

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.

Y. Mébarki et al.

yassine.mebarki@cnrso-orleans.fr

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We thank the referee for the very thorough review of the manuscript and 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:

General comments

A significant part of their argument that I did not find convincing is that the HCl in the TTL was entirely the result of the breakdown of VLSL, which was based on two 7-day

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back trajectories. Although I wholly agree that these back trajectories do not indicate any contribution from stratospheric air, I do not think that two 7-day back trajectories are sufficient for the assumption that the HCl in the TTL is entirely the result of the breakdown of VSLS. TTL transport is a complicated problem and there is much evidence that the tropical troposphere consists of isolated regions of convective ascent among weaker large-scale descent, which together give net ascent. More work needs to be done to show that the measurements have not been exposed to any air carrying HCl from the stratosphere (...) Can the authors show some evidence that this argument is sound for the bulk of the TTL?

According to this comment, the paper has been revised with the aim of providing a clearer discussion. First we have gathered in Section 3.1 (“Air mass origin”) the comments about the 2008 backward trajectories (page 16172, lines 26-29; page 16173, lines 1-3) with those about 2005 (page 16172, lines 10-15) and have added the following new arguments as a conclusion at the end of this section: “Since the TTL is an exchange zone, air masses in this region might be exposed to those from above. On short time-scales, episodic stratospheric intrusions may penetrate from the extratropics down to the TTL. Potential vorticity fields, which are useful tools to highlight such relatively “sporadic” phenomena (see, e.g. Waugh and Polvani, 2000), have been calculated over the few days preceding the SPIRALE observations and did not show any evidence for stratospheric intrusions likely to affect the HCl amounts. So these results suggest that the HCl amounts measured by SPIRALE in the TTL in June 2005 and June 2008 were not influenced by layers below or above this region on a short time scale.” Secondly, it is to be noted that dynamical processes between stratosphere and troposphere also take place on longer time-scales. Indeed, extensive aircraft observations in the tropical and the subtropical upper troposphere - lower stratosphere have shown that between 350 K and 400 K, without the influence of convective events, the abundances of species are controlled by transport and mixing processes occurring over periods of one month or more (James and Legras, Atmos. Chem. Phys., 9, 25-38, 2009) with stratospheric air proportion of not more than 20% (see their figure 10). We

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examine this point in the section 3.2.1 (“HCl measurements in the TTL”) by comparing our measurements with previous aircraft measurements of HCl performed in the TTL by Marcy et al. (2007) and so we have added the new following arguments: “Our HCl low values are in agreement with those presented by Marcy et al. (2007) around the LZRH (at approximately 15 km). These authors reported HCl mixing ratios ranging from about 0 to 40 pptv at the LZRH, and gradually increasing to 20–80 pptv at the top of the TTL. However their more elevated HCl mixing ratios were attributed to mixing of stratospheric air in the TTL, as revealed by enhanced O₃ amounts. Thus a clear tendency in the vertical profile of HCl with increasing values toward those typical of the stratosphere is to be expected as a consequence of a significant stratospheric influence. Given that our vmr values were below SPIRALE detection limit (iĀĀ 30 pptv) for the whole range of the upper TTL and without significant increase toward stratospheric values, they reasonably suggest a weak or insignificant contribution of stratospheric air at the time of our observations.” Finally, other parts of the text mentioning this subject have been corrected accordingly: (i) in the Abstract (page 16165, line 12), “Backward trajectory calculations and such low amounts [of HCl] suggest that the air masses sampled correspond to typical background conditions. . .”; (ii) at the end of the Introduction, page 16167, after line 18 slightly modified in “Air mass backward trajectory calculations have been performed and indicate that air characteristics in this region were not influenced by lower or higher levels”, we have added “This is further corroborated by the very low HCl amounts we found.”; (iii) in the Conclusion (page 16179, line 16), we have removed “according to backward trajectory calculations”.

It should also be acknowledged that chemical transport modeling work indicates that essentially all meteorological fields (ECMWF included) have difficulty accurately representing stratosphere-troposphere exchange.

We agree with the reviewer’s comment. We are aware of the limitations of trajectory calculations, especially regarding subgrid processes such as convection. We have then added the following sentence at the end of the second paragraph of section 3.1:

“Of course, one must keep in mind that subgrid convection is not resolved in three-dimensional trajectories (e.g. Berthet et al. 2007b) so that our calculations possibly miss advection due to individual convective cells.”

COC12 values in the WMO report come from the work of Toon et al. (2001). The original work must be cited to give credit appropriately. That being said, these values may be seriously outdated for an analysis of 2005 and 2008 observations. The recent work of Fu et al. (2007...) must also be cited and the more extensive measurements in that work must be considered for the interpretation of the COC12 contribution.

We thank the reviewer for making us aware of the paper from Fu et al. (2007). We took into account his comment by rewriting the paragraph concerning COC12 in the Introduction (page 16166, from line 26) as follows: “Phosgene (COC12) 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 COC12 vmr of 22.5 ± 2.5 pptv, i.e. 45 ± 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 VSLs 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 COC12 vmr values should be adapted for tropical latitudes and updated by more recent ones. Fu et al. (2007) recently performed COC12 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 ± 5 pptv to 18 ± 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 et al. (2008), we arrive at an updated total VSLs contribution to stratospheric chlorine of about 50–80 pptv, or more safely 50–100 pptv if all the associated uncertainties and variabilities are accounted for. In addition,

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the contribution of the final VLSL degradation product, HCl, should be included.” In addition, this recent work from Fu et al. (2007) has been considered as the most relevant and hence cited in the Abstract and in the Conclusion in place of WMO (2007).

Specific comments

I would personally prefer expansion of the acronym VLSL in the title, but I think this is an editorial decision, not mine.”

As the long title expands the VLSL acronym, we think it is not necessary to expand it again in the short title, all the more so as it is now well-known in the atmospheric research community. However we agree this is an editorial decision.

Figure 7 in Froidevaux et al. (2008) describes the difference between MLS HCl versions 1.5 and 2.2 in detail. Please explain why two different versions of MLS data were used in this work, instead of just the newer version 2.2. There are some significant differences between MLS HCl and ACE-FTS v2.2 HCl, although agreement with ACE-FTS v2.2 is better for MLS v2.2, especially in the upper stratosphere. Please also restate the MLS version numbers in section 3.3.

The reason to use two versions, i.e. v1.5 for year 2005 and v2.2 for year 2008, is that the v2.2 data are not publicly available on the MLS website for 22 June 2005 around SPIRALE location. The sentence in Section 2.2 (page 16170 line 18) has been rewritten more clearly as: “MLS HCl measurements around SPIRALE location (5°S-43°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.” At present the different MLS version numbers are restated in Section 3.3, in Table 1 and in Figure 7 of the current paper draft.

Could the values given in the second last paragraph of section 2.1 be shown as a table or figure for improved clarity?

We think it is not worth to make a table for so few values and only 2 types of variables

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(uncertainty value and altitude). Table use is more relevant for presenting at least three variables. We believe it is a very minor point and hope the referee will accept this point of view.

It is not clear to me at all what the thickness of the lines in Figure 4 below 19 km represents. Is this representing variability which is not shown for higher altitudes? Please explain this in the text and caption.

Also answering the Referee #2 question, the inset of Fig. 4 has been rebuilt and provided in attachment. The text has been revised as follows: “The HCl volume mixing ratios . . . are below the detection limit for both flights, i.e. below 30 pptv on 22 June 2005 and below 20 pptv on 10 June 2008, on average over the whole upper TTL. . . These detection limits are found to be variable with altitude because of optical interference fringes. These fringes generate an undulating background structure on the signal, which is sometimes mistaken for the HCl ro-vibrational line. Consequently the detection limits quoted above are the result of smoothing the signal with a moving average over 500 m altitude to lower them a maximum. In addition, this reduces their variations over the whole altitude range of the upper TTL to less than 20% (2 sigma). In the inset of Fig. 4, the shaded areas [i.e. the line thicknesses] in red and blue for 2005 and 2008 profiles, respectively, represent the ranges of HCl possible values, between 15 km and the first altitude points where HCl has been unambiguously detected, i.e. at 18.6 km in the 2005 flight and at 17.7 km in the 2008 flight.” This leads to shaded areas given that the measurements are initially every 5 m (as written in the initial figure caption). The figure caption has also been modified accordingly.

On page 16178 where MkIV, FIRS-2 and ALIAS-II are mentioned, a distinction must be made between remote and in situ measurements. The balloon-borne remote sensing observations are in many ways more like satellite observations than balloon-borne in situ measurements.

This distinction has been made. In addition it is to be noted that ALIAS-II is an in

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situ laser diode method and so, the text has been corrected accordingly as: "...other remote (MkIV, FIRS-2) and in situ tunable laser diode (ALIAS-II) balloon-borne measurements, ...". Note that the paper by Froidevaux et al. (2008) does not indicate significant differences between these remote and in situ comparisons with MLS.

On page 16178-79 the discussion of the ACE and MLS comparison "ACE HCl values have been shown to be 2 to 10% larger than MLS ones from 50 to 10 hPa (21–31 km) and from 1 to 0.2 hPa (48–60 km); the agreement was better than 3% in the range 10–1 hPa" is a bit sloppy and possibly misleading. In the lower altitude range (21–31 km), the agreement is very good, but the values are low whereas in the higher altitude range (48-60 km), the two datasets actually diverge but since HCl VMR is much higher, as a percentage, the difference is coincidentally similar to the lower range.

We agree the discussion is misleading. Our goal is not to compare the quality of the agreement between ACE and MLS data as a function of altitude but to indicate that SPIRALE and MLS are in better agreement with each other than they are with ACE, which gave larger values. So we removed the allusion to the better than 3% agreement in the range 10-1 hPa, and we added that "ACE values were larger than MLS values by about 200 pptv" at 53 km where MLS agrees very well with modelling including VLSL contribution of 100 pptv. In addition we followed the corrections suggested by Referee #2, since this discussion in percentage is based on his paper (L. Froidevaux et al., JGR 2008, Fig. 12).

The sentence "As a conclusion, the present paper answers the WMO (2007, p. 2.42) requirement for accurate HCl measurements in the TTL," in the final paragraph is too strong of a statement since HCl was actually below the detection limit, so accurate and quantitative measurements are still elusive.

This conclusion has been weakened as: "As a conclusion, the present paper, based on HCl in situ measurements combined with examination of dynamical conditions, helps to quantify the influence of VLSL on the stratospheric chlorine content as required by

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WMO (2007)".

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

page 16168, line 2: Omission of the expanded SPIRALE acronym seems common for SPIRALE papers. I would like to see it expanded even though it is French. Surprisingly, this was done for another French acronym MIMOSA, which is much less central to the work

The SPIRALE acronym has been expanded once: the first time it is quoted, i.e. in the last paragraph of the Introduction, just before the Instrument section where it is described.

Figure 1: Why are the zeros on the left and right axes not aligned? What is the significance (if any) of this offset? Also, the fonts for the exponents are too small and difficult to read.

The zeros have been aligned, leading to no more offset. The fonts of the exponents have been enlarged to improve clarity.

Figure 2: Could the LZRH also be shown?

The LZRH has been added on this figure as suggested.

Figure 3: It would be helpful to label the location of Teresina.

The location of Teresina has been indicated by a black cross on the maps, and specified in the caption.

Figure 4: Explain the thickness below 19 km.

See above in the answer to the specific comments.

Figures 5&6: Black background is not standard for journal figures and makes for poor quality printing.

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The black background has been replaced by a white background.

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

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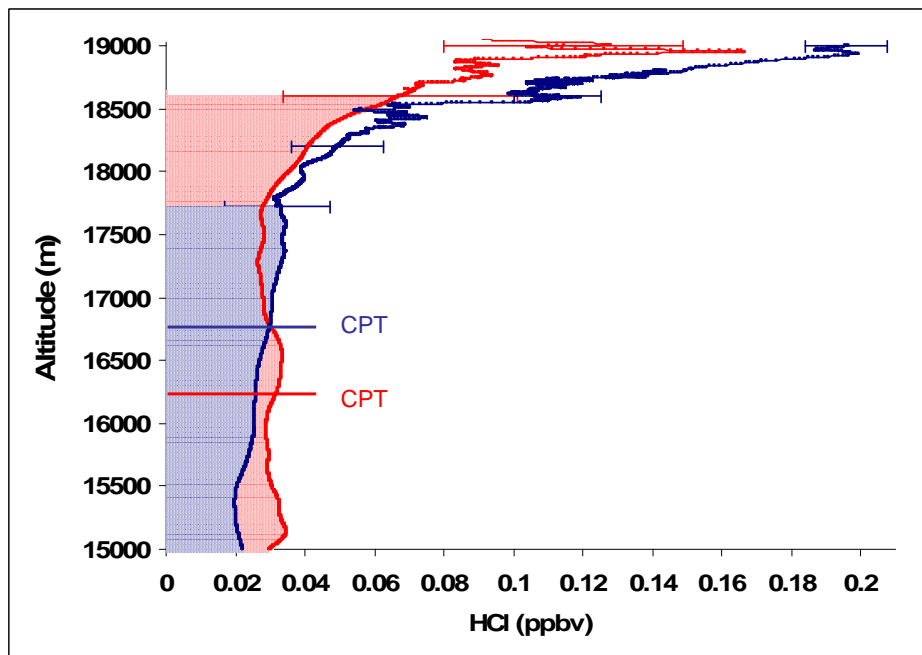
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Fig. 1. Modified version of the inset of Figure 4.

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