here because no vertical information is given or discussed. Based upon the trajectories it is concluded "that the air sampled in the TTL has most probably been influenced from continental air masses" but we have no indication of the past vertical history of the airmass. Are you making some assumptions regarding the probable influence of the continent on sampled air in a region of vigorous convection. Clearly state your assumptions.

p. 9, The ranges for Cl and Br from VSLS given in the WMO report and quoted here

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are based on a root-mean square manipulation of measurements, so I do not understand the point of the clause: "but measurements show a much higher variability and uncertainty." Is there additional data not included in the report that you are bringing in here? I do not believe this is a point of the report... Certainly the range in the WMO report is an attempt to provide a best estimate given much variability; what additionally are you adding here?

Finally, the authors could improve citations. They rely heavily on citations of the WMO report in lieu of citing original work. They also cite "NOAA/ESRL" extensively, yet no publications are mentioned;what data are you using, in particular? Furthermore, global trend information from NOAA is critical to their analysis, yet no specific trends or citations are given for the data they are incorporating. This represents an inclusion of undocumented but critical results in their analysis. Perhaps the specific global trends critical to their determination of total Cl in the stratosphere need to be displayed in a table of the paper.

Intro, line 11 and/or line 13, Reference to the Salawitch work seems warranted here.

It also seems some citations might be warranted in section 3.1: who indicated 538 ppt for a global CH3Cl mixing ratio?

Technical issues: p. 3, line 4. I do not believe the WMO report is cited appropriately here. It is an assessment of existing data and should be indicated as such. So "Law and Sturges (2007) assessed available data at altitudes..." In this same vein (p. 3, line 9-12) the WMO does not make estimates; this is better described as "A recent assessment of available observations in the upper trop..."

The coauthor of the WMO (2007) report was C. Clerbaux.

p. 13, Is there no information to provide the reader with some estimate of tropospheric mixing ratios and Br contributions of any of the tentatively identified compounds?

Why are different ranges for VSLS contributions to Cl and Br different in the conclusion

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and Abstract?

Abstract, p. 2. line 1. It is a bit confusing to state "the amount of Cly or Bry from organic source gases", how about "from the decomposition of both long- and short-lived organic source gases."

Intro, line 4, only certain brominated inorganic gases actually react with ozone, please clarify.

p. 3, line 9-12, "Current estimates..." I presume this refers to VSLS, but does this also refer only to organic forms, or a sum of organic and inorganic halogen from the VSLS?

Section 3.1, Be clear that you are talking about cylinders as air samples, not calibration samples. When was the initial analysis performed? Consider quoting the corrections in total ppt as well as %, given the importance of absolute amounts in this work.

p. 5, last line. What does "quality of our measurements' refer to specifically?

p. 8, what is "Due to the limited amount the samples where measured only twice?" p. 8, for samples not analyzed at UEA, are these compounds likely to add a significant amount of Br? Guide the reader as appropriate.

p. 9, have any of these compounds (PCE-see Simpson et al; perhaps also CH2Cl2) undergone atmospheric changes over time, and could this influence your comparison of total Cl from these VSLS gases given that total Cl determinations quoted in the WMO assessment were likely based on measurements in years before 2005, on average?

p. 11, What is "product gas injection"? How is Chi(NOAA) determined specifically? Is the uncertainty related to global means increased when the two hemispheres have large mixing ratio differences? Is an error added for compounds increasing very rapidly in the troposphere, such that errors in transport time affect the analysis?

p. 12, A bit more (i.e., some) detail about the calibration scale transfer from other labs would be useful. How was it done? What do the years indicated for the scales in Table

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Interactive Comment

1 denote?

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