

Spaceborne measurements of the upper stratospheric HCl vertical distribution in early 1992 and the trend in total stratospheric chlorine since 1985

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Abstract. The GRILLE infrared spectrometer was part of the shuttle payload during the first ATLAS mission in March–April 1992. This experiment measured the vertical distribution of several important minor constituents in the middle to high atmosphere by solar occultation mid-infrared absorption spectroscopy. Among the molecules observed is the stratospheric chlorine reservoir species HCl. This paper discusses the vertical profiles measured, including their validation with respect to correlative measurements from ATMOS on board the same mission and from HALOE on board UARS. The most important conclusion drawn from the measured HCl volume mixing ratio of (3.6 ± 0.2) ppbv above 50 km presently measured by GRILLE in comparison with published ATMOS data from 1985 is that the actual GRILLE data confirm the increase of the upper stratospheric total chlorine loading by about 40% with respect to 1985, as reported and/or predicted earlier.

Introduction

The HCl molecule is an important reservoir for the family of atmospheric chlorine species. It is produced in various chemical processes involved in the stratospheric degradation of the CFCs and particularly through direct attack of methane by Cl atoms resulting from the photodissociation of halocarbons. Under this rather stable form, HCl accounts for more than 90% of all the available chlorine above 40 km, i.e., in the higher stratosphere, and above 50 km its concentration is representative of the effective total chlorine burden in the stratosphere. Measuring the concentration of HCl at these altitudes is therefore very important to assess the increase of stratospheric chlorine resulting from anthropogenic releases of CFCs and their substitutes. In the lower stratosphere the chlorine species partitioning involves many additional species including the other reservoir species ClONO₂, the active ClO_x species (Cl, ClO, and so on), and the source gases containing chlorine. At these altitudes the balance of chlorine between active and reservoir species also needs detailed quantification, since HCl can be converted back to species that participate in the ozone destruction through heterogeneous processes.

Therefore the precise measurement of vertical mixing ratio profiles of HCl from the tropopause to the mesopause is of particular importance. But because the abundance of this species is in the parts per billion by volume (ppbv) range

(10⁻⁹), not many techniques can measure HCl quantitatively. In situ methods usually are not sensitive enough, and only a limited number of mass spectrometric measurements [Arnold and Spreng, 1994] and diode laser absorption measurements [Webster *et al.*, 1994] have been obtained from balloon. Therefore remote sensing techniques that benefit from the geometrical amplification factor afforded by limb-viewing techniques are of special interest. Far-infrared thermal emission measurements have been obtained by using Fourier transform spectrometry [Traub and Chance, 1981; Carli and Park, 1988], but solar occultation measurements in the infrared around 3.4 μm allow a better signal-to-noise ratio. Such measurements have been performed originally from balloon [Farmer *et al.*, 1976, 1990; Buijs *et al.*, 1980] and from aircraft [Mankin and Coffrey, 1983], but recently, a larger data set has been obtained from space experiments using gas correlation techniques such as the Halogen Occultation Experiment (HALOE) [Russell *et al.*, 1996] on board UARS or high-resolution spectroscopy like the Atmospheric Trace Molecule Spectroscopy experiment (ATMOS) [Zander *et al.*, 1990; Gunson *et al.*, 1994] or GRILLE [De Mazière *et al.*, 1993] on board the shuttle flights.

We report here a set of HCl measurements in the altitude range 30–60 km produced by the GRILLE experiment during the ATLAS 1 mission flown between March 24 and April 2, 1992. After a brief presentation of the data and the retrieval methods the resultant vertical profiles are discussed and compared with correlative measurements by ATMOS (which flew on board the same mission) and HALOE on board UARS, and conclusions are drawn about the long-term evolution of the stratospheric chlorine.

Observations

The GRILLE spectrometer measures infrared absorption spectra between 2 and 10 μm, during sunrises or sunsets,

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Table 1. Tangent Point Locations for the HCl GRILLE and ATMOS/ATLAS 1 and HALOE/UARS Correlative Measurements

Event	Date	time, UT	Latitude, deg	Longitude East, deg
GRILLE SS09	March 25, 1992	02:03:31	-17.8	240.0
		02:03:54	-19.2	239.9
ATMOS SS03	March 25, 1992	09:37:19	-21.9	126.4
GRILLE SS38	March 26, 1992	21:49:32	-31.7	302.4
		21:49:54	-33.0	302.2
ATMOS SS10	March 26, 1992	20:20:22	-32.6	324.9
GRILLE SS79	March 29, 1992	11:39:23	-45.1	92.7
		11:39:42	-46.1	92.5
ATMOS SS25a	March 29, 1992	10:09:17	-45.9	115.2
HALOE SS	March 29, 1992	10:41:50	-45.36	106.4
HALOE SS	March 29, 1992	12:18:06	-45.16	82.3
GRILLE SS124	April 1, 1992	07:26:37	-52.8	153.2
		07:26:53	-53.3	152.9
ATMOS SS42	April 1, 1992	07:27:01	-53.5	152.9

For GRILLE data the upper and lower values correspond to tangent altitudes of about 55 and 30 km, respectively; elsewhere, corresponding specifications are given at 30 km tangent height. Tangent altitudes are calculated without atmospheric refraction. SS, sunset; SR, sunrise.

using the limb occultation technique. Two different spectral windows of about 10 cm^{-1} extent are scanned simultaneously, with a resolution of about 0.1 cm^{-1} ; one is recorded with an InSb detector, and the other is recorded with a HgCdTe detector. The optical design is fully described by *Besson et al.* [1978] and *Camy-Peyret et al.* [1992].

The HCl window covers the line at 2944.9 cm^{-1} , some CH_4 lines and some solar lines, and is recorded with the InSb detector at a spectral resolution of 0.120 cm^{-1} . Four HCl profiles in the latitude range 18°S to 53°S have been derived; the space and time locations of their tangent points are listed in Table 1. Included also are the corresponding specifications for the correlative observations by ATMOS/ATLAS 1 (R. Zander, private communication, 1992) and HALOE/UARS (J. M. Russell, private communication, 1992) that we restricted to be quasi-coincident observations, i.e., within at most 1° in latitude and 1 hour difference, except for the tropical observation (7 hours and 2.5° latitude difference). For each GRILLE occultation, six to eight spectra have been used to retrieve the HCl mixing ratio profile. As an example for the occultation at 53°S , Figure 1 shows the observed and best fit synthetic HCl spectra and corresponding residuals. In this case the S/N ratio is large enough to allow retrievals up to 52 km, where the depth of the line (at the GRILLE resolution) is less than 2%.

Retrieval Method

Three independent inversion algorithms running at the Office National d'Etudes et de Recherches Aérospatiales (ONERA), the Belgian Institute for Space Aeronomy (BISA) and the Centre National de Recherches Météorologiques (CNRM) have been used to retrieve the

HCl volume mixing ratio (VMR) profiles. The comparison of the individual results has proved very effective for assessing the quality of the retrievals and for producing final profiles with reliable error bars.

1. The algorithm developed at ONERA is based on a least squares global fit method: all spectra containing strong enough absorption lines are considered simultaneously in order to retrieve the vertical mixing ratio profiles, together with some parameters of the instrumental function. The method has been improved, because sometimes oscillations appear in the retrieved profiles as a result of compensating effects between the different layers in the inversion. To minimize these oscillations, the new least squares algorithm has the capability to reduce the vertical resolution of the retrievals when necessary. The new algorithm also takes into account the field of view of about 9 arc min of the GRILLE spectrometer. These improvements have been described by *Achard et al.* [1995].

2. The algorithm developed at BISA is based on the Mill's method [*Alamichel et al.*, 1986], which performs a fit to a selection of observed spectra in an iterative way, starting from the lowest tangent heights and proceeding upward. It searches for a minimum rms residual between observed and synthetic spectra by adjusting the molecular concentrations in the individual layers, the continuum level (linear regression), and a wavenumber shift; the instrument function parameters are adjusted separately. The algorithm needs initial model vertical distributions for the absorbing molecules, but their actual choice does not bias the final result [*Eichen*, 1981]. The method has been optimized for the GRILLE data retrieval and allows an additional smoothing of the derived vertical profile, based on all or a reduced number of individual spectra; as such, oscillations in the resultant profile are minimized without significantly increasing the residual.

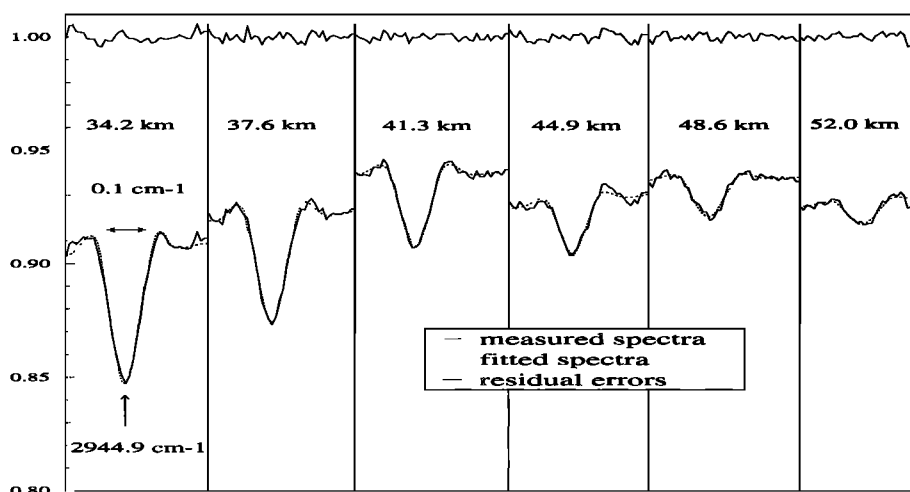


Figure 1. Experimental and best fit HCl spectra for tangent heights in the 34.2 to 52 km range; ordinate is in transmission units; abscissa is in wavenumber units. The residual error is defined as the measured minus fitted spectrum (in transmission units); for reasons of display it has been plotted around 1.

3. The algorithm developed at CNRM performs a global fit of a set of selected absorption spectra. Retrieved variables are volume mixing ratios for given levels (with assumed linear variation versus altitude between the levels), parameters of the instrumental function, and a set of linear background coefficients. In the present version of the algorithm the levels at which the mixing ratios are fitted are chosen as the tangent heights corresponding to the recording time of the HCl line. To estimate the uncertainty of the measurements, the inversion has been performed 64 times for each event, using input synthetic spectra instead of experimental ones, which are the sum of the fitted (calculated) spectra and of a random noise having the same characteristics as the difference (observed minus calculated) obtained in the initial inversion of the experimental spectra. The final CNRM profile is given as an average mixing ratio in each layer between levels.

The calculations of the geographical locations of the tangent points are based on the postmission orbital parameters provided by NASA (the so-called PATH data). The Earth ellipticity has been taken into account to a good approximation, in all retrievals. Temperature and pressure profiles are fixed model parameters in all three algorithms; for each observation they were provided by Météo-France and by U.K. Meteorological Office (data from the stratospheric sounding unit instrument on board the NOAA polar orbiting satellites). The spectroscopic parameters are taken from HITRAN92.

Because of the Pinatubo aerosols, only spectra at tangent altitudes above about 35 km could be used reliably to retrieve concentration profiles. Below these altitudes the actual azimuth and elevation angles of the heliostat differ from those expected according to a simulation of the observation geometry during sunrise or sunset with Earth ellipticity and atmospheric refraction taken into account; the approximations involved in these calculations should be 1 order of magnitude smaller than the observed discrepancies. Radiative transfer calculations indicate that the combined effect of enhanced forward scattered light and reduced direct solar irradiance in the visible may have perturbed the sun

tracker (basically a 4-quadrant silicon Sun edge sensor of 4° full-aperture angle), which controls the heliostat orientation. The influence of a high aerosol burden is also confirmed by the early decrease of the IR signal below 35 km tangent altitude. This additional absorption present in our HCl spectral window would not affect the retrieved HCl VMR values, since they depend on the local continuum that is fitted in the retrieval process itself, as underlined also by *Rinsland et al.* [1994]. But the uncertainties in the actual pointing direction of the heliostat and in the corresponding tangent height assignments discussed above led us to discard the spectra at the lowest altitudes.

Results And Discussion

An example of profiles obtained by the three independent methods discussed above is shown in Figure 2. A final profile was obtained from these individual profiles in the following way. The individual results for mixing ratio and corresponding error bar have been interpolated to a common grid of sampling altitudes that is consistent with the effective 5 km vertical resolution of GRILLE. Then a weighted average was produced, and a final error bar was estimated combining the dispersion around the average of the individual values and their associated uncertainties. As such the final error bar accounts for uncertainties originating in the retrieval algorithm and the measurement noise; it does not account for uncertainties in the spectroscopic parameters, which for the HCl line at 2944.914 cm^{-1} are less than 2%, or for the errors in the adopted atmospheric model parameters and tangent height assignments. As will be shown hereafter, uncertainties on temperature vertical profiles are of a random nature and contribute 2% HCl VMR uncertainties at most. Tangent height assignments have been verified with respect to ATMOS observations, and no significant systematic discrepancies have been found; optical path calculations above 35 km do not suffer from refraction uncertainties either.

The final GRILLE HCl volume mixing ratio profiles for the four events of Table 1 are given in Table 2 and shown in

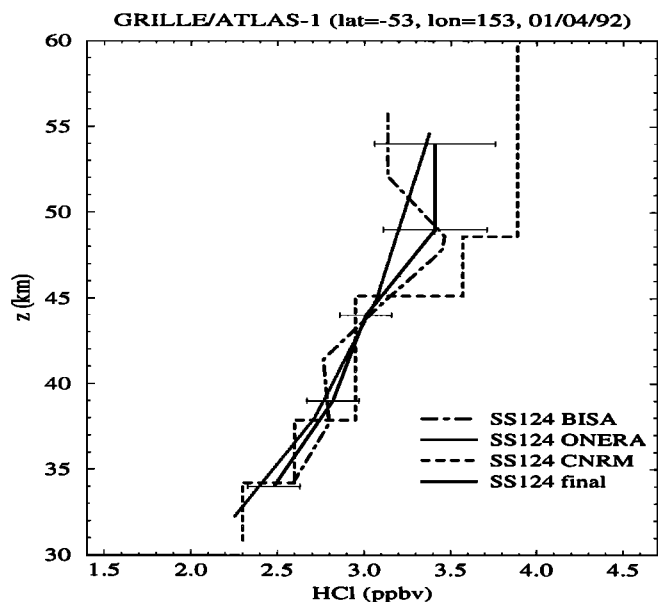


Figure 2. Individual and final HCl retrieval profiles for SS124 (53°S; 153°E; April 1, 1992).

Figures 3a to 3d, together with the ATMOS and HALOE collocated measurements. The comparison shows a good overall agreement between the ATMOS and GRILLE results within their respective uncertainty limits. Some structures observed by ATMOS are not resolved in the GRILLE data: indeed, their typical vertical extension is about 5 km, which can be resolved at the ATMOS vertical resolution of about 2.5 to 3 km. Similar structures were observed in some of the individual GRILLE retrievals, as illustrated in Figure 2.

Keeping in mind, however, the GRILLE vertical resolution of about 5 km and the fact that the retrieval procedure itself can induce some oscillatory behavior of the resultant profile, we considered them not statistically significant.

Apparent systematic differences between the correlative measurements may be due to real longitudinal variability for noncoincident observations with longitudes differing by more than 20° (Figures 3a, 3b, and 3c). Such differences of about 10–15% in the HCl VMR can be observed in the HALOE longitudinal cross sections at the corresponding space-time locations. This explanation does not hold for the differences above 45 km between ATMOS and GRILLE for the perfectly coincident case of Figure 3d, for which, however, the agreement is quite satisfactory at lower altitudes.

In addition, the GRILLE data in Figure 3c confirm the systematic negative offset of the order of 15–20% of the HALOE HCl results with respect to the ATMOS (ATLAS 1) data [Russell *et al.*, 1996]. As to the HALOE observations, it should be noted that in the ATLAS 1 time frame the beta angle was always smaller than 35° (22.6° on March 29), which was found to induce errors of the order of 10%, especially above 30 km [Russell *et al.*, 1996].

We also compared the atmospheric pressure-temperature profiles used by each experiment. Contrary to GRILLE, ATMOS can retrieve local P,T profiles from simultaneously measured CO₂ spectra [Stiller *et al.*, 1995]. Compared to GRILLE, the ATMOS density profiles are almost identical, and T differences are at most 10 K, which can account for about 2% of VMR differences. However, the comparison between HALOE and GRILLE shows that HALOE adopted a systematically higher density (by 12–18%), which can explain part of the observed offset.

Table 2. HCl Vertical Profiles Retrieved From GRILLE Observations During the ATLAS 1 Mission (March 24 to April 2, 1992)

Altitude, km	T, K	P, hPa	Air density, molecules/cm ³	HCl Concentrations, molecules/cm ³	HCl VMR, ppbv
SS09					
38.	246.7	3.91	1.15E+17	2.35E+08	2.05 ± 0.25
43.	256.2	2.01	5.68E+16	1.57E+08	2.76 ± 0.20
48.	262.7	1.05	2.90E+16	8.65E+07	2.98 ± 0.25
53.	260.1	0.56	1.55E+16	4.83E+07	3.12 ± 0.30
58.	247.7	0.29	8.36E+15	2.96E+07	3.54 ± 0.35
63.	235.3	0.15	4.77E+15	1.70E+07	3.57 ± 0.40
SS38					
35.	238.2	5.93	1.80E+17	3.61E+08	2.00 ± 0.30
40.	249.2	3.02	8.77E+16	2.44E+08	2.78 ± 0.15
45.	256.5	1.55	4.38E+16	1.46E+08	3.33 ± 0.20
50.	264.7	0.81	2.22E+16	8.67E+07	3.90 ± 0.30
55.	252.8	0.42	1.20E+16	4.69E+07	3.90 ± 0.30
SS79					
36.	238.0	4.99	1.52E+17	3.31E+08	2.18 ± 0.20
41.	247.8	2.51	7.35E+16	1.93E+08	2.62 ± 0.15
46.	255.4	1.30	3.67E+16	1.07E+08	2.90 ± 0.20
51.	261.3	0.67	1.87E+16	5.87E+07	3.15 ± 0.20
56.	247.6	0.35	1.01E+16	3.45E+07	3.40 ± 0.25
SS124					
34.	229.9	6.49	2.05E+17	5.07E+08	2.48 ± 0.15
39.	239.2	3.17	9.61E+16	2.71E+08	2.82 ± 0.15
44.	247.1	1.58	4.64E+16	1.40E+08	3.01 ± 0.15
49.	261.2	0.81	2.26E+16	7.70E+07	3.41 ± 0.30
54.	252.4	0.42	1.22E+16	4.15E+07	3.41 ± 0.35

SS*n* (SR*n*): sunset (sunrise) in orbit *n*.
Read 1.15E+17 as 1.15 × 10¹⁷.

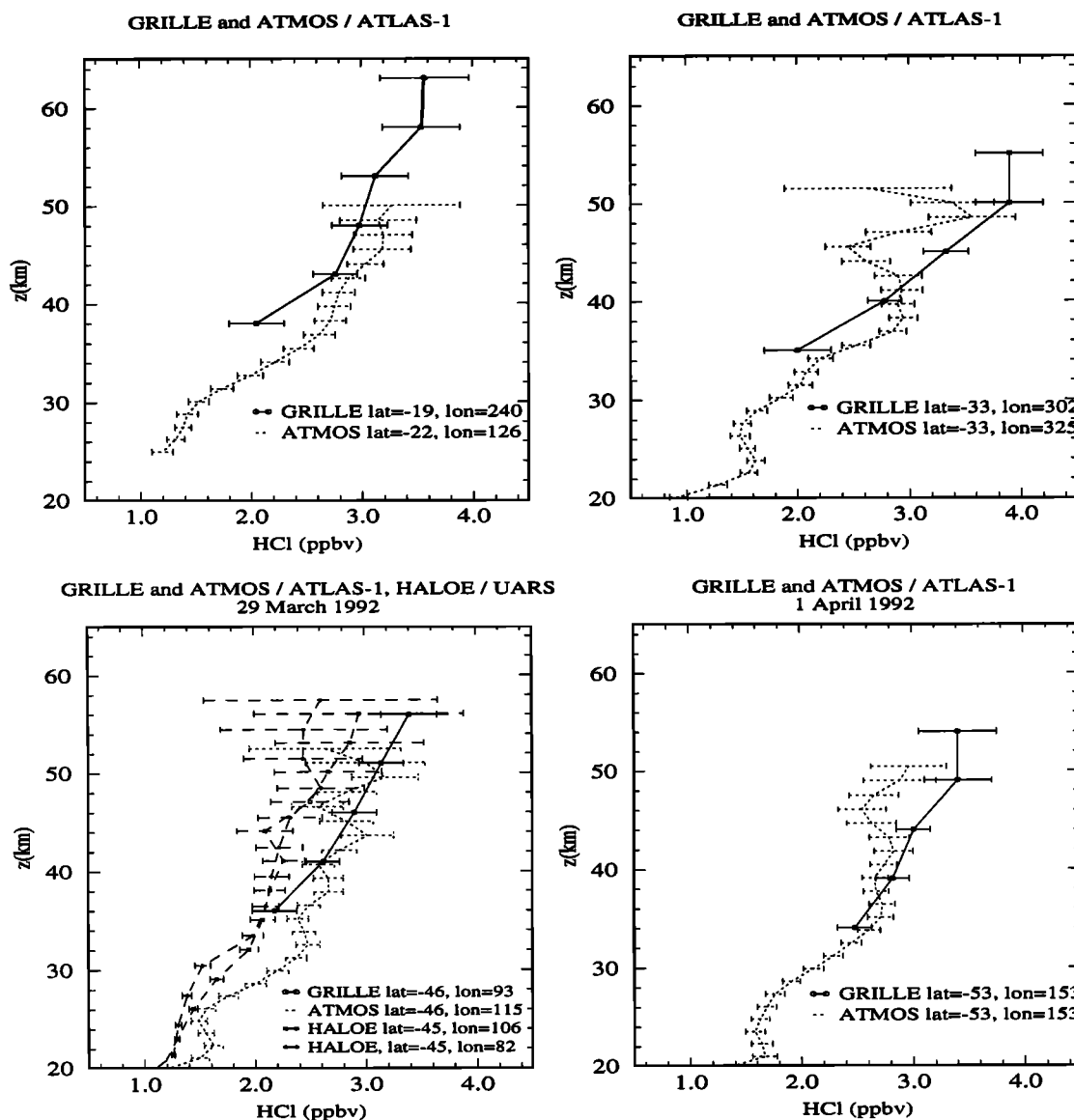


Figure 3. HCl volume mixing ratio profiles retrieved from GRILLE, in comparison with ATMOS and HALOE collocated measurements.

The HCl mixing ratio above 50 km is a prime measurement of the effective stratospheric chlorine loading. According to the GRILLE spectrometer observations at 55 km, it amounts to (3.6 ± 0.2) ppbv, in good agreement with the mean asymptotic value of (3.4 ± 0.3) ppbv estimated from averaged HCl spectra from ATMOS on board the same mission [Gunson *et al.*, 1994] and confirming the preliminary findings from De Mazière *et al.* [1993]. In comparison with the mean 1985 HCl volume mixing ratio above 50 km of (2.55 ± 0.28) ppbv, measured by ATMOS during the Spacelab 3 mission [Zander *et al.*, 1990], the present value measured by GRILLE demonstrates an increase of (0.15 ± 0.05) ppbv/yr, only slightly higher than model predictions that evaluate to 0.11 to 0.13 ppbv/yr [Sanhueza *et al.*, 1995, and references therein]. The data set presented here is too limited, however, to derive any significant latitudinal variations.

Conclusions

The set of HCl vertical profiles measured by the GRILLE spectrometer during the 1992 ATLAS 1 mission, after comparison with the 1985 Spacelab 3 ATMOS measurements, consistently shows an increase of the upper stratospheric HCl concentration of somewhat less than 6% per year, in agreement with the rate deduced from ATLAS 1 ATMOS measurements and very close to theoretical predictions. This increase of HCl above 50 km is representative of that of the total chlorine burden in the stratosphere.

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