

Observations of Stratospheric HCl:
1975-1985.

M. De Mazière, C. Lippens and C. Muller.
Belgian Institute for Space Aeronomy.
circular avenue , 3
B1180 Brussels, Belgium.

ABSTRACT

Since the first observations of HCl in 1975 by balloon borne infrared absorption spectroscopy, several other observations from airborne and space borne vehicles, using mostly infrared techniques, have been published . The first spectra are reinterpreted using the latest AFGL HITRAN spectroscopic parameters in order to check for a secular trend of stratospheric HCl and compare it with the known variations of the main chlorine source gases. No significant variation can be deduced from the presented data set and an upper limit of 3% for the annual HCl increase is proposed.

Introduction

HCl was observed for the first time in the stratosphere by limb sounding using a stratospheric balloon borne grille infrared spectrometer in the fall of 1975 (Ackerman et al, 1976) and from high altitude aircraft flights of an interferometer (Farmer et al, 1976). These first observations were important at the time because they identified a sink for the chlorine introduced in the stratosphere by chlorofluoromethanes which had been recently discovered in the atmosphere and identified as interfering with stratospheric ozone (Lovelock ,1971 , Molina and Rowland, 1974, Cicerone et al., 1974). The near simultaneous first observation of HF in the stratosphere by Zander (1975) proved that the CFC's, which are considered as its only source, were reaching altitudes where their photodissociation releases atomic chlorine in possibly sufficient amounts to affect ozone chemistry.

Using mainly the infrared technique from balloons and airplanes, other observations rapidly followed (Williams et al, 1976, Farmer et al,1980, Zander, 1981, Fast and Evans, 1987, Mankin and Coffey, 1983 and references therein). Later, during the first and third flights of the European built SPACELAB, infrared limb occultation spectra were obtained using respectively the GRILLE spectrometer (Girard et al, 1988) and the ATMOS interferometer (Raper et al, 1987). The GRILLE spectrometer HCl data were unfortunately partially lost due to transmission difficulties and were

limited to 4 spectra ranging in limb altitudes from 25 to 35 km and thus corresponding to a balloon flight. This paper presents the interpretation of these spectra together with the reinterpretation of the 1975 balloon data, making use consistently of the most accurate line parameters available nowadays.

Observations and interpretation.

The SPACELAB 1 spectra are shown on figure 1 with the corresponding limb altitudes, the results have been obtained on 2-12-1983 at 8:24 G.M.T. for a latitude of 32° North and a longitude of 127° East. In these spectra, the equivalent width of the 2944.91 cm^{-1} HCl R2 line was measured and inverted using an iterative onion peeling technique. The obtained vertical distribution is shown on figure 2, the dip at 34 km might be an artefact due to the transmission difficulties encountered during this occultation, and which could have altered the time information on one spectrum and consequently led to an error in altitude determination. During the next flight of the grille spectrometer on ATLAS 1, the communication situation will be much improved and similar problems should not arise anymore. The 1986 AFGL HITRAN line set (Rothman et al, 1987) was used for interpretation of the data; this data set differs from the previous ones by improved values of all parameters and especially a better treatment of the line widths and their temperature dependences. However in the case of the HCl line we use, the position and intensities are identical to the ones of the 1982 edition. The new 1990 edition will include revised values (Tipping, private communication, 1989). A check was performed by interpreting several weak CH_4 absorptions in the same spectral interval which gave reasonable agreement with our previously published methane data (Girard et al, 1988). This verification will be performed again when new methane line parameters (Malathy-Devi, private communication, 1989) will be available in order to use again this interval for accurate methane determinations instead of the stronger lines which were considered for SPACELAB 1 and which saturate in the lower stratosphere. At this occasion the revised onion peeling algorithm used in this paper will be compared with an updated version of the Mills technique (Alamichel et al, 1986) used for the Girard et al (1988) interpretations. This simultaneous accurate observation will later allow us to correlate the variations of methane and hydrogen chloride and verify the current coupling theories between these two molecules (Mc.Elroy and Salawitch, 1983, and references therein). Simultaneously with the HCl spectra, the HF line at 3920.31 cm^{-1} was measured. Despite the small number (3) of spectra available in consequence of the telemetry problems, an estimate of the HF vertical profile has been made. The profile's shape is similar to that of HCl, showing also a minimum at 35 km altitude. The HF/HCl ratio is of

order 0.12-0.18 over the whole altitude range, as expected.

The same interpretation technique was used on the previous (Ackerman et al., 1976) data obtained on October 2, 1975 at Sunset from the CNES launching range at Aire-sur-l'Adour (43°N, 0°). The results are shown on figure 3 together with the error limit given at the time. The new values agree surprisingly with the older interpretation and are almost entirely within the earlier error bars. The new error bar includes only the actual uncertainty on the measurement of equivalent widths; the error increases significantly above 30 km due to the smaller equivalent widths and this upper part was not plotted. The older interpretation used the (Toth et al., 1970) data set as later did most authors reviewed by Raper et al (1977). The vertical distributions obtained are shown on figure 2 together with the ATMOS vertical distribution as published by Raper et al (1987) using a line data set similar to Rothman et al (1987). Other data sets were not reinterpreted due to the difficulties of reconstituting the intensity scales for most published spectra and the general absence of tables of equivalent widths. This shows the necessity of an agreement in the geophysical spectrometry community for a standard publication format for the unprocessed data either in the scientific journals or by an international dedicated data center.

Stratospheric HCl trend.

The sample shown is too small in both time and spatial coverage to deduce a trend in the total atmospheric column abundance, however the comparison of the values obtained at 30 km can be indicative. It is clear that they agree quite well with a constant value close to 1.8 ppb, a yearly 5% increase leading to values of HCl 1.6 times higher in 10 years which would fall outside the error limits of the present values. However, a 3% growth or decrease would correspond to a 35% HCl variation and would fall within the error limits of the current infrared remote sensing technique. This 3% increase is however well below the observed trend of the man-made chlorofluoromethanes which are now considered as causing ozone depletion in the stratosphere and which increased in the atmosphere by about a factor 2.5 over the same period. Moreover, HF, the parent gas of HCl in the elimination of stratospheric halocarbons has been shown by Zander et al (1987) to increase by 8% per year while HCl remained quasi constant in the same ground-based infrared measurements. This observation was attributed to the influence of tropospheric chlorine originating from marine chemistry. Clearly, a still to be determined source or sink of HCl also influences the stratosphere. Other trends values already published are the 8% increase reported by Fast and Evans (1986) for the years 1978-1985 and the 5% increase indicated by Mankin and Coffey (1983) for the

period 1978-1982. If our observation of a constant HCl within the observational error were to be confirmed, the consequence would be that the man-induced perturbations of chlorine would add up to an existing natural stratospheric chlorine cycle which was never considered. This HCl source would also explain the discrepancy between a theoretical model and observations noticed by Rodriguez et al (1986) and not present in the more recent Mc.Elroy and Salawitch (1989) model.

In conclusion, this data set does not permit to deduce a significant increase of HCl and is consistent with a $\pm 3\%$ yearly variation, excluding the 8% increase indicated by the models quoted by Mankin and Coffey (1983). The present measurements and especially the observations obtained from space (ATMOS and the SPACELAB GRILLE spectrometer) must be preserved in their raw form so that reinterpretation will be possible in the next century with the best data available then. The atmospheric community has now the duty of incorporating this curatorial requirement in all future observation proposals.

References

Ackerman, M., Frimout, D., Girard, A., Gottignies, M. and Muller, C., Stratospheric HCl from infrared spectra, *Geophys. Res. Lett.*, 3, 81-83, 1976.

Alamichel, C., Laurent, J., Brard, D. and Mendez, F., An automatic program for retrieving atmospheric mixing ratio profiles from occultation spectra, *Ann. Geophys.*, 4, 201-206, 1986.

Cicerone, R.J., Stolarski, R.S. and Walters, S., Stratospheric ozone destruction by man-made chlorofluoromethanes, *Science*, 185, 1165-1167, 1974.

Farmer, C.B., Raper, O.F. and Norton, R.H., Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere, *Geophys. Res. Lett.*, 3, 13-16, 1976.

Farmer, C.B., Raper, O.F., Robbins, B.D., Toth, R.A. and Muller, C., Simultaneous spectroscopic measurements of stratospheric species: O₃, CH₄, CO, CO₂, N₂O, H₂O, HCl and HF at Northern and Southern mid-latitudes, *J. Geophys. Res.*, 85, 1621-1632, 1980.

Fast, H. and Evans, W.F.J., Stratospheric profiles of HCl and CH₄ at 32 deg N obtained on project Stratoprobe from 1978 to 1985, *Adv. in Space Res.*, 7, 127-131, 1987.

Girard, A., Besson, J., Brard, D., Laurent, J., Lemaître, M.P., Lippens, C., Muller, C., Vercheval, J. and Ackerman, M., Global results of grille spectrometer experiment on board SPACELAB 1, *Planet. Space Sci.*, 36, 291-300, 1988.

Lovelock, J.E., Atmospheric fluorine compounds as indicative of air movements, *Nature*, 230, 379, 1971.

Mankin, W.G. and Coffey, M.T., Latitudinal distributions and temporal changes of HCl and HF, *J.*

Geophys. Res., 88, 10776-10784, 1983.

Mc.Elroy, M.B. and Salawitch, R.J., Changing composition of the global stratosphere, Science, 243, 763-770, 1989.

Molina, M.J. and Rowland, F.S., Stratospheric sink for chlorofluoromethanes: chlorine atoms catalysed destruction of ozone, Nature, 249, 810-814, 1974.

Raper, O.F., Farmer, C.B., Toth, R.A. and Robbins, B.D., The vertical distribution of HCl in the stratosphere, Geophys. Res. Lett., 4, 531-534, 1977.

Raper, O.F., Farmer, C.B., Zander, R. and Park, J.H., Infrared spectroscopic measurements of halogenated sink and reservoir gases in the stratosphere with the ATMOS instrument, J. Geophys. Res., 92, 9851-9858, 1987.

Rodriguez, J.M., Ko, M.K.W. and Nien Dak Sze, Hydrogen chloride in the middle stratosphere: comparison of observations with model results, Planet. Space Sci., 34, 655-664, 1986.

Rothman, L.S., Gamache, R.R., Goldman, A., Brown, L.R., Toth, R.A., Pickett, H.M., Poynter, R.L., Flaud, J.M., Camy-Peyret, C., Barbe, A., Husson, N., Rinsland, C.P. and Smith, M.A.H., The HITRAN database: 1986 edition, Appl. Optics, 26, 4058-4097, 1987.

Toth, R.A., Hunt, R.H. and Plyler, E.K., Line strengths, line widths, and dipole moment function for HCl, J. Molecul. Spectry., 35, 110-126, 1970.

Williams, W.J., Kusters, J.J., Goldman, A. and Murcray, D.G., Measurement of the stratospheric mixing ratio of HCl using infrared absorption technique, Geophys. Res. Lett., 3, 383-385, 1976.

Zander, R., Présence de HF dans la stratosphère supérieure, C.R. Acad. Sci. Paris, Ser. B, 281, 213-214, 1975.

Zander, R., Recent observations of HF and HCl in the upper stratosphere, Geophys. Res. Lett., 8, 413-416, 1981.

Zander, R., Roland, G., Delbouille, L., Sauval, A.J., Farmer, C.B. and Norton, R.H., Monitoring the integrated column of hydrogen fluoride above the Jungfrau Joch station since 1977 -the HF/HCl column ratio, J. Atm. Chem., 5, 385-394, 1987.

Legends of the figures.

Figure 1: observed spectra of the HCl R2 line obtained during the Spacelab One flight with the Girard et al(1988) Grille Spectrometer. Spectra labeled (a) to (e) are recorded at the following tangential heights (at the line positions): (a) 21.8 km, (b) 24.9 km, (c) 32.3 km, (d) 34.4 km, (e) >200 km.

Figure 2: comparison of the partial HCl data obtained during SPACELAB 1 with ATMOS data (SPACELAB 3) and the Aire-sur-l'Adour 1975 balloon flight data.

Figure 3: comparison of the reinterpretation of the R2 HCl line in the Ackerman et al (1976) spectra with the previously published vertical distribution.

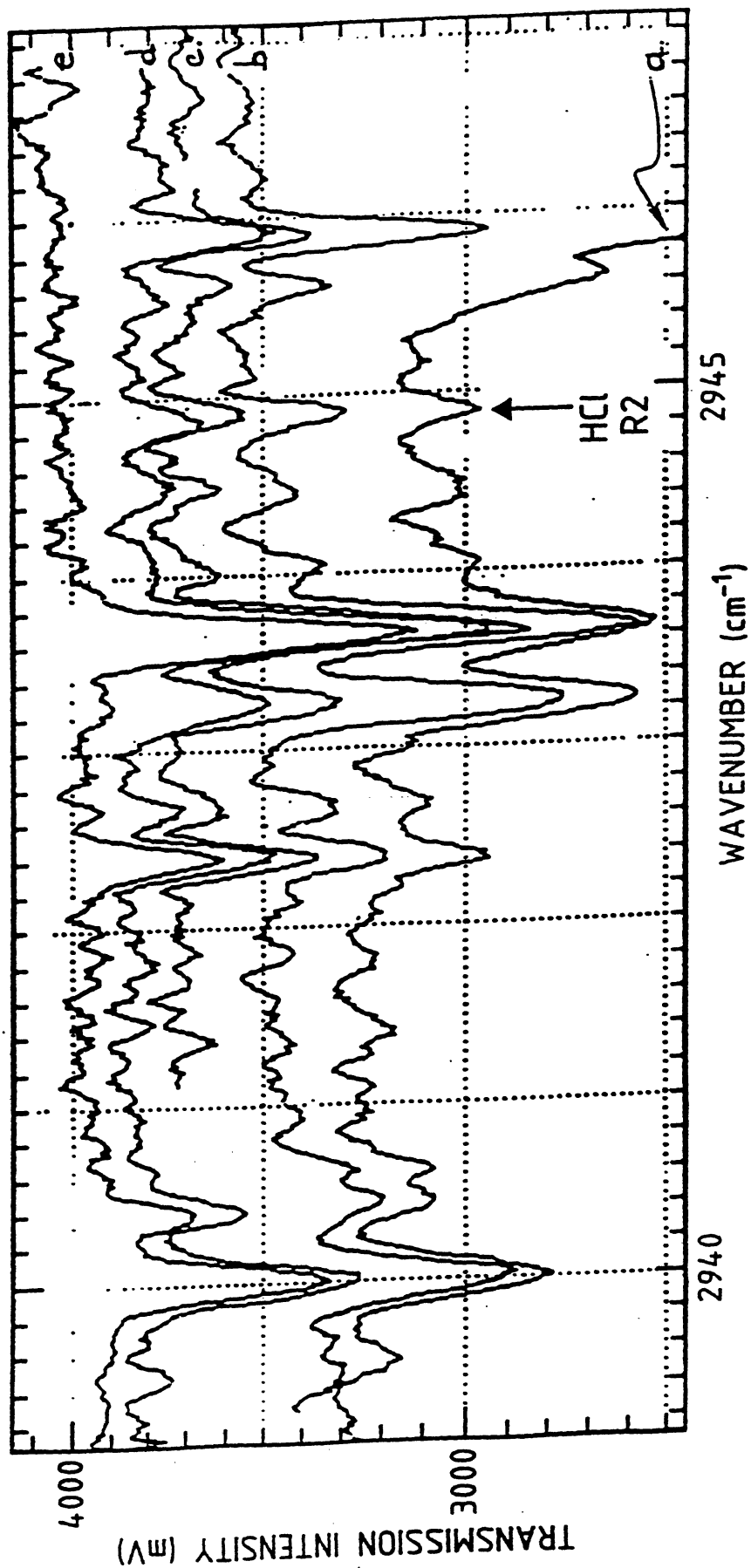


FIGURE 1

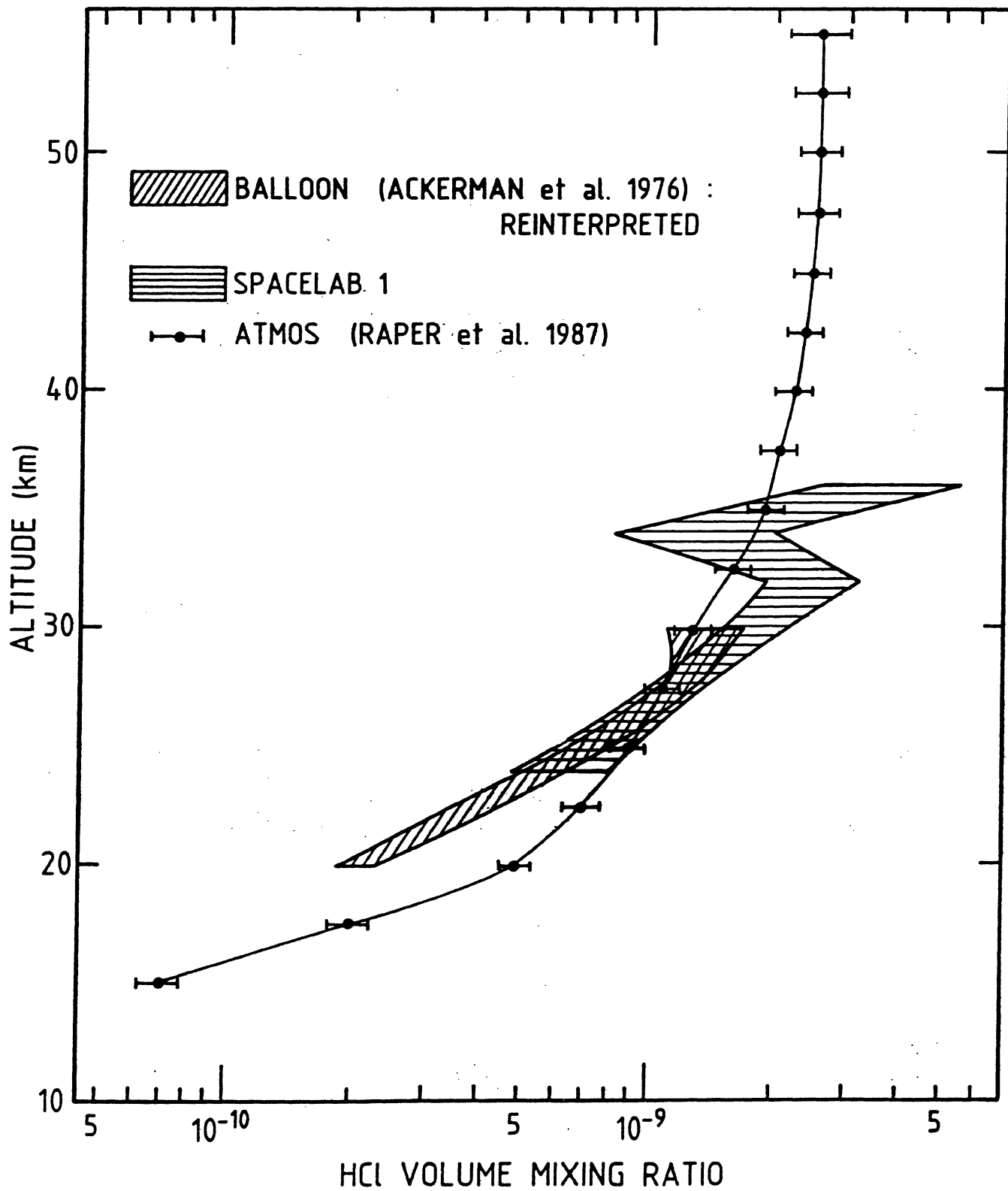


FIGURE 2

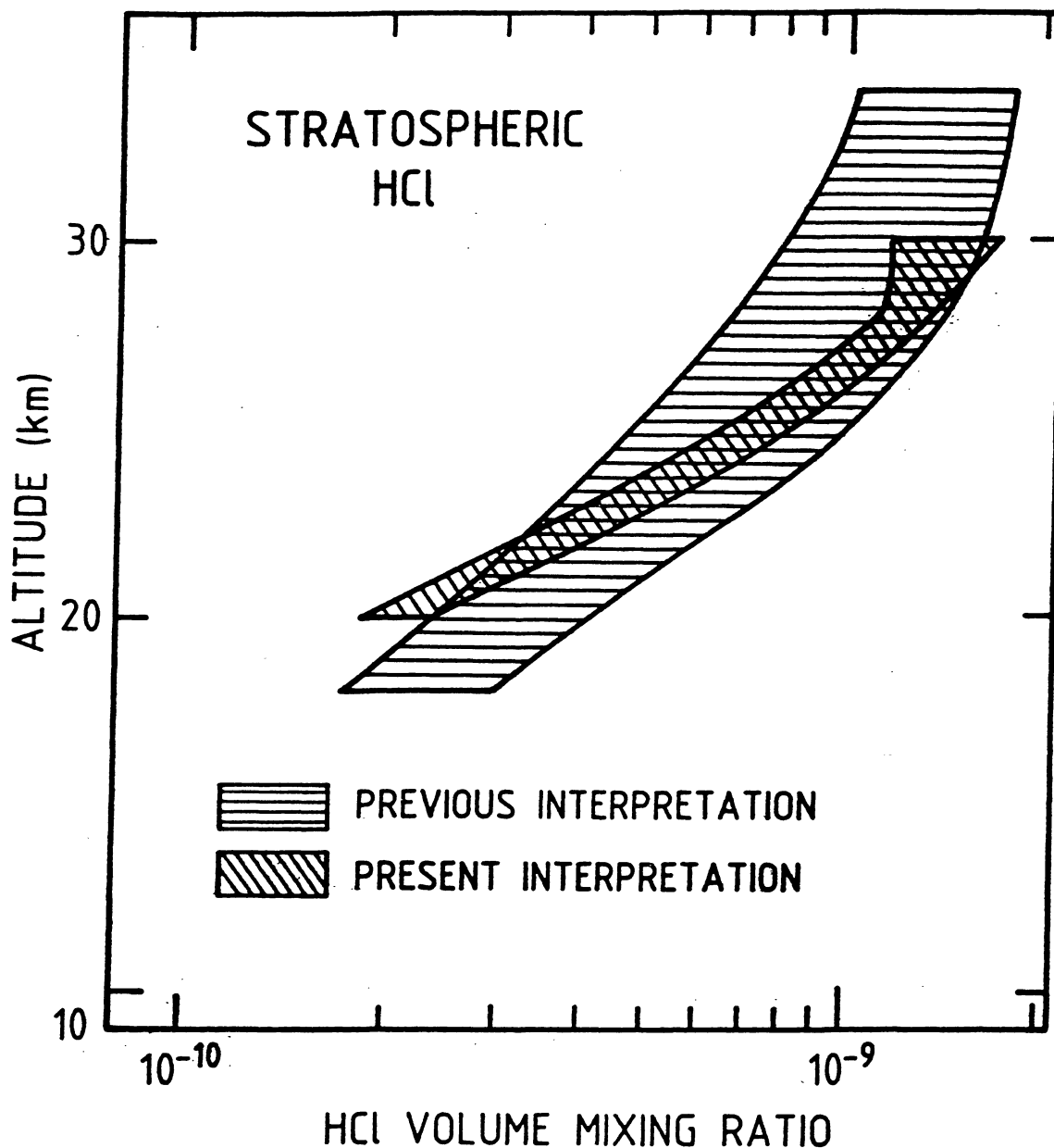


FIGURE 3

DISCUSSION

MARTENS : Individual contributions of chloro(fluoro)carbons to the total chlorine budget are often given (CFC-11, CFC-12, carbon tetrachloride, methylchloroform). Are these contributions consistent with the measured HF/HCl ratios ?

MULLER : The HF/HCl ratio is a differential measurement and is affected by the error on HF and HCl and difficult to use. However, as appears, HCl does not seem to increase despite a growth in HF. This is not consistent with the present knowledge of the chlorine budget.

ZANDER : How many spectra are used to cover the altitude range over which you showed SL1 results for HCl ?

MULLER : Four.

KAYE : By directly comparing data from 10/75 at 48°N, 12/83 at 32°N and 5/85 at 30°N you are assuming no contribution from changes due to seasonal or meridional dependence of HCl, as well as no short-term variability. Are you suggesting that there has been no change in stratospheric amounts of HCl or are you saying only that the three different spectra give essentially undistinguishable amounts ?

MULLER : They give undistinguishable amounts.

COMMENTS

McELROY : COF_2 is a significant component of the stratospheric F budget, perhaps comparable to HF. It needs to be considered in assessing the stratospheric F budget.

ZETSCH : To the occurrence of COF_2 in the stratosphere : we observed the formation of COCl_2 in heterogeneous reactions of atomic Cl with plain hydrocarbons in our aerosol smog chamber. Hence the halogenated phosgenes may be produced not only from a degradation of halo- and fluoro- carbons.