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Atmospheric Chemistry and Physics Discussions

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 the very thorough review of the manuscript and for helpful comments and suggestions aimed at improving the clarity of the paper. We agree with all the comments and suggestions. Our responses are presented below.

1) General and specific comments about the VSLS contribution to chlorine and associated uncertainties

Question: It would be nice to have a clearer statement regarding the uncertainties, as

the level of significance for the in situ data appears to be masked by random errors. Showing average values at the lowest altitudes might help the readers in this respect. . . . . .The current manuscript is a worthwhile study and, if nothing else, an indication of an upper limit [of HCl]. . . There are comments regarding the random uncertainties for the SPIRALE data, but can you state that systematic errors are most likely lower than 20 (or 10) pptv, so that the total error estimate arises mostly from the random errors? Further comments on this issue would be desirable, for clarification of the error bars. This is important because the total uncertainty will be a key number to associate with the likely VSLS contribution. The note (e.g., pg. 16173) on experimental scatter being 30 or 20 pptv at the 1 sigma level would seem to imply that this study is almost dealing with an upper limit. . . It may be difficult to state that 90 pptv HCl is not present, unless you can use some averaging arguments over a wider height range, possibly (why not?). In this respect, why not show actual average values as a solid line especially at the lower altitudes?

Answer: We agree with the referee's comment we have to clarify our statement regarding the uncertainties. We have made several changes described as follows: We have added the following sentence in Section 2.1, pg 16169, line 21 at the beginning of the paragraph concerning the uncertainties: "An assessment of the error sources on the vmr retrieved has been already performed in a previous paper (Moreau et al., 2005). In brief, [uncertainties in the pressure and temperature. . .]". In the same paragraph just below, it was already written, lines 25-26: "The two important sources of random errors are the fluctuations of the laser background emission signal and the signal-to-noise ratio. At lower altitudes, these are the main contributions to overall uncertainties." (Note that the term "global" has been replaced by "overall"). More important, we have removed the note "uncertainties representing only experimental scatter at 1ïĄş level" and rewritten the beginning of Section 3.2.1 (pg 16173) as: "The HCl volume mixing ratios measured by SPIRALE in the upper TTL are shown in the inset of Fig. 4. They 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 lower limits of

detection correspond to a signal-to-noise ratio of one with the noise defined as the 2ïĄş precision of the signal. The systematic errors have been evaluated to negligibly contribute (< 6%) to the overall uncertainties in the TTL and up to 21 km, consistently with our previous paper (Moreau et al., 2005), so that the precisions reported as detection limits in the TTL are the only important uncertainties. 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% (2ïĄş). In the inset of Fig. 4, the shaded areas (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." The inset of Fig.4 has been revised and provided in attachment.

Comment: If this is not more clearly discussed or demonstrated, readers may have some trouble with the numbers you arrive at, in terms of "global" [total] uncertainties for the VSLS contribution.

Answer: This has been clarified several times throughout the manuscript. First the Introduction has been rewritten from line 26 pg 16166 in order to specify the VSLS contribution according to the COCl2 budget updated thanks to the reference suggested by Referee #1, as follows: "Phosgene (COCl2) 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 COCl2 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 34–68°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 COCl2 vmr values should be adapted for tropical latitudes and updated by more recent ones. Fu et al. (2007) recently performed COCl2 measurements using the ACE-FTS satellite instrument in agreement with those of MkIV over the same latitudes (30–35°N) and the same period (2004-2006). Averaging more than fifty FTS vertical profiles at 0–5°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$15–17 km). Combining them with the VSL SG contribution reported by Laube et al. (2008), we arrive at an updated total VSLS contribution to stratospheric chlorine of about 50–80 pptv, or more safely of 50–100 pptv if all the associated uncertainties and variabilities are accounted for. In addition, the contribution of the final VSLS degradation product, HCl, should be included." Secondly, concerning the numbers we arrive at for the VSLS contribution to stratospheric chlorine and associated uncertainties, the end of Section 3.2.1 (pg 16174, from line 17) has been rewritten as: "From this mean upper limit of 25$\pm$5 pptv for HCl, a CH3Cl mean contribution of 5$\pm$3 pptv (Marcy et al., 2007; see Sect. 3.1) should be subtracted, indicating that no more than 20$\pm$5 pptv of VSLS is converted into HCl in the TTL. This represents the maximum contribution of VSLS in the form of final degradation product to stratospheric chlorine. Hence chlorinated VSLS are essentially present in their source and intermediate product gas forms in this region. Then summing this range of HCl values (0 to 20$\pm$5 pptv) with the value of 49$\pm$6 pptv for total chlorine coming from tropospheric VSL SGs measured in situ under the same conditions (Laube et al., 2008) and with a COCl2 contribution to VSLS of 0–(33$\pm$11) pptv (Fu et al., 2007; see Sect. 1), we can estimate a total contribution of VSLS to stratospheric chlorine ranging from about 45 to 125 pptv if all the associated uncertainties are accounted for, or in other words of about 85$\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." Finally, in the Abstract, the overall uncertainties on HCl (ïĆś20, ïĆś30 pptv) have been removed (line 10), and the VSLS contribution changed to 85±40 pptv. And also in the Conclusion, where the range has been specified again (pg 16179, line 20) as ". . . an estimate of 45 to 125 pptv (or 85±40 pptv). . .".

2) General and specific comments about transport

Comment: If transport from above does affect the low altitude measurements, the estimated values are likely to represent upper limits for a contribution from VSLS; this may be a useful statement to make as well.

Answer: We have provided new arguments to show that transport from above negligibly affects our TTL measurements, as detailed in the answer to the first question of Referee #1. In brief, Section 3.1 ("Air mass origin", pg 16172) contains now the following text: "On short time-scales, episodic stratospheric intrusions may penetrate from the extra-tropics 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. Therefore 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." And Section 3.2.1. (pg 16173, from line 23) has been revised as: "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 (ïĆč 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."

Comment: [In the discussion on pg 16174, Section 3.2.1]: . . . Finally, the point is made elsewhere that aircraft data (Marcy et al.) have indicated very low HCl values in the tropics before. This is worth some emphasis and possibly further comments, as your data appear to confirm this previous information (correct?).

Answer: Yes, our data confirm this information. This has been emphasized in the preceding answer.

3) General and specific comments about agreement between SPIRALE, satellite data and models

Comment: Some consistency with satellite data is discussed, although this argument is fairly weak, given the error bars in total chlorine implied from upper stratospheric satellite data. One should understand that, regarding the issue of satellite data agreement versus models, including the previous (rough) estimates of about 100 pptv for VSLS, such comparisons do not carry significance at the better than 200 pptv level, given the possible systematic errors in MLS (or other satellite) measurements in the upper stratosphere; of course, the model estimates have additional uncertainties. Therefore, measurements of VSLS in the UT/LS and measurements such as the SPIRALE HCl data are likely to carry the "burden of significance" in terms of possible VSLS contributions to total chlorine in the stratosphere. If the current manuscript (coupled with other evidence) can convincingly imply 85±35 pptv for this VSLS contribution [see comments on uncertainties below], the consistency with satellite data is only a mild connection, given the larger satellite data uncertainties. Pg. 16180, L6-10: A shorter summary sentence is suggested, possibly as follows: "Our result regarding a VSLS contribution of XYpptv to stratospheric chlorine supports the previous agreement between MLS-inferred upper stratospheric total chlorine and model chlorine, taking into

account about 100 pptv from VSLS, although satellite results do not constrain the VSLS contribution to better than 200 pptv."

Answer: Concerning this last comment, we thank the reviewer for his suggestion. The sentence has been included in the Conclusion (with the contribution put at 85$\pm$40 pptv). The manuscript has been changed in this way, according to the more general comment just above. First, the last sentence of the Abstract has been replaced by: "The previous agreement between MLS-deduced upper stratospheric total chlorine content and modelled values including 100 pptv of VSLS (Froidevaux et al., 2006) is thus supported by our present result about the VSLS contribution." At the end of the Introduction (from line 22, pg 16167), the sentence has been rewritten according to the technical comments suggested: "The result of such comparisons [between SPIRALE and MLS] can lead to an assessment of the validity of previous estimates regarding the potential contribution of about 100 pptv from VSLS to total stratospheric chlorine." What is interesting to note is the very good agreement between SPIRALE and MLS data, suggesting that no bias affects the data of this satellite instrument, in contrast with the apparent ACE-FTS data shift on Figure 1.12 of WMO 2007 (i.e. Fig. 5 from Froidevaux et al., 2006). The last two sentences of Section 3.3, pg 16179 lines 1-6, have been modified in this way and in order to state again that the uncertainties in the satellite measurements are larger than the 100 pptv contribution of VSLS: "Among these satellite measurements at about 53 km, the MLS value were found in excellent agreement with calculated HCl vmr based on tropospheric measurements of ground-based networks and modelling including long-lived source gases and 100 pptv of VSLS contribution (Froidevaux et al. 2006), whereas the ACE values were larger than calculated HCl values by about 200 pptv. The very good agreement between SPIRALE and MLS measurements suggests further evidence for the VSLS contribution of about 85$\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."

4) Other Specific comments

Comment: It is also worth noting that 2 balloon flights may not suffice to "nail down" the upper limit for VSLS contribution to chlorine, so additional data may be useful as further confirmation in the future... This could mean that the error bars are somewhat too low, although this is difficult to estimate... A cautionary note about this would still be worthwhile.

Answer: To answer both this comment and the same comment of Referee #3 on the last paragraph (page 16174) of Section 3.2.1 (HCl measurements in the TTL), we have added the following sentence at the end of this paragraph: "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 initial paper that: (i) "even though the SPIRALE measurements have limited spatial sampling, they lead us to conclude..." (pg 16179 line 22), (ii) "further investigations in the TTL and tropical stratosphere would help to quantify the influence of season, location and deep convection on this contribution" (last lines of pg 16180). The error bars have been refined as explained in the second part of our answer to question 1 above (paragraph "General and specific comments about the VSLS contribution to chlorine and associated uncertainties").

Comment: Pg. 16167, lines 19/20 (L19/20) and pg. 16172: It would be useful to have (or point to) a good (quantitative) argument, regarding the possible direct (and local, if one can really ignore transported HCl) contribution to measured HCl from the (longer-lived) CFC's? The local photolysis rate should be very small at low "enough" altitude in the tropics, but is this really a zero pptv contribution or possibly a small number approaching the 20 pptv that you measure? Without quantification (or a reference to this), one cannot have a really firm conclusion (with zero error). Only if this number (and associated uncertainty) provides less than 5-10 pptv can that source of error be ignored, in terms of assigning tropical HCl values to VSLS only.

Answer: The CFC contribution to HCl content is negligible, as also indicated by Marcy et al. (2007). The text (Section 3.1 corresponding to line 20 page 16172) has been

revised according to the following argument: “Thus HCl potentially present in the TTL appeared to be the result from photochemical degradations only, including those of VSLS. More precisely, from a simple calculation based on typical residence timescale of two months in the TTL we derived a contribution of CFC and other long-lived species to HCl budget lower than 1 pptv in this region. This negligible contribution was also indicated by Marcy et al. (2007). In addition, using the lifetimes of CH3Cl towards photolysis and reaction with OH, these authors have shown that the depletion of CH3Cl over a 1–2 month period in the TTL is only 3–8 pptv.”

Comment: Along these lines, the discussion on pg. 16174 mentions the possibility (and ref. to Laube et al., 2008) that up to 56 pptv inorganic Cl could come from CH3Cl (or maybe a similar SG). So how much of this might (or might not) end up in the measured HCl? In the limit, could there not be zero VSLS contribution, with all the (25 pptv) measured HCl [from SPIRALE] really coming from longer-lived product degradation?

Answer: The mention of 0 up to 56 pptv of CH3Cl has been removed as we have hazardously inferred it from the Laube et al (2008) paper. Furthermore this paper was not taking into account the intermediate product gas COCl2 and so, conclusions were not so straightforward. Actually, using the CH3Cl lifetimes towards photolysis and reaction with OH, Marcy et al. (2007) have shown that the depletion of CH3Cl over a 1-2 month period in the TTL is only 3–8 ppt. We have added this information in Section 3.1, as written in the just above question. In addition for the calculation of the VSLS contribution to stratospheric HCl, we have removed this CH3Cl contribution as explained in the revised section 3.2.1.

Comment:Regarding the MLS data in Table 1 and Fig. 7: it is not clear that the version 1.5 data should be included, given that the latest data version (v2.2) should typically be viewed as a replacement (unless otherwise stated). If there is no obvious reason to do this (please state if there is), it would be best to simply include v2.2 data (and the Table does not mention what version is used). Fig. 7 does not make it clear which symbols refer to what version anyway.

Answer: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 (line 18 page 16170) 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.

Comment:Finally, it is not obvious why some heights (shown in Table 1) have 3 “selected points” and one has 6 points – some clarification would be useful.

Answer: The explanation is detailed in the text pg 16177, lines 5-21. This has been specified in the Table caption as: “a Selections based on comparisons of the dynamical situation between SPIRALE et MLS, as illustrated on Fig. 6. See the text (Sect. 3.3) for details.”

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

Pg 16166, L21: check that the value from Laube et al. is really 49ïĆś6 pptv at 15.2 km

Actually, Laube et al measured 47.1 pptv of chlorine, coming from all VSLS except chloroethane. This result has been specified in the text as follows: “. . . with a chlorine vmr estimated to 49ïĆś6 pptv at 15.2 km, resulting from their VSL SGs measurements and an additional contribution of 1.5 pptv from chloroethane (WMO, 2007).”

Pg 16176, the reference to ATMOS is indeed too difficult to use as a comparison point, given the time difference, so I would simply delete this. And L23: change “this chlorine content slow decay” to “a slow decay in chlorine content”

The comparison with ATMOS has been deleted and the last sentence of this Section 3.2 has been rewritten as: “Additionally it has to be mentioned that the two SPIRALE

measurements performed at only three years interval cannot confirm the current slow decay in chlorine content expected since 2000 (WMO, 2007)."

Fig. 5: The white crosses are somewhat hard to see (a thicker/larger symbol would help); brighter labels would also help (and black background is less desirable than white, but other colors would also need to change, e.g. white symbols, in this case). "Fig. 6: Same as for Fig. 5; also, the black symbols for MLS measurement locations are not visible enough, so white might be useful for these symbols also (with a dot or other symbol rather than a cross).

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 been replaced by white backgrounds.

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

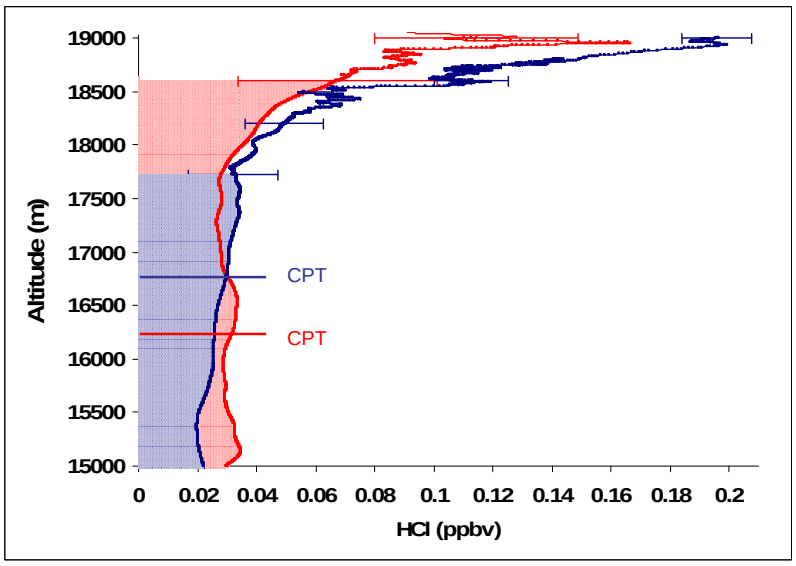

Fig. 1. Modified version of the inset of Figure 4.