

## ***Interactive comment on “More evidence for very short-lived substance contribution to stratospheric chlorine inferred from HCl balloon-borne in situ measurements in the tropics” by Y. Mébarki et al.***

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We thank the referee for helpful comments and suggestions aimed at improving the clarity of the paper. We essentially agree with all the comments and suggestions. Our responses are presented below:

### Specific comments

Issue 1: Page 16166, line 20: It would be useful to list here the most important VSL SGs measured by Laube et al. and which species mainly contributed.

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This paragraph has been rewritten accordingly as follows: “. . . Laube et al. (2008) have confirmed this result, with a chlorine vmr estimated to  $49 \pm 6$  pptv at 15.2 km, resulting from their VSL SGs measurements and an additional contribution of 1.5 pptv from chloroethane (WMO, 2007). These authors performed simultaneous measurements of  $\text{CH}_2\text{Cl}_2$  (11.2 pptv),  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (6.2 pptv),  $\text{CHCl}_3$  (2.7 pptv),  $\text{C}_2\text{Cl}_4$  (1.0 pptv) and other very minor contributors to chlorine vmr during a balloon flight in the tropics (near Teresina, Brazil,  $5.0^\circ\text{S}$ – $42.9^\circ\text{W}$ ).”

Issue 2: Page 16166, line 29: Why don't you cite the original studies instead of WMO (2007). We have now cited the original work from Toon et al. (2001) and referred to another more relevant and recent study by Fu et al. (Geophys. Res. Lett., 34, L17815, 2007).

Issue 3: Page 16170, line 18: Why are two different MLS data versions used for the comparison? Please explain, or change and compare both flights with the newer version.

Two versions were used, the v1.5 for year 2005 and the v2.2 for year 2008, since the v2.2 data are not publicly available on the MLS website for 22 June 2005 around SPIRALE location. This sentence (page 16170 line 18) has been rewritten more clearly as: “MLS HCl measurements around SPIRALE location ( $5^\circ\text{S}$ – $43^\circ\text{W}$ ) are publicly available in version 1.5 (v1.5) for 22 June 2005 and in version 2.2 (v2.2) for 9 June 2008, and are used for comparisons.” The different MLS version numbers are specified in Section 3.3, in Table 1 and in Figure 7 of the current paper draft.

Issue 4: Page 16174, line 17 and the whole paragraph: When calculating the uncertainties and making the conclusion that  $85 \pm 35$  ppt of VSLs contribute to total stratospheric chlorine, it should also clearly be stated that this estimate is based on: only 2 SPIRALE balloon observations at the same location and during the same season (more observations are needed), one measurement of VSLs from the Laube et al. study, and a maximum contribution from phosgene of 45 pptv (what might the real uncertainties of

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this number be ?). Therefore, the error bars of 35 ppt are probably too low, but the real value is also difficult to estimate.

To answer both this comment and the same comment of Referee #2, we have added the following sentence at the end of the last paragraph of Section 3.2.1 (HCl measurements in the TTL): "However it should be stated that this estimate is based on only two balloon flight observations at the same location and during the same season. So, further data are still required." Note that it was already mentioned in the Conclusion of the submitted paper, (i) pg 16179 line 22: "even though the SPIRALE measurements have limited spatial sampling, they lead us to conclude...", and (ii) last lines of pg 16180: "further investigations in the TTL and tropical stratosphere would help to quantify the influence of season, location and deep convection on this contribution." Concerning the VSL contribution to stratospheric chlorine and associated uncertainties, the phosgene value has been updated thanks to the remark of Referee #1, and the error bars have been refined by rewriting: - the end of the Introduction section (pg 16166, from line 26) as: "Phosgene ( $\text{COCl}_2$ ) is the main intermediate product present in the upper troposphere, resulting from the degradation of VSL SGs, since its lifetime is much longer than any other intermediate products (WMO, 2007). The last WMO report (2007), based on the work of Toon et al. (2001), indicates a  $\text{COCl}_2$  vmr of  $22.5 \pm 2.5$  pptv, i.e.  $45 \pm 5$  pptv of chlorine, from measurements of the MkIV balloon-borne instrument performed in the latitudinal zone  $34\text{--}68^\circ\text{N}$ , between 1992 and 2000. Phosgene is also produced by long-lived SGs so that the total VSL contribution to stratospheric chlorine in the form of organic species (SGs and intermediate PGs) ranges between about 50 and 100 pptv according to WMO (2007). The  $\text{COCl}_2$  vmr values should be adapted for tropical latitudes and updated by more recent ones. Fu et al. (2007) recently performed  $\text{COCl}_2$  measurements using the ACE-FTS satellite instrument in agreement with those of MkIV over the same latitudes ( $30\text{--}35^\circ\text{N}$ ) and the same period (2004-2006). Averaging more than fifty FTS vertical profiles at  $0\text{--}5^\circ\text{S}$  latitudes they reported vmr ranging from  $15 \pm 5$  pptv to  $18 \pm 6$  pptv, i.e.  $\sim 33 \pm 11$  pptv of chlorine, on average, in the upper TTL ( $\sim 15\text{--}17$  km). Combining them with the VSL SG contribution reported by Laube

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et al. (2008), this leads to an updated total VSL contribution to stratospheric chlorine of about 50–80 pptv, or more safely to 50–100 pptv if all the associated uncertainties and variabilities are accounted for. In addition, the contribution of the final VSL degradation product, HCl, should be included." - the end of Section 3.2.1 (pg 16174, from line 17): "From this mean upper limit of  $25 \pm 5$  pptv for HCl, a  $\text{CH}_3\text{Cl}$  mean contribution of  $5 \pm 3$  pptv (Marcy et al., 2007; see Sect. 3.1) should be subtracted, indicating that no more than  $20 \pm 5$  pptv VSL is converted into HCl in the TTL. This represents the maximum contribution of VSL in the form of final degradation product to stratospheric chlorine. Hence chlorinated VSL are essentially present in their source and intermediate product gas forms in this region. Then summing this range of HCl values (0 to  $20 \pm 5$  pptv) with the value of  $49 \pm 6$  pptv for total chlorine coming from tropospheric VSL SGs measured in situ under the same conditions (Laube et al., 2008) and with a  $\text{COCl}_2$  contribution to VSL of  $0\text{--}(33 \pm 11)$  pptv (Fu et al., 2007; see Sect. 1), we can estimate a total contribution of VSL to stratospheric chlorine ranging from about 45 to 125 pptv if all the associated uncertainties are accounted for, or in other words of about  $85 \pm 40$  pptv by simply averaging the lower and higher limits of this range. This refines the estimated 50–100 pptv range of WMO (2007), which was not taking into account the final VSL PG (HCl) due to a lack of measurements. However it should be stated that this estimate is based on only two balloon flight observations at the same location and during the same season. So, further data are still required." We believed the 40 pptv uncertainty is not so much underestimated since it takes into account a pessimistic large range contribution of VSL to  $\text{COCl}_2$  production.

Issue 5: Page 16179, line 1 to 6: I guess that the uncertainties in the satellite measurements are larger than the 100 pptv contribution of VSL derived with the help of the model. This should be stated in the text, besides possible model uncertainties (which are probably unknown).

In consistence also with the remark of Referee #2, the sentence pg 16179 lines 4-6 has been modified as: "The very good agreement between SPIRALE and MLS mea-

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surements suggests further evidence for the VSLS contribution of about  $85\pm 40$  pptv that we derived in the TTL from the present analysis, even if satellite accuracy cannot constrain this VSLS contribution to better than 200 pptv.”

Technical corrections All the technical corrections have been accounted for and changed in the text. In particular:

10. Page 16168, line 9: '(Berthet et al., 2006, 2007)' - As far as I know both references are from 2007, so they should be labelled 2007a and 2007b.

Actually the 2006 reference was missing and has been maintained here with the complete reference added in the Reference Section. The 2007 reference (Berthet, Renard, et al.) has been labelled 2007a and the second one from 2007 (Berthet, Esler, and Haynes), now labelled 2007b, has been quoted in the Section 3.1.

11. Page 16168, line 10 and following lines: Add 'the' before the instruments names, e.g. '...such as the Sub-Millimeter...'. Why is the acronym ACE-FTS not explained?

“The” has been added before the instrument names. The acronym ACE-FTS is already explained in the Introduction section page 16165, line 18.

16. Page 16172, line 21: Briefly describe the BONBON instrument, e.g. what does the acronym mean?

On page 16172, line 21, the following description has been added: “The BONBON instrument performed a balloon flight on 8 June 2005 near Teresina (Laube et al., 2008). This cryogenic whole air sampler allows for the collection of several whole air samples at different altitudes, which are analysed by gas chromatography mass spectrometry after the flight. Backward trajectories associated with the BONBON flight presented the same characteristics as ours in the TTL region. . .” The acronym is even not indicated by the instrument owner (Laube et al., 2008) and has not been found.

22. Page 16187 and 16188: You could combine the tables, since the structure, caption and footnotes are basically the same.

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The tables have the same the structures and captions, but combining them will only save 1 line and 1 column and make the reading less easy; so we think it is not worth. We removed the footnotes of Table 1b and referred them to Table 1a.

23. Page 16189, Figure 1: The lower panel is missing an x-axis. Furthermore, the labelling on the y-axis is hardly readable and the zero position of the left and right axis are off.

The x-axis on the lower panel has been added. The labelling on the y-axis, including the fonts of the exponents, has been enlarged. The zeros have been aligned, leading to no more offset.

24. Page 16191, Figure 3: The upper left panel is missing a scale. The units of the colour-scale are not given in the Figure, nor in the caption. Maybe you can enlarge the figure, or at least the axis labels, and indicate the position of Teresina in the right panels.

The upper left panel scale and the units of the colour scale have been added, the axis labels have been enlarged with the location of Teresina indicated. The figure caption has been rewritten as follows: “Seven-day backward trajectories associated with SPIRALE measurements on (a) 22 June 2005 at 12:00 UT and (b) 10 June 2008 at 03:00 UT. The different trajectory colours indicate the altitude ranges. Left panels represent the altitude evolution with Time = 0 corresponding to the time of measurements. Right panels represent the geographical locations of the air masses along the trajectories ending at the measurement location, near Teresina (indicated by a black cross)

25. Page 16193, Figure 5: The white cross in the lower panel is hardly visible. You should use another colour. The black background is also very unusual. Same for Figure 6.

The white crosses denoting SPIRALE locations have been enlarged; the black crosses for MLS have been replaced by large white triangles. The black backgrounds have

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been replaced by white backgrounds.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 16163, 2009.

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