CHAPTER 11

HALOGENATED SPECIES

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CHAPTER 11

HALOGENATED SPECIES: OBSERVATIONS AND INTERPRETATION

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11.0 INTRODUCTION

In this chapter stratospheric measurements of halogen containing species are reviewed and compared with model predictions. Emphasis is placed here on new developments since the previous assessment [WMO Report -11, 1982].

The bulk of the chapter deals with chlorinated species. In fact, HF is the only inorganic compound containing a halogen other than chlorine for which there are measurements not already reported in the earlier 1979 assessment [NASA Reference Publication 1049]. There are, however, new stratospheric observations of organic source species containing bromine ($CBrClF_2$, $CBrF_3$ and CH_3Br).

The most important findings in the chapter are summarized in Section 7. Section 8--the final one-- refers to future research needs involving stratospheric measurements of species within the chlorine family. These needs represent only a fraction of the research accomplishments required to significantly advance current understanding of stratospheric chlorine chemistry.

11.1 CHLORINE MONOXIDE (ClO)

11.1.1 Introduction

The principal fate of the chlorine atoms released in the stratosphere by photodecomposition of CFC's is reaction with ozone to form ClO, the chlorine monoxide radical, which in turn reacts with atomic oxygen to regenerate the chlorine atom, thereby completing a catalytic cycle which destroys ozone. Understanding of stratospheric ClO is thus crucial for prediction of stratospheric ozone depletion by CFC's.

First measurements of stratospheric ClO were made from *in-situ* resonance fluorescence detected by instrumentation on parachutes dropped from high-altitude balloons [Anderson *et al.*, 1977, 1980]. Tentative detection of millimeter-wavelength emission lines of ClO was made by aircraft-based instruments [Waters *et al.*, 1979], followed by definitive measurements from ground-based [Parrish *et al.*, 1981] and balloon-based [Waters *et al.* 1981] millimeter wavelength spectrometers. An early measurement of stratospheric ClO by balloon based infrared absorption spectroscopy was also reported [Menzies, 1979; amended, 1983]. The status of ClO measurements up to 1981 is summarized in the previous assessment report [WMO, 1982].

Since the 1981 assessment, the stratospheric ClO data base has been improved in the following ways:

1. The diurnal variability of ClO has been measured by both ground-based and balloon-based millimeter-wavelength techniques.

2. The time-base on measurements of the ClO column abundance has been extended, and observations have now been made at latitudes of 20°, 32°, and 42°N by ground-based millimeter-wavelength techniques.

3. Additional *in situ* profile measurements have been obtained from the recently developed reel down technique.

4. Balloon-borne infrared laser heterodyne results have been reevaluated, and are now generally consistent with other measurements.

5. Initial results from ground-based infrared heterodyne measurements failed to detect stratospheric ClO; preliminary results from more recent measurements, however, have indicated the presence of a ClO signal.

6. Observations of stratospheric ClO have been obtained from balloon-borne submillimeter measurements.

Continued refinements in theoretical modeling, adjustments in laboratory-measured rate constants and in uv solar flux, and improvement in the observational data base for ClO, including the 24-hour cycle of diurnal variation, have by now produced a state of reasonable agreement between theory and experiment in both the average altitude profile and diurnal behavior. On the other hand, existing experimental data is inadequate to measure seasonal and latitudinal variations or long term trends which are theoretically predicted. Also, simultaneous measurements of ClO at the same location by independent techniques have not yet been performed, although agreement in the mean value of measurements from various techniques appears good.

11.1.2 Midday ClO

11.1.2.1 Vertical Profile

Figure 11-1 summarizes existing measurements of the mid-day stratospheric ClO vertical profile. The *in situ* resonance fluorescence measurements, are (a) the average of eight profiles measured between
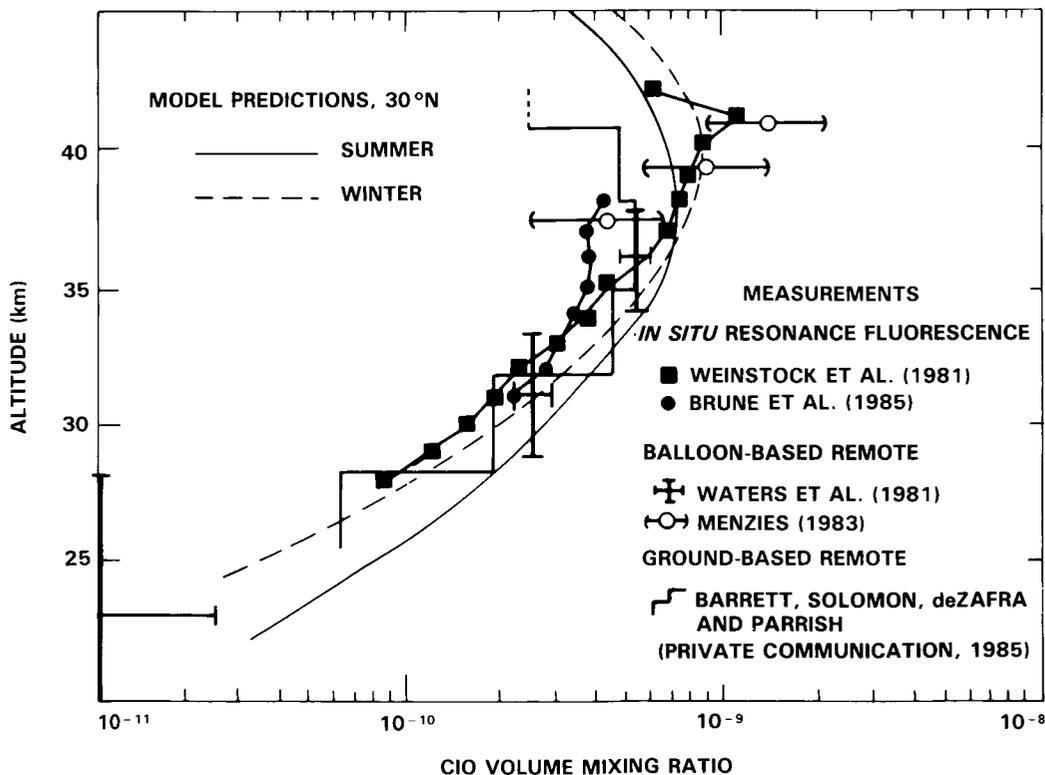
Figure 11-1. ClO vertical profiles from measurements and theoretical models. See text for details.

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9 Dec. 1976 and 26 Sept. 1979; (with the omission of the anomalously high mixing ratio profiles measured on 28 July 1976 and 14 July 1977 [Weinstock et al., 1981]), and (b) a profile measured on 14 Sept. 1984 using an entirely reengineered fluorescence instrument in a repeatable reel-down mode [Brune et al., 1985]. The two anomalously high profiles measured in July of 1976 and 1977 are omitted since they have been previously discussed in the literature and represent data well outside the norm (and in the case of July 1977, exceeding the total accepted chlorine budget for the stratosphere). The points from Waters et al., [1981] were obtained from balloon-borne millimeter-wavelength heterodyne spectrometer measurements of limb thermal emission by the 204-GHz ClO line. The Menzies [1983] points are a reevaluation of earlier published data from balloon-borne infrared laser heterodyne spectrometer measurements of atmospheric absorption against the setting sun. The ground-based profile results from a deconvolution of the pressure broadened ClO spectral line shape obtained at Mauna Kea, Hawaii (20°N) in December 1982 [Barrett et al., private communication 1985]. The data used to obtain this profile do not differ by more than 15% from the mean of other data taken in 1982, 1983, and 1984 at Mauna Kea, although having a better overall signal/noise ratio. These data also do not differ qualitatively from line shapes obtained at 32° and 42°N using the same technique and equipment. The measurements reported in Weinstock et al., Brune et al., Waters et al. and Menzies were all made at 32°N.

Also shown in Figure 11-1 are two calculated noontime vertical profiles of ClO from the model of Ko and Sze [1984] with updated chemistry [see Appendix A]. These profiles were calculated for 30°N latitude and solar declination angles + 20° (summer) and −20° (winter). Note the larger abundances near the peak and the shift of the profile to higher altitudes in the winter. The calculated midday ClO profiles appear to be in reasonably good agreement with the measurements as presented in Figure 11-1. Since 1981 there has been significant improvement in the agreement between measured and calculated ClO profiles, due to improved values for reaction rates.

11.1.2.2 Variations

The *in situ* resonance fluorescence measurements of 1976-1979 by Anderson and co-workers were reviewed in the previous Assessment Report [WMO, 1982] and in Weinstock et al., [1981]. With the exception of the anomalous data of 28 July 1976 and 14 July 1977, the remainder, all taken near local noon (whose average is given in Figure 11-1), show vertical profiles between 25 and 40 km which lie within a region whose bounds differ from the mean by about a factor of 2. According to Anderson [private communication, 1985], the standard deviation in calibration accuracy between the individual profiles evolved from about 30% in the earlier flights, to about 15% in the later ones. Table 11-1 gives statistics on the *in situ* ClO measurements reported in [Weinstock et al., 1981]. The standard deviation in these data, excluding the 28 July 1976 and 14 July 1977 measurements, varies from about 65% at 25 km to about 45% at 40 km. Accounting for the expected calibration uncertainty, as shown in the table, the residual standard deviation (which is the maximum that can be attributed to stratospheric ClO variability) varies between about 60% at 25 km, to 30-40% at 40 km. Figure 11-2 shows the *in situ* measurements from Weinstock et al., [1981] with those from the recent reel down [Brune et al., 1985] added. It is the opinion of Brune et al., that the rather different shape of the reel down profile is real and not an instrumental artifact related to the change of experimental methods.

Millimeter-wavelength ground-based measurements of ClO [Parrish et al., 1981; Solomon et al., 1984; de Zafra et al., 1985a] now extend from January 1980 to December 1984, and include data taken at 20°, 32°, and 42°N, with observations near both the winter and summer solstices from the southernmost location.

Table 11-1. Statistics on the *in situ* ClO measurements given in Figure 2 of Weinstock *et al.,* [1981]. The mean μ and standard deviation σ are in units of ClO volume mixing ratio in ppbv. The quantity $(\sigma/\mu)_R$ is the residual relative variation after quadrature subtraction of a random calibration error having the indicated value.

		HEIGHT			
		25 km	**30 km**	**35 km**	**40 km**
WITHOUT 28 JULY 76 OR 14 JULY 77					
	mean μ	0.03	0.16	0.45	0.91
	std. dev. σ	0.02	0.08	0.20	0.40
	σ/μ	0.66	0.50	0.44	0.44
$(\sigma/\mu)_R(0.3)$	$\sqrt{(\sigma/\mu)^2-(0.3)^2}$	0.59	0.40	0.32	0.32
$(\sigma/\mu)_R(0.15)$	$\sqrt{(\sigma/\mu)^2-(0.15)^2}$	0.64	0.48	0.41	0.41
WITH 28 JULY 76 AND 14 JULY 77					
	mean μ	0.09	0.39	0.82	1.50
	std. dev. σ	0.15	0.54	0.95	2.14
	σ/μ	1.66	1.38	1.16	1.43
$(\sigma/\mu)_R(0.3)$	$\sqrt{(\sigma/\mu)^2-(0.3)^2}$	1.63	1.35	1.12	1.40
$(\sigma/\mu)_R(0.15)$	$\sqrt{(\sigma/\mu)^2-(0.15)^2}$	1.65	1.37	1.15	1.42

The results are summarized in Figure 11-3. No latitudinal or seasonal variations in column density above 30 km are discernable in these data at a level greater than ± 20% about the mean and the data set is not yet long enough in time to detect the expected 5% per year increase in ClO due to industrial chlorocarbon release. The two-dimensional model of Solomon and Garcia [1984b] predicts about ± 20% latitudinal variation in ClO concentration at the peak (~ 38 km) between the latitudes of the ground-based measurements at solstice. This model also predicts (at the peak of the mixing ratio profile) approximately 50% more ClO at 40° latitude in winter than in summer, and approximately 25% more in winter at 20° latitude. More ground-based millimeter-wavelength measurements at different latitudes and seasons would provide tests of these predictions.

A smaller overall variation exists in the ClO data base from the groundbased millimeter-wavelength technique than that from the *in situ* resonance fluorescence technique. This contrast in measured variability is illustrated in Figure 11-4 where the measured *in situ* profiles have been used to calculate millimeter-wavelength emission lines which are compared with the ground-based measurements. The origin of this difference in measured variability is not completely resolved at present, but it should be noted that the
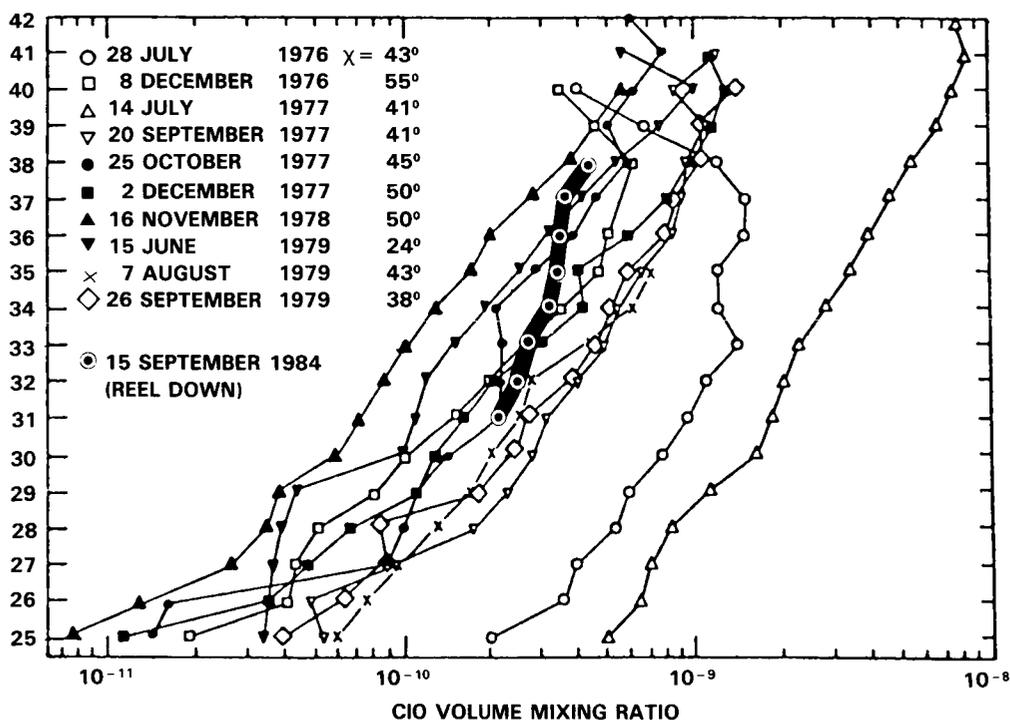
Figure 11-2. Comparison of the average reel down ClO profile of 15 September 1984 [Brune *et al.*, 1985] with earlier "fast" parachute drop profiles measured by *in situ* resonance fluorescence [Weinstock *et al.*, 1981]. Concentrations from the reel down measurement have been converted to mixing ratios using the 1976 U.S. Standard Atmosphere.

claimed accuracy for the ground-based technique is about twice that of the *in-situ*, (which is about the same as the ratio of variations in the *in situ* data set to that in the ground-based millimeter data set), and that the integration times for the two measurement techniques differ greatly. The *in situ* profile points are measured in less than a minute, whereas the ground-based millimeter wavelength measurements are averages over typical periods of several days or more.

Pyle and Zavody [1985a] and Solomon and Garcia [1984b] estimated the variability of ClO using LIMS and SAMS satellite data. Neither of these instruments made measurements of chlorine compounds. However, species which determine the partitioning among odd chlorine compounds were measured or can be derived the partitioning among odd chlorine compounds were measured or can be derived.

For example,

$$\frac{[HCl]}{[ClO]} \approx \frac{k_1 [CH_4] + k_2 [HO_2]}{k_3 [OH]} \times \frac{k_4[O] + k_5[NO]}{k_6 [O_3]}$$

$[O_3]$ and $[CH_4]$ were measured by LIMS and SAMS, respectively. $[OH]$, $[HO_2]$, $[NO]$ and $[O]$ can all be derived from LIMS and SAMS measurements of H_2O, CH_4, O_3 and NO_2 using photochemical steady-state arguments (see, for example, Pyle and Zavody [1985b]).

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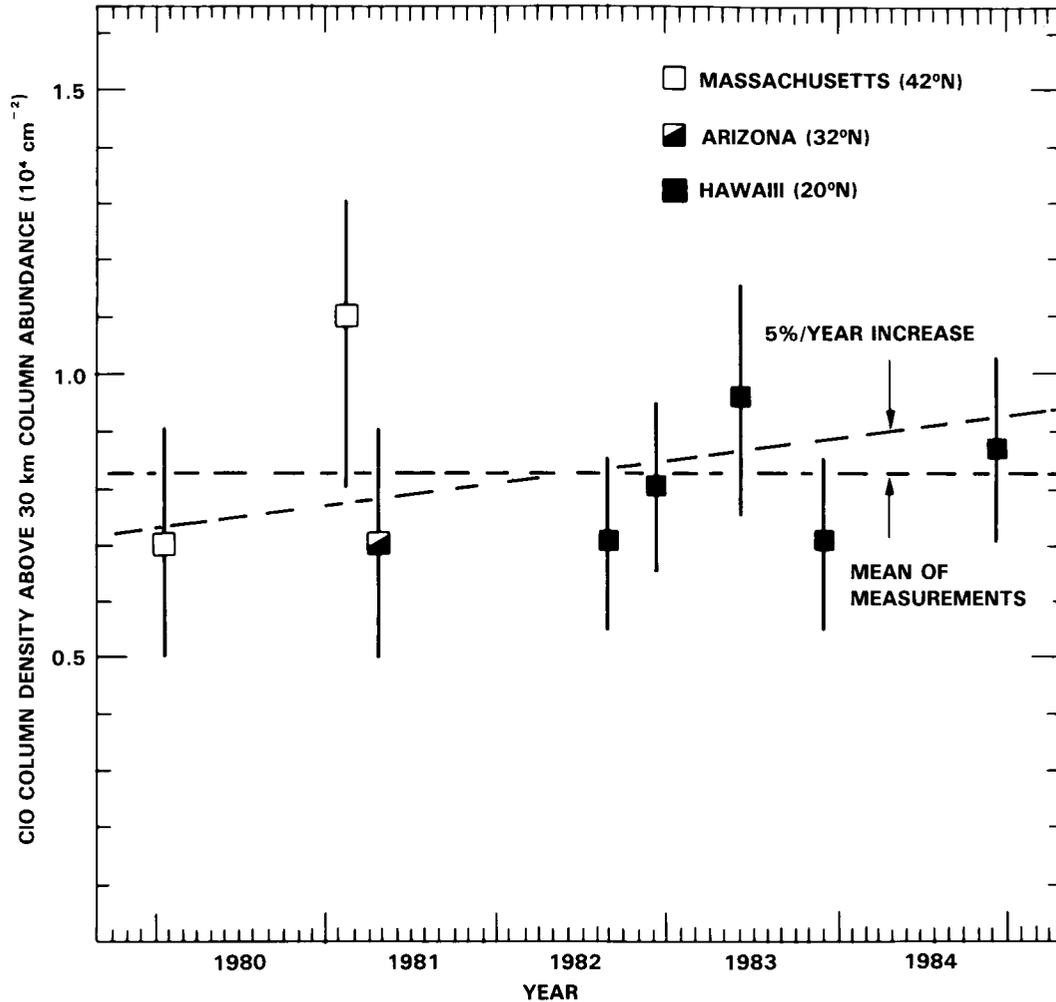
Figure 11-3. Midday ClO column abundances above 30km measured by ground-based millimeter-wavelength spectrometry [from de Zafra *et al.*, 1985a, with data for December 1984 added and a slight change in error bars on the February 1981 data]. The January-February measurements are from the 204 GHz ClO line; all others are from the 278 GHz ClO line.

Similar expressions can be used to derive the partitioning between all the odd chlorine species (Cl, ClO, HCl, HOCl and ClONO$_2$). Then, if an odd chlorine profile is specified, the partitioning can be computed for each sounding of the LIMS mission.

Taking satellite data at 32 °N, Pyle and Zavody [1985a] have estimated the variability of the derived ClO about the monthly zonal mean. Between 25 and 40 km the standard deviation of the monthly zonal mean is ~20% or less. Using all the LIMS data in 1979 (the five months from January to May) the variability of any one month about the five-month mean amounts to less than 10%.

These values are smaller than suggested by the measurements of Weinstock *et al.*, [1981] but agree well with estimates from the ground- based microwave measurements. It should perhaps be remembered
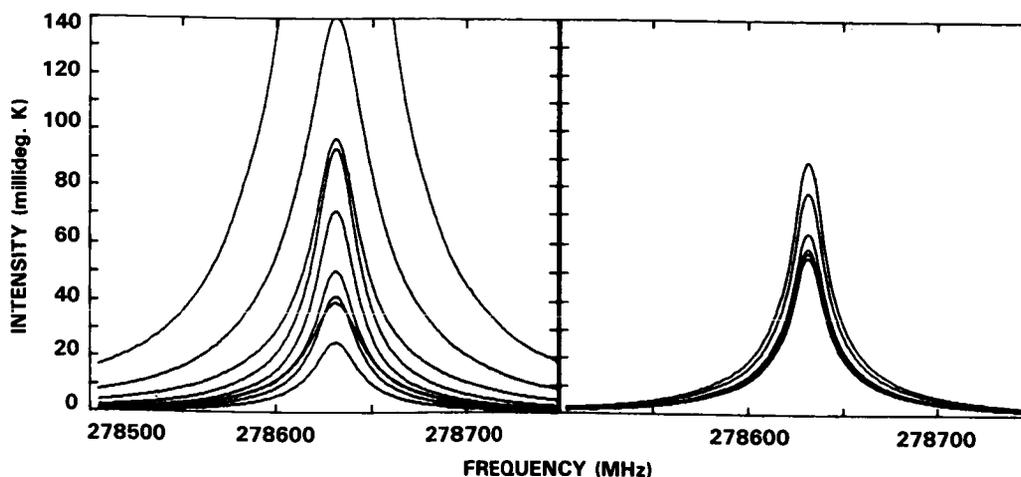
Figure 11-4.

Left: 278 GHz ClO emission lines calculated for ClO profiles measured by *in situ* resonance fluorescence between 1976 and 1979 and reported in Weinstock *et al.* [1981] (see Figure 11-2). The line of greatest intensity is for the *in situ* measurements of 14 July 1977 and the next highest is for 28 July 1976. All intensities shown here are somewhat lower than true intensities would be, because no allowance has been made for ClO above 40 km where there are no *in situ* measurements.

Right: 278 GHz ClO emission lines measured from the ground, covering observations from Massachusetts (Winter, 1980, 1981), Arizona (May 1981), and Hawaii (October, Dec. 1982, June 1983, Dec. 1983, and Dec. 1984). All lines are scaled to zenith-looking observations with no tropospheric absorption.

Essentially all of the contribution to the lines is from ClO above ~30 km, [from de Zafra *et al.*, 1985a with data for Dec. 1984 added].

that remotely sensed data are averages over a large volume of air so that small scale variability cannot be inferred. Short term local variations in methane, as indicated by balloon measurements [Ehhalt *et al.*, 1983] could possibly explain much of the variation in midday ClO observed by *in situ* resonance fluorescence [Solomon and Garcia, 1984b]. Given the scatter in the *in situ* data and calibration uncertainty, and the lack of simultaneous measurements of interacting species, however, it is at present difficult to assess the variability of stratospheric ClO from the *in situ* measurements.

11.1.2.3 Additional Results

11.1.2.3.1 Ground-Based Infrared Laser Heterodyne Measurements

An upper limit for stratospheric ClO obtained with a ground-based infrared heterodyne spectrometer measuring absorption against the sun was reported by Mumma, *et al.* [1983]. These measurements were made at the McMath solar telescope (Kitt Peak National Observatory 32 °N, 112 °W) in May and October of 1981. Three lines of ClO were searched for near 12μm (~856 cm^{-1}) with primary emphasis on the R9.5 line of ^{35}ClO at 856.50137 cm^{-1}. Measurements were made in early morning and late afternoon, to increase the absorption path length. The early morning measurements were made to establish the atmospheric spectral transmittance at a time when ClO was expected to be minimal. By comparing their

observed transmittance spectra with modelled spectra, the authors concluded that the absence of a detectable ClO line indicated the "stratospheric ClO abundance to be smaller by at least a factor of 7 than the currently accepted value" based on an average of all previous balloon-borne *in situ* measurements. This conclusion depends in part upon the assumption that the infrared line strengths and pressure broadening parameters for several nearby lines (primarily HNO_3, but also including NO_2 and OCS) are correctly known, as well as those for ClO, since the R9.5 line falls near the middle of an absorption minimum between two significantly stronger HNO_3 lines. Most of the molecular line parameters have been measured at doppler-limited spectral resolution [Maki *et al.*, 1982; Weaver *et al.*, 1983] and the early morning (no ClO) spectra are satisfactorily modelled using them.

Recently, these observations have been repeated [M. J. Mumma; J. Olivero, private communications], extending the observing period throughout the day. Preliminary analysis indicates the presence of a ClO signal in the new data, and a variation in this signal during the daylight hours when measurements were made. Hence, considering uncertainties, the ground-based infrared measurements no longer appear to be in significant conflict with all other observations as was initially thought.

11.1.2.3.2 Balloon-borne Submillimeter Measurements

Carli *et al.*, [1985] have recently reported balloon measurements of stratospheric ClO emission by the rotational transition $J = 37/2 \rightarrow 35/2$ of ^{35}ClO located at 22.8976 cm^{-1} (686 GHz). The instrument is a Martin-Puplett type Fourier transform spectrometer [Carli *et al.*, 1984] observing thermal emission from the limb with 0.0033 cm^{-1} unapodized spectral resolution. Data were obtained from flights in April 1979 and November 1982. Assignment of the ClO feature in the spectra from these flights has recently been made possible by compilations of submillimeter spectral lines [Baldecchi *et al.*, 1984; Poynter and Pickett, 1984]. Results from analysis of this line indicate the observed ClO daytime profile is consistent with the mean of measurements discussed above to within the experimental uncertainty of approximately 50%, and also support diurnal variability in ClO as discussed below.

This submillimeter result at 686 GHz gives a total of four pure rotational lines of ClO which have now been either measured or tentatively detected in the stratospheric spectrum. Lines at 204 and 278 GHz have been measured with good signal to noise by ground [Parrish *et al.*, 1981; Solomon *et al.*, 1984; de Zafra *et al.*, 1985a] and, at 204 GHz, by balloon-based [Waters *et al.*, 1981] millimeter spectrometers. Tentative detection of an additional line at 241 GHz, as well as the 278 GHz line, were made by aircraft-based millimeter-wavelength spectrometers [Waters, *et al.*, 1979]. Results from all the rotational line measurements for stratospheric ClO are consistent to within the measurement accuracies. The positions and strengths [Poynter and Pickett, 1984], as well as the pressure broadening parameters for these transitions are known with sufficient accuracy so as to not limit the measurement interpretation. (Pure rotational line strengths can be accurately determined from the measured dipole moment and are not subject to the substantial uncertainties which often exist in experimental line or band strength values for vibrational and electronic transitions).

11.1.3 Diurnal Variation of ClO

Measurements of the diurnal variation in ClO provide a critical test of theoretical predictions of the coupling between chlorine and nitrogen/hydrogen chemistries in the stratosphere. Interpretation of such measurements is also relatively free from uncertainties caused by longer-term variations due to transport, which are more difficult to predict.

Results from ground-based millimeter-wavelength measurements of the stratospheric ClO diurnal variation [Solomon, *et al.*, 1984] are shown in Figure 11-5 and compared with predictions of theoretical models. These measurements were conducted from the Hawaii Mauna Kea Observatory (19.7 °N) during two observing periods in October and December of 1982. Approximately eight 24-hour cycles of measured emission from the $15/2 \rightarrow 13/2$ ClO rotational transition at 278.630 GHz were averaged to improve the signal to noise ratio, and the data were binned in two-hour time intervals to give the diurnal variation in ClO column density above ~30 km altitude which is shown in Figure 11-5. The observed day-to-night ratio of ClO column density is in reasonable agreement with predictions as shown in Table 11-2. However, current theory predicts approximately 50% more in the column above 30 km than measured. Agreement is also found with the predicted hour-by-hour variations except that a somewhat slower post-dawn increase in ClO is measured. The measured narrowing in the pressure-broadened line shape also qualitatively confirmed the predicted night-time disappearance of nearly all ClO below 35 km.

Data from the balloon-borne microwave limb sounder, which measures ClO by thermal emission from the $J = 11/2 \rightarrow 9/2$ rotational transition at 204.352 GHz [Waters *et al.*, 1981 and 1984], have also been analyzed for the diurnal variability in ClO. The results, given in Figure 11-6, show the variation of ClO in a 4 km thick vertical layer centered at 30 km altitude, as a function of time with 1/2 hour temporal resolution, for noon through 7 p.m. on 20 February 1981 and for midnight through 11 a.m. on 12 May
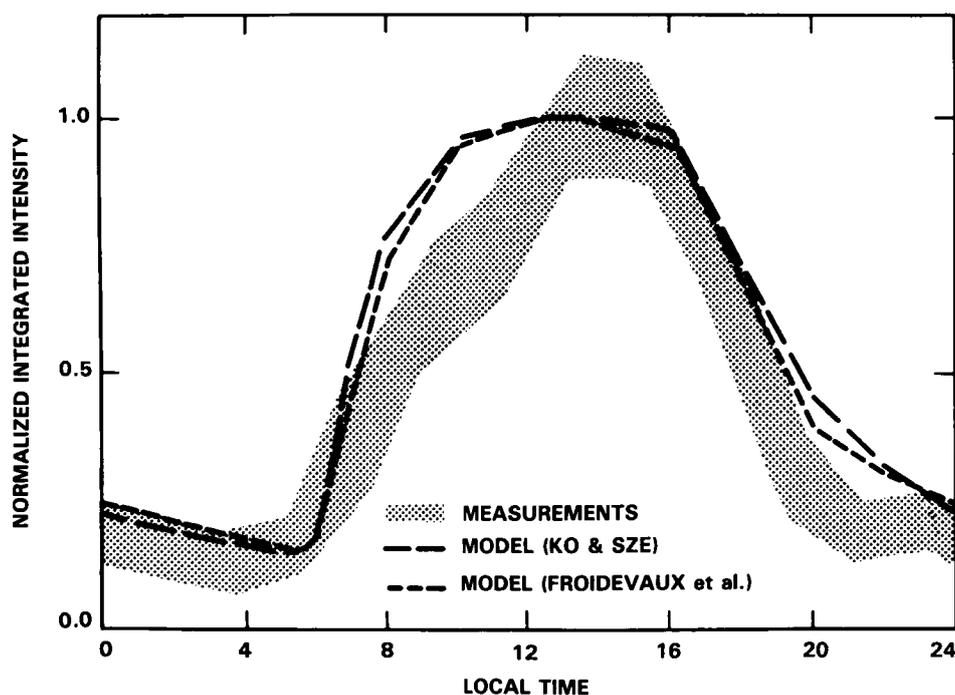
Figure 11-5. Diurnal variation of ClO measured by ground-based millimeter-wavelength spectroscopy and compared with theoretical predictions of Ko and Sze [1984] and Froidevaux *et al.* [1985a]. Measurements and predictions have both been normalized to unity at midday. Measurements were binned in two-hour intervals and smoothed; the shaded area represents estimated error limits about the mean. The measurements have been analyzed so that the normalized integrated intensity shown here is proportional to the ClO column density above ~30 km, although a small contribution from lower material is present. (From Solomon *et al.* [1984]).

Table 11-2. Day and night ClO column densities measured by ground-based millimeter measurements [Solomon *et al.,* 1984, with correction of typographical error on quoted uncertainty for measured day column above 40 km] and calculated from the photochemical model of Ko and Sze [1984] with updated chemistry (see Appendix A). The measurements were made in October and December 1982 from Mauna Kea, Hawaii (20 °N). The model results were also for winter 20 °N.

	ClO column density		
	Day (10^{13}cm^{-2})	Night (10^{13}cm^{-2})	Day/Night ratio
Above 30 km			
Measurement (8–11 Oct 82)	7 ± 1	1.0 ± 0.2	7^{+3}_{-2}
Measurement (9–16 Dec 82)	7.5 ± 1	1.3 ± 0.3	5.7^{+3}_{-2}
Model	12	1.5	8
Above 40 km			
Measurement (8–11 Oct 82)	1.3 ± 0.6		
Measurement (9–16 Dec 82)	2.0 ± 0.6	1.0 ± 0.3	2.0^{+2}_{-1}
Model	2.1	1.1	1.9

1981. Comparisons with theoretical predictions show general agreement in the rate of decrease around sunset, but the observed increase after sunrise is slower than predicted. This result is similar to that from the ground-based millimeter-wavelength measurements discussed above, which cover a longer time period and a larger vertical layer.

The measured diurnal variation of ClO column density above 30 km and of local ClO around 30 km can be explained by exchange processes between ClOx (Cl + ClO) and ClONO$_2$ operating during the day (via photolysis of ClONO$_2$) and the night (via recombination of ClO with NO$_2$). The measured morning rise in ClO appears to be somewhat more gradual than predicted. Ko and Sze [1984] argue that this observed feature rules out the possiblity of any appreciable formation of ClNO$_3$ isomers such as ClOONO or OClONO which are expected to have shorter photolytic lifetimes than ClONO$_2$. Laboratory studies [Margitan, 1983; Cox *et al.,* 1984] have recently demonstrated that ClONO$_2$ is the sole product from the recombination of ClO with NO$_2$. The apparent experimental evidence of a postdawn rise in ClO even slower than that predicted from photolysis of ClONO$_2$ may be, at least in part, an effect due to advection by stratospheric zonal winds across the day-night terminator [Ko and Sze, 1984].
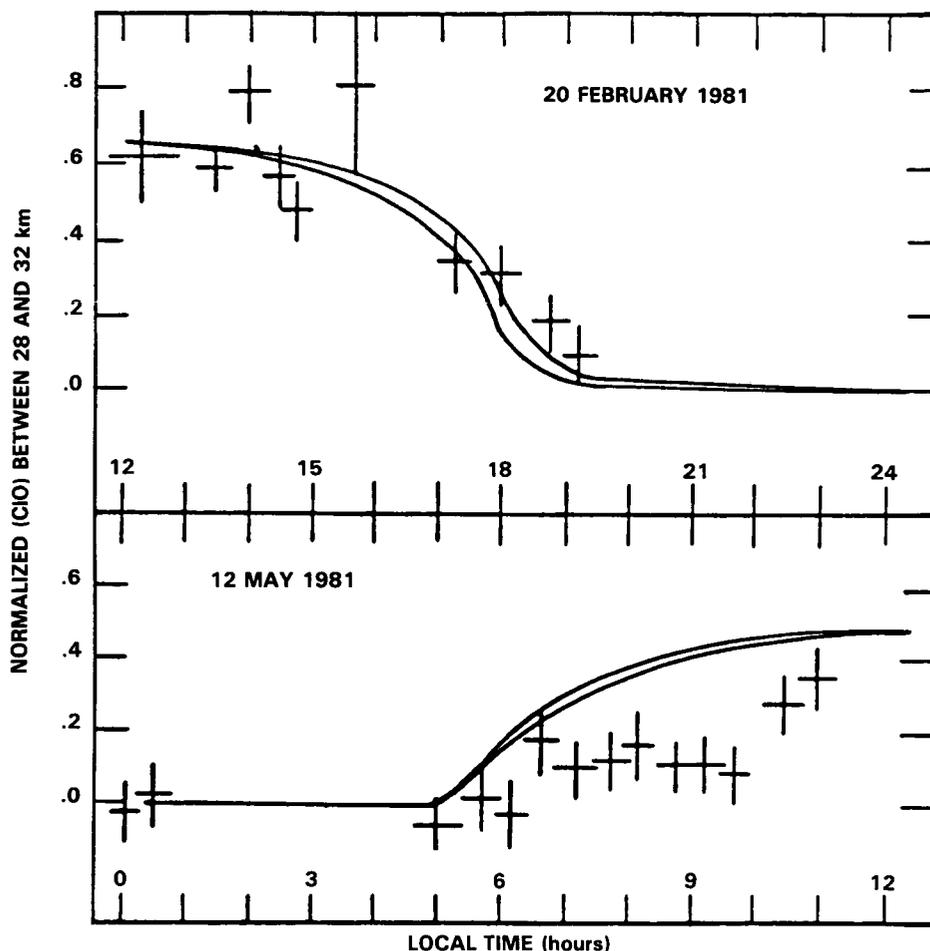
Figure 11-6. Diurnal variation in ClO measured by balloon-borne microwave limb sounding (crosses) on two flights (from Palestine, TX, 32 °N) and compared with theoretical predictions (curves). The vertical scale is an average of the measured brightness temperature of the 204 GHz line which is proportional to the abundance of ClO between heights of approximately 28 and 32 km. The vertical bars on the measurements are ±one standard deviation of instrument noise. The two theoretical curves for each flight are normalized to noon and are for the same latitude and solar conditions as the measurements, but for 6 km thick layers centered, respectively, at 29 and 31 km altitude. [From Froidevaux *et al.,* 1985a].

The observed diurnal variation of about a factor of two (see Table 11-2) in ClO above 40 km, however, is not explained by $ClONO_2$ chemistry alone. Ko and Sze argue that formation of $HOCl$ via the recombination of ClO with HO_2 can provide an additional nighttime sink for upper stratospheric ClO, while photolysis of $HOCl$ can enhance daytime ClO above 40 km. These effects are included in the model whose results are given in Table 11-2.

Measurements of the diurnal variation in the *shape* of the ClO vertical profile, with better vertical resolution and coverage than is available in the diurnal data to date, would provide important additional tests of the theoretical models. The capability of such measurements now exists with the recently-developed *in situ* reel-down technique whose initial results are given by Brune *et al.,* [1985] and a 10x improvement

in the sensitivity of the balloon microwave limb sounder [Waters *et al.*, 1984] which was flown successfully in May 1985 obtaining data over a full diurnal cycle.

11.2 ATOMIC CHLORINE (Cl)

Chlorine atoms have been directly measured in the stratosphere only on two occasions (on July and December 1976), betwen ~35 km and 42 km altitude [Anderson *et al.*, 1977, 1980; NASA RP 1049, 1979]. The technique employed was *in situ* resonance fluorescence. The extremely low concentration of Cl make the observations very difficult. Current models (e.g., Ko and Sze [1984]) predict a Cl-atom concentration which is within a factor of two of these measurements, which can be considered as satisfactory agreement particularly in view of the sparcity of the data.

Indirect information on the Cl-atom profile below 35 km has been obtained from ethane (C_2H_6) measurements [Rudolph *et al.*, 1981], since the main stratospheric sink for this hydrocarbon is reaction with atomic chlorine. No new stratospheric ethane measurements have been reported since the time of the last assessment (1981). Figure 11-7 shows the existing C_2H_6 data together with a calculated profile, which was obtained by Ko and Sze [1984] with a 1-D model. The agreement is significantly better than with the older models [WMO, 1982] which overestimated the OH abundance in the lower stratosphere.

11.3 CHLORINE NITRATE ($ClONO_2$)

Chlorine nitrate ($ClONO_2$) is predicted to be a major temporary reservoir of chlorine in the middle stratosphere (25-35 km). It is formed by the recombination of ClO with NO_2 and removed in the daytime by photolysis. Chlorine nitrate plays several important roles in stratospheric chemistry. For instance, the observed diurnal variation of ClO (as discussed in the ClO section) is thought to be driven mainly by $ClONO_2$ chemistry. Formation of $ClONO_2$ also leads to strong coupling between the stratospheric chlorine
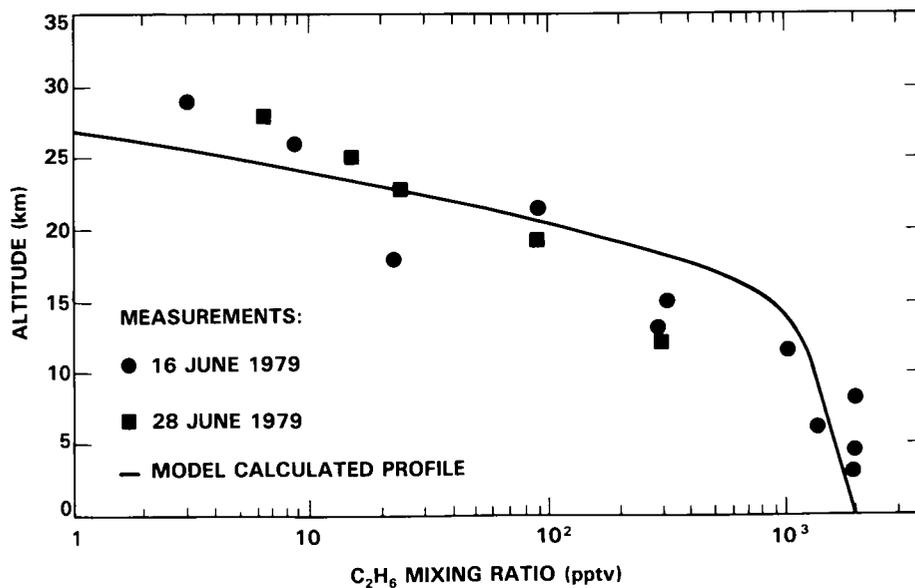
Figure 11-7. Comparison of C_2H_6 measurements [Rudolph *et al.*, 1981] with a one-dimensional calculation [Ko and Sze, 1983].

and nitrogen cycles. At high concentrations (> 12 ppbv) of stratospheric chlorine, this coupling involving $ClONO_2$ chemistry could lead to highly nonlinear response of ozone to chlorine perturbations (see Chapter 13 for a discussion of nonlinear chemistry). Measurements of $ClONO_2$ are not only important for better understanding of stratospheric chemistry, but also for the assessment of impacts on ozone of chlorine perturbations.

Evidence for the presence of chlorine nitrate ($ClONO_2$) in the lower stratosphere has improved during the period since the previous assessment report. The first claimed detection [Murcray et al., 1979] was based on measurements of the $ClONO_2$ band at 1292 cm^{-1}. This occurs in a spectral region of strong, closely spaced absorptions of several of the minor gases, making the positive identification and quantitative analysis of $ClONO_2$ very difficult. More recently, the same group has reported the results of balloon observations of the Q-branch of the longer wavelength band at 780 cm^{-1} [Rinsland et al., 1985b]. This feature, while still contaminated by weak absorptions of CO_2 and O_3, is generally more suitable for analysis. The necessary laboratory work to establish the frequencies and strengths of the interfering lines has been done, so as to allow the identification of residual $ClONO_2$ absorption to be made with confidence. The vertical distribution of $ClONO_2$ determined from these observations is reproduced here and found to be in reasonable agreement with model calculations (Figure 11-8).
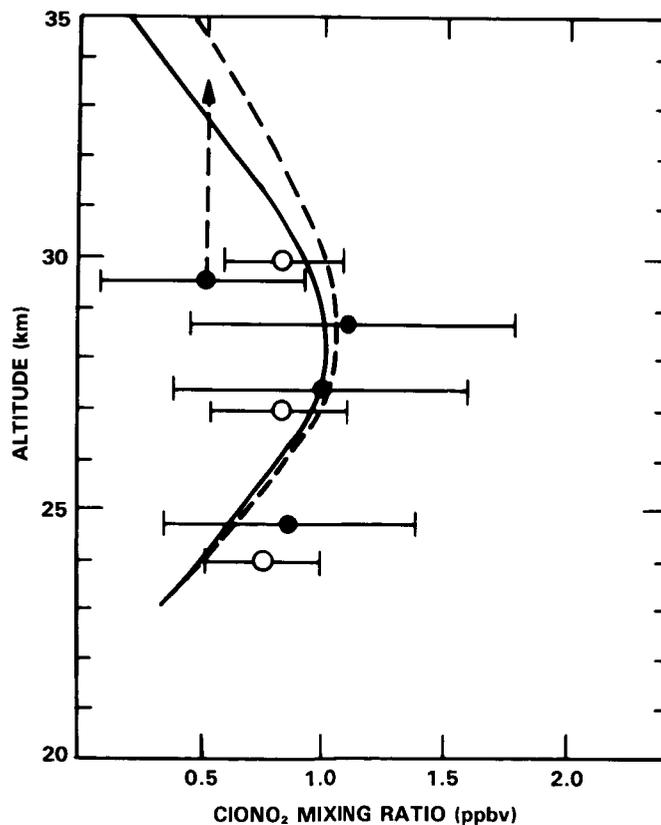
Figure 11-8. Mixing ratio profile of $ClONO_2$. The open circles are from Murcray et al. [1979] and the closed circles from Rinsland et al. [1985b]. Both sets of measurements were made at 33° N latitude. Model results corresponding to 30° N for noon (——) and sunset (——) are from Ko and Sze [1984], calculated with updated chemistry (Appendix A).

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The quantitative analysis of $ClONO_2$ at relative concentrations less than 10^{-9} by volume requires data of very high resolution and signal-noise ratio, and is hampered by the need to model the spectral structure of the Q-branch absorption from laboratory measurements which have been made under very different partial pressure conditions than occur in the stratosphere. Nevertheless within the realistic errors given with the profile derived by Rinsland et al. [1985b], it appears that the measured $ClONO_2$ distribution is in reasonable agreement with model predicitions. It is noted here that, at the time of writing, a preliminary examination of the ATMOS spectra obtained during the May 1985 Spacelab-3 flight confirms the presence of the $ClONO_2$ feature at 780.2 cm^{-1} [C. B. Farmer, private communication].

11.4 HYDROGEN CHLORIDE AND HYDROGEN FLUORIDE (HCl, HF)

11.4.1 Introduction

HCl has sources in both the troposphere and stratosphere; the principal tropospheric source is natural - the interaction between SO_4 and NO_3 ions and NaCl in ocean spray - although some tropospheric HCl originates from burning of plastics and from certain industrial processes. By contrast, the stratospheric source is primarily anthropogenic, (photolysis of halocarbons) with a minor fraction resulting from the reaction of OH with CH_3Cl released from the oceans and burning vegetation, and from direct injection of HCl into the stratosphere from volcanic eruptions. We thus expect HCl to show a characteristic vertical distribution having a minimum in the upper troposphere and lower stratosphere. The variability in this distribution might be expected to reflect the distribution of its surface sources, as modified by circulation and temperature, its sinks (primarily rainout) and perturbations to the stratospheric steady state chemistry resulting from volcanic activity.

HF, while in many ways the analog of HCl, differs from HCl in the respect that its source is stratospheric and (as far as is known) anthropogenic involving only the photolysis of halocarbons. HF has no known tropospheric source of significance. Thus monitoring the relative abundances of HCl and HF can provide the means for distinguishing between the man-made and the natural components of the stratospheric halogen burden and their variation with time. In addition, the ratio of HCl:HF provides an indirect check on stratospheric OH.

Almost all of the measurements of HCl and HF have been made by remote sensing spectroscopic methods, both at near IR wavelengths (by absorption) and, more recently, in the far infrared (by emission). Because the infrared spectrum of these gases is relatively simple and well understood, the techniques for their measurement have been developed to the point where a comparatively high level of precision and absolute accuracy can now be achieved. The situation regarding the shapes of the vertical distributions of HCl and HF, and the variability in their total column abundances, has improved considerably over the past three or four years. Current understanding of stratospheric HCl and HF is reviewed here under the headings of the vertical profile of concentration, latitude distribution, seasonal effects, temporal variation, and the effects of volcanic activity.

Measurements of stratospheric HCl have been made since 1975. Apart from the early in situ measurements of total acidic chlorine by filter collection techniques [Lazrus et al., 1976], the available data have almost exclusively been obtained from spectroscopic observations of the 1-0 vibration-rotation band at around 3000 cm^{-1} (3 μm), with the recent addition of far infrared emission measurements of pure rotation lines in the frequency range from 40 to 160 cm^{-1}.

Since the time of the last assessment (1981) there have been a number of additional studies of HCl from the ground, from aircraft and from stratospheric balloons. These include the accumulation of data on the total HCl column density and its variability from ground-based sites, aircraft surveys of the latitude dependence of the stratospheric HCl component, and extensive profile and column measurements made at 32 °N latitude during the two international Balloon Intercomparison Campaigns (BIC-1 and -2) in 1982 and 1983.

The improvement in the experimental techniques and the corresponding data quality achieved during these more recent investigations have yielded results which are of sufficient precision to reveal variability over a variety of spectral and temporal scales, including a systematic latitude dependence. The data from the balloon observations of June 1983 (BIC-2) provide a stratospheric vertical concentration profile (for the particular latitude and season) with an estimated accuracy of $\pm$ 15% over most of the 18 to 40 km altitude range - a considerable advance over the confidence that could be attached to the mean HCl profile given in the previous assessment. This result includes agreement between the data obtained from five different experiments, three of which were carried on the same gondola, (i.e., observing the same airmass).

The magnitude of the variability of HCl, seen particularly in the total column data taken from the surface, is too large to allow a long-term trend in the total HCl abundance to be established with confidence. However, the groundbased and aircraft results are in apparent disagreement in this regard. These separate aspects of the current status of knowledge of HCl in the atmosphere are discussed in detail in the following sections.

11.4.2 Hydrogen Chloride (HCl)

11.4.2.1 Vertical Concentration Profile

The large uncertainties and the wide spread of possible values associated with the mean vertical mixing ratio profile in the 1981 assessment report resulted from the fact that the data were obtained from a variety of different experimental methods and that the observations were made at different latitudes and seasons. From the earliest ground-based measurements of the total column abundance of HCl [Farmer et al., 1976] and the aircraft observations of the column above about 12 km by Mankin and Coffey [1983] it was apparent that the HCl concentration is variable both temporally (on relatively short time scales) and spatially (i.e., latitudinally, see later). It was not known to what extent the large spread of data combined into the 1981 profile was due to this variability as opposed to systematic differences between the results of techniques which had not been carefully intercompared. It was for this reason, together with the importance of HCl in the overall knowledge of the characteristic properties of the present stratosphere, that HCl was chosen as one of the principal molecular species for inclusion in the international Balloon Intercomparison Campaigns (BIC), which were conducted in fall of 1982 and summer of 1983. Although there have been additional observations of the stratospheric mixing ratio profile of HCl in the time period under consideration here, it is from the BIC observations that significant progress in obtaining high precision and confidence in the stratospheric vertical distribution has been obtained and which, in turn, has allowed the effects of experimental uncertainty and natural variability to be separated.

Figure 11-9 shows the individual concentration profiles obtained from the BIC-2 measurements [Farmer et al., private communication 1985]; details of the instruments and their observation modes are given in the figure caption. Three of the five profiles were obtained from instruments carried on the same gondola (i.e., observing the same airmass); these were the near-IR absorption measurements of AES and ONERA, and the far infrared emission results of SAO. The remaining two BIC profiles (from the UL absorption
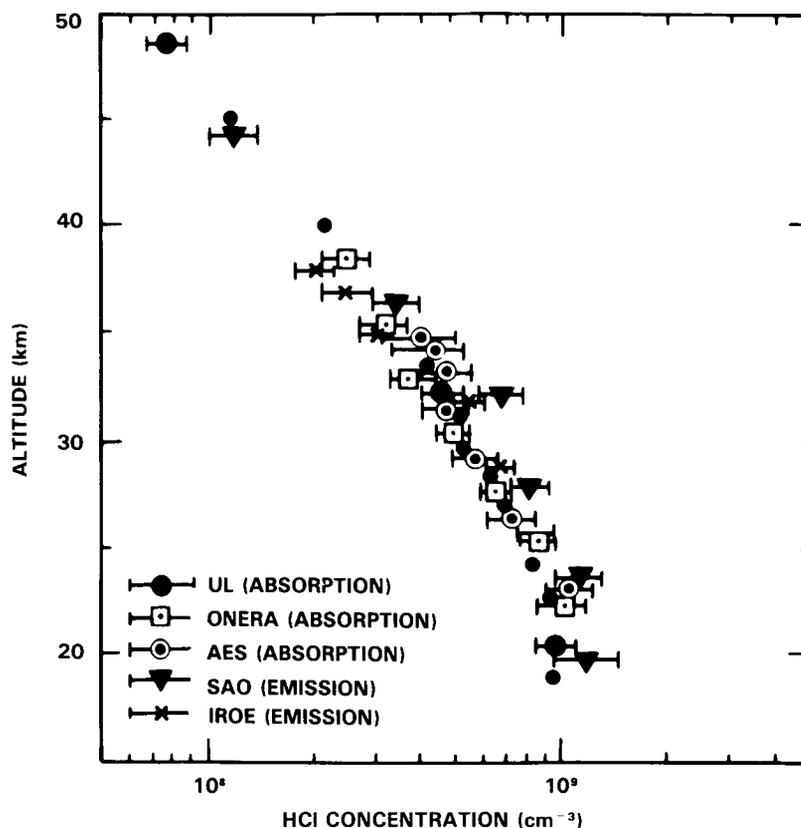
Figure 11-9. Results of measurements of the vertical distribution of HCl from BIC-2. The University of Liege (UL) and the Office National D'Etudes et de Recherches Aerospatiales (ONERA) data were obtained by absorption spectroscopy using grating instruments. The Atmospheric Environment Service, Canada, (AES) measurements were also by absorption, but used a Michelson Interferometer. The Smithsonian Astrophysical Observatory (SAO) and the Instituto di Ricerca sulle Onde Electromagnetiche (IROE) measurements were both made in the far infrared by emission, using high resolution Michelson Interferometers. The five instruments were carried on three separate flights (see text). The error bars represent the estimated errors from all sources except the uncertainty in the values of the molecular spectroscopic constants.

and the IROE emission measurements) were obtained on separate flights, one on the same day and one 3 days before the 3-instrument flight. The meteorological observations of the stratosphere made during the period of time covered by these flights indicate that all of the profile measurements sampled the same atmospheric parcel, so that differences between the profiles arising from any short-term or spatial variability are minimized.

The estimated final accuracies of the profiles are included in Figure 11-9. The weighted mean profile derived from the combination of all of the data is shown in Figure 11-10 together with the extreme values required to emcompass all of the estimated errors. The maximum uncertainty in the profile is not expected to exceed $\pm 15\%$. Figure 11-11 shows the same mean distribution in terms of volume mixing ratio together with the earlier (1981) profile for comparison. It should be noted that the observations of HCl made thus far have not been able to reach high enough altitudes to locate a maximum in the volume mixing ratio of HCl as a function of height.
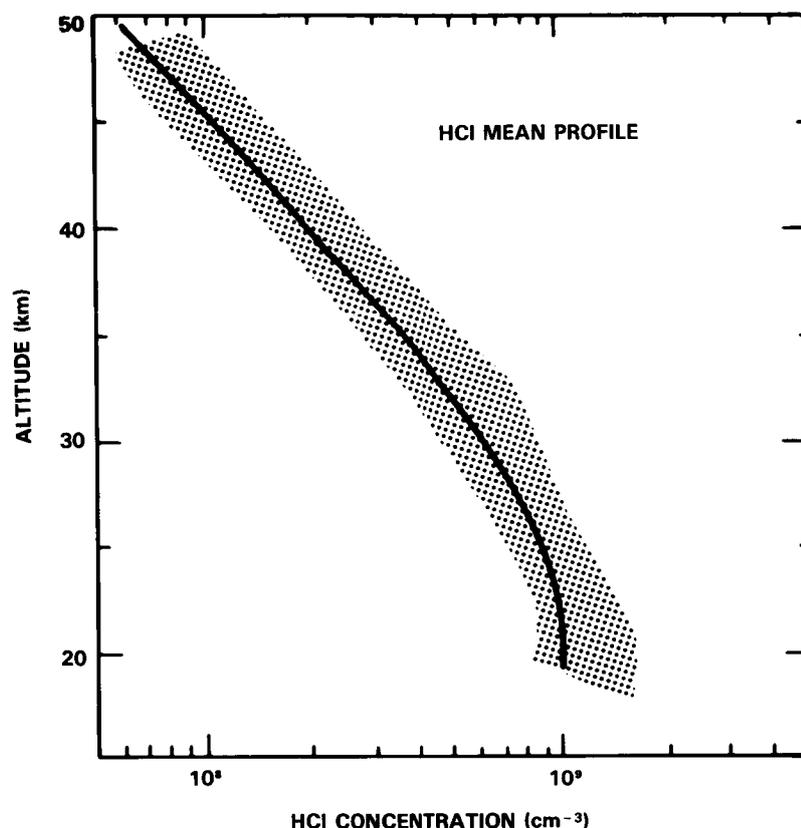
Figure 11-10. Weighted mean profile of concentration of HCl from data of Figure 11-9 (solid line). The hatched area represents the envelope of the estimated errors of all of the individual measurements.

The BIC-1 flights, which were made in late 1982 and involved some of the instruments used for BIC-2, gave profiles which were generally similar to the BIC-2 results but were associated with rather larger errors and uncertainties. The mean of the BIC-1 data gives a profile on the high side of the BIC-2 profile by about 20%, suggesting a marginally significant decrease from fall-winter of 1982 to the summer of 1983.

Observations of the vertical distributions of HCl are not only important for diagnosing certain key aspects of stratospheric chlorine chemistry, but also important for defining the stratospheric chlorine budget. The abundance of HCl in the upper stratosphere, for instance, is often taken as an approximate measure of total chlorine in the stratosphere. Since HCl is an inactive form (towards destruction of O_3) of stratospheric chlorine, its abundance relative to other active chlorine species (e.g., ClO) provides important clues to the efficiency of chlorine catalysis of ozone removal.

Plotted in Figure 11-11 is a theoretical profile of HCl calculated by Ko and Sze [1984] with updated rate data (see Appendix A). The model profile corresponds to summer conditions at 30 °N latitude. Comparing with the BIC data, the calculated concentration of HCl at around 30 km is about a factor of 2 lower. The agreement, however, is much better at around 20 and 40 km, where $ClONO_2$ is expected to be a minor form of chlorine. Interestingly, the observed HCl concentrations are closer to the sum of the calculated HCl and $ClONO_2$ concentrations. One possible interpretation of the HCl data is that models might have overestimated the abundance of stratospheric $ClONO_2$. However, $ClONO_2$ in amounts comparable to those
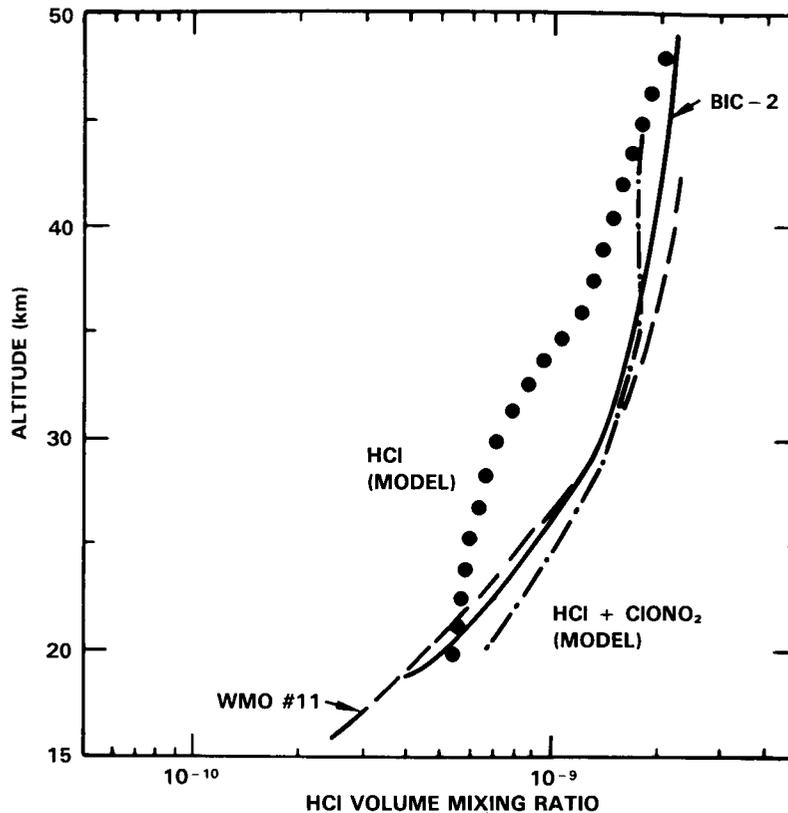
Figure 11-11. The weighted mean profile from Figure 11-9 reproduced as HCl mixing ratio by volume
(——) BIC-2 and compared with the mean profile of the last assessment (---), and the model prediction
of Ko and Sze [1984] for HCl (•••) and for HCl + ClONO₂ (·—·—).

predicted by models is needed to account for the observed diurnal variation of ClO (see Section 11.1.3). Another possible interpretation is that models might have underestimated the total stratospheric chlorine (Cl_x) burden. But higher total Cl_x would imply too much ClO in the model compared with observations (see Section 11.1.2). If this discrepancy persists, it could have serious implications for stratospheric chemistry and/or the chlorine budget. However, the discrepancy is not very significant at present, considering the lack of data on variability and on simultaneous observations for HCl, $ClONO_2$ and ClO.

11.4.2.2 Latitude Distribution of the Stratospheric Column

Whereas balloons have the advantage of altitude over other platforms for obtaining vertical profiles from limb scanning, they are generally not suitable for measurements of latitude distributions because they can be launched at only a few locations. Aircraft, on the other hand, can operate over a wide geographic range, and can cover a large range of latitude in a few days. Such measurements are extremely useful for understanding meridional transport. Aircraft observations, however, being made from below the bulk of the stratospheric HCl, are unable to obtain the detailed distribution of HCl in the stratosphere, although some information on the distribution is available in the variation of line of sight amount of absorber with observation angle. Since aircraft cannot reach altitudes at which the HCl concentration peaks, remote sensing methods from aircraft are required for measuring the latitudinal distribution of stratospheric column HCl.

Two groups, Girard and his colleagues [Girard *et al.*, 1978/79, 1982, 1983] and Mankin and Coffey [1983, 1984] have used spectrometers flown on aircraft to measure column HCl.

Girard *et al.*, made a series of nine flights in April and May of 1980, covering the latitude range from 62 °N. to 60 °S. They report the total vertical column of HCl and HF, along with several other trace gases, above, the flight altitude of 11.5 km. The analysis is based on measurements of the R2 line of $H^{35}Cl$ at 2944.92 cm^{-1}. Their results, which have an estimated precision of 15% and an estimated accuracy of 25%, show a minimum, below their detection limit of 0.8 x 10^{15} molec-cm^{-2}, at the equator, rising in both hemispheres. Their maximum value of 3.0 x 10^{15} is observed at 60 °N. [Girard *et al.*, 1983]. An earlier analysis of the same data [Girard *et al.*, 1982] was based on older values of the line parameters both for HCl and for interfering species, principally CH_4; these results have been superseded by the newer analysis and should be disregarded [N. Louisnard, private communication].

Mankin and Coffey [1983] made flights in both winter and summer over a five year period from 1978 through 1983, covering the Northern hemisphere only, from the equator to 70 °N. Their estimated precision and accuracy are 10% and 25% respectively. Generally their values are lower than those of Girard *et al.*, except that at 4.6 °N. they report a column of 0.54 x 10^{15} and at 6.1 °N. a value of 0.97 x 10^{15} molec-cm^{-2}. On average, their values are 45% lower than those of Girard *et al.* [1983]. The shape of the distribution is very similar to the findings of Girard *et al.*, Mankin and Coffey find that their data fit the equation

$$[HCl] = (3.41 - 2.77 \times \cos(\phi)) \times 10^{15} \text{ molecule } cm^{-2}$$

where ϕ the North latitude.

Figure 11-12 shows the aircraft measurements of the column amounts for both HCl and HF. In addition, the column amounts predicted by two different models are shown. There is good agreement between models and measurements for the shape of the latitude distribution, although there is still some question about the magnitudes of the values. We can conclude that the latitude distribution of HCl shows a minimum in the tropics and a strong latitude gradient to a value at 60-70° which is three or four times the tropical value. It is difficult to explain the difference in magnitude of the HCl column in the two similar experiments. Both experiments use a spectroscopic technique, Girard, a grille spectrometer and Mankin and Coffey a Fourier transform spectrometer; Mankin and Coffey have better spectral resolution (0.06 cm^{-1} as opposed to 0.15 cm^{-1}). Mankin and Coffey analyze two lines, R_1 and R_2, and both lines give comparable results. The differences in the two data sets are less than the errors in absolute accuracy, but many of the systematic errors should be common to both.

11.4.2.3 Temporal Variability of the Stratospheric Column

11.4.2.3.1 Seasonal Effects

The only data for stratospheric HCl obtained with a single instrument, which are extensive enough to allow any variation of HCl with season to be discerned, are the aircraft measurements of Mankin and Coffey [1983]. Their measurements were made in winter (December through early February) or in summer (late June and July) in the Northern hemisphere. There is some tendency for the summer measurements to be higher in total column, particularly at the higher latitudes, but the effect is small and it is difficult to distinguish the seasonal effects from the short-term variability. Zander (private communication, 1985)
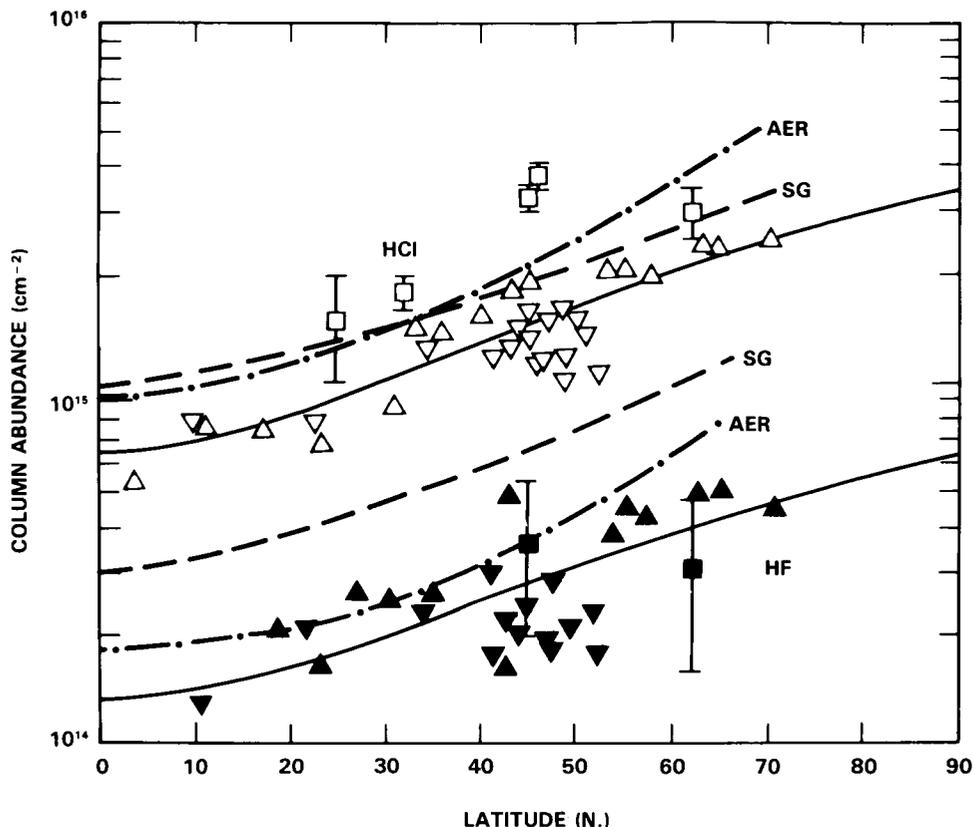
Figure 11-12. Latitude variation of the stratospheric column abundance of HCl and HF. The open and closed symbols correspond respectively to HCl and HF. The triangles are data from the aircraft measurements of Mankin and Coffey [1983], and the squares from Girard *et al.* [1983]. The solid lines are parametric fits to the Mankin and Coffey data (see text). The dashed lines are model predictions: AER from Ko *et al.* [1985], and SG from Solomon and Garcia [1984b].

has a long time series of observations of total column of HCl from the Jungfraujoch; here the stratospheric effects are somewhat obscured by variability in the tropospheric column (see discussion below), and no seasonal effects are clearly shown. Model calculations indicate that the HCl abundance should be smaller in the summer because of the larger amounts of OH corresponding to higher insolation. The seasonal variation should be small at equatorial latitudes and perhaps as large as 40% at high latitudes.

11.4.2.3.2 Short-Term Variability

When the aircraft data of Mankin and Coffey are corrected for the latitude dependence of the column amount above the cruising altitude of 12 km, the results show day-to-day differences which exceed the precision of the individual measurements, indicating some short-term variability of the stratospheric HCl burden. The authors note that, when interpreting their results in terms of both latitudinal and temporal variability, the residuals in the analysis are irregular; this may reflect monthly or seasonaly variability but will require further observations for a satisfactory description.

Figure 11-13 shows monthly means of the total HCl column content as deduced from observations carried out at the Jungfraujoch Station, Switzerland (3580 m altitude: 46.65° N; 8.0° E) between 1977 and 1984 [Zander, 1985]. Referring to that figure, the scatter of the arithmetic means (full points) is a direct indication of the variability of the total column of HCl on a monthly time scale. Furthermore, as the vertical bars between arrows correspond to the observational and analytical errors while their full amplitudes show the rms dispersions of the observations about the monthly arithmetic means, the differences between these two amplitudes are direct indications of the HCl variability on a day-to-day time scale. HCl column variations above the Jungfraujoch as large as 30% have been observed among measurements made during the same day.

Other, less extensive series of measurements from the ground-based sites have been made - e.g., at the Kitt Peak National Observatory, Tucson, Arizona, USA (hereafter KPNO: 2064 m altitude; 31.95° N; 111.60° W) and at the Observatoire de Haute Provence, Chiran, France (hereafter OHP: 1905 m altitude; 43.88° N; 6.18° E). The result of these measurements support variabilities of similar amplitudes as those observed above the Jungfraujoch [Zander and Johnson, private communication; Marche and Meunier, 1983].

In summary, the ground-based measurements show larger and more frequent changes in the total atmospheric content, on various time scales, than do the data for the stratosphere only. This result indicates that the tropospheric component of HCl is of significance relative to the total abundance both in quantity and in its variability.
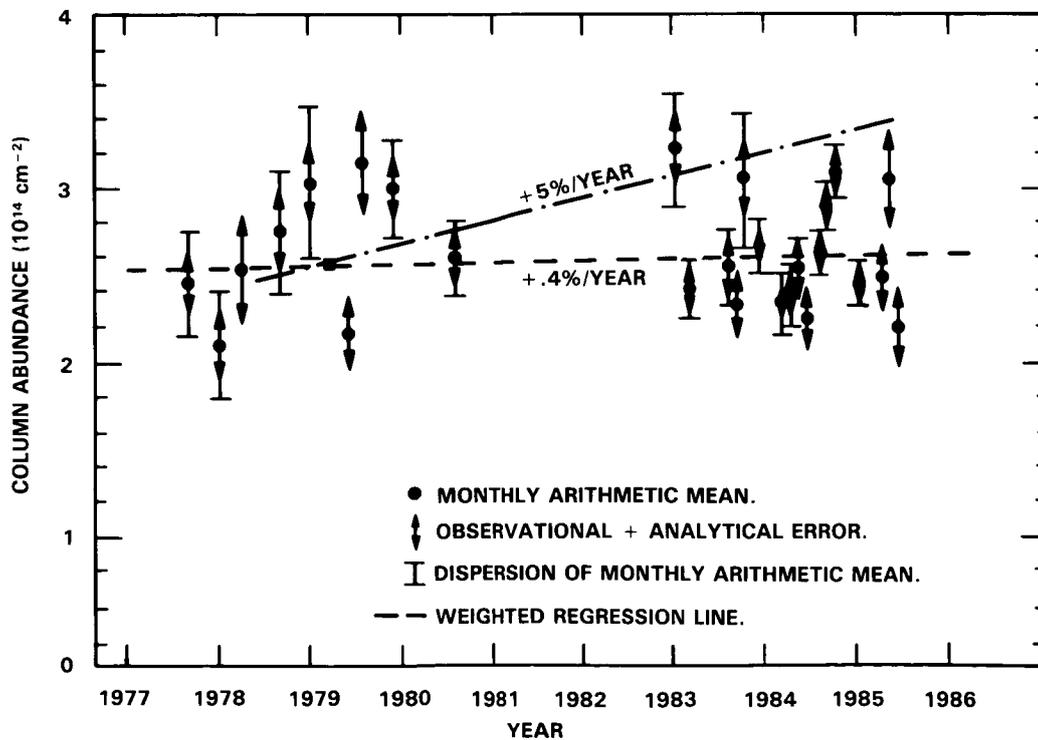
Figure 11-13. Observations of the total atmospheric column abundance of HCl over the Jungfraujoch Scientific Station from 1977 to 1984 (from Zander, [1985]).

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The first measurements in which an attempt was made to separate the tropospheric and stratospheric components were those of Farmer *et al.* [1976]. Their results indicated (as expected) a small scale height for tropospheric HCl, coupled with day-to-day variability of as much as a factor of 2. Recently, Vierkorn-Rudolph *et al.*, [1984] have reported on vertical profiles of hydrogen chloride in the troposphere. Their paper gives an idea of the background values of gaseous HCl in the mid-troposphere, between 1 and 7 km altitude. The mean results deduced from their *in situ* samplings by airplane, at 3 different locations, are reproduced on Figure 11-14. Although the data are far from being representative, they show that mixing ratios of 50 to 100 pptv are not unusual over the whole 3 to 7 km range. In air masses not influenced by continental sources, below 3 km, the variations are larger, with maximum values of up to 500 pptv. It is worth noticing here that Marche and Meunier [1983], investigating variability observed over OHP during June 1981, suggest that the total HCl could be inversly correlated with the tropopause height.
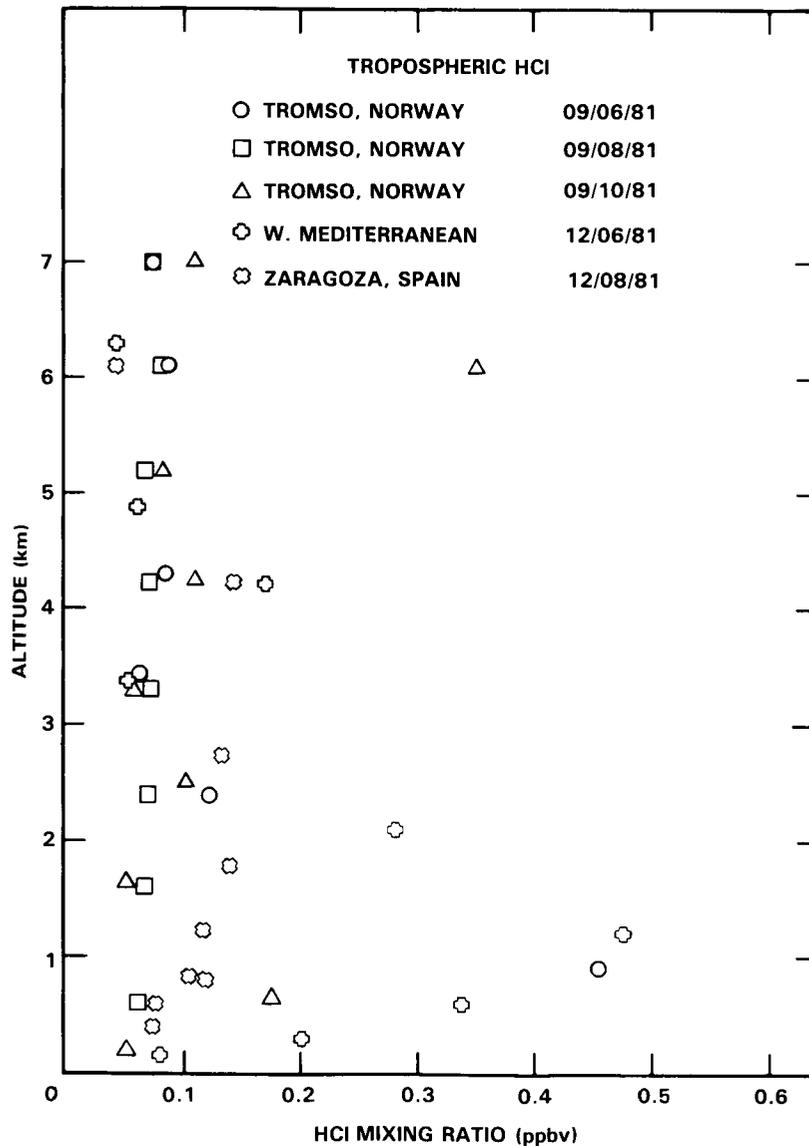
Figure 11-14. *In situ* measurements of the volume mixing ratio of tropospheric HCl at three locations (from Vierkorn-Rudolph *et al.* [1984]).

11.4.2.3.3 Long-Term Trend in HCl

On the basis of balloon observations carried out in May 1976, October 1978 and September 1979, Zander [1981] concluded that there was no significant change in the content of HCl above 30 km altitude, over the three year period covered by his flights up to that time. However, conflicting results deduced from the two most extensive series of observations available at the present time characterize the secular trend of hydrogen chloride; these are the airplane results from Mankin and Coffey [1983] and the ground-based observations from the Jungfraujoch.

From their airborne observations made between 1978 and 1982, Mankin and Coffey [1983] deduced a long-term trend in the integrated column of HCl above 12 km, amounting to an average increase of 5% per year. The conclusion was based on spectra in the latitude range 35-55° N, because that is the range with the largest number of observations, but the conclusion was the same if all of their data were included. The authors note that the fit of this rate of increase to their data leaves negative residuals for 1980 and positive residuals for earlier and later years. The measurements of Mankin and Coffey were made in four observation periods - winter 1978, summer 1978, winter 1979-80 and summer 1982. Measurements later in 1982 and 1983 were excluded from the fit because of the observation of a large amount of HCl injected into the stratosphere by the volcano El Chichon [Mankin and Coffey, 1984]. The summer 1982 observations were made at latitudes above 34° N where it is believed (based on lidar studies) that the volcanic debris had not yet reached. It is possible, however, that the HCl data in summer 1982, which have a strong effect on the magnitude of the fitted trend, were influenced by volcanic HCl.

Determination of the existence of a long-term trend is dependent upon the magnitude of any short-term variability that may be present. The available data base of aircraft measurements does not cover a long enough period, nor is it sampled frequently enough, to allow a long-term trend in the presence of substantial random variability to be determined. It is important that the aircraft program be continued in order to establish with certainty the secular trend of the HCl content of the stratosphere.

The weighted regression line drawn through the ensemble of monthly means from the Jungfraujoch observations, shown in Figure 11-13, indicates a linear increase in the total column of HCl of 0.4% per year. A sizable and highly variable portion of the HCl column measured from the Jungfraujoch is tropospheric, so the rate of increase of the stratospheric HCl could be significantly larger. Unfortunately, the magnitude of the tropospheric contribution is not known. It should be noted that if the fit had been restricted to observations up through July 1982 (as was the case with the data fit by Mankin and Coffey) the indicated trend would have been around 5% per year (dash dotted line in Figure 11-13). This illustrates the importance of a long time series in determining trends in the presence of short-term variability.

The KPNO observations carried out between 1977 and 1983 indicate a yearly increase in the total HCl content equal to about 1%. Measurements of the integrated column of HCl above Reims and OHP, published by Marche et al. [1980a,b] and Marche and Meunier [1983] covering the period 1979 to 1981, do not reveal any significant trend. The OHP results obtained in 1983 during the Map-Globus intercomparison campaign also support this conclusion [Marche, private communication].

While model calculations predict a trend in stratospheric HCl of 3 to 5% per year, it is not possible to draw any satisfactory conclusion as to its actual magnitude from the available observational data. Further measurements from aircraft and from the ground, made more frequently and with better coordination, are needed to provide a clear understanding of the variability and trend of the tropospheric and stratospheric components of the HCl burden.

11.4.2.4. Effects of Volcanos

In their original paper on the effects of chlorine on stratospheric chemistry, Stolarski and Cicerone [1974] considered volcanos as a possible source of stratospheric chlorine, concluding that they are probably one of the most important sources. Until recently, there was little evidence of significant volcanic input to the stratospheric chlorine budget. Johnston [1980] estimated from studies of the chlorine content of magma and ash, and from morphology of the volcanic plume, that the Augustine volcano in Alaska injected 84,000 to 180,000 tons of HCl into the stratosphere during its January 1976 eruptions. Mankin and Coffey, observing six months after the eruptions of El Chichon in March and April 1982, saw approximately 40% enhancements of the HCl column at latitudes where they were under the cloud of volcanic debris [Mankin and Coffey, 1984]. They estimated that the increased HCl amounted to 40,000 tons. These amounts are equivalent to a sizable fraction of the annual production of fluorocarbons. Thus, we conclude that volcanoes can occasionally be a substantial contributor to the stratospheric chlorine budget. Volcanic eruptions that inject a large amount of material into the stratosphere can perturb the ozone layer by a variety of chemical, radiative, and dynamical effects. The major eruptions, however, are infrequent events and their effects are transitory; they probably have a minor effect on the stratospheric ozone in the long term.

11.4.3 Hydrogen Fluoride (HF)

Hydrogen fluoride is the only sink for fluorine in the stratosphere. So far as is known, it does not actively participate in the chemistry of the stratosphere. It is quickly formed after the photolysis of fluorocarbons and is stable, ultimately diffusing to the troposphere where it is rained out. It has no known source except photodecomposition of fluorcarbons. Comparison of HCl and HF can give some indication of the relative abundances of natural and anathropogenic halogens in the stratosphere, since HCl has both natural and manmade sources.

HF has a strong infrared spectrum, both in the pure rotation region and the rotation-vibration fundamental near 4000 cm^{-1}. Both of these bands have been used for the measurement of HF from balloons, the near infrared in absorption against the sun and the far infrared in emission. The near infrared band includes lines that may be seen from the surface and both ground-based and aircraft observations have been used to measure the total column. Because there is very little tropospheric HF, the ground based measurements give essentially the stratospheric column.

11.4.3.1 Vertical Concentration Profile

Since the time of the last assessment, additional measurements of the vertical profile of HF have been made as part of the Balloon Inter-comparison Campaigns (BIC-1 in Sept. 1982, BIC-2 in June 1983). HF was a molecule of secondary importance for BIC, so there are comparatively few measurements.

The vertical profile from BIC-2 is shown in Figure 11-15. Measurements from three instruments are shown: vertical profiles from two far infrared interferometers and a single point from a near infrared grating spectrometer (open circle). The single point gives the total column above the 34 km float altitude, interpreted as a uniform mixing ratio above that altitude. The error bars are somewhat wider than for HCl because there are fewer measurements and less effort has been used in refining them. Also plotted in Figure 11-15 is a theoretical HF profile calculated by Ko and Sze [1984] with the updated kinetic data of Appendix A.
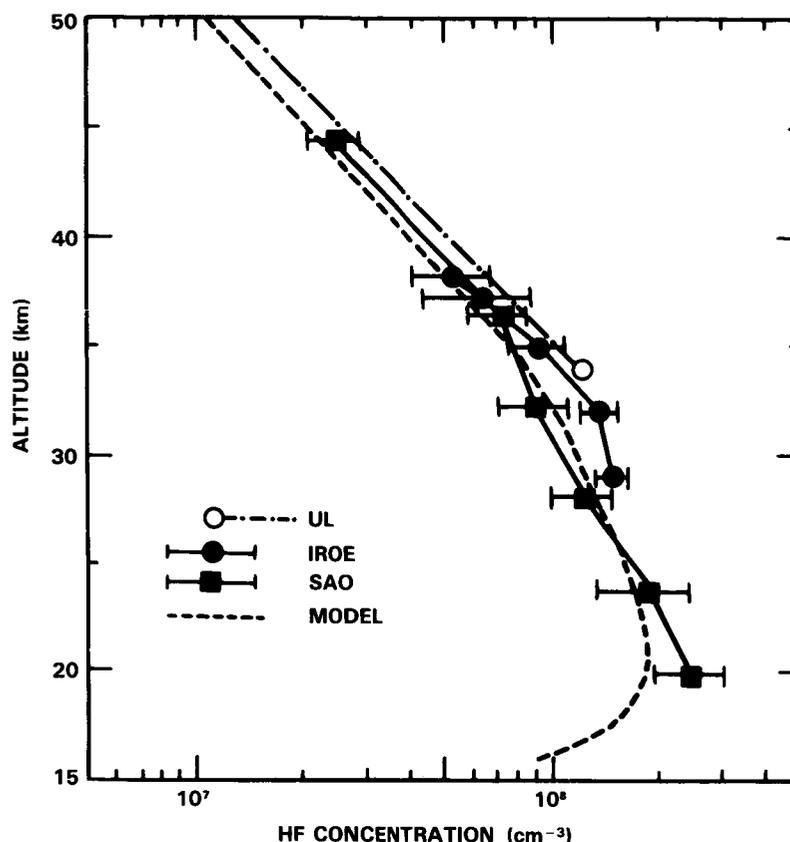
Figure 11-15. Results of measurements of the vertical distribution of HF from BIC-2. The flights on which the data were obtained are the same as for Figure 11-9. The dashed line is the model prediction of Ko and Sze [1984].

The BIC-1 results, from only two instruments, are similar in magnitude but show an intriguing difference in shape of the profile, with a mixing ratio minimum near 27 km. The aircraft and ground based measurements of the total column of HF are consistent with the integrated profiles from the balloons.

11.4.3.2 Latitude Distribution

Measurements of the total column of HF above 12 km as a function of latitude have been made from aircraft by two groups, on the same flights as those on which they measured the HCl columns. Girard et al. [1983] made a series of nine flights covering the range 62 °S to 60 °N. Mankin and Coffey [1983] report data from 26 flights from 10 °N to 70 °N. In the Northern Hemisphere, there is generally good agreement between the measurements of the two groups (see Figure 11-12), although Girard et al. report only upper limits for latitudes between 40 °N and the equator.

The shapes of the distributions are very similar for HCl and HF. The Southern Hemisphere measurements of Girard et al. do not show any significant differences from the Northern Hemisphere measurements.

11.4.3.3 Temporal Variability

There is some evidence for short term temporal variability from measurements of the total column of HF. Figure 11-16 reproduces the monthly means of the total column amount as deduced from near-infrared solar observations made at the Jungfraujoch, between October 1976 and December 1984 [Zander, private communication, 1985]. The vertical scatter of the monthly arithmetic means (full points) gives an indication about variability of the total column of HF. As for HCl, the vertical bars between the arrows correspond to the observational errors, while their full amplitudes give the rms deviations of the means. The differences between these two amplitudes are indicative of the HF variability on a day-to-day time scale: the largest differences (e.g., March 1977, March 1978, Feb. 1984) occur when stratospheric polar air, enriched in HF, intrudes towards lower latitudes and lower altitudes. (The correlation with increasing ozone column amounts is striking on some occasions).

Between June and July 1981, Marche and Meunier [1983] observed a decrease of 13% in the monthly mean total HF content above Haute Provence. Observations carried out during 1982 at KPNO show monthly and daily variabilities exceeding 15% on many occasions [R. Zander and D. Johnson, private communication].

The aircraft measurements of Mankin and Coffey in the 40-50 °N range (containing the largest number of observations) provide further evidence of variability. The standard deviation of these points from their mean (corrected for the observed latitude variation) is 37%, substantially greater than the estimated precision of 10%. Part of this variance is doubtless due to a long term trend (see below), but a portion is clearly
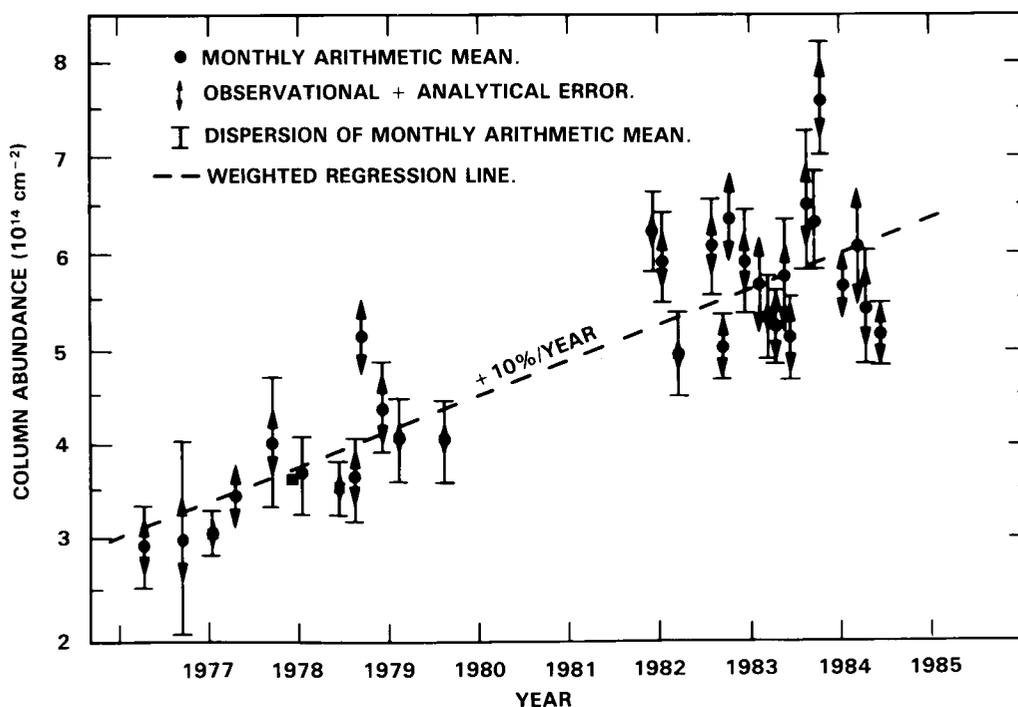
Figure 11-16. Observations of the total column of HF above the Jungfraujoch Station from 1976 through 1984 (from Zander private communication, 1985).

short term variation. Because the aircraft data set is less extensive than the ground based data set, it is not possible to establish as clearly from it the magnitude and time scale of the variability. There is no detectable seasonal variation in either the ground based or aircraft columns from the data availabe to date.

11.4.3.4 Trend in HF

There is good agreement among the various results deduced during recent years regarding the hydrogen fluoride secular increase in the atmosphere.

First, from their airplane observations at 12 km altitude, Mankin and Coffey [1983] have reported a linear temporal trend in the total column of HF above cruising altitude, equal to 12% per year for the period 1978-1982: that trend, because of the latitudinal variation of the HF content (discussed elsewhere), was based on data obtained between 35 and 55 °N, normalized to an effective latitude of 45 °N. Second, from the ground-based measurements of the total column of HF above the Jungfraujoch station, the weighted regression line drawn through the total set of the data (shown in Figure 11-16) leads to a linear increase of 10% per year between 1977 and 1984. Treating the data as two separate but representative groups of results, a cumulative increase of 9% per year between mid-1978 and the fall of 1983 is obtained.

The HF observations of Marche and Meunier [1983], obtained between 1979 and 1981, support a trend of 10% per year. The observations at KPNO, made between 1977 and 1984, confirm a yearly increase in the integrated amount of HF equal to ~10% [R. Zander, private communication].

The Jungfraujoch, data of Figure 11-16 gives HF column abundances which are almost a factor of two larger than the corresponding aircraft results (Figure 11-2), at the appropriate latitude and time. Although the discrepancy cannot be satisfactorily explained, much of it can be attributed to the intrinsic uncertainties associated with the measurement techniques themselves. It might be pointed out that a comparison of Figures 11-12 and 11-13 also indicates an apparent discrepancy in the HCl data, but in this case it can be attributed to the tropospheric HCl contribution, which can be 30–50% of the total column.

11.4.4 HCl/HF RATIO

While HF measurements can serve as an indicator for monitoring the quantities of chlorofluoromethanes destroyed by photolysis in the stratosphere, the concentrations of HCl provide insight into both the total chlorine budget of the stratosphere and the importance of competing reservoirs (such as HOCl and $ClONO_2$). Their relative long-term trends provide a test of the validity of the chemistry of the present models. Furthermore, HF and HCl measurements, when carried out simultaneously, may help in establishing the relative influence of natural versus anthropogenic sources of stratospheric chlorine. From the results reported in the previous paragraphs, the following HF/HCl ratios can be derived:

Mankin and Coffey [1983], using all their reported data for 1978 through 1982, and ignoring temporal variations, obtain an average HF/HCl ratio of 0.2 ± 0.08, with no significant latitude variation. This value corresponds to the mean time of their observations, i.e., 1980, and it is an average for the whole stratosphere above 12 km altitude.

Due to the variability seen in the total columns of both HF and HCl observed from the ground, an isolated measurement of the ratio will not be representative of the mean atmospheric content of these molecules above the point of observation. Therefore, the values of that ratio given below are averages of series of measurements made over selected time intervals.

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When treating the Jungfraujoch results as two separate ensembles the following mean values for the HF/HCl ratio are obtained:

Group A (March, 1977 to September, 1978) HF/HCl = 0.15 ± 0.03
Group B (June, 1982 to December, 1984) HF/HCl = 0.22 ± 0.03

The HF/HCl ratio deduced from the results for Haute Provence [Marche and Meunier, 1983] is 0.29 ± 0.05. Marche and Meunier suspect the presence of a local source of hydrogen fluoride which enhances the tropospheric content of HF above OHP; while this possibility needs further assessment, it would explain the higher values of the HF/HCl ratios above central France. Above KPNO the mean HF/HCl ratio is 0.15 ± 0.04 for the period May 1977 through October 1979.

It should be noted that the Jungfraujoch as well as the Haute Provence data include tropospheric contributions, while the Mankin and Coffey results are for the stratosphere only. The theoretical HF/HCl ratio for the stratosphere estimated for the year 1982 by Ko and Sze [1984] is 0.18, a value which is in good agreement with observations.

11.5 STRATOSPHERIC DISTRIBUTION OF HALOCARBONS

Since 1980 stratospheric profiles of many halocarbons have become available. These include fully halogenated methanes, such as CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, CF_4, $CBrClF_2$, and $CBrF_3$; fully halogenated ethanes, such as CCl_2FCClF_2, $CClF_2CClF_2$, $CClF_2CF_3$, and CF_3CF_3; and hydrohalocarbons whose overall atmospheric lifetimes are longer than 1 year: CH_3Cl, CH_3Br, $CHClF_2$, and CH_3CCl_3.

The origins and sources of halocarbons are discussed in Chapter 3. These compounds are transported into the stratosphere where they are photochemically decomposed to provide sources of chlorinated free radicals. The most important halocarbons are CCl_4, CCl_3F, CCl_2F_2, CH_3CCl_3 and CH_3Cl--all of which have a tropospheric abundance in excess of 100 pptv. These are also the halocarbons that have been included in most models used in the assessment of stratospheric ozone perturbations (see Chapter 13).

Knowledge about the vertical distributions of halocarbons is important for several reasons. First, the vertical gradients of these species provide important information regarding their photochemical removal rates, and also regarding transport processes. Second, stratospheric abundances of each halocarbon help define its relative contribution to the stratospheric chlorine or fluorine budget.

Most of the available data on the vertical distribution of halocarbons have resulted from the analysis of air samples collected aboard aircraft and balloon platforms. The analytical techniques employed, i.e., gas chromatography (GC) and mass spectrometry (MS), have been reviewed by Penkett [1981]. Both grab-sampling (with and without a compressor) and cryogenic sampling have been applied successfully. Only very few data have so far been obtained by means of other methods such as infrared spectroscopy. This section focuses on new stratospheric data, most of which have been obtained by cryogenic sampling experiments carried out in southern France (44 °N). Previous stratospheric data for CCl_3F, CCl_2F_2, and CH_3Cl have been compiled and reviewed in the WMO Report #11 [1982].

11.5.1 CCl₄ (FC-10)

Prior to 1980, aircraft samples provided scattered CCl_4 data for various latitudes and altitudes of the lower stratosphere [Lovelock, 1974; Robinson *et al.*, 1977; Seiler *et al.*, 1978; Tyson *et al.*, 1978; Rasmussen

and Khalil, 1980], and sampling aboard U2 aircraft provided data up to about 20 km [Krey *et al.*, 1977; Vedder *et al.*, 1978; Leifer *et al.*, 1979a, 1979b, 1981]. These early measurements are compiled in a review article by Fabian [1985].

The first stratospheric profile of CCl_4 was obtained by Borchers *et al.* [1983]. Stratospheric samples collected cryogenically on September 20, 1982, by means of the MPAE sampler were analyzed in turn at Max Planck Institut fur Aeronomie (MPAE) Lindau/Germany by GC with Electron Capture Detection (ECD) (profile "a" in Figure 11-17) and by gas chromatography mass spectrometry (GC-MS) at AERE Harwell, Great Britain (profile "b"). The precision of both sets of analyses was ± 10% or 0.1 pptv, whichever is greater. The absolute calibration by 2-step static dilution was made at AERE to better than ± 10%. The 4 lowest samples were used to determine the calibration factor for the MPAE profile.

Two data sets obtained from stratospheric samples collected with the cryogenic sampler of KFA Julich, on October 21, 1982, and on September 10, 1983 [Knapska *et al.*, 1985a] are also displayed in Figure 11-17 (c-f). The analyses of these samples were made at KFA by GC-ECD (c and e) and at AERE by GC-MS (d and f) in turn. The precision of both sets of analyses is given as ± 10% or ± 0.2 pptv, whichever is greater. The absolute calibration was performed to better than ± 5% against a Harwell standard.
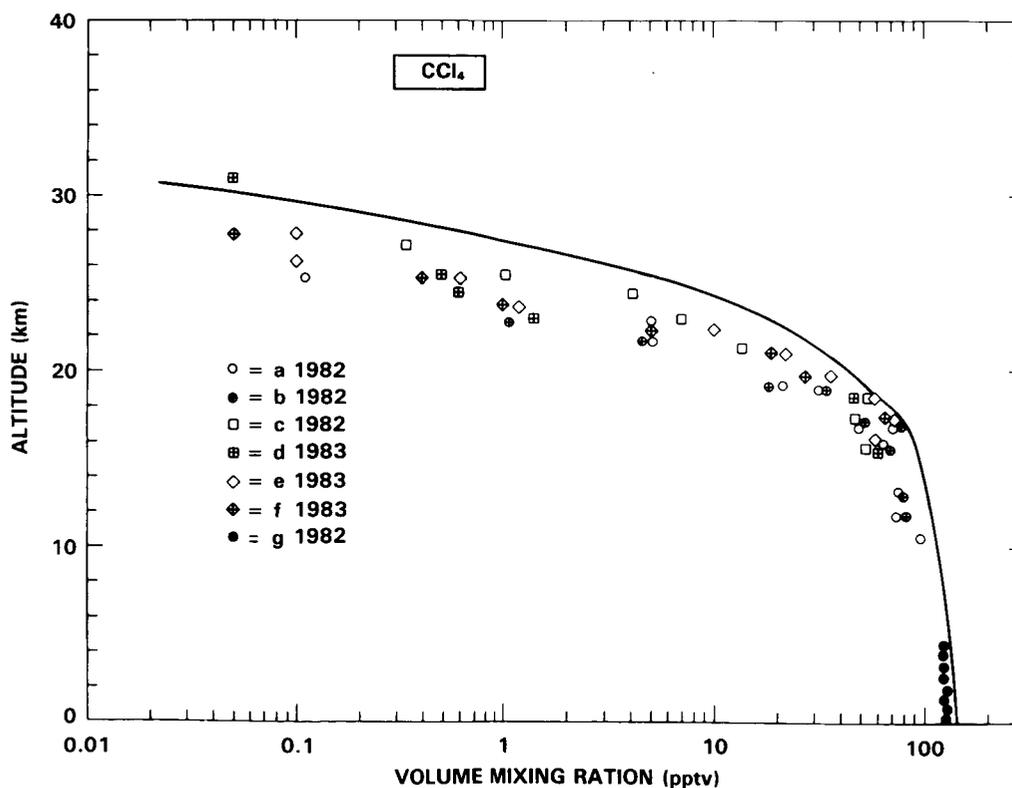
Figure 11-17. Vertical distribution of CCl_4 (FC-10) at northern midlatitudes.

a,b: [Borchers *et al.*, 1983]

c-f: [Knapska *et al.*, 1985a]

g: [Rasmussen and Khalil, 1983b]

The year of measurement is indicated in the figure. The solid line is for latitude 47°N calculated by a 2-D model [Ko *et al.*, 1985].

Although these published data sets appear to agree reasonably well, the data by Borchers *et al.* are generally lower than those by Knapska *et al.* On the other hand, the latter ones show larger discrepancies between the GC-ECD and GC-MS results as compared to Borchers *et al.* It should be noted again that both data sets are based on the same absolute calibration method. A tropospheric CCl_4 profile obtained by Rasmussen and Khalil [1983b], at about 70°N, is shown for comparison (profile "g"). It indicates CCl_4 mixing ratios of about (120 ± 2) pptv. This profile has been scaled down by a factor of 0.8 to take into account a recent recalibration of the measurements, as is the case for CH_3CCl_3 [Khalil and Rasmussen, 1984a].

The height dependence of the older aircraft data is consistent with the stratospheric profiles presented here (see Fabian [1985]), although absolute values were generally lower at that time. It appears reasonable to establish a mean 1982/83 profile of CCl_4, representative of northern midlatitude conditions, as an average of the data presented in Figure 11-1. The absolute scale of this profile may have an error of up to ± 10%.

11.5.2 CCl_3F (FC-11)

Stratospheric profiles of CCl_3F measured prior to 1980, at northern midlatitudes and in the tropics, are compiled in the WMO-Report #11 [1982]. New CCl_3F data from northern midlatitudes are displayed in Figure 11-18. The stratospheric data resulting from GC analyses of air samples collected with the MPAE
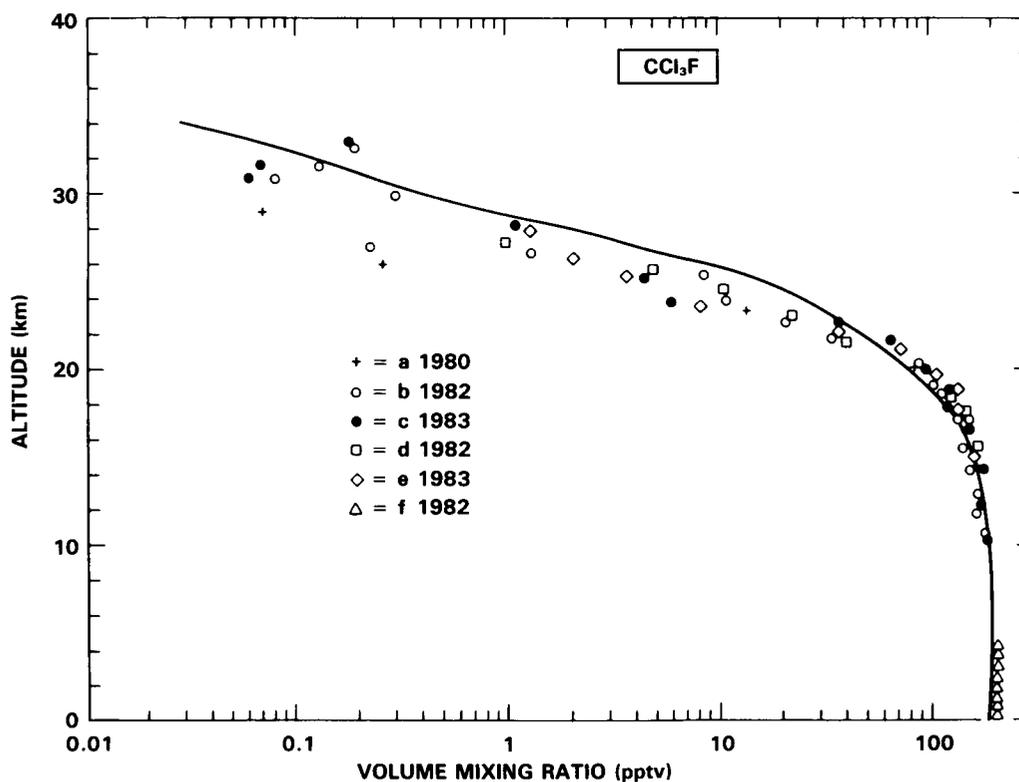
Figure 11-18. Vertical distribution of CCl_3F (FC-11) at northern midlatitudes.
a: [Fabian *et al.*, 1981a]
b: [Borchers and Fabian, private communication 1985]
c,e: [Schmidt *et al.*, 1985a]
d: [Schmidt *et al.*, 1984, Knapska *et al.*, 1985a]
f: [Rasmussen and Khalil, 1983b]
The solid line is for latitude 47°N calculated by a 2-D model [Ko *et al.*, 1985].

(profiles a-c) and KFA cryogenic samplers (profiles d and e) are supplemented by a tropospheric profile of (205 ± 2) pptv measured at 70°N [Rasmussen and Khalil, 1983].

While profile "a" results from GC-MS analysis made at AERE Harwell with a precision of ± 15% [Fabian et al., 1981a], analyses of "b" and "c" were performed at MPAE Lindau by GC-ECD, with ± 5% precision [Borchers and Fabian, private communication 1985; Schmidt et al., 1985a], and "d" and "e" by GC-ECD at KFA Julich with ± 3% quoted precision [Schmidt et al., 1984, 1985b]. The detection limit was 0.1 pptv for all profiles, while the quoted error of the absolute calibration was ± 10% and ± 5% for a-c and d-e, respectively.

11.5.3 CCl$_2$F$_2$ (FC-12)

As CCl_2F_2 is usually analyzed along with CCl_3F, the data base of both halocarbons is almost identical. The new profiles a-f shown in Figure 11-19 refer to the same groups and techniques as those in Figure 11-18. The quoted precisions for CCl_2F_2 are ± 15% for a, ± 5% for b and c, and ± 3% for d and e. The detection limit was 0.2 pptv for a-e, while the absolute calibration was achieved to better than ± 10% and ± 5% for a-c and d-e, respectively. The tropospheric abundances of CCl_2F_2 as measured in May 1982, at 70°N (f), are (353 ± 3) pptv. As for CCl_3F, the slope of the profiles shown in Figure 11-19 is consistent with that of the older data compiled in the WMO-Report #11 [1982], while the absolute values are clearly higher indicating the growth of the CCl_2F_2 abundance with time.

11.5.4 CClF$_3$ (FC-13)

This halocarbon is used as a refrigerant either by itself or in an azeotropic mixture with CHF_3 (refrigerant 503) for very low temperature applications [Chou et al., 1978]. It was measured in the atmosphere for the first time in 1979: while Rasmussen and Khalil [1980] found (3.6 ± 0.7) pptv and (3.2 ± 0.5) pptv in clean tropospheric air of Antarctica, Penkett et al. [1981] measured 3 pptv for both hemispheres.

The first stratospheric profile of $CClF_3$ was obtained by GC-MS analysis of air samples collected On September 25, 1980, with the MPAE cryogenic sampler, at 44°N [Fabian et al., 1981a]. The analytical precision was ± 15% or ± 0.5 pptv, whichever is greater, while the absolute calibration was achieved to better than ± 10%.

$CClF_3$ data are shown in Figure 11-20. More measurements of this halocarbon, for which no data of global release rates are available, would be useful.

11.5.5 CF$_4$ (FC-14)

Atmospheric CF_4 is thought to originate from anthropogenic (aluminum production) and possibly natural sources (see reviews by Cicerone [1979] and Fabian [1985]). Its tropospheric abundance was first measured by Rasmussen et al. [1979] and Penkett et al. [1981] as (67 ± 10) pptv. In the stratosphere, CF_4 was first measured by Goldman et al. [1979], who determined a mixing ratio of 75 pptv at 25 km. A complete stratospheric profile (Figure 11-21) was obtained by GC-MS analysis of air samples collected on September 25, 1980 [Fabian et al., 1981a]. It confirms that CF_4 must have a very long atmospheric lifetime which had been estimated by Cicerone [1979] as more than 10,000 years. From the quoted precision of the stratospheric data given as ± 15%, it cannot be concluded whether or not the slight decrease from 72 pptv at 10 km to 60 pptv at 33 km is real; more measurements are needed to settle this question.
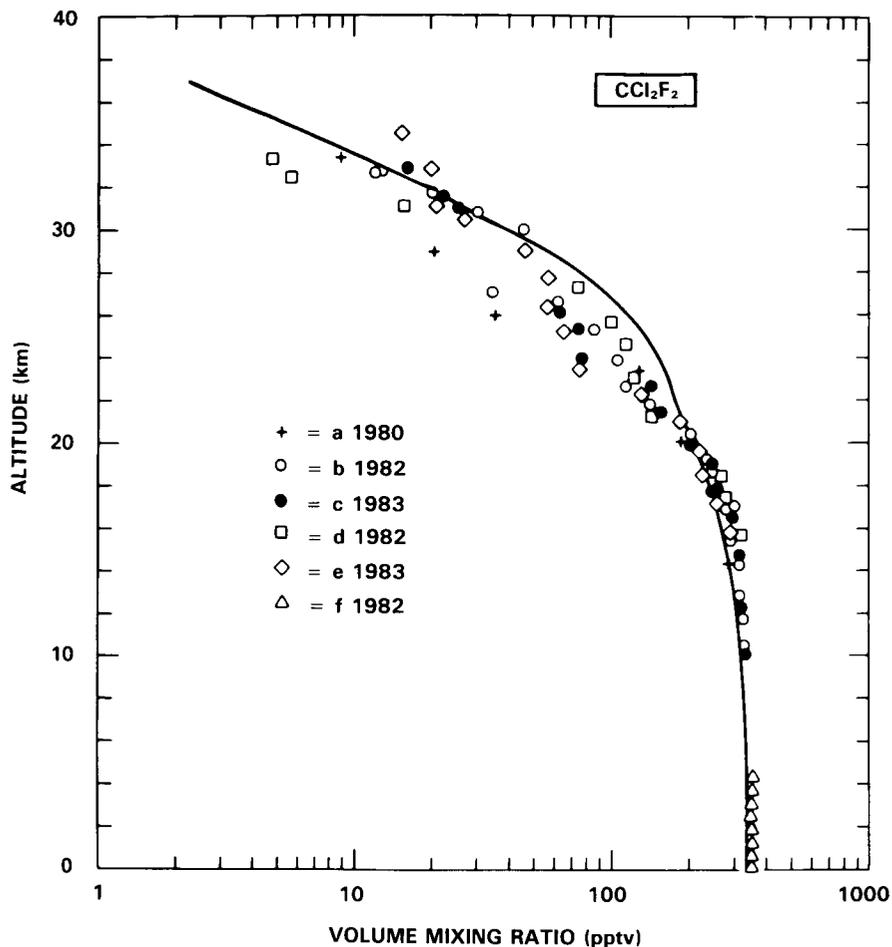
Figure 11-19. Vertical distribution of CCl_2F_2 (FC-12) at northern midlatitudes.

    a: [Fabian *et al.,* 1981a]
    b: [Borchers and Fabian, private communication 1985]
    c,e: [Schmidt *et al.,* 1985a]
    d: [Schmidt *et al.,* 1984, Knapska *et al.,* 1985a]
    f: [Rasmussen and Khalil, 1983b]
The solid line is for latitude 47 °N calculated by a 2-D model [Ko *et al.,* 1985].

11.5.6 CBrClF₂ (FC-12B1)

This bromine-containing methane is used as fire extinguisher. Rasmussen and Khalil [1984c] report tropospheric abundances of (1.1 ± 0.1) pptv measured at 70 °N during 1983. A tropospheric profile resulting from GC-ECD analysis of aircraft samples collected at 70 °N, during May 1979, is shown in Figure 11-22.

Stratospheric profiles of $CBrClF_2$ were obtained for the first time by Lal *et al.* [1985] by GC-ECD analysis of samples collected with MPAE cryogenic samplers, on September 20, 1982, September 10, 1983, and October 1, 1984 (Figure 11-22). Thus, the vertical stratospheric distribution could be measured for 3 consecutive years, with an analytical precision of ± 5% or 0.03 pptv, whichever is greater. The absolute calibration was achieved by 2-step static dilution within ± 10% accuracy. Repetitive analyses
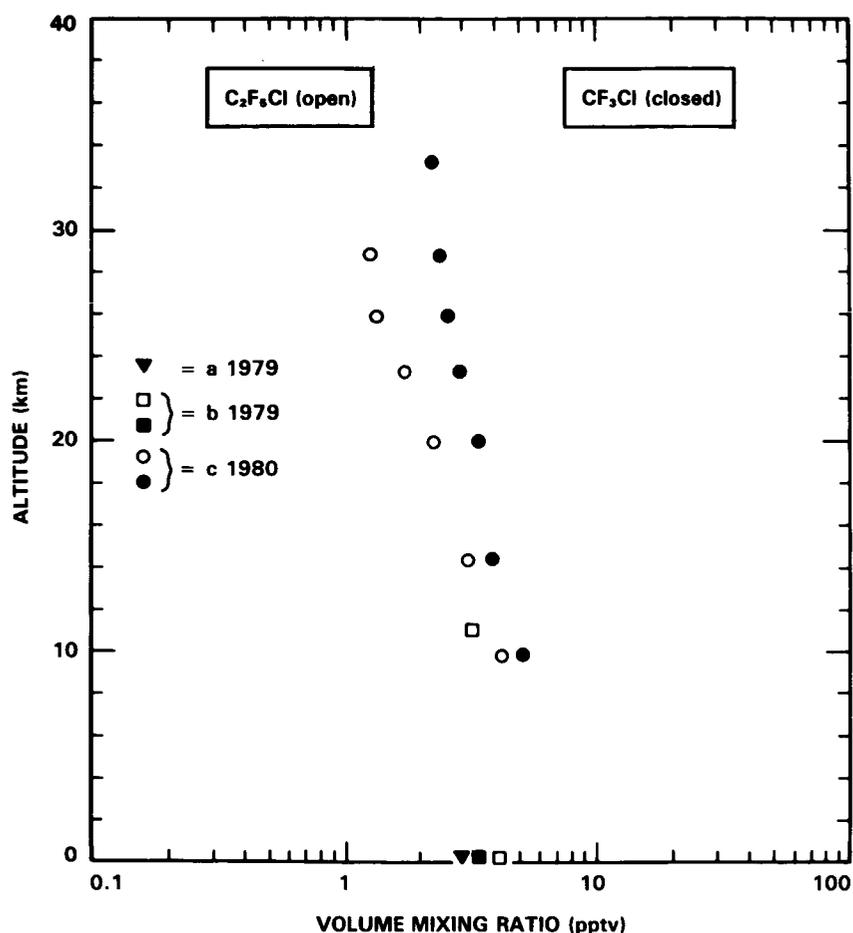
Figure 11-20. Vertical distribution of CF_3Cl (FC-13) and of $CClF_2CF_3$ (FC-115) at northern midlatitudes.

a: [Rasmussen and Khalil, 1980]
b: [Penkett *et al.*, 1981]
c: [Fabian *et al.*, 1981a]

and cross-checks were carried out to ensure that the rapid increase of $CBrClF_2$ mixing ratios observed in the lower stratosphere, which amounts to about 20%/year, is real [Lal *et al.*, 1985].

11.5.7 CBrF₃ (FC-13B1)

Like FC-12B1, this bromine-bearing halocarbon is used as fire extinguisher. In 1979, its tropospheric abundance was first measured by Penkett *et al.* [1981] as 0.7 pptv. The first stratospheric profile obtained by Fabian *et al.* [1981a] is shown in Figure 11-22. GC-MS analysis of samples collected on September 25, 1980, was made with a precision of ± 15%. The detection limit was about 0.05 pptv, and the absolute calibration was made to within ± 10%.

11.5.8 CCl₂FCClF₂ (FC-113)

FC-113 is used primarily as a solvent. According to Wuebbles [1983a] its global release rate into the atmosphere is 91 x 10³ tons/year. It was first measured in the atmosphere by Singh *et al.* [1979] who
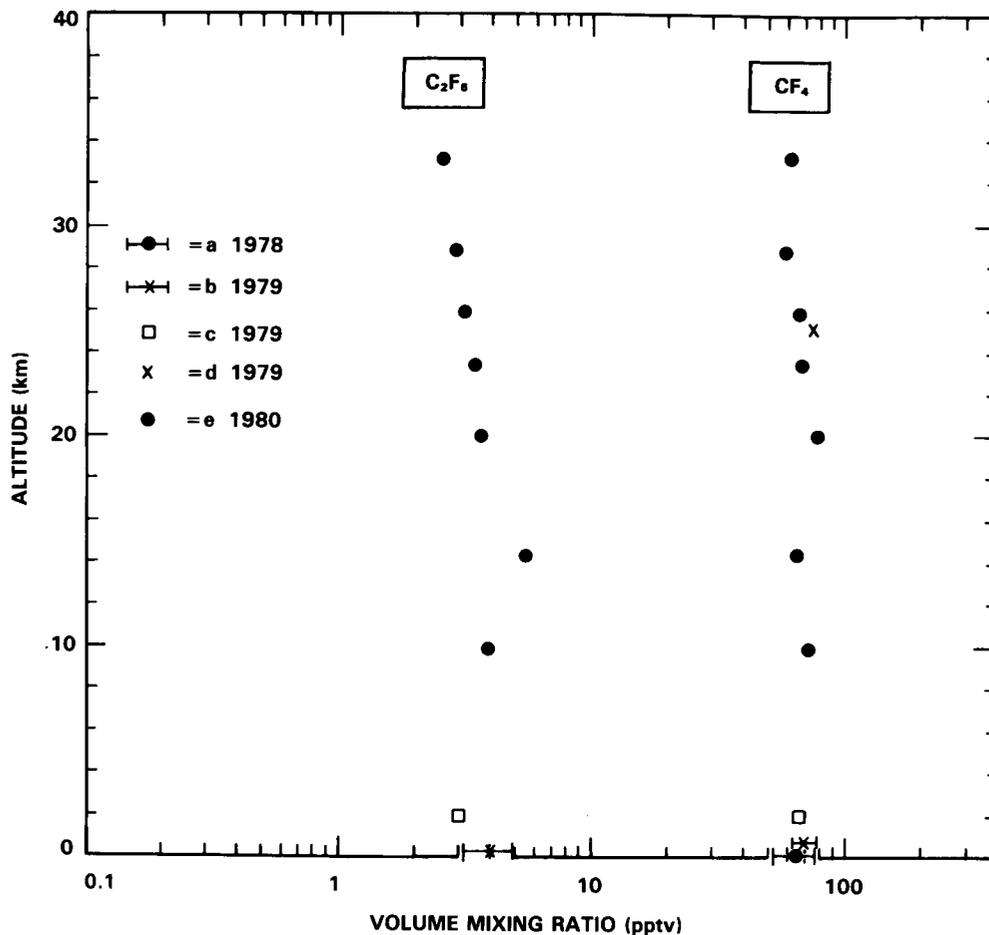
Figure 11-21. Vertical distribution of CF₄ (FC-14) and of CF₃CF₃ (FC-116) at northern
midlatitudes.
a: [Rasmussen et al., 1979]
b: [Penkett et al., 1981]
c: [Rasmussen and Khalil, 1980]
d: [Fabian et al., 1981a]

found in 1975, (19 ± 3.5) pptv and (12 ± 1.9) pptv on the northern and southern hemispheres, respectively, on a latitudinal survey between 60 °N and 40 °S. Rasmussen and Khalil [1981c, 1982, 1983b] and Rasmussen et al. [1983] measured FC-113 abundances ranging between 13 and 23 pptv.

The first stratospheric profile was obtained by Fabian et al. [1981a] by GC-MS analysis (AERE Harwell) of samples collected with a MPAE sampler on September 25, 1980 (Figure 11-23). The analytical precision of these data points was ± 15% or ± 0.1 pptv, whichever is greater. The absolute calibration was achieved to better than ± 10%.

Two profiles resulting from GC-ECD analyses at KFA (b and d) and GC-MS analyses at AERE (c and e) of samples collected with the KFA sampler, on October 21, 1982 and September 10, 1983, showed a factor of 3 larger FC-113 mixing ratios [Knapska et al., 1985a]. Their analytical precision against a
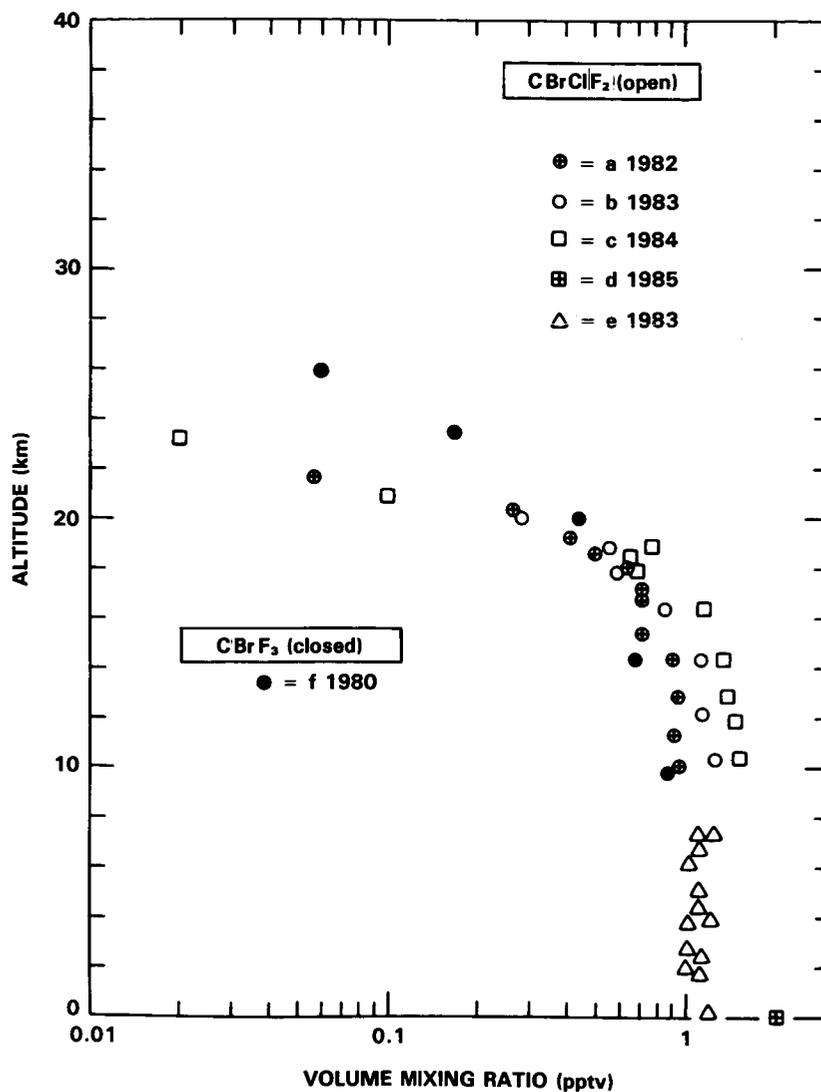
Figure 11-22. Vertical distribution of CBrClF₂ (FC-12B1) and CBrF₃ (FC-13B1) at northern midlatitudes.

a-d: [Lal *et al.,* 1985]
e: [Rasmussen and Khalil, 1983b]
f: [Fabian *et al.,* 1981a]

standard is quoted as ± 10% or ± 0.2 pptv, whichever is greater. The absolute calibration of this standard was made at AERE only.

Three FC-113 profiles (not presented in Figure 11-23) measured by MPAE during 1982, 1983 and 1984 showed that the first 1980 profile is certainly too low by a factor 2 [Borchers *et al.,* 1985]. They match the tropospheric profile of (23 ± 1) pptv measured by Rasmussen and Khalil [1983b] at 70°N (profile "f" in Figure 11-23). This would imply that the KFA profiles b-e have to be reduced by about 30%. More measurements and intercalibrations are needed for FC-113 whose absolute calibration is extremely difficult to achieve.

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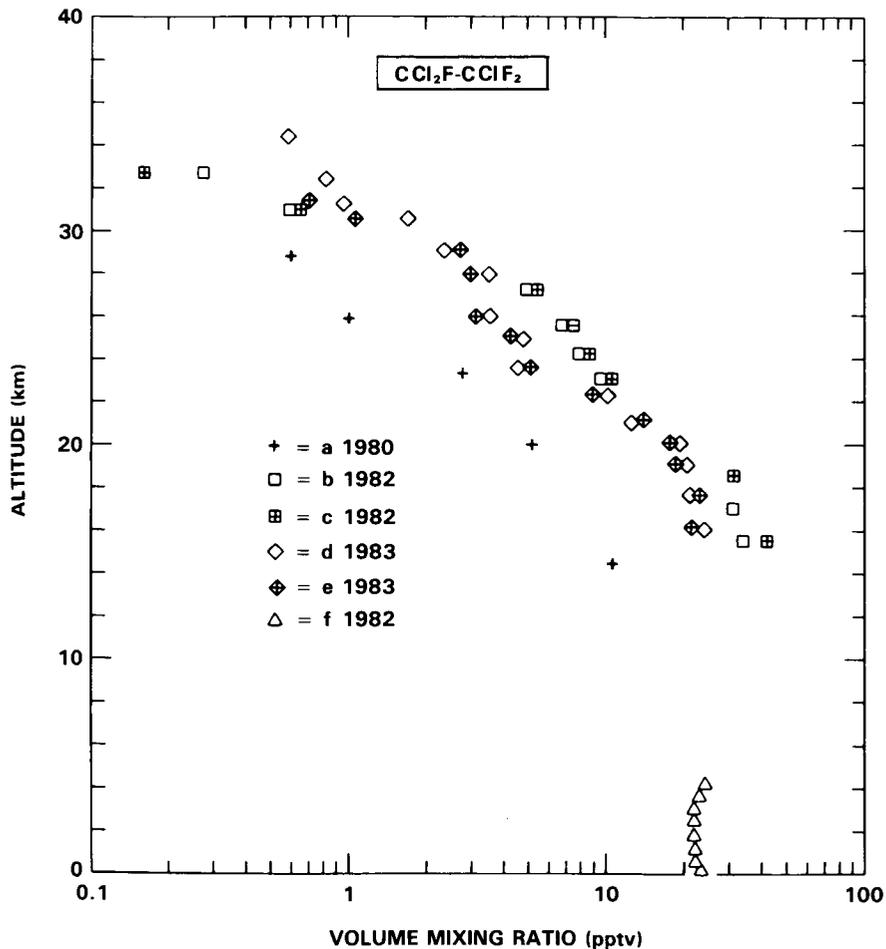
Figure 11-23. Vertical distribution of CCl_2FCClF_2 (FC-113) at northern midlatitudes.

    a: [Fabian *et al.,* 1981a]

    b-e: [Knapska *et al.,* 1985a]

    f: [Rasmussen *et al.,* 1983]

11.5.9 $CClF_2CClF_2$ (FC-114)

FC-114 is used as an aerosol propellant and as a refrigerant, with present global emission rates being estimated as 18 x 10^3 tons/year [Wuebbles, 1983a]. This halocarbon was first measured in 1975 by Singh *et al.* [1979] who found (12 ± 1.9) pptv and (10 ± 1.3) pptv at sea level for the northern and southern hemispheres, respectively.

Figure 11-24 shows the first stratospheric profile of FC-114 [Fabian *et al.,* 1981a]. Samples collected on September 25, 1980 with the MPAE cryogenic sampler at 44 °N were analyzed by GC-MS at AERE Harwell. The precision was ± 15% or ±0.5 pptv, whichever is greater, and the error of the absolute calibration was within ± 10%. Three as yet unpublished profiles obtained by GC-ECD analysis of samples collected with the MPAE sampler on September 20, 1982, September 10, 1983, and October 1, 1984 are consistent with the profile shown in Figure 2-8 [Fabian and Borchers, private communication 1985].
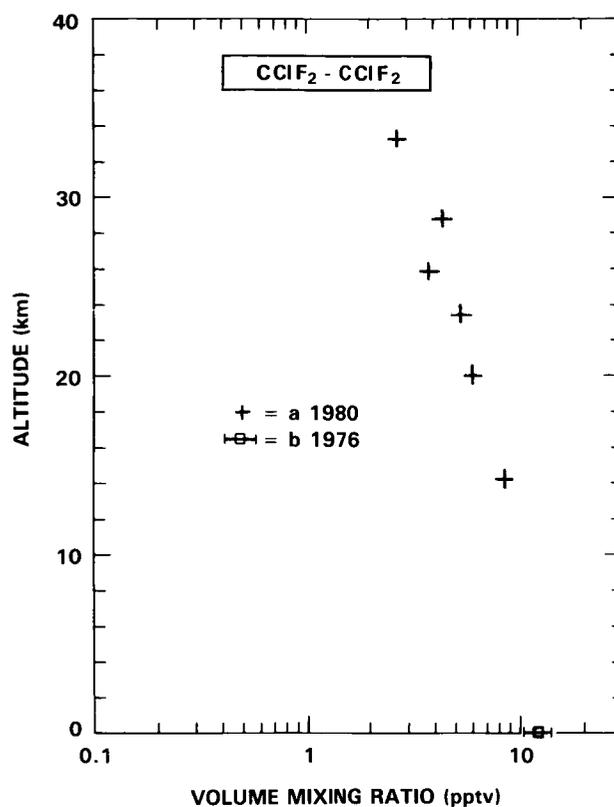
Figure 11-24. Vertical distribution of CClF₂CClF₂ (FC-114) at northern midlatitudes.
a: [Fabian *et al.*, 1981a]
b: [Singh, 1977]

11.5.10   CClF₂CF₃ (FC-115)

This halocarbon is used as a propellant for foods dispensed from aerosols, and as a refrigerant either directly or in mixture with FC-22 in the azeotropic refrigerant 502. Its present global release rate into the atmosphere, as evaluated by Wuebbles [1983a], is 4.5 x 10³ tons/year.

Penkett *et al.* [1981] measured the tropospheric abundance of FC-115 as 4.1 pptv in 1979. The first stratospheric profile, shown in Figure 11-20, was obtained by GC-MS analysis of cryogenically collected samples [Fabian *et al.*, 1981a]. The quoted precision was ± 15% with a detection limit of about 0.5 pptv, while the absolute calibration was made to within ± 10%.

11.5.11   CF₃CF₃ (FC-116)

Like CF₄, this halocarbon is thought to be released from aluminum plants. Its tropospheric abundance was measured to range between 3 and 5 pptv with no indication of latitudinal or hemispheric differences [Penkett *et al.*, 1981; Rasmussen and Khalil, 1980]. The first stratospheric profile obtained by GC-MS of cryogenically collected midlatitude samples [Fabian *et al.*, 1981a] shows a slight decrease from 4 pptv at 10 km to 2.5 pptv at 33 km (Figure 11-21). The precision of these data points was ± 15% with a detection limit of about 0.5 pptv. The absolute calibration was made with an error of ± 10%.

11.5.12 CH₃Cl (Methyl Chloride)

A first stratospheric midlatitude profile of methyl chloride, the most important natural halocarbon, was already presented in the WMO Report #11 [Penkett *et al.*, 1980]. More stratospheric data which have become available since then are presented in Figure 11-25, supplemented by a tropospheric profile measured at 70°N by Rasmussen and Khalil [1983b].

The profiles "a" and "b" result from analyzing cryogenically collected midlatitude samples of the MPAE sampler. For profile "a" [Fabian *et al.*, 1981a], GC-MS analysis was made at AERE, with a
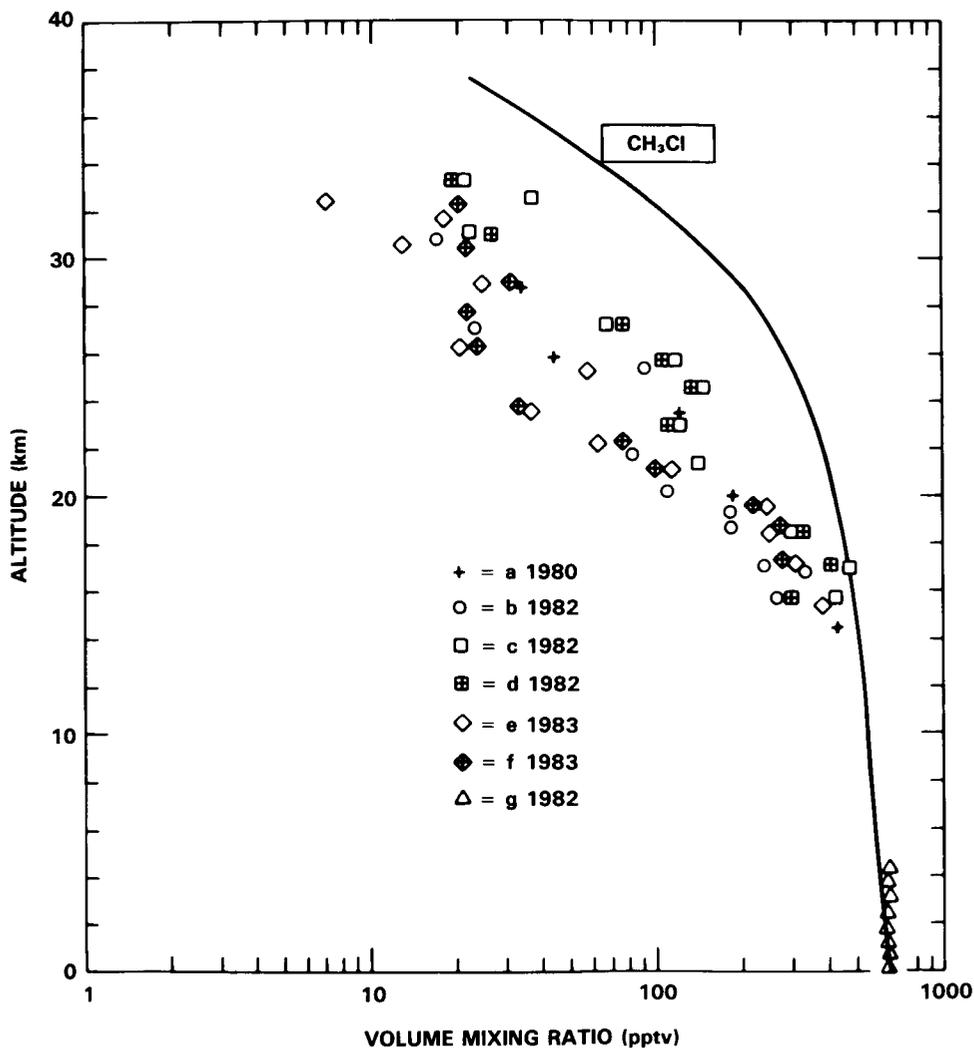
Figure 11-25. Vertical distribution of CH₃Cl at northern midlatitudes.
a: [Fabian *et al.*, 1981a]
b: [Borchers and Fabian, private communication 1985]
c-f: [Knapska *et al.*, 1985a]
g: [Rasmussen and Khalil, 1983b]
The solid line is for latitude 47°N calculated by a 2-D model [Ko *et al.*, 1985].

precision of ± 15%, while profile "b" [Borchers and Fabian, private communication 1985] results from GC-MS analysis at MPAE with ± 10% precision. The detection limit was about 1 pptv, while the absolute calibration was performed to within ± 10% in both cases. The profiles c-f result from samples collected with the KFA sampler during two balloon flights in 1982 and 1983, respectively. The samples were analyzed both by GC-ECD and KFA (c and e) and GC-MS of AERE (d and f). The quoted precision was ± 15% and ± 10%, and the detection limits were about 10 pptv and 1 pptv for the GC-ECD and GC-MS analyses, respectively. The absolute calibration was made against an AERE standard calibrated to within ± 5%.

Some of the scatter noticeable in Figure 11-25 may reflect real variations due to large-scale advection. To a larger extent, however, this scatter is likely to be due to contamination and alteration of the samples during sampling in the presence of ozone, and to storage [Schmidt et al., 1985b].

11.5.13 CHClF₂ (FC-22)

This hydrohalocarbon has been used in refrigeration and as a foam blowing agent, and global release data have been assessed [Jesson, 1980]. Since FC-22 was first measured in 1979 by Rasmussen et al. [1980], an increase of its abundance of about 12%/year was found in both hemispheres [Khalil and Rasmussen, 1981].

For the lower stratosphere, the first profile was reported by Leifer et al. [1981], who found FC-22 mixing ratios decreasing from about 55 pptv at the tropopause to 35 pptv at 19 km. Goldman et al., [1981d] reported 100 pptv measured at 15 km by infrared spectroscopy.

Two complete midlatitude profiles up to 33 km were reported by Fabian et al. [1985]. They are shown in Figure 11-26 along with a tropospheric profile measured at 70°N [Rasmussen and Khalil, 1983b]. Cryogenically collected samples of two balloon flights, on September 20, 1982 and September 10, 1983 at 44°N, were analyzed by GC-MS. Samples of the first flight were analyzed at MPAE (a) and AERE (b) in turn, with a precision of ± 10% or ± 3 pptv, whichever is greater. The absolute calibration was made at Harwell to within ± 10%, and a calibration factor was applied to the MPAE data. The samples collected during the 1983 flight were analyzed at MPAE only, with a precision of ± 5% or ± 3 pptv, whichever is greater, the error of the absolute calibration being ± 10%.

This data base confirms that FC-22, although being decomposed in the troposphere by OH attack, is fairly stable in the stratosphere. Its mixing ratios decrease by a factor of 3 only, while those of its fully halogenated counterpart, CCl₂F₂ decrease by about a factor of 30, within the height range discussed here.

11.5.14 CH₃Br (Methyl Bromide)

Like methyl chloride, methyl bromide is mostly of natural origin. Singh [1977] and Singh et al. [1977, 1979] measured tropospheric background mixing ratios of 5 pptv or less, with values as high as 20 pptv in the marine environment. Rasmussen and Khalil [1980] reported CH₃Br mixing ratios varying between 5 and 25 pptv, while Penkett et al. [1981] found about 10 pptv in the upper troposphere. Rasmussen and Khalil [1984c] measured a tropospheric profile at 70°N up to 7 km yielding (10 ± 2) pptv. The first stratospheric measurement indicates that CH₃Br falls off rapidly above the tropopause: 1.2 pptv was measured at 14.4 km, while a sample collected at 20 km was already below the detection limit [Fabian et al., 1981a]. As these data are considered preliminary, more measurements are needed to establish a realistic profile.
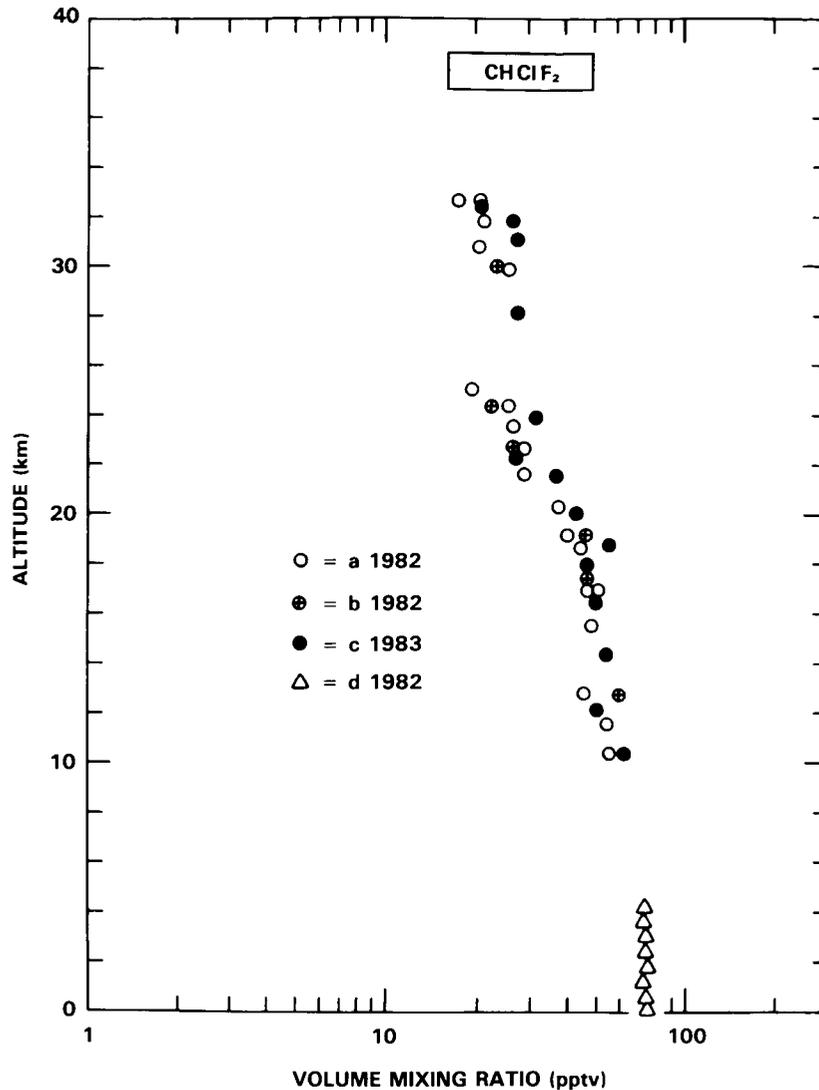
Figure 11-26. Vertical distribution of CHClF₂ (FC-22) at northern midlatitudes.
a-c: [Fabian *et al.*, 1985a]
d: [Rasmussen and Khalil, 1983b]

11.5.15 CH₃CCl₃ (Methyl Chloroform)

Tropospheric measurements of methyl chloroform were reviewed in the WMO Report #11 [1982], but no stratospheric data were available then. From analyses of air samples collected aboard aircraft some CH_3CCl_3 data for the lower stratosphere were obtained by Leifer *et al.* [1981], showing midlatitude mixing ratios decreasing from about 100 pptv at the tropopause to 30 pptv at 19 km.

A first complete stratospheric profile of CH_3CCl_3 was obtained by Borchers *et al.* [1983]. Samples collected on September 20, 1982, with an MPAE cryogenic sampler at 44 °N were analyzed by GC-ECD at MPAE and GC-MS at AERE Harwell. The results are plotted as profiles "a" and "b" in Figure 11-27.
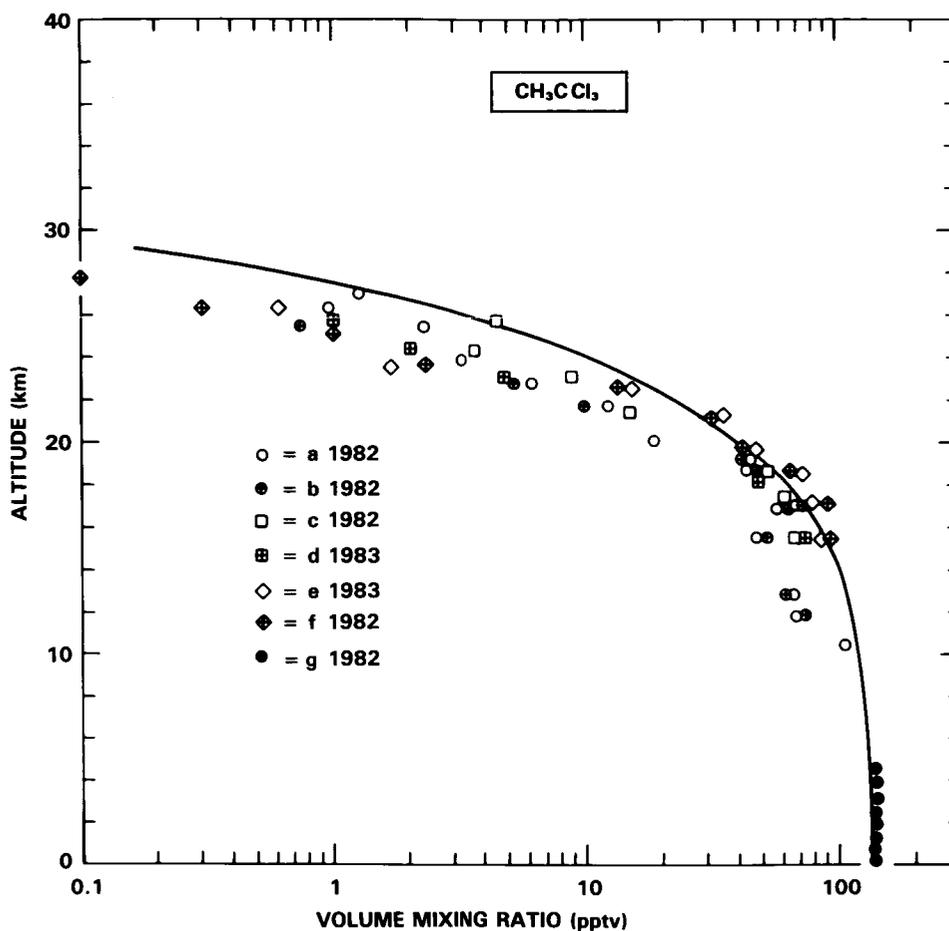
Figure 11-27. Vertical distribution of CH₃CCl₃ at northern midlatitudes.

a,b: [Borchers *et al.,* 1983]

c-f: [Knapska *et al.,* 1985a]

g: [Rasmussen and Khalil, 1983b; Khalil and Rasmussen, 1984a]

The solid line is for latitude 47°N calculated by a 2-D model [Ko *et al.,* 1985].

The quoted precision and detection limit was ± 10% and 0.1 pptv, respectively, for both data sets, while the absolute calibration was made at AERE to within ± 10%, with a calibration factor applied to the MPAE data points.

From samples collected during two flights of the KFA sampler, on October 21, 1982, and September 10, 1983, two more CH₃CCl₃ profiles were established [Knapska *et al.,* 1985a]. The analyses of these samples were made by GC-ECD at KFA (c and e) and by GC-MS at AERE (d and f), and the quoted analytical precision was ± 10% or ± 2 pptv, whichever is greater, for both data sets. All analyses were made against an AERE standard calibrated to within ± 5%. A tropospheric profile measured at 70°N, also shown in Figure 11-27, indicates (175 ± 2) pptv of CH₃CCl₃ in 1982. The data of Rasmussen and Khalil [1983b] have been scaled down by a factor of 0.8 to reflect a recent recalibration of the measurements [Khalil and Rasmussen, 1984a].

Although the data set presented in Figure 11-27 reveals some scatter which may, as in the case of CH_3Cl, reflect contamination effects, it appears reasonable to establish a mean profile representative of 1982/83 midlatitude conditions as an average of the data points presented here.

11.5.16 Comparison With Models

Among the various halocarbons discussed above, model profiles are only presented for the most abundant halocarbons, i.e., CCl_4, CCl_3F, CCl_2F_2, CH_3Cl and CH_3CCl_3. The stratospheric sinks for these species are reasonably well established, but the transport processes controlling their vertical distributions are less well characterized (see Chapter 12 for a discussion on the uncertainties in transport-related parameters).

Plotted in Figures 11-17, 11-18 and 11-19 are vertical profiles of CCl_4, CCl_3F and CCl_2F_2 at 47 °N latitude taken from AER's 2-D model calculations [Ko et al., 1985]. With the new O_2 cross section in the Herzberg continuum (see Chapter 6), the calculated profile of CCl_3F (Figure 11-18) is now in better agreement with observations, and the serious discrepancy noted earlier in the WMO Report #11 [1982] is now partially resolved.

The calculated concentration of CCl_4 (Figure 11-17) appears to be somewhat higher than observations. It should be noted, however, that because of the very steep vertical gradient of stratospheric CCl_4, the difference between model and observations may be attributed to a shift of as small as ~ 1 km in vertical scale. Such a shift may occur when the model profiles are transformed from pressure coordinates to height coordinates.

Figure 11-25 shows the calculated profile of CH_3Cl along with observations which indicate a much steeper vertical gradient. Unlike its fully halogenated counterparts, CH_3Cl is mainly removed by reaction with OH. The discrepancy between the calculated and observed profiles of CH_3Cl could be indicative of uncertainties in transport coefficients or higher OH in the lower stratosphere. However, more and better data will be required to establish the variability of CH_3Cl and to assess in more detail the discrepancy with model profiles.

Figure 11-27 shows the calculated profile of CH_3CCl_3 along with observations. The agreement appears to be quite satisfactory.

Two-dimensional model calculations have not been made for other halocarbons whose data are summarized in Figures 11-20 through 11-24, and 11-26 and whose UV absorption cross sections are listed in JPL Publication 85-37 [1985]. This body of data should provide an additional test for models in the future.

11.6 TOTAL CHLORINE

The total amount of chlorine is determined largely by the amount of organically bound chlorine in the troposphere, whose background concentration is estimated to be in the range 2.4 - 2.8 ppbv chlorine (see Chapter 3). Hence, an equivalent mixing ratio for total chlorine is expected in the stratosphere. Berg et al. [1980] have measured total halogens at ~ 20 km altitude and at various latitudes, using activated charcoal traps and neutron activation analysis, obtaining values ranging between 2.7 ± 0.9 and 3.2 ± 0.7 ppbv chlorine.

More recently, Gallagher et al. [1985] employed cryogenic whole air samplers to measure individual halogenated hydrocarbons, and filter samplers to measure acidic and particulate chlorine, in order to estimate

the total chlorine content (excluding possibly Cl and ClO) at altitudes between 15 and 30 km. They measured total chlorine mixing ratios that decreased from 2.6 ppbv at 15 km, to 2.2 - 2.5 ppbv for the higher altitudes. Hence, at present there appears to be no significant discrepancy between measured and calculated total stratospheric chlorine abundance.

11.7 CONCLUSIONS

11.7.1 Chlorine Monoxide (ClO)

Since 1981 the stratospheric ClO data base, measurement techniques and theoretical models have been considerably improved. Between altitudes of about 28 and 38 km there is now agreement within a factor of two between the mean of the measurements and model predictions. The ClO diurnal variation has now been monitored and is also in reasonable agreement with model predictions, although observations indicate a somewhat slower morning rise than expected. The existing data base, however, is not yet adequate to establish seasonal and latitudinal variations or long term increases in ClO which are all predicted by theoretical models. Furthermore, the experimental precision and accuracy need to be improved in order to assess with confidence the magnitude of the shorter term variations in midday ClO which might be caused by transport-induced fluctuations in CH_4, H_2O and NO_X.

11.7.2 Chlorine Nitrate (ClONO₂)

There is now improved evidence for the presence of the reservoir species $ClONO_2$ with measurements made in a second spectral region, and there is also indirect evidence coming from the observed diurnal behavior of ClO.

11.7.3 Hydrogen Chloride (HCl) and Hydrogen Fluoride (HF)

Several different remote sensing techniques for HCl and HF were carefully intercompared during the balloon intercomparisons carried out in 1982 and 1983. The vertical concentration profile of HCl, for which many more observations were made, can now be measured to 15% accuracy with confidence. Total column values from the surface (i.e., including the tropospheric component) can be determined with a precision approching 5%. Significant variability in the column amount of HCl in the stratosphere in space and in time has been established. Column values for the total HCl seen from the surface show even greater variation with time. The expected trend in stratospheric HCl is presumably masked by this variation and has not yet been observed. For HF the measured latitude variation and long-term trend are compatible with theoretical prediction.

11.7.4 Stratospheric Halocarbon Profiles

There is now general agreement between calculated and measured profiles for the halogen source molecules. Some differences remain, but these are most likely due to imperfections in the modeling of transport processes. The least satisfactory agreement occurs with CH_3Cl, a species removed predominantly by reaction with OH. However, CH_3Cl is among the halocarbons presenting greatest measurement difficulties.

The discrepancy in the previous assessment [WMO Report #11, 1982] between models and observations, most apparent in CCl_3F, has been partially resolved by the new O_2 absorption cross sections around 200 nm (Chapter 7).

11.8 FUTURE RESEARCH NEEDS

In summarizing the future needs for measurements of radiatively and chemically active trace species in the stratosphere, it should be mentioned that a new source of data, the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment had its first flight as part of the Spacelab-3 mission in May of 1985. Although the results of this flight cannot be made available in time for inclusion in the present assessment, it can be stated that the experiment was successful and that data pertaining to many of the molecular species discussed in this and other chapters were obtained. The results, which provide simultaneous measurements of a large number of species at various locations over the globe, are expected to satisfy several of the specific needs discussed here.

One of the higher priority research items should be the simultaneous measurements of chlorine-bearing species, mainly HCl, $ClONO_2$ and ClO. Such observations should resolve questions concerning the total chlorine budget and its spatial and temporal variability. Measurements of high altitude HCl, e.g., at 50 km (which are probably available from ATMOS) would also be very useful in this context, since at those altitudes chlorine is expected to be present predominantly as HCl.

A more stringent test of the models, related to the partitioning of chlorine among the various species, would be possible with simultaneous measurements of O_3, H_2O, CH_4, NO_x and temperature, besides HCl, ClO and $ClONO_2$.

It is important to continue monitoring stratospheric HCl and HF. The long term increase expected as a result of CFM release is apparent in the HF, but not in the HCl data so far. Also, the latitudinal variation of these two species in the stratosphere needs to be better established by continued measurements.

It appears that $ClONO_2$ can now be added to the list of species positively identified in the stratosphere. Given its relative abundance--next to HCl in the inorganic chlorine family--higher sensitivity measurements are now required in order to establish reliably a stratospheric concentration profile.

Measurements of stratospheric ClO have matured considerably since the first observations pioneered by Anderson and co-workers. An intercomparison of the several existing techniques is clearly needed at present. Furthermore, with state-of-the-art instrumentation it should now be possible to measure the diurnal, the seasonal and the latitudinal variation in ClO to about $\pm$ 15%. Also, measurements of the profile shape should be continued in order to better establish the behavior of this important species.

Techniques to measure HOCl to about 0.1 ppbv should be developed: detection of this species in the stratosphere is important in testing current knowledge of the chemistry of the chlorine family.

There are only two direct measurements of Cl-atoms, both by the in situ resonance fluorescence technique. Additional observations would be useful, particularly if coupled to measurements of other key species, as discussed above. Also, improved measurements of the shape of the C_2H_6 profile would provide important information on Cl-atom abundance in the lower stratosphere, where direct measurements are not practical due to the exceedingly small concentrations expected.