

## ***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.**

**J. C. Laube et al.**

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Referee comment(s)

I would urge the authors to consider making changes to the manuscript to improve its message and readability. 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.

Author response

The structure of the manuscript was reworked to improve its readability. The mentioned section of the introduction was moved to section 2 as a new subsection (2.1

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Sampling techniques). Moreover, two additional subsections of section 2 were created (2.2 Measurement techniques and 2.3 Air mass origin &#8211; the latter was moved from section 3.1). The main part of section 3.1 (Quality assurance) does not fit to the Analytical procedures section nor to the discussion. Thus, a new section was created (3 Quality Assurance) which subdivided in three subsections: 3.1 Concentration drift and blank corrections, 3.2 Intercomparison with ground-based observations and in addition 3.3 Error bar calculations (moved from former subsections 3.1 and 3.2).

Referee comment(s) Specific comments

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 CH<sub>3</sub>Br 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?

Author response

The statement on local convection was changed to: &#8220;In combination with the observed low VLS mixing ratios (see below) this indicates that a well mixed air mass with little influence from local deep convection was sampled (VLS should be super-elevated in the case of convective influence).&#8221; Moreover we assume that the referee is referring to methyl chloride as &#8220;this gas&#8221; and the corresponding paper of Khalil and Rasmussen, 1999. It was added as a citation. We agree with the referee, that it would be difficult to sample the global mixing ratio but we did so

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within 3 % for the HCFCs. For CH<sub>3</sub>Br the latitudinal gradient was added as an additional possible cause for the observed discrepancy. Furthermore the fact, that we were able to observe the global mean mixing ratio for most longer-lived substances is supporting our conclusion, that the sampled air masses were well-mixed, originated from both hemispheres and were little influenced by local convection.

Referee comment(s)

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??

Author response

In order to improve its message and understandability the first statement was corrected and expanded to: "However, due to the high variability of VLSLs in the troposphere and since many processes influence the composition of the tropical region around 15 km (see e. g. Tuck et al., 2004) we do not claim global significance for the mixing ratios found in the lowest altitude sample"; The second statement was changed to "should be more representative";.

Referee comment(s)

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 air mass. 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.

Author response

Information on vertical transport was added. Above the level of zero radiative heating the quasi-isentropic transport leads to realistic results. We admit that below the calculations of vertical winds in the tropical upper troposphere are connected with high uncertainties. Thus the statement on continental air mass origin is indeed a questionable suggestion and was removed. Nevertheless the trajectories are supporting the finding that we sampled an air-mass originating from both hemispheres which enabled us to measure global mean mixing ratios for most longer-lived substances.

#### Referee comment(s)

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

#### Author response

The ranges given by the WMO report are indeed based on a root-mean square manipulation which is why the respective best estimate shows lower variability and uncertainty than the original measurements. This is exactly our point.

Referee comment(s) 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.

## Author response

We do not agree with the referee, that we rely heavily on the WMO report. Only three of the 26 citations (revised version: 4 out of 36) refer to a Chapter of a WMO report. We admit, that Law and Sturges, 2007 is cited quite often. But this is simply due to the fact, that we compare our data with this latest and most complete assessment of upper tropospheric data for chlorinated and brominated organic substances. Regarding NOAA/ESRL: A statement including an URL was added to clarify the origin of the data (These mixing ratios are publicly available and can be accessed as anonymous ftp data under <http://www.esrl.noaa.gov/gmd/>). We have no intention or permission to publish these time trends again.

## Referee comment(s)

Intro, line 11 and/or line 13, Reference to the Salawitch work seems warranted here. p. 3, line 9-12, "Current estimates..." I presume this refers to VLSL, but does this also refer only to organic forms, or a sum of organic and inorganic halogen from the VLSL? It also seems some citations might be warranted in section 3.1: who indicated 538 ppt for a global CH<sub>3</sub>Cl mixing ratio?

## Author response

We assume, that the referee is referring to the paper by Salawitch et al. (2005) which deals with BrO observations. The adjective organic was added to clarify, that the discussion includes organic VLSL observations only. The NOAA/ESRL web page was added as the reference for the global CH<sub>3</sub>Cl mixing ratio.

## Referee comment(s)

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

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available observations in the upper trop..." The coauthor of the WMO (2007) report was C. Clerbaux. Abstract, p. 2. line 1. It is a bit confusing to state "the amount of Cl<sub>y</sub> or Br<sub>y</sub> from organic source gases", how about "from the decomposition of both long- and shortlived organic source gases." Section 3.1, Consider quoting the corrections in total ppt as well as %, given the importance of absolute amounts in this work.

Author response

The manuscript was adapted as requested.

Referee comment(s)

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 VLSL contributions to Cl and Br different in the conclusion and Abstract?

Author response

To our knowledge there are no published global tropospheric time series for the listed candidate species up to now. Moreover, as mentioned in the manuscript, in NICl detection mode the size of a peak is not indicative for the substance's concentration, which makes an estimate of the mixing ratios observed in the samples impossible without having a calibration. The intention of the authors was to stimulate further research by questioning the completeness of the list of brominated substances that are currently believed to reach the stratosphere. Moreover, the VLSL contributions mentioned in the abstract were replaced by the mixing ratio ranges from the conclusions.

Referee comment(s)

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

Author response

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All mentioned chlorine and bromine containing inorganic species play a role in ozone depletion. To explain further details on stratospheric ozone destruction mechanisms would exceed the scope of the paper. The information requested can be looked up in most environmental textbooks.

Referee comment(s)

Section 3.1, Be clear that you are talking about cylinders as air samples, not calibration samples. When was the initial analysis performed?

Author response

The various used prescriptions (cylinders, canisters, containers) were unified to containers;. Moreover, three cylinders; was replaced by three of the sample containers;. The time of the initial analysis was already given and can now be found in the measurement techniques subsection.

Referee comment(s)

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

Author response

Longer-lived trace gases show rather uniform concentrations in the global background troposphere. If we find good agreement of our measurements on samples originating from the upper troposphere with ground-based observations;this indicates that a well mixed air mass with little influence from local deep convection was sampled;. Moreover it provides evidence, that the samples were not contaminated e.g. by balloon exhaust. The latter statement was added to the manuscript.

Referee comment(s)

p. 8, what is "Due to the limited amount the samples where measured only twice?"

Author response

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This means that, the amount of sampled air available from the containers was limited. The statement was extended accordingly.

Referee comment(s)

p. 8, for samples not analyzed at UEA, are these compounds likely to add a significant amount of Br? Guide the reader as appropriate.

Author response

A reference to the corresponding mixing ratios in Table 3 and 4 was added.

Referee comment(s)

p. 9, have any of these compounds (PCE-see Simpson et al; perhaps also CH<sub>2</sub>Cl<sub>2</sub>) 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?

Author response

The concentrations of all organic VSLS are highly variable in the troposphere which makes the corresponding time series very uncertain. This is why the WMO gives mixing ratio ranges in their assessment. Nevertheless in 15 km altitude we find good agreement with these ranges for Cl from organic VSLS.

Referee comment(s)

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?

Author response

A product gas injection is bringing inorganic bromine species contained in

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the upper tropospheric aerosol or in gaseous form into the stratosphere; as explained in the manuscript.  $\chi(\text{NOAA})$  is determined as the sum of the standard deviations of the global mixing ratios averaged over 2001 as provided by NOAA-ESRL; as explained in the manuscript. These standard deviations are estimates of the instrumental precisions only. The source of data (<http://www.esrl.noaa.gov/gmd/>) and an additional statement (Uncertainties which could originate from hemispheric mixing ratio gradients were not estimated;) were added for clarification.

#### Referee comment(s)

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 1 denote?

#### Author response

Additional information on calibration is now given in the header of Table 1 (All NOAA calibrations originate from a calibrated container obtained from NOAA-ESRL and were transferred to an internal secondary calibration container used for sample measurements. The years indicate the revision of the calibration scale. The University of East Anglia (UEA), UK calibrations originate from a direct cross-comparison of that secondary container with an internal secondary UEA calibration container for  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$ . Four substances were calibrated using air samples from UEA which were measured twice at both institutes: F115, F114, F114a and H2402. The remaining substances; 1,2-dichloroethane and F124; were quantified via a cross-comparison with a container calibrated by E. Atlas of the University of Miami, USA which is owned by the Max-Planck-Institute for Chemistry in Mainz, GER.)

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8491, 2008.

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