

# More evidence for very short-lived substance contribution to stratospheric chlorine inferred from HCl balloon-borne in situ measurements in the tropics

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**Abstract.** Volume mixing ratio (vmr) vertical profiles of hydrogen chloride (HCl) are retrieved from in situ measurements performed by a balloon-borne infrared tunable diode laser absorption spectrometer (SPIRALE) during two balloon flights in the tropics (Teresina, Brazil, 5.1° S–42.9° W) in June 2005 and June 2008. HCl vertical profiles obtained from 15 to 31 km are presented and analysed to estimate the contribution of very short-lived substances (VSLs) to total stratospheric chlorine. Both retrieved vertical profiles of HCl from these flights agree very well with each other, with estimated overall uncertainties of 6% on vmr between 23 and 31 km. Upper limits of HCl vmr as low as 20 pptv in June 2008 and 30 pptv in June 2005 are inferred in the upper part of the tropical tropopause layer (TTL). Backward trajectory calculations and such low amounts suggest that the air masses sampled correspond to typical background conditions, i.e. neither influenced by recent tropospheric nor stratospheric air. Taking into account the recently reported VSL source gas measurements obtained in similar conditions (Laube et al., 2008) and the main intermediate degradation product gas COCl<sub>2</sub> (Fu et al., 2007), a total VSLs contribution of 85±40 pptv to stratospheric chlorine is inferred. This refines the WMO (2007) estimation of 50 to 100 pptv, which was not taking into account any HCl contribution. In addition, comparisons of HCl measurements between SPIRALE and the Aura MLS satellite instrument in the tropical lower and middle stratosphere lead to a very good agreement. 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.

## 1 Introduction

Active chlorine species (Cl, ClO) have been recognized to be very efficient for stratospheric ozone depletion (WMO, 2007 and references therein). For a vast majority, they originate from long-lived source gases (in the troposphere) that release chlorine atoms in the stratosphere, directly through photodissociation or indirectly through reactions with radicals (e.g., O(<sup>1</sup>D), OH). The ozone destruction catalytic cycles are mainly terminated by recombination reactions of the Cl atoms with hydrogenated compounds, especially methane (CH<sub>4</sub>). These reactions produce the most abundant stratospheric chlorine reservoir, hydrogen chloride (HCl). Satellite observations are relevant for providing the total stratospheric chlorine abundance (Cl<sub>TOT</sub>) through measurements of HCl at high altitudes. In the upper stratosphere Cl<sub>TOT</sub> is dominated by HCl, which thus serves as a good proxy for estimating this budget. For example, HCl/Cl<sub>TOT</sub> ratios ranging from 0.89 to 0.98 at ~46–55 km height have been determined, depending on the altitude and the latitude (Nassar et al., 2006; Froidevaux et al., 2006). The last WMO review (2007), based on the Froidevaux et al. (2006) study, compared the HCl observations from the most recent satellite instruments, including HALogen Occultation Experiment (HALOE) aboard UARS (Russell et al., 1993), Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) aboard SCISAT-1 (Bernath et al., 2005) and Microwave Limb Sounder (MLS) aboard EOS Aura (Waters et al., 2006). It highlights that the upper stratospheric HCl measurements agree with each other within the stated accuracies (at the 2 standard deviations (2σ) level), but not sufficiently well to definitely answer the open questions about chlorine content. In particular, these satellite observations were compared to calculated HCl volume mixing ratios (vmr) at about 53 km based on tropospheric source gas (SG)



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measurements of ground-based networks and modelling taking into account the air mixing and the delay for the transport to the stratosphere. ACE and MLS showed good agreement in 2006 (within 6% at this altitude, i.e. 0.2 parts per billion in volume (ppbv)), with the generally lower MLS values in very good agreement with HCl vmr derived from the tropospheric data taking into account chlorine contributions from long-lived source gases (SGs) and 0.10 ppbv from very short-lived substances (VSLS). In contrast there was a systematic difference in HCl observations of about 0.2–0.4 ppbv (i.e. about 7–15%) between MLS and HALOE in 2004–2006, with lower HALOE values being consistent with supply of chlorine from long-lived source gases only. These differences precluded any firm conclusion about a possible total contribution from VSLS of about 0.05–0.10 ppbv (or 50–100 parts per trillion by volume (pptv)) to stratospheric chlorine and demonstrate the need for more accurate HCl measurements (WMO, 2007) or a more direct determination of the abundance of VSLS in the upper troposphere and lower stratosphere.

In the light of observed and predicted decreases of anthropogenic ozone-depleting long-lived substances regulated by the revised Montreal Protocol, it is important to quantify the contribution of the VSLS to the chlorine loading in the stratosphere, both from anthropogenic origin (but without regulation until now) and from natural origin (in a changing climate which should be favourable to emission increase). The uncertainty in the amount of VSLS reaching the stratosphere is due to the high chemical reactivity of these species in the troposphere leading to short lifetimes (from hours to a few months) with respect to transport time to the stratosphere, and to the paucity of the measurements in the tropical tropopause layer (TTL), the main entrance region of the chemical species into the global stratosphere. In the last WMO report (2007), a VSL SGs contribution of  $55 \pm 3$  pptv to the chlorine budget has been estimated in the upper tropical troposphere (>10 km height) including the TTL. Since then, 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 (Teresina, Brazil,  $5.0^\circ \text{S}$ – $42.9^\circ \text{W}$ ).

In order to fully quantify the VSLS contribution to total inorganic chlorine in the stratosphere, one must also include the intermediate and final product gases (PGs) from VSLS degradation injected into the stratosphere. 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  $34$ – $68^\circ \text{N}$ , 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  $\text{COCl}_2$  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 ( $30$ – $35^\circ \text{N}$ ) and the same period (2004–2006). Averaging more than fifty FTS vertical profiles at  $0$ – $5^\circ \text{S}$  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 ( $\sim 15$ – $17$  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, the contribution of the final VSLS degradation product, HCl, should be included. However, measurements of HCl in the tropical upper troposphere and stratosphere are particularly missing, leading to uncertainty in the total VSLS contribution. To our knowledge, only one recent study using in situ HCl measurements in this region has been reported, but only up to 19 km (Marcy et al., 2007), with values ranging from 0 to 80 pptv, depending on the occurrence of stratosphere to troposphere transport.

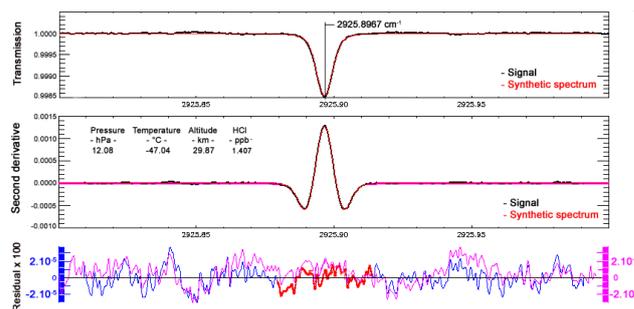
Our in situ balloon-borne instrument SPIRALE (Spectroscopie InfraRouge par Absorption de Lasers Embarqués, i.e. infrared absorption spectroscopy by embarked tunable laser diodes) is able to perform measurements of HCl vertical profiles with high vertical resolution and accuracy in the upper troposphere and the stratosphere. Within the framework of the ENVISAT satellite chemical species validation campaign and the SCOUT-O<sub>3</sub> integrated project of the European Commission, it was flown, on 22 June 2005 and on 9–10 June 2008 near Teresina, giving unique tropical in situ vertical profiles of HCl. In the present paper, we give upper limits of HCl vmr in the TTL for each of the two SPIRALE flights. Air mass backward trajectory calculations have been performed and indicate that air characteristics in this region were not influenced by lower or higher levels. This is further corroborated by the very low HCl amounts we found. The total contribution of VSLS to stratospheric chlorine is then deduced, including HCl potentially produced from their degradation. In addition, the SPIRALE HCl measurements in the lower and middle stratosphere are used for validation purpose of the Aura MLS profiles in spatial and temporal coincidence. The result of such comparisons 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.

## 2 Instrument and model descriptions

### 2.1 SPIRALE instrument

SPIRALE is a balloon-borne instrument devoted to in situ measurements of trace gases from the upper troposphere to the middle stratosphere. SPIRALE measurements have been used to study the dynamical structure of the mid-latitude stratosphere (Huret et al., 2006; Pirre et al., 2008) and the high-latitude stratosphere (Engel et al., 2006; Müller et al., 2007), as well as the modelling of the  $\text{NO}_y$  partitioning (Berthet et al., 2006; Berthet et al., 2007a). They have been also used for validation of both long-lived and short-lived species abundances measured by satellite instruments such as the Sub-Millimeter Radiometer (SMR) aboard Odin (Urban et al., 2005), the Global Ozone Measurement by the Occultation of Stars (GOMOS) and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) aboard Envisat (Renard et al., 2008; Wang et al., 2007) and ACE-FTS (Mahieu et al., 2008; Wolff et al., 2008). A detailed description of the SPIRALE instrument measurement concept and the concentration retrieval can be found in Moreau et al. (2005). This optical absorption spectrometer uses six lead salt laser diodes as light sources in the mid-infrared region (3 to 8  $\mu\text{m}$ ), enabling the simultaneous measurements of a number of chemical species (e.g.,  $\text{O}_3$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{OCS}$ ,  $\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{HCl}$ ,  $\text{COF}_2$ ,  $\text{H}_2\text{O}_2$ ) with high frequency sampling ( $\sim 1$  Hz). The laser beams are injected into a multipass Herriott cell located under the gondola and fully open to the atmosphere for reducing the pollution by the latter. Laser absorptions take place in the cell ( $\sim 3.5$  m long) deployed during the ascent and descent when pressure is lower than 300 hPa, limiting the lower altitude measurements to  $\sim 10$  km. The absorption limit is close to  $10^{-5}$ , and with the very high spectral resolution ( $0.0005$ – $0.0010$   $\text{cm}^{-1}$ ) and the long optical path (300.31 m in June 2005 and 430.78 m in June 2008), it allows measuring trace gas vmr with a good sensitivity and with a vertical resolution of a few metres ( $\sim 5$  m), depending on the vertical velocity of the gondola.

Species concentrations are retrieved on direct infrared absorption signal or after derivative processing, by adjusting synthetic spectra calculated using the HITRAN 2004 database (Rothman et al., 2005) to match the observation. Specifically, the ro-vibrational line at  $2925.8967$   $\text{cm}^{-1}$  was used for HCl (Pickett et al., 1998). Figure 1 presents an example of an in situ HCl absorption spectrum acquired in the stratosphere during the balloon flight of 9–10 June 2008. Signal variations due to the fluctuations of the laser background emission signal and to fringes of interferences between the laser emission and the scattered light from optical components complicate retrievals with the direct absorption line fitting method, because the zero absorption signal is difficult to reconstruct. An adopted alternative method consists of applying a numerical derivative that efficiently removes the continuous component of the signal. The sec-



**Fig. 1.** Retrieval of HCl near  $2925.9$   $\text{cm}^{-1}$  from spectra obtained on 10 June 2008 at 12.08 hPa ( $\sim 29.87$  km). The signal is the average of 3 consecutive spectra over 3.3 s. The optical path length is 430.78 m. Top: Experimental transmission (black curve) with the retrieval of the baseline and synthetic spectrum (red curve); Middle: Second derivative of the synthetic and experimental spectra; Bottom: Residual of the direct absorption signal (pink line) and of the second derivative signal (blue line). Statistical precision on the fit is 1.6% ( $2\sigma$ ).

ond derivative is preferred, because it transforms absorption lines into symmetrical signatures (which are easier to handle) and reduces the fringes efficiently for very weak lines. The numerical second derivative retrieval method has a physical link with the high frequency modulation technique (Cooper and Warren, 1987). Statistical noise is smaller in the second derivative due to the associated filtering. This is illustrated in Fig. 1 with the residual for the direct absorption larger than the second derivative one. Measurements of pressure (from two calibrated and temperature-regulated capacitance manometers) and temperature (from two probes made of resistive platinum wire) aboard the gondola allow the species concentrations to be converted to volume mixing ratios.

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 parameters have been evaluated to be negligible relative to the other uncertainties discussed below. The overall uncertainties have been assessed by taking into account the random and systematic errors, and combining them as the square root of their quadratic sum. 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. Systematic errors originate essentially from the laser linewidth (an intrinsic characteristic of the laser diode), which contributes more at lower pressure (higher altitudes) than at higher pressures. The impact of the spectroscopic parameter uncertainties (essentially the molecular line intensities and pressure broadening coefficients) on the vmr retrievals is almost negligible ( $< 2\%$ ; Rothman et al., 2005). The overall uncertainties are estimated to be 100% below 18.6 km in 2005 and 17.7 km in 2008, decreasing to 50% at these minimum altitudes at which HCl is unambiguously detected,

and continuously decreasing to 30% at 19 km, 20% at 20 km, 15% at 21 km, 10% at 22 km and to an almost constant value of 6% from 23 to 31 km (i.e. from 0.04 to 0.1 ppbv).

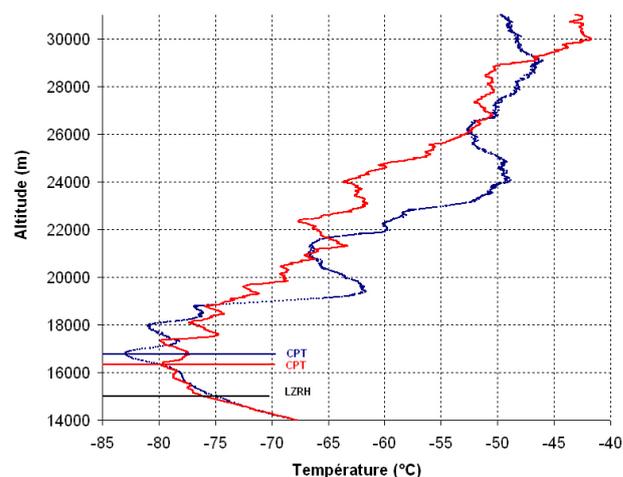
The SPIRALE HCl measurements were performed on 22 June 2005, from 09:30 to 14:30 UT (i.e. 06:30–11:30 local time), and during the night of 9 to 10 June 2008, from 23:30 to 05:30 UT (i.e. 20:30–02:30 local time).

## 2.2 MLS measurements

The MLS instrument aboard the EOS Aura satellite observes the millimetre and sub-millimetre thermal emission from the limb of Earth's atmosphere. Detailed information on the measurement technique, spectral bands and target molecules can be found in Waters et al. (2006). MLS HCl measurements in the lower and middle stratosphere have a  $\sim 3$  km vertical resolution and a precision typically ranging from 0.2 ppbv (at 100 hPa) to 0.5 ppbv (at 1 hPa). Publicly available MLS HCl measurements in version 2.2 (v2.2) for 22 June 2005 and for 9 June 2008 are used for comparisons with SPIRALE measurements. They were filtered to include only measurements with values of status even, of quality  $>1.0$ , of convergence  $<1.5$ , and of precision positive. Detailed descriptions of the characteristics of the MLS HCl measurements used in this study can be found in "EOS MLS Level 2 data quality and description document" available for v2.2 (Livesey et al., 2007). Early detailed validation of MLS HCl, including comparisons with other satellite and balloon data (further discussed in Sect. 3), are provided by Froidevaux et al. (2008).

## 2.3 Backward trajectory model

Backward trajectories have been computed by the FLEXTRA trajectory model (Stohl et al., 1995). As input data, three-dimensional (3-D) wind fields from the (ECMWF) analysis are used, with a 6-hour temporal resolution and a  $1^\circ \times 1^\circ$  horizontal resolution. There were 60 vertical levels from the ground to 1 hPa for June 2005 and 91 levels from the ground to 0.1 hPa for June 2008. In our study, trajectories have been performed in a geographical domain around SPIRALE measurement locations. Hence, each trajectory was initialised at  $5^\circ$  S latitude and longitudes ranging from  $43^\circ$  W to  $42.5^\circ$  W at  $0.1^\circ$  intervals on 22 June 2005, and at  $5.1^\circ$  S latitude and longitudes ranging from  $43.6^\circ$  W to  $42.8^\circ$  W at  $0.1^\circ$  intervals on 10 June 2008, for an altitude range between 15 and 17.5 km, with 500 m vertical resolution. All the trajectories originated from 12:00 UT on 22 June 2005 and from 03:00 UT on 10 June 2008 and were integrated 7 days backward in time.



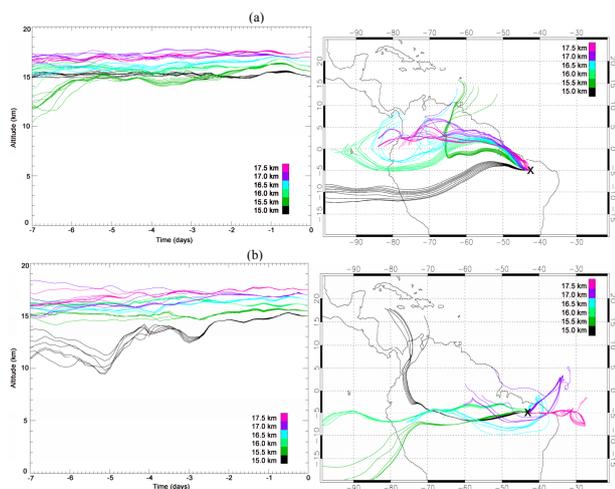
**Fig. 2.** Vertical profiles of temperature measured on the payload during the June 2005 flight (red line) and the June 2008 flight (blue line). The cold points (CPT) and level of zero radiative heating (LZRH) are indicated on each profile.

## 3 Results and discussion

### 3.1 Air mass origin

The trajectory calculations have been performed to determine the origin of the air masses sampled by SPIRALE in the upper part of the TTL. This upper TTL corresponds to the TTL defined by Folkins et al. (1999) as the region extending from the level of zero net radiative heating (LZRH; Gettelman et al., 2004) to the cold point tropopause (CPT). The LZRH is found at an almost constant value of 360 K, i.e.  $\sim 15 \pm 0.5$  km (Gettelman, et al., 2004; Fueglistaler et al., 2008). The tropopause heights for both flights were derived from high resolution measurements of temperature performed aboard the gondola. Vertical profiles of temperature are shown in Fig. 2 with the CPT indicated. The CPT was higher and colder in June 2008 (16.78 km;  $-83.0^\circ\text{C}$ ) than in June 2005 (16.25 km;  $-79.9^\circ\text{C}$ ).

Since air parcels above the LZRH are expected to move slowly to the stratosphere (Gettelman et al., 2004), the HCl amounts potentially present above this level will be further transported into the stratosphere. Strong convection in combination with HCl tropospheric source areas arising from dechlorination of sea-salt aerosols (WMO, 2007; Kim et al., 2008) or volcanoes (Edmonds et al., 2002) can influence the HCl amounts present in the TTL. Stratosphere-to-troposphere transport can also affect the chlorine content of the TTL (Marcy et al., 2004). Therefore trajectory calculations are a useful tool to determine if such upward or downward transport has occurred prior to SPIRALE measurements. 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.



**Fig. 3.** 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).

Figure 3 shows the 7 day backward trajectories of air masses reaching the SPIRALE measurements vicinity in the 15–17.5 km altitude range (i.e. including the upper TTL and lower stratosphere) for the June 2005 and the June 2008 flights. According to this figure, the air masses sampled in June 2005 originated southwest and northwest of Teresina. The air masses probed by SPIRALE in 2005 at and above the LZRH did not undergo significant upward or downward transport at least 7 days before the flight. For June 2008, the backward trajectories reveal that air masses originated west (around 15.5 km) and east (around 17 km) of Teresina. Despite these distinct air mass origins, an agreement is found with the corresponding HCl values obtained in 2005 in the upper TTL. As in 2005, Fig. 3b also indicates that transport inside this region in June 2008 occurred predominantly at constant altitudes with no downward motion and limited upward motion prior to the SPIRALE flight. This reveals unfavourable conditions for fast transport of trace gases vertically from the troposphere to the TTL as well as transport of stratospheric air into the TTL. 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 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. Thus HCl potentially present in the TTL appeared to be the result of photochemical degradations only, including those of VLS. 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  $\text{CH}_3\text{Cl}$  lifetimes towards photolysis and reaction with OH, these authors have shown that the depletion of  $\text{CH}_3\text{Cl}$  over a 1–2 month period in the TTL is only 3–8 pptv.

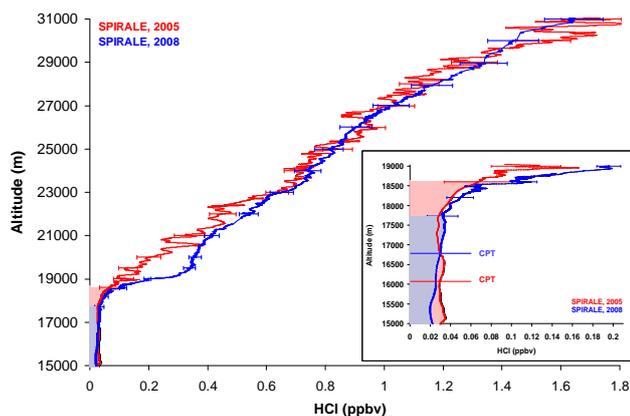
Besides, the BONBON instrument performed a balloon flight on 8 June 2005 near Teresina (Laube et al., 2008). This cryogenic whole air sampler allows for the collection of several whole air samples at different altitudes, which are analysed by gas chromatography mass spectrometry after the flight. Backward trajectories associated with the BONBON flight presented the same characteristics as ours in the TTL region. This further supports the use of the VLS mixing ratio values presented in their study in combination with our HCl measurements to assess the contribution of the VLS to chlorine budget of the upper TTL.

### 3.2 SPIRALE in situ measurements of HCl in June 2005 and June 2008

For both flights, retrievals of volume mixing ratios have been performed using ascent and descent spectra, leading to four vertical profiles of HCl. Unfortunately, the ascent vertical profiles were sporadically affected by chemically polluted air arising from the gondola. Nevertheless, it has to be mentioned that they agree perfectly with the descent ones in the vertical ranges where they were not affected by this contamination. We only present the descent vertical profiles.

#### 3.2.1 HCl measurements in the TTL

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  $2\sigma$  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



**Fig. 4.** Vertical profiles of HCl volume mixing ratios measured in situ by SPIRALE on 22 June 2005 (red line) and 9–10 June 2008 (blue line) above Teresina ( $5.1^{\circ}\text{S}$ – $42.9^{\circ}\text{W}$ ). Inset: zoom on the TTL measurements with the altitude of the cold points (CPT). The overall uncertainties are represented by horizontal error bars displayed every km between 20 km and 31 km, every 400 m between 20 km and the first altitude points where HCl has been unambiguously detected (18.6 km in 2005 and 17.7 km in 2008), and every  $\sim 5$  m below, leading to the shaded areas representing the ranges of HCl possible values.

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 (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.

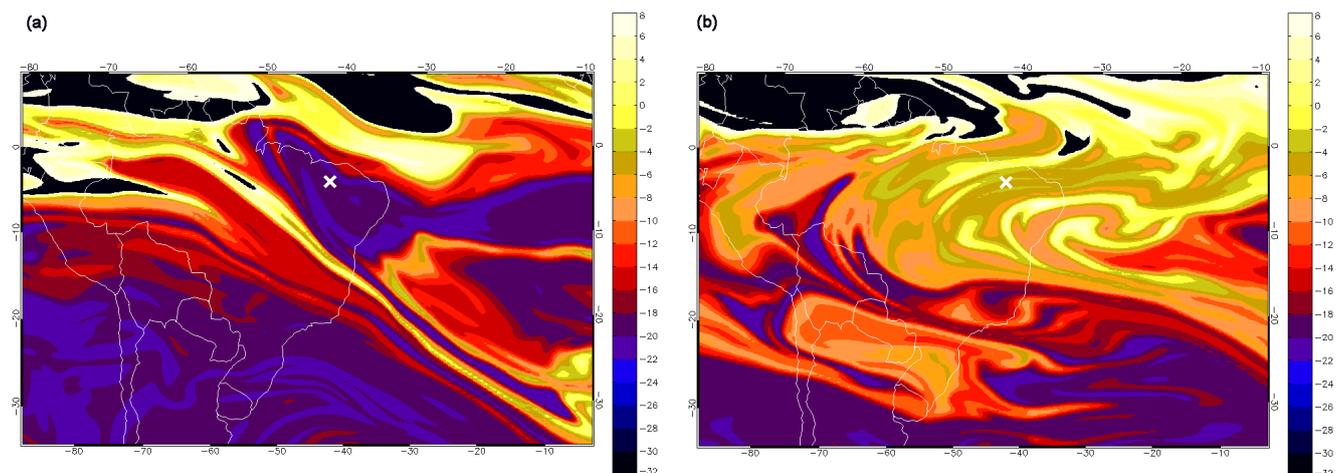
Thus the HCl content in this region was very low in June 2005 and June 2008. Besides a higher detection limit for the 2005 measurements due to a poorer laser diode quality, the HCl upper limit values did not change dramatically, though being performed at a three year interval. These low values are in 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  $\text{O}_3$  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 ( $\leq 30$  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 strato-

spheric air at the time of our observations. Since our measurements were also negligibly affected by tropospheric air (see Sect. 3.1), we conclude that they provide a reasonable quantification of HCl under typical background conditions. Moreover, we confirm that in the absence of convection, HCl coming from the VLSL degradation in the lower and middle troposphere is rather removed by scavenging by clouds and aerosols before being transported into the TTL (WMO, 2007).

Such low amounts of HCl reveal important insights into the chlorine content of the TTL, at least at the time of our observations, especially with regards to the contribution of chlorinated VLSL. From the 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 of VLSL is converted into HCl in the TTL. This represents the maximum contribution of VLSL in the form of final degradation product to stratospheric chlorine. Hence chlorinated VLSL 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 VLSL of  $0$ – $(33 \pm 11)$  pptv (Fu et al., 2007; see Sect. 1), we can estimate a total contribution of VLSL 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.

### 3.2.2 HCl measurements in the lower and middle stratosphere

Between the CPT (16.25 km in 2005 and 16.78 in 2008) and 31 km, both the 2005 and 2008 vertical profiles of HCl show a monotonic increase with altitude. This can be explained as a result of the reaction of Cl with  $\text{CH}_4$  following photolyses and reactions with radicals (e.g.,  $\text{O}(^1\text{D})$ , OH) of chlorinated source gases rising into the tropical stratosphere. Between 21 and 31 km, both vertical profiles agree very well with each other within the estimated overall uncertainties of 6%. One remarkable feature revealed by the high resolution of the SPIRALE measurements (shown in Fig. 4) is a specific layer visible between 19 and 21 km on the vertical profile of the June 2008 flight, with enriched values of HCl compared to those of June 2005. In this layer, the average values were  $0.34 \pm 0.04$  ppbv in June 2008 and  $0.22 \pm 0.09$  ppbv in June 2005. In addition, temperature values in this layer were significantly higher compared to those obtained in June 2005.



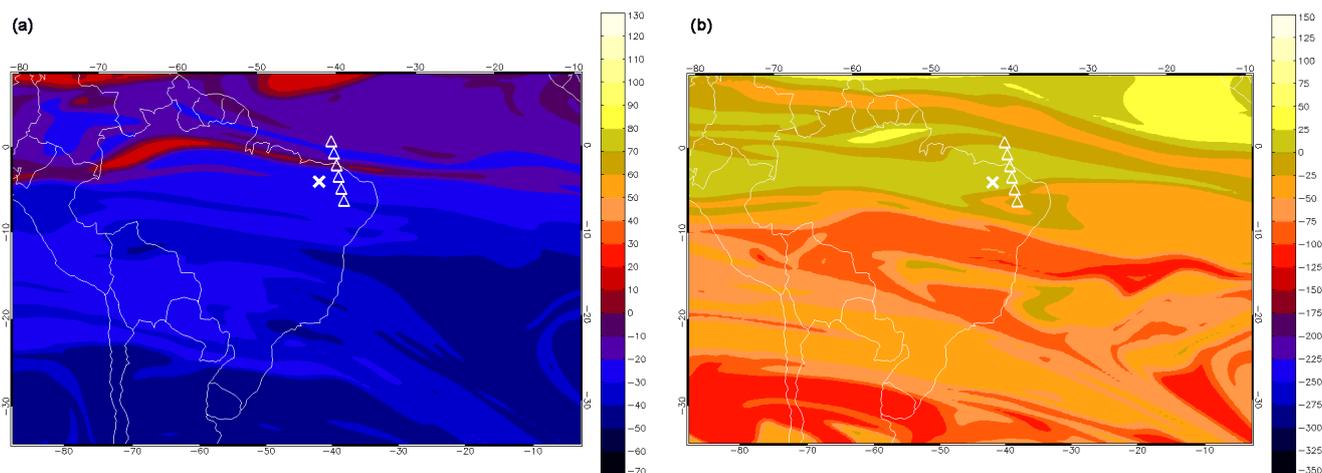
**Fig. 5.** Latitudinal and longitudinal maps of potential vorticity isocontours ( $1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ s}^{-1} \text{ kg}^{-1}$ ) calculated by the MIMOSA model on (a) 22 June 2005 at 13:00 UT for the 465 K isentropic surface ( $\sim 19.5 \text{ km}$ ) and (b) 10 June 2008 at 03:00 UT for the same isentropic surface. The white cross denotes the SPIRALE instrument locations.

The average values were  $-64.2 \pm 1.8^\circ\text{C}$  in June 2008 and  $-68.6 \pm 1.7^\circ\text{C}$  in June 2005. These 2008 HCl and temperature values are higher than typical tropical ones and shifted toward expected mid-latitude ones.

In order to investigate the origin of these differences, potential vorticity (PV) maps have been calculated using the “Modèle Isentropique de transport Mésos-échelle de l’Ozone Stratosphérique par Advection” (MIMOSA) contour advection model (Hauchecorne et al., 2002). This model performs high resolution advection calculations based on the ECMWF wind fields to provide PV fields on isentropic surfaces. These PV maps give information about the location of the SPIRALE measurements relative to the different dynamical barriers. Distributions of PV have been calculated at the time of SPIRALE measurements in the 440 K to 500 K range (corresponding to the 19–21 km altitude range) every 5 K. Figure 5 shows the PV maps derived at 465 K ( $\sim 19.5 \text{ km}$ ) on (a) 22 June 2005 and (b) 10 June 2008. On each map, the instrument location is indicated by a white cross. It appears that SPIRALE sampled air masses of low PV values on 22 June 2005 and was located on the south side of the strong dynamical barrier (marked by a high PV contour gradient around  $0\text{--}5^\circ \text{N}$ ). On 10 June 2008 the situation was strongly different as SPIRALE sampled air masses on the north side of this barrier (marked by a high PV contour gradient around  $15\text{--}20^\circ \text{S}$ ) with much higher PV values. Interestingly, the PV map of 10 June 2008 does not show a clear filament coming from mid-latitudes as higher HCl values could have suggested. Another explanation for this phenomenon could come from the influence of the different quasi biennial oscillation (QBO) phases in which the two flights occurred. In the altitude range of interest, the 2008 flight took place in a well-established easterly phase

whereas in 2005 the flight was performed at the end of a westerly QBO-phase (see <http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html>). Based on the study of Chen et al. (2005), for pressures larger than 50 hPa (below  $\sim 21 \text{ km}$ ), the easterly and westerly QBO phase are not associated with the same induced circulation. During the easterly phase, the tropical region is characterized by a convergent wind flow from higher latitudes. As a consequence, the SPIRALE instrument might have captured the effect of this easterly QBO phase with air masses under the influence of mid-latitude air at these low altitude levels leading to higher HCl values.

Between 21 and 30 km, both the 2005 and 2008 SPIRALE measurements agree very well with each other (see Fig. 4). This good consistency suggests an atmospheric state without strong dynamical and chemical perturbations over the middle tropical stratosphere. At these altitudes, our measurements were made in very favourable conditions for direct absorption detection because of the higher HCl vmr values and the lower pressure reducing the ro-vibrational line broadness. We find vmr values ranging from  $0.37 \pm 0.05 \text{ ppbv}$  at 21 km to  $1.49 \pm 0.09 \text{ ppbv}$  at 30 km for 2005 and 2008, on average. These results are in fairly good agreement with previous measurements for  $30^\circ \text{S}\text{--}30^\circ \text{N}$  during 2004 by ACE-FTS, yielding  $0.50 \pm 0.14 \text{ ppbv}$  of HCl at 20 km and  $1.8 \pm 0.3 \text{ ppbv}$  at 30 km (Nassar et al., 2006; Mahieu et al., 2008), with ACE-FTS measuring about 20% more than SPIRALE at 30 km. 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. 6.** Latitudinal and longitudinal maps of potential vorticity isocontours ( $1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ s}^{-1} \text{ kg}^{-1}$ ) calculated by the MIMOSA model on 22 June 2005 at 16:00 UT for (a) the 570 K isentropic surface ( $\sim 23.5 \text{ km}$ ) and (b) the 753 K isentropic surface ( $\sim 28.6 \text{ km}$ ). The white crosses and triangles denote the SPIRALE and MLS measurement locations, respectively.

### 3.3 Comparison of SPIRALE with MLS measurements

In this section we compare SPIRALE HCl measurements with those from MLS obtained during the Aura satellite overpass on the days of the SPIRALE flights. On 22 June 2005 and 9 June 2008, a set of several HCl measurements from MLS are available in the neighbourhood of the SPIRALE measurement locations. On 22 June 2005, HCl measurements from MLS were separated from those of SPIRALE by  $\sim 455 \text{ km}$  and were acquired only 3 h after the flight. The spatial and temporal differences were larger on 9 June 2008, as the MLS measurements were performed  $\sim 11 \text{ h}$  before the SPIRALE flight and  $\sim 1000 \text{ km}$  away. Therefore, in order to ensure the consistency of the comparisons, the dynamical situation at the time and location of each measurement was examined using PV maps derived from MIMOSA model. Distributions of PV have been calculated over the isentropic surface levels listed in Tables 1a and b and corresponding to each pressure level of the MLS measurements. As an illustration, Fig. 6a and b present PV maps derived from MIMOSA at 570 K ( $\sim 23.5 \text{ km}$ ) and 753 K ( $\sim 28.6 \text{ km}$ ) at the time of MLS measurements (22 June 2005 at 16:00 UT). The white triangles denote all the geographical locations of the available HCl measurements of MLS obtained on that day. Also shown is the location of the SPIRALE flight (indicated by a white cross), which occurred 3 h earlier. Clearly, in both cases, three MLS measurements out of six are found to be relevant with SPIRALE data. Indeed, at 570 K (Fig. 6a) SPIRALE and three MLS measurements are located southward of the weak dynamical barrier and are in the same PV range; at 753 K (Fig. 6b) the PV values are similar for SPIRALE and three MLS measurement locations only. Following the same approach, the MLS measurements made on 9 June 2008 were selected based on the analysis of MIMOSA output PV-maps

on 9 and 10 June 2008. Table 1a and b summarize the results of the data set averaging the selected individual measurements. Furthermore, in order to take into account the difference in the vertical resolution of the two instruments, a triangular weighting function of width equal to 3 km at the base (corresponding to the MLS estimated vertical resolution) was applied to SPIRALE measurements. HCl vertical profiles of both instruments are shown in Fig. 7a and b. In June 2008, the negative values of MLS retrieved at 100 hPa were excluded.

Between 46.4 hPa and 10.0 hPa (i.e.  $\sim 21 \text{ km}$  and 31 km) the percentage differences are  $0.4 \pm 5.5\%$  on average for June 2005 and  $6.5 \pm 26.8\%$  on average for June 2008. Despite the major differences between the remote and in situ methods and the geographical distance between the two measurements, these comparisons indicate very good agreement between SPIRALE and MLS in the tropical middle stratosphere. Low HCl mixing ratios for pressures larger than 46.4 hPa ( $< 21.1 \text{ km}$ ) lead to more uncertain agreement between the two instruments, being excellent for June 2005 and just fair for June 2008. A comparison of MLS HCl measurements with in situ aircraft ones has been performed up to  $\sim 18.8 \text{ km}$  (68 hPa) and revealed a rather mediocre agreement (Froidevaux et al., 2008). In the same study, other remote (MkIV, FIRS-2) and in situ tunable laser diode (ALIAS-II) balloon-borne measurements yielded good agreement ( $\leq 10\%$  difference) with those of MLS from the middle to the upper stratosphere ( $\geq 21.1 \text{ km}$ ) where HCl abundances are larger, but poorer agreement (about 20 to 40% difference) at lower altitudes. As a conclusion, MLS measurements of HCl are essentially valid in the tropical middle and upper stratosphere, as demonstrated by SPIRALE and other balloon-borne instruments.

**Table 1a.** HCl mixing ratios derived from SPIRALE and MLS measurements in June 2005.

Pressure (hPa)	MLS				SPIRALE		
	N <sup>#</sup> of selected points <sup>a</sup>	Mean HCl (ppbv)	Precision <sup>b</sup> (ppbv)	Approximate altitude (km)	HCl (ppbv)	Overall uncertainty <sup>c</sup> (ppbv)	Theta (K)
100.00	3	0.00	0.23	16.5	0.030	0.030	374
68.13	3	0.10	0.18	18.9	0.092	0.044	434
46.42	3	0.35	0.16	21.3	0.362	0.049	501
31.62	3	0.65	0.15	23.5	0.66	0.04	570
21.54	6	0.90	0.17	26.1	0.91	0.05	668
14.68	3	1.17	0.21	28.6	1.19	0.07	753
10.00	5	2.07	0.25	31.3	1.86	0.11	878

<sup>a</sup> Selections based on comparisons of the dynamical situation between SPIRALE and MLS, as illustrated on Fig. 6. See the text (Sect. 3.3) for details. <sup>b</sup> Averaged values based on random errors only, affecting the selected single measurements. Estimated systematic errors are generally equal to the estimated random ones in the given altitude range and are provided by Froidevaux et al. (2008). <sup>c</sup> Taking into account the random and systematic errors, and combining them as the square root of their quadratic sum.

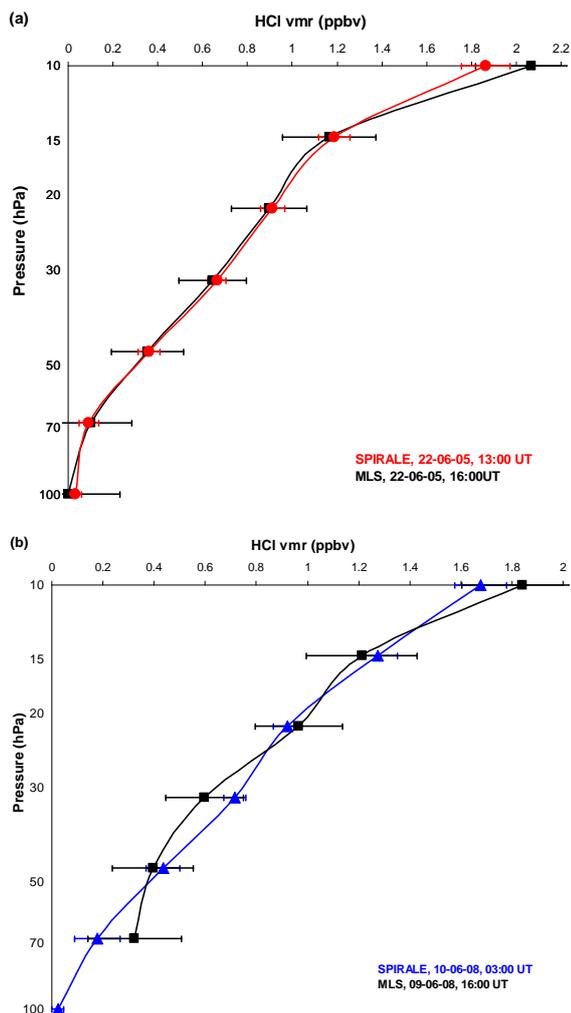
**Table 1b.** HCl mixing ratios derived from SPIRALE and MLS measurements in June 2008.

Pressure (hPa)	MLS				SPIRALE		
	N <sup>#</sup> of selected points <sup>a</sup>	Mean HCl (ppbv)	Precision <sup>b</sup> (ppbv)	Approximate altitude (km)	HCl (ppbv)	Overall uncertainty <sup>c</sup> (ppbv)	Theta (K)
100.00				16.6	0.020	0.020	369
68.13	3	0.32	0.18	18.8	0.180	0.090	430
46.42	3	0.40	0.16	21.2	0.430	0.065	502
31.62	6	0.60	0.15	23.6	0.72	0.04	597
21.54	5	0.97	0.17	26.1	0.92	0.05	656
14.68	3	1.21	0.22	28.6	1.27	0.07	760
10.00	2	1.84	0.24	31.2	1.68	0.10	850

<sup>a</sup> Selections based on comparisons of the dynamical situation between SPIRALE and MLS, as illustrated on Fig. 6. See the text (Sect. 3.3) for details. <sup>b</sup> Averaged values based on random errors only, affecting the selected single measurements. Estimated systematic errors are generally equal to the estimated random ones in the given altitude range and are provided by Froidevaux et al. (2008). <sup>c</sup> Taking into account the random and systematic errors, and combining them as the square root of their quadratic sum.

Froidevaux et al. (2008) also compared the MLS HCl measurements to other satellite instruments (HALOE and ACE-FTS). They found MLS HCl values  $\sim 7$  to 20% larger than those of HALOE for the whole stratosphere, consistent with previous studies illustrating a similar offset in HALOE measurements (Russell et al., 1996; McHugh et al., 2005). Over a great range of latitudes and longitudes including thousands of collocated measurements, ACE HCl values have been shown to be 2 to 10% larger than MLS ones from 50 to 10 hPa ( $\sim 21$ – $31$  km) and from 1 to 0.2 hPa ( $\sim 48$ – $55$  km). On the other hand, a SPIRALE single profile recorded at high latitude (near Kiruna,  $67.6^\circ$  N– $21.5^\circ$  E) in January 2006 was compared to a ACE-FTS profile collocated 413 km away. The agreement was fairly good in the altitude range where

the SPIRALE HCl measurements were not perturbed by the presence of a polar stratospheric cloud (Grossel et al., submitted), i.e. from 16.5 to 19.5 km and from 23.5 to 27.5 km, but with a slight positive bias (ACE-SPIRALE) of about 4–11%. In summary, ACE measurements are larger by about  $7 \pm 4\%$  than SPIRALE and MLS values between 21 and 31 km height and than MLS values between 48 and 55 km. 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 (Froidevaux et al., 2006), whereas the ACE values were larger than calculated HCl values by about 200 pptv. The very good agreement between



**Fig. 7.** HCl mixing ratios vertical profiles derived from SPIRALE measurements on (a) 22 June 2005 (red circles) and (b) 10 June 2008 (blue triangles) compared to the selected MLS associated averages (black squares) at each MLS pressure level. Error bars represent overall uncertainties for SPIRALE instrument and only precision at  $1\sigma$  level for MLS instrument.

SPIRALE and MLS measurements suggest 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 Conclusions

Hydrogen chloride (HCl) has been measured in situ for the first time in the tropical tropopause layer (TTL) and the tropical stratosphere ( $5.1^{\circ}\text{S}$ – $42.9^{\circ}\text{W}$ ), by the infrared tunable diode laser spectrometer balloon-borne instrument SPIRALE. Two vertical profiles were obtained at three year interval (in June 2005 and June 2008), from 15 to 31 km height, with very high vertical resolution. These measurements allowed for a study of the HCl content in the TTL and the tropical middle stratosphere, as well as an investigation of the total contribution from VSLs to stratospheric chlorine content. In the upper TTL, HCl mixing ratios were below 30 pptv in June 2005 and below 20 pptv in June 2008, neither influenced by tropospheric nor stratospheric air. By combining these HCl vmr with a VSL source gas contribution to chlorine of  $49\pm 6$  pptv derived from another balloon-borne instrument performed on 8 June 2005 near Teresina under similar atmospheric conditions (Laube et al., 2008) and a  $33\pm 11$  pptv contribution at most from phosgene  $\text{COCl}_2$  (Fu et al., 2007), an estimate of 45 to 125 pptv (or  $85\pm 40$  pptv) for the total VSLs contribution to stratospheric chlorine is inferred. Thus, even though the SPIRALE measurements have limited spatial sampling, they lead us to conclude that the current estimated contribution of 50–100 pptv from VSLs to stratospheric chlorine presented in WMO (2007) is approximately correct.

From 19 to 21 km height in the 2008 flight, SPIRALE sampled air masses of significantly enhanced HCl and temperature values. These anomalies have been tracked and lead to the reasonable assumption that they may come from transport of mid-latitude air into the tropics induced by the quasi-biennial oscillation.

From the lower to the middle stratosphere (21–31 km), SPIRALE HCl measurements are found to be in excellent agreement with each other as well as with those from Aura MLS instrument, acquired in the neighbourhood of SPIRALE locations. This consolidates the reliability of the tropical MLS measurements of HCl in this altitude range. Our result regarding a VSLs contribution of  $85\pm 40$  pptv 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.

As a conclusion, the present paper, based on HCl in situ measurements combined with an examination of dynamical conditions, helps to quantify the influence of VSLs on the stratospheric chlorine content as required by WMO (2007). Further investigations in the TTL and tropical stratosphere would help to quantify the influence of season, location and deep convection on this contribution.

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