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**VLS contribution to
stratospheric
chlorine**

Y. Mébarki et al.

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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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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) at three year interval in June 2005 and June 2008. HCl vertical profiles obtained from 15.0 to 31.0 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 globally 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±20) pptv in June 2008 and (30±30) pptv in June 2005 are inferred in the upper part of the tropical tropopause layer (TTL). Backward trajectory calculations suggest that these low amounts were sampled in air masses corresponding to typical background conditions, i.e. neither influenced by recent tropospheric nor stratospheric air. Taking into account the recently reported VSLs source gas measurements obtained in similar conditions (Laube et al., 2008) and the main intermediate product gas (COCl₂), a VSLs contribution of about (85±35 pptv) to total 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 MLS-Aura satellite instrument in the tropical lower and middle stratosphere lead to a very good agreement. Since HCl modelled values derived from a total stratospheric chlorine budget including 100 pptv of VSLs agree with MLS measurements in the upper stratosphere, the consistency between SPIRALE and MLS measurements provides another evidence for this VSLs contribution.

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VSLs contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Chlorine active 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(¹D), OH). The ozone destruction catalytic cycles are mainly terminated by recombination reactions of the Cl atoms with hydrogenated compounds, essentially methane (CH₄). These reactions produce the most abundant stratospheric chlorine reservoir, hydrogen chloride (HCl). Satellite observations are relevant for providing the total stratospheric chlorine abundance (Cl_{TOT}) through measurements of HCl at high altitudes. In the upper stratosphere Cl_{TOT} is dominated by HCl, which thus serves as a good proxy for estimating this budget. For example, HCl/Cl_{TOT} 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 Souder (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 gases (SG) 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 generally lower MLS values in perfect agreement with HCl vmr derived from the tropospheric data taking into

VLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



account chlorine contributions from long-lived source gases (SG) and 0.10 ppbv from very short-lived substance (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 in volume (pptv)) to stratospheric chlorine and demonstrate the need for more accurate HCl measurements (WMO, 2007).

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 VSLS SG budget of (55 ± 3) pptv 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 VSLS SG vmr of (49 ± 6) pptv at 15.2 km obtained by summing up the simultaneous VSLS vmr measurements acquired during a balloon flight in the tropics (Teresina, Brazil, 5.0° S–42.9° 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 (PG) from VSLS degradation injected into the stratosphere. Phosgene (COCl_2), which has been estimated to about (22.5 ± 2.5) pptv, i.e. ~ 45 pptv of chlorine, is the main intermediate product resulting from degradation of VSLS SG present in the upper troposphere, since its lifetime is much longer than any other intermediate products (WMO, 2007). However it is also produced by long-lived SG, so that

VSLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the total VLSL contribution to stratospheric chlorine in the form of organic species (SG and intermediate PG) entering the stratosphere is comprised between 49 and 100 pptv, to which the contribution of the final VLSL degradation product, HCl, should be added. However, measurements of HCl in the tropical upper troposphere and stratosphere are particularly missing, leading to uncertainty in the total VLSL 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 (french acronym for infrared absorption spectroscopy by embarked tunable diode lasers) is able to perform measurements of HCl vertical profiles with high vertical resolution and accuracy in the upper troposphere and the stratosphere. Within the frame of the Envisat satellite chemical species validation campaign and the SCOUT-O₃ integrated project of the European Commission, it has been flown at three year interval, on 22 June 2005 and 9 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. We performed air mass backward trajectory calculations allowing for indicating that air characteristics in this region are not influenced by lower or higher levels. The total contribution of VLSL to stratospheric chlorine is then deduced, including HCl potentially produced from their degradation. In addition, the SPIRALE HCl vertical profiles in the lower and middle stratosphere are used for validation purpose of coincident ones from MLS-Aura satellite instrument. The result of the comparison between MLS and SPIRALE measurements leads to assess the validity of modelling the total stratospheric chlorine budget in the stratosphere with taking into account a 100 pptv VLSL contribution.

VLSL contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2 Instrument and model descriptions

2.1 SPIRALE instrument

SPIRALE (French acronym for infrared absorption spectroscopy by embarked tunable laser diodes) 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 (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 NO_y partitioning (Berthet et al., 2006, 2007). They have been also used for validation of both long-lived and short-lived species abundances measured by satellite instruments such as Sub-Millimeter Radiometer (SMR) aboard Odin (Urban et al., 2005), Global Ozone Measurement by the Occultation of Stars (GOMOS) and 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, the concentration retrieval and an assessment of error sources 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., O_3 , CH_4 , CO , CO_2 , OCS , N_2O , HNO_3 , NO_2 , HCl , COF_2 , H_2O_2) with a high frequency sampling ($\sim 1\ \text{Hz}$). 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 ($\sim 3.5\ \text{m}$ long) deployed during the ascent and descent when pressure is lower than 300 hPa, limiting the lower altitude measurements to $\sim 10\ \text{km}$. The absorption limit is close to 10^{-5} , and with the very high spectral resolution ($0.0005\text{--}0.0010\ \text{cm}^{-1}$) and the long optical path (300.31 m in June 2005 and 430.78 m in June 2008), it allows measuring the trace gases vmr with a good sensitivity and with a vertical resolution of a few meters ($\sim 5\ \text{m}$), depending on the vertical velocity of the gondola.

VLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**VLS contribution to
stratospheric
chlorine**

Y. Mébarki et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 cm^{-1} was used for HCl. Figure 1 presents an example of an in situ HCl absorption spectrum acquired in the stratosphere during the balloon flight of 9 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 alternative method adopted consists in applying a numerical derivative that efficiently removes the continuous component of the signal. The second 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 (vmr).

Uncertainties in the pressure and temperature parameters have been evaluated to be negligible relative to the other uncertainties discussed below. The global uncertainties on the vmr 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 global uncertainties. Systematic errors originate essentially from the laser line-width (an intrinsic characteristic of the laser diode), which contributes more at lower pressure (higher altitudes) than at higher pressures. The impact of the spectroscopic parameters

**VLS contribution to
stratospheric
chlorine**Y. Mébarki et al.

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 31.2 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 ~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 1.5 (v1.5) and version 2.2 (v2.2) are used on 22 June 2005 and 9 June 2008, respectively. The v2.2 of MLS HCl profiles have been shown to agree closely with v1.5, within about 5 to 10% on average in the lower stratosphere (Froidevaux et al., 2008). Both were filtered to include only measurements with values of status even, of quality >1.0 for v2.2 (or >1.5 for v1.5), 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 v1.5 (Livesey et al., 2005) and 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).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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-h temporal resolution and a $1^\circ \times 1^\circ$ horizontal resolution.

5 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° S latitude and longitudes ranging from 43° W to 42.5° W at 0.1° intervals on 22 June 2005, and at 5.1° S latitude and longitudes ranging from 43.6° W
10 to 42.8° W at 0.1° 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.

3 Results and discussion

15 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 located higher and colder in June 2008 (16.78 km; -83.0°C) than in June
20 2005 (16.25 km; -79.9°C).
25

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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.

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) for the June 2005 and the June 2008 flights. According to this figure, the air masses sampled in June 2005 originated from south-west and north-west 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. This reveals unfavourable conditions for a fast transport of trace gases vertically from the troposphere to the TTL as well as an intrusion of stratospheric air into the TTL. In particular this demonstrates that HCl amounts measured by SPIRALE in the TTL in June 2005 were not influenced by those from layers below or above this region. Thus HCl potentially present in the TTL is assumed to be the result from VSLS degradation only. Furthermore, backward trajectories associated with the BONBON instrument flight performed on 8 June 2005 present the same characteristics as ours in the TTL region (Laube et al., 2008). This further supports the use of the VSLS mixing ratio values presented in their study in combination with our HCl measurements to assess the chlorinated VSLS budget of the upper TTL.

On 9 June 2008, the backward trajectories associated with the SPIRALE flight reveal that air masses originated from 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. 3 reveals that

VSLS contribution to stratospheric chlorineY. Mébarki et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

transport inside this region in June 2008 occurred predominantly at constant altitudes and that no downward motion and limited upward motion to this region occurred prior to the SPIRALE flight.

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

5 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 perfectly agree to the descent ones in the vertical ranges where they were not affected by this contamination. We
10 only present the descent vertical profiles.

3.2.1 HCl measurements in the TTL

In the upper TTL (inset of Fig. 4), HCl amounts were below SPIRALE detection limit for both flights, i.e. below (30 ± 30) pptv in June 2005 and below (20 ± 20) pptv in June 2008, with uncertainties representing only experimental scatter at 1σ level. This indicates that
15 HCl content in this region was very low on June 2005 and June 2008. Besides more variability visible in the 2005 vertical profile due to a poorer laser diode quality, the SPIRALE measurements of HCl did not change dramatically, though being performed at a three year interval. Hence, since our measurements in this region were negligibly affected by tropospheric or stratospheric air (see Sect. 3.1), we conclude that they provide a reasonable quantification of HCl under typical background conditions. So,
20 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). This is further supported by comparing our measurements with those presented by Marcy et al. (2007). In the later study they used aircraft measurements performed in January 2004 in the tropics to
25 quantify HCl from ~ 12 to 19 km altitude. They reported HCl mixing ratios ranging from

VLSL contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



0 pptv at ~12 km to nearly 40 pptv at the LZRH (at approximately 15 km), increasing to 20–80 pptv at the top of the TTL (~17.5 km altitude). These more elevated HCl mixing ratios were attributed to mixing of stratospheric air in the TTL, as revealed by enhanced O_3 amounts.

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 VSLS. They suggest that no more than 20–30 pptv (i.e. 25 pptv on average) of VSLS is converted into HCl in the TTL, since some HCl may also come from long-lived SG degradation such as CH_3Cl , in accordance with Laube et al. (2008) who derived 0 to 56 pptv of inorganic chlorine vmr in the TTL (15.2–16.4 km) essentially originating from this species. Hence chlorinated VSLS are essentially present in their source and intermediate product gas forms in this region. Then, combining the value of (49±6) pptv for total chlorine coming from tropospheric VSLS SG obtained in the same conditions (Laube et al., 2008) with an additional maximum contribution of 45 pptv from phosgene (WMO, 2007) and (25±25) pptv from HCl according to our findings, we can estimate a total contribution of VSLS to stratospheric chlorine ranging from about 50 to 120 pptv, or in other words about (85±35) pptv. On that account, our measurements of HCl combined to those of VSLS SG by Laube et al. (2008) both performed in situ in the same conditions refine the estimated 50–100 pptv range of WMO (2007) for this contribution without taking into account the final VSLS PG (HCl) due to a lack of studies.

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 31.3 km, both the 2005 and 2008 vertical profiles of HCl show a monotonic increase with altitude, as a result from the reaction of Cl with CH_4 following photolyses and reactions with radicals (e.g., $O(^1D)$, OH) of chlorinated source gases rising the tropical stratosphere. 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,

VSLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the average values were (0.34 ± 0.04) ppbv in June 2008 and (0.22 ± 0.09) ppbv in June 2005. In addition, temperature values in this layer were significantly higher compared to those obtained in June 2005. 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 Mesoéchelle 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 to 21 km altitude range) every 5 K. Figure 5 shows the PV maps derived at 465 K (~ 19.5 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 $0-5^\circ\text{N}$). 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 $15-20^\circ\text{S}$) 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 on 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>). Regarding the study of Chen et al. (2005) it comes out that above 50 hPa (below ~ 21 km) the easterly and westerly QBO phase are not associated with the same induced circula-

VSLs contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tion. 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 in 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 atmosphere 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 ranging from (0.37 ± 0.05) ppbv at 21 km to (1.49 ± 0.09) ppbv at 30 km on average over 2005 and 2008 years. These results are in fairly good agreement with previous measurements of HCl for 30°S – 30°N during 2004 by ACE-FTS, yielding (0.50 ± 0.14) ppbv of HCl at 20 km and (1.8 ± 0.3) ppbv at 30 km (Nassar et al., 2006; Mahieu et al., 2008), with a 20% higher value of ACE at 30 km. These values can be also compared to those presented by Michelsen et al. (1996), derived from the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment obtained in November 1994 for 3°N – 13°N and ranging from 0.4 ppbv at 20 km to 1.9 ppbv at 30 km altitude. These results however do not reveal consistency with SPIRALE ones since in this 1980–2000 period stratospheric chlorine content was strongly increasing and so, the HCl vmr are expected to be lower than in 2005 and 2008, included in the period (2000–2008) of slow decrease (WMO, 2007). Additionally it has to be mentioned that the two SPIRALE measurements performed at only three years interval in this period cannot confirm this chlorine content slow decay.

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 in coincidence with the days of the SPIRALE flights. On 22 June 2005 and 9 June 2008, a set of several HCl measurements from

VSLs contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 ~ 455 km and were acquired only 3 h after the flight. This spatial and temporal proximity was less close on 9 June 2008 as the MLS measurements were performed ~ 11 h before the SPIRALE flight and ~ 1000 km away from its location. 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 (~ 23.5 km) and 753 K (~ 28.6 km) at the time of MLS measurements (22 June 2005 at 16:00 UT). The black crosses 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 over six are found to be relevant for comparison 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 for comparison.

Between 46.4 hPa and 10.0 hPa (i.e. ~ 21.1 km and 31.1 km) the percentage differences are $(1.8 \pm 8.3)\%$ on average for June 2005 and $(6.5 \pm 26.8)\%$ on average for June

**VLS contribution to
stratospheric
chlorine**

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2008. Given the major differences in the remote and in situ methods of measuring HCl and the geographical distance between the two measurements, these comparisons indicate very good agreement between SPIRALE and MLS in the range of the tropical middle stratosphere. Low HCl mixing ratios above 46.4 hPa (<21.1 km) lead to a poorer agreement between the two instruments where the MLS HCl mixing ratios are less accurate (see Sect. 2.2). Similarly a comparison of MLS HCl measurements with in situ aircraft ones has been performed up to ~18.8 km (68 hPa) and revealed a rather mediocre agreement (Froidevaux et al., 2008). In the same study, other balloon-borne (MkIV, FIRS-2, ALIAS-II) measurements have yielded a good agreement ($\leq 10\%$ difference) with those of MLS from the middle to the upper stratosphere (≥ 21.1 km) where amounts of HCl are higher, but again a 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.

Froidevaux et al. (2008) also compared the MLS HCl measurements to other satellites (HALOE and ACE-FTS). They found MLS HCl values ~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 (~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. On the other side, a SPIRALE single profile recorded at high latitude (near Kiruna, 67.6° N–21.5° 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., 2009), 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%. So, to summarize, ACE measurements are consistently higher by about $(7\pm 4)\%$ than SPIRALE and MLS ones between 21 and 31 km height and than MLS ones between

VLS contribution to stratospheric chlorine

Y. Mébarki et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

48 and 60 km. Among these three satellite HCl vmr measured at about 53 km, the MLS value was found in perfect 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. Therefore the very good agreement between SPIRALE and MLS measurements provides further evidence for the VSLS contribution of about 50 to 120 pptv that we derived in the TTL from SPIRALE.

4 Conclusions

Hydrogen chloride (HCl) has been measured in situ for the first time in the tropical tropopause layer (TTL) and the stratosphere in the tropics (5.1° S–42.9° W), with the balloon-borne instrument SPIRALE, an infrared tunable diode laser spectrometer. Two vertical profiles were obtained at three year interval (June 2005 and June 2008), from 15.0 to 31.3 km height, with very high vertical resolution. These measurements allow for studying the HCl content in the TTL and the tropical middle stratosphere as well as to investigate the total contribution from VSLS to stratospheric chlorine. 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 according to backward trajectory calculations. By combining our HCl vmr with a VSLS SG vmr of (49±6) pptv acquired from another balloon-borne measurement performed on 8 June 2005 near Teresina under similar atmospheric conditions (Laube et al., 2008) and a 45 pptv contribution at most from phosgene COCl₂ (WMO, 2007), an estimate of (85±35) pptv for the total contribution of VSLS to stratospheric chlorine is inferred. Thus, even though the SPIRALE measurements have limited spatial sampling, they lead to conclude that the current estimated contribution of 50–100 pptv from VSLS to stratospheric chlorine presented in WMO (2007) is correct.

From 19 to 21 km height in the 2008 flight, SPIRALE has 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-

VSLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



latitude air into the tropics induced by the quasi-biennial oscillation.

From the lower to the middle stratosphere (21.2–31.1 km), SPIRALE HCl measurements are found to be in excellent agreement with each other as well as with those of MLS-Aura satellite acquired in the neighborhood of SPIRALE locations, which consolidates the reliability of MLS measurements of tropical HCl amounts in this altitude range. In addition, HCl values from MLS are also in excellent agreement with HCl vmr calculated from the combination of tropospheric source gases measurements of ground-based networks and modelling results taking into account the air mixing and the delay for the transport to the stratosphere, including the degradation of 100 pptv of VSLS (WMO, 2007). This further supports the need to consider a contribution of (85±35) pptv for VSLS to stratospheric chlorine.

As a conclusion, the present paper answers the WMO (2007, p. 2.42) requirement for accurate HCl measurements in the TTL, combined with an examination of dynamical conditions and air mass origins, to quantify the influence of VSLS on the stratospheric chlorine content. Finally, 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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**VSLS contribution to
stratospheric
chlorine**

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5

10

15

20

25

References

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VLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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VLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**VLS contribution to
stratospheric
chlorine**

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**VLS contribution to
stratospheric
chlorine**Y. Mébarki et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**VSLs contribution to
stratospheric
chlorine**

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**VSLs contribution to
stratospheric
chlorine**

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



VLS contribution to stratospheric chlorine

Y. Mébarki et al.

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

Pressure (hPa)	MLS				SPIRALE			Theta (K)
	N [#] of selected points	Mean HCl (ppbv)	Precision ^a (ppbv)	Approximate altitude (km)	HCl (ppbv)	Global uncertainty ^b (ppbv)		
100.00	3	0.13	0.17	16.5	0.030	0.030	374	
68.13	3	0.23	0.12	18.9	0.092	0.044	434	
46.42	3	0.39	0.11	21.3	0.362	0.049	501	
31.62	3	0.60	0.11	23.5	0.66	0.04	570	
21.54	6	0.99	0.12	26.1	0.91	0.05	668	
14.68	3	1.13	0.15	28.6	1.19	0.07	753	
10.00	5	2.00	0.17	31.3	1.86	0.11	878	

^a 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).

^b Taking into account the random and systematic errors, and combining them as the square root of their quadratic sum.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


VLS contribution to stratospheric chlorine

Y. Mébarki et al.

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

Pressure (hPa)	MLS				SPIRALE			Theta (K)
	N [#] of selected points	Mean HCl (ppbv)	Precision ^a (ppbv)	Approximate altitude (km)	HCl (ppbv)	Global uncertainty ^b (ppbv)		
100.00				16.6	0.020	0.020	369	
68.13	3	0.15	0.18	18.8	0.180	0.090	430	
46.42	3	0.14	0.16	21.2	0.430	0.065	502	
31.62	6	0.47	0.15	23.6	0.72	0.04	597	
21.54	5	0.81	0.17	26.1	0.92	0.05	656	
14.68	3	1.07	0.22	28.6	1.27	0.07	760	
10.00	2	1.77	0.24	31.2	1.68	0.10	850	

^a 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).

^b Taking into account the random and systematic errors, and combining them as the square root of their quadratic sum.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



VLS contribution to stratospheric chlorine

Y. Mébarki et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

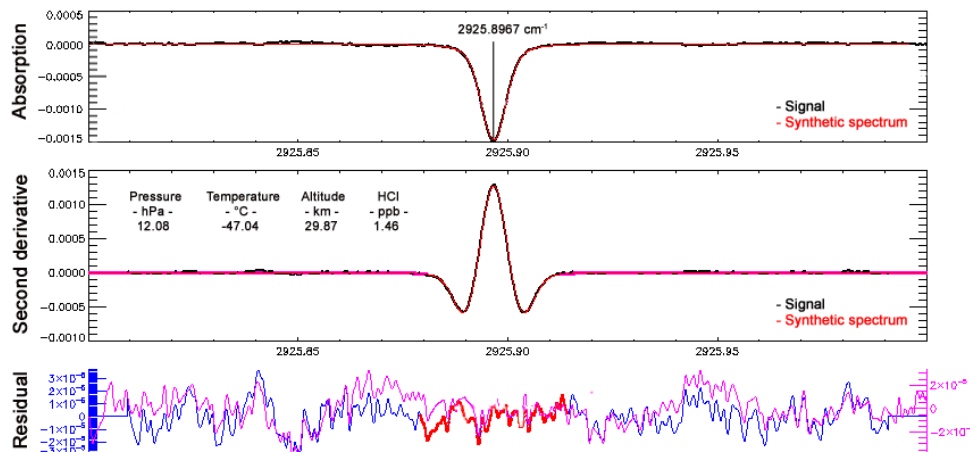


Fig. 1. Retrieval of HCl near 2925.9 cm^{-1} from spectra obtained on 9 June 2008 at 12.08 hPa ($\sim 29.87 \text{ km}$). The signal is the average of 3 consecutive spectra over 3.3 s. The optical path length is 430.78 m. Top: experimental absorption (black curve) with the retrieval of the baseline and 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 0.82% (1σ).

**VLSL contribution to
stratospheric
chlorine**

Y. Mébarki et al.

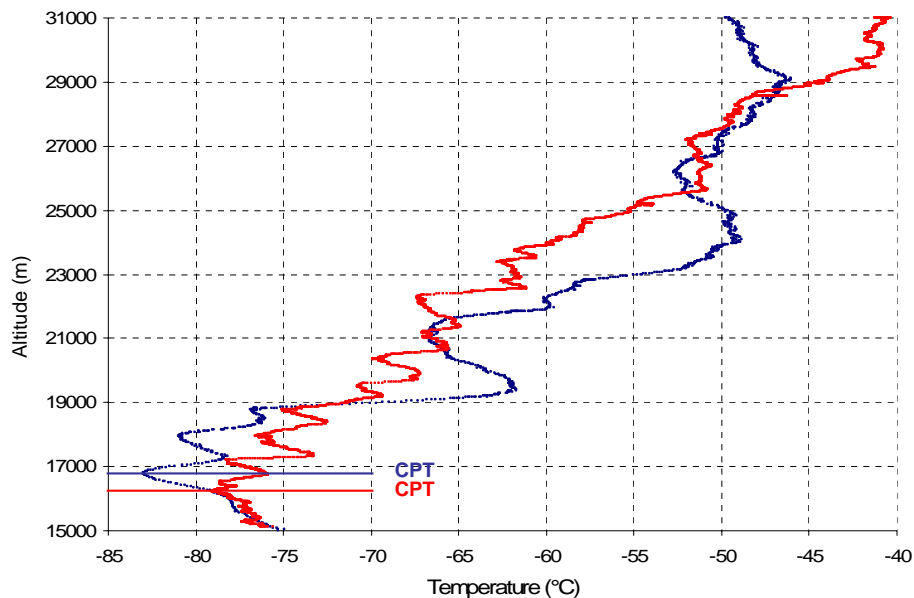


Fig. 2. Vertical profiles of temperature measured on the payload during the June 2005 flight (red line) and the June 2008 flight (blue line). The cold points (CPT) are indicated on each profile.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

VSLs contribution to
stratospheric
chlorine

Y. Mébarki et al.

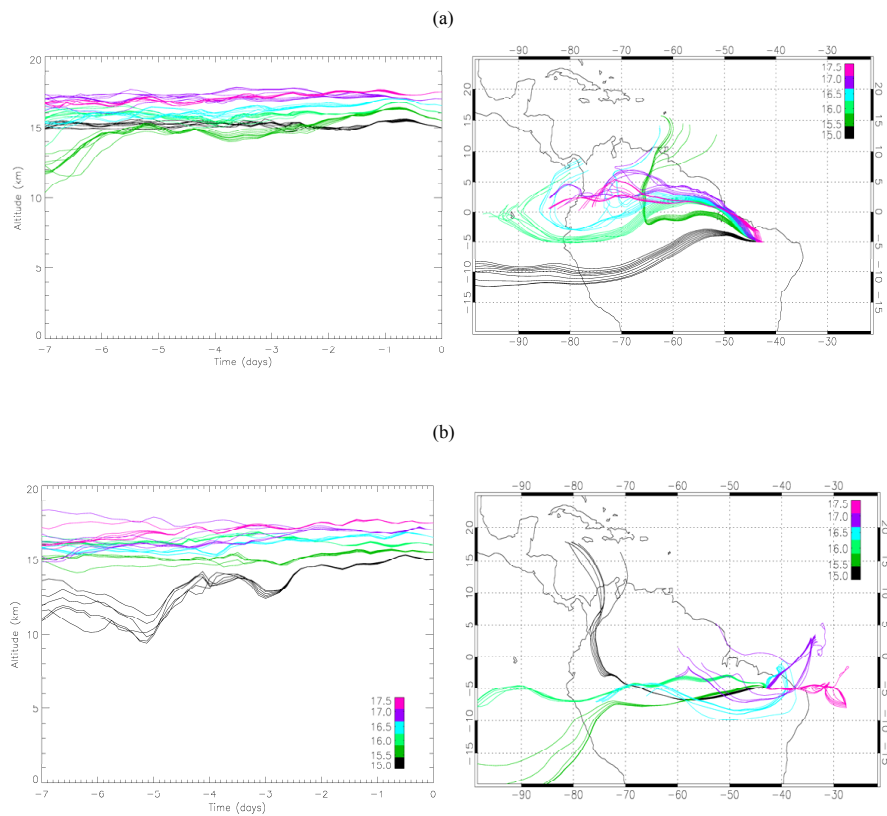


Fig. 3. Seven-day backward trajectories associated with SPIRALE measurements on **(a)** 22 June 2005 at 12:00 UT and **(b)** 10 June 2008 at 03:00 UT. The respective trajectory colours indicate the altitude. Time=0 corresponds to the time of measurements. Left panels represent the altitude evolution and right panels represent the geographical locations of the air masses along the trajectories.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

VLSL contribution to
stratospheric
chlorine

Y. Mébarki et al.

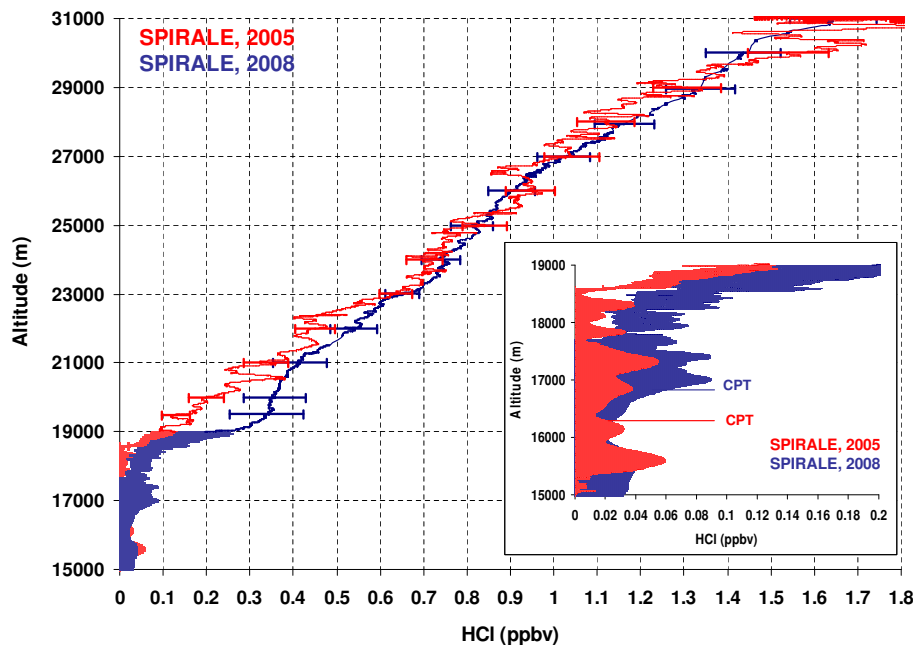


Fig. 4. Vertical profiles of HCl volume mixing ratios measured in situ by SPIRALE on 22 June 2005 (red line) and 9 June 2008 (blue line) above Teresina (5.1° S– 42.9° W). Inset: zoom on the TTL measurements with the altitude of the cold points (CPT). The global uncertainties are represented by horizontal error bars (1σ) every km between 20 and 31 km (and at 19.5 km) and every ~ 5 m between 15 and 19 km.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

VLSL contribution to
stratospheric
chlorine

Y. Mébarki et al.

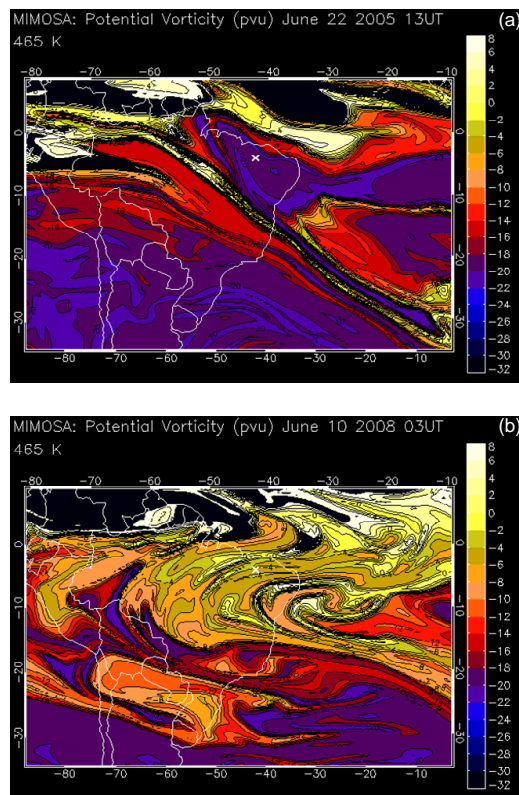


Fig. 5. Latitudinal and longitudinal maps of potential vorticity isocontours ($1\text{PVU}=10^{-6}\text{K m}^2\text{s}^{-1}\text{kg}^{-1}$) calculated by the MIMOSA model on **(a)** 22 June 2005 at 13:00 UT for the 465 K isentropic surface ($\sim 19.5\text{ km}$) and **(b)** 10 June 2008 at 03:00 UT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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

VLSL contribution to
stratospheric
chlorine

Y. Mébarki et al.

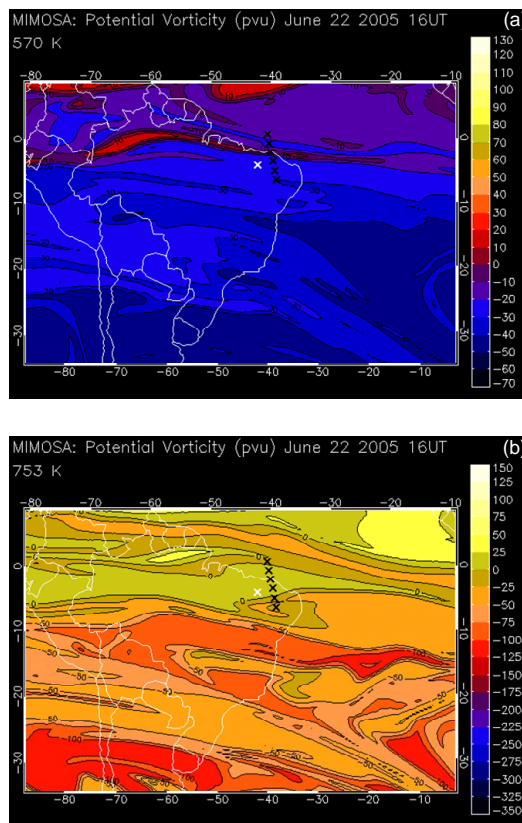


Fig. 6. Latitudinal and longitudinal maps of potential vorticity isocontours ($1 \text{ PVU} = 10^{-6} \text{ K m}^2 \text{ s}^{-1} \text{ kg}^{-1}$) calculated by the MIMOSA model on 22 June 2005 at 16:00 UT for **(a)** the 570 K isentropic surface ($\sim 23.5 \text{ km}$) and **(b)** the 753 K isentropic surface ($\sim 28.6 \text{ km}$). The white and black crosses denote the SPIRALE and MLS measurement locations, respectively.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

VLS contribution to
stratospheric
chlorine

Y. Mébarki et al.

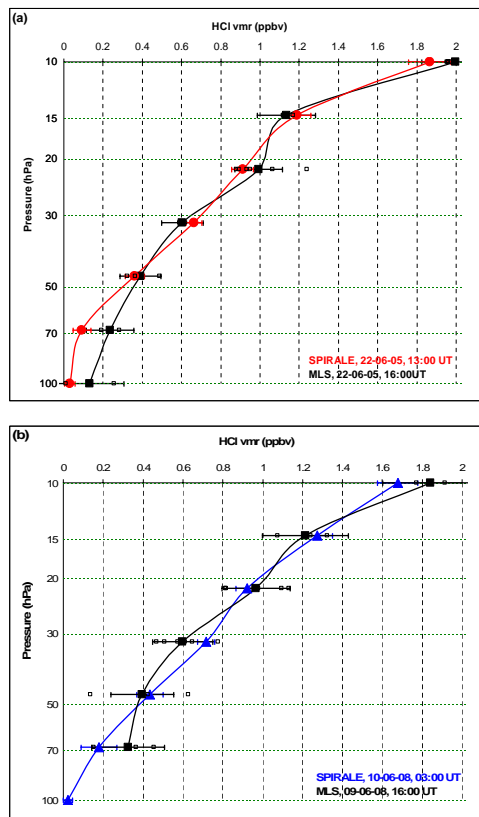


Fig. 7. HCl mixing ratios vertical profiles derived from SPIRALE measurements on **(a)** 22 June 2005 and **(b)** 10 June 2008 compared to the selected MLS v1.5 and v2.2 HCl data (open black squares) and associated averages (solid black squares connected by lines) at each MLS pressure level. Error bars represent global uncertainties for SPIRALE instrument and only precision at 1σ level for MLS instrument.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)