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Analysis of Halogen Occultation Experiment HF versus CH₄ correlation plots: Chemistry and transport implications

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Abstract. The relationship between stratospheric CH₄ and Hydrogen Fluoride (HF) observed simultaneously by the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) has been examined globally. The meridional structures of the two long-lived species for the equinox and solstice seasons are found to be very similar. Their surfaces of constant mixing ratio, however, are found to not quite coincide. The isopleth of CH₄ graphed as pressure versus latitude shows a steeper slope than that of HF. This feature can be clearly seen from the scatterplots of CH₄ versus HF for a sequence of latitude regions. In general, CH₄-HF correlation plots are characterized by tightly fitted curves for different latitude bands; curves for the tropics and high latitudes define the envelope for the correlations. The NCAR two-dimensional model simulation of CH₄ and HF agrees well with HALOE observations, and it shows that the altitude-latitude dependences of CH₄ removal and HF production rates play an important role in determining global CH₄-HF correlations. It is found that the CH₄-HF correlation inside the Antarctic vortex is nearly linear and is shifted from that of outside the vortex and from that of polar late-summer before the formation of the vortex. HALOE observations of CH₄ and HF indicate that the two species are not in states of perfect "slope equilibrium" or "gradient equilibrium" globally. The obvious shift of HF values on CH₄ surfaces or vice versa is usually found across dynamical barriers. There is no universal relationship between CH₄ and HF. The HF mixing ratios are observed to change up to 20-35% for a given CH₄ from different dynamically isolated regions such as the polar vortex, midlatitudes, and the tropics, and the same magnitudes of change in CH₄ could also be found for a fixed HF. Therefore one must be cautious in the usage of correlation-inferring methods for any pair of tracers in place of unavailable measurements or for evaluating chemical disturbances.

1. Introduction

Several chemical species in the stratosphere are regarded as long-lived tracers because the timescales for their chemical sinks or sources are usually longer than the timescales for atmospheric dynamical processes. The mixing ratios of those trace gases, for example, can therefore be used as labels of moving air parcels for a time period shorter than the chemical timescale or diffusive mixing timescale. In fact, satellite observations [Jones and Pyle, 1984; Kumer et al., 1993; Russell et al., 1993a, b] and model simulations [e.g., Solomon et al., 1986; Mahlman et al., 1986; Gray and

Pyle, 1987; Brasseur et al., 1990; Prather and Remsberg, 1993] show that the global zonal mean distributions of the long-lived tracers, represented by their volume mixing ratio (VMR) isopleths have similar shapes, bulging up in the tropical region due to upwelling motion and extending downward to the higher latitudes due to poleward-downward transport. Theoretical studies indicate that a few dominant processes determine the meridional structure of the tracer VMR distributions [Holton, 1986a, b; Mahlman et al., 1986; Plumb and McConalogue, 1988; Ko et al., 1991]. These processes include advection by the global circulation, which tends to steepen the slopes of tracer VMR surfaces, and eddy mixing processes which tend to flatten tracer mixing ratio surfaces. Chemical loss or production would flatten the tracer VMR surfaces near the tropics. The global distributions of stratospheric CH₄ and Hydrogen Fluoride (HF) for different seasons have been obtained

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by the Halogen Occultation Experiment (HALOE) instrument on UARS since October 1991. *Luo et al.* [1994] described HALOE global observations of HF and demonstrated that stratospheric HF, which is an inert reservoir of fluorine in CFCs, can also be treated as a long-lived tracer in the stratosphere. We will present the HALOE CH₄ global distribution here and discuss its similarities and differences with HF.

Theoretical model studies also indicate that the mixing ratios of long-lived tracers can have simple interrelationships [*Plumb and Ko*, 1992]. An ideal pair of tracers which are in the state of "slope equilibrium" (the chemical timescales for the species are longer than quasi-horizontal transport timescales) will share surfaces of constant volume mixing ratio and their correlation plot would fall in a compact curve globally. Limited tracer observations prior to UARS and the correlation plots between them were collected at the NASA 1992 Models and Measurement Workshop for comparing with model simulations [*Prather and Remsberg*, 1993]. While observations have very limited latitudinal and seasonal coverage, model results seem to suggest that a "universal" compact, nearly linear correlation between very long-lived tracers does exist, such as N₂O versus CH₄ and N₂O versus CFC-12 for example. Some models also show a slight latitudinal departure of the correlation curves. HALOE observations provide long-term nearly global measurements of CH₄ and HF and the data are of excellent quality. In this paper we will study the correlations between HALOE-observed CH₄ and HF and compare them with NCAR two-dimensional model results [*Brasseur et al.*, 1990] which provide global distributions of stratospheric tracers. The model however, is not able to simulate polar vortex conditions.

The interrelationship between long-lived tracers has been a very powerful tool used in studies of polar ozone-hole related transport and chemical processes. Their correlation curves have been used to infer unavailable measurements or to identify chemical perturbations, such as denitrification and ozone loss [*Fahey et al.*, 1990; *Proffitt et al.*, 1990]. A commonly used assumption in such studies is that the correlation between tracers is universal. By this it is meant, for example, that it is reasonable to assume that observed tracer correlation curves in the midlatitude are also applicable in the polar vortex and any departure from the curve would be due to perturbed chemistry. Although some tracer fields in the lower stratosphere are indeed very close to "slope equilibrium" and their VMR correlations should merge to a universal nearly compact curve, it should be borne in mind that air in the polar region and near the ozone hole has been isolated from the rest of the atmosphere for a long season and it originated from a higher altitude [*Russell et al.*, 1993a] where chemical processes may not be negligible. *Hall and Prather* [1995] studied N₂O-O₃ correlations for a modeled vortex with only normal gasphase chemistry. Their results showed that the correlation curves of the two species in the lower stratosphere inside the vortex depart from that of outside, which suggests less ozone would be found on a N₂O surface across the vortex boundary. In this pa-

per we will examine the correlation curves for HALOE simultaneously measured CH₄ and HF in the polar vortex and compare them with those outside the vortex. HALOE data clearly show that CH₄-HF correlations follow different curves for measurements made inside and outside the vortex.

2. HALOE Observations of CH₄ and HF

Since launch in September 1991, the HALOE instrument on UARS has been operating essentially without flaw. This solar occultation instrument consists of eight optical channels measuring atmospheric absorption features by various stratospheric gases and provides retrieved volume mixing ratio profiles of a number of key chemical species at every spacecraft sunrise and sunset event. A detailed description of the instrument and its measurement coverage can be found in the work of *Russell et al.*, [1993b]. The measurement line-of-sight tangent point of HALOE moves gradually between the south and the north and scans nearly the whole globe in about a month. The accumulated global data set then can be used to create a zonal mean pressure versus latitude cross section for the volume mixing ratio of the species measured.

The HALOE HF and CH₄ channel validation papers [*Russell et al.*, 1995; *Park et al.*, 1995] provide further information on data quality and comparisons with correlative measurements. In general, HALOE HF observations agree with correlative balloon underflight observations to within 7% or less throughout the stratosphere above the 70 mbar level. The precision (repeatability) of the measurements is ≤ 0.04 part per billion by volume (ppbv) over the range from the tropopause to the stratopause. The estimated CH₄ error (random plus systematic) is of the order of 7% over the altitude range from 12 to 40 km. The precision is ≤ 0.05 part per million by volume (ppmv) from 25 to 75 km degrading below 25 km to 0.1 ppmv at 16 km.

Luo et al. [1994] described HALOE-measured stratospheric hydrogen fluoride (HF) in detail, including its zonal mean meridional structures for different seasons, its global column amounts and comparisons with previous measurements, and results from the NCAR two-dimensional model. HALOE has provided the first global observations of HF, the dominant reservoir species for fluorine released from man-made CFCs. HF is believed to be very inactive chemically with no known chemical (photochemical) removal processes in the stratosphere. The conversion of the fluorine in CFCs to HF in the middle-high stratosphere leads to a monotonically increasing HF field with altitude. Its seasonally dependent global distributions, as described by *Luo et al.* [1994], show a very similar pattern to the long-lived tracers, such as CH₄ and N₂O observed by the Stratospheric and Mesospheric Sounder (SAMS) and CH₄ observed by HALOE itself. The production timescale for HF is equivalent to the timescale for CFC dissociation. This species is therefore a good dynamical tracer in the stratosphere, as discussed, for example, by *Brasseur and Solomon* [1986].

The tropospheric source gas CFCs have roughly a few percent annual increase rate, and the observations of stratospheric HF and CF₂O also show similar rates of increase with a few years delay time [Zander *et al.*, 1994; Luo *et al.*, 1994]. The total fluorine amount in different regions in the stratosphere is predicted to be different depending on the average "age" of the air. Simultaneous measurements of fluorine-containing species globally should therefore provide useful data in studies of air exchanges in different regions of the atmosphere. The HF distribution itself, however, is hard to use as an indicator of the air age because the fluorine partitioning among F-containing species depends on altitude, latitude, and seasons.

Among several long-lived tracers in the stratosphere (e.g., CH₄, N₂O, CFC-11, and CFC-12), theoretical calculations indicate that CH₄ has the longest chemical lifetime (e-folding time for decay in the stratosphere). It is therefore considered to be a better tracer than the others for use in studies of dynamical processes in the upper stratosphere. As pointed out by Mahlman *et al.* [1986] and Holton [1986], chemical effects would tend to flatten the mixing ratio surfaces of long-lived tracers. We expect that the isopleth (or isosurfaces) for CH₄ VMR graphed as pressure versus latitude would be steeper compared to other tracer fields, such as HALOE HF.

Plate 1 shows HALOE CH₄ pressure versus latitude cross sections for the same four time periods in 1993 used by Luo *et al.* [1994] for the HF fields. These four periods are basically representative times for northern winter, spring, summer, and fall. We will not repeat the detailed discussions on implications of the seasonal characterized structures of the CH₄ field as we did for HF. The HALOE-observed CH₄ and HF global patterns are very similar. For example, both CH₄ and HF fields show a pronounced "double-peak" structure in the April-May midstratosphere and a less pronounced "double-peak" in October-November; the two fields show similar tiltings of their tropical minimum and maximum regions in the solstice seasons; as the result of strong mixing by waves, both tracer VMR surfaces show a relatively flat area (the "surf zone") in the midlatitude October-November period; and distinct vortex-descent features are shown in both CH₄ and HF in the spring Antarctic region. The similarities in HALOE-measured CH₄ and HF global patterns indicate that HALOE measurements are internally consistent and that our current understanding of fluorine chemistry in the stratosphere is roughly correct. HF is indeed a long-lived trace gas and HALOE global observations of HF provide us with useful data for studies of stratospheric transport and its coupling with the halogen chemistry.

Although the similarity in meridional structures of tracers can be qualitatively explained by seasonally dependent dynamical processes, detailed observation-model comparisons reveal problems in the understanding and in the model treatment of realistic dynamical processes and their coupling with chemical processes. The correlations between chemical tracers, in-

cluding model-simulated hypothetical tracers, are powerful tools in diagnosing the effect of interactive processes. As a step toward quantitatively using HALOE-measured CH₄ and HF fields, we will examine the interrelationship between these two simultaneously measured species, which we believe will reveal the differences between the two very similar fields and the role of stratospheric chemistry and transport in determining their distributions and relationship.

3. Correlations Between CH₄ and HF

Global Measurements and Model Simulations

As described earlier and in several other papers [Russell *et al.*, 1993b; Luo *et al.*, 1994], HALOE daily sunrise and sunset events are usually located at two latitude circles and they gradually sweep between south and north. The measurement tangent point passes the equator about 15-20 times annually or at least once a month. HALOE observes each polar region (60° latitude and poleward) in three time periods every year. In addition to a summer month when observations are limited to below 70° latitude, there are two time periods in each hemisphere when the observations reach nearly 80° latitude; i.e., mid-March to the end of April and mid-August to mid-September in the Arctic and mid-February to mid-March and the end of September to end of October in Antarctica. The global coverage of HALOE measurements allows us to survey the CH₄ and HF relationship for different latitude bands and seasons. We found an interesting shift of CH₄-HF correlations for data taken inside the polar vortex relative to those measured outside. The discussion on the vortex tracer correlation will be in the next subsection. In this subsection we focus on the HALOE global CH₄-HF relationships without considering the polar vortex and compare with results from the NCAR two-dimensional model, which does not simulate the polar vortex.

Examinations of HALOE simultaneously measured stratospheric CH₄ and HF for different latitude bands and seasons show that in general, measurement pairs in CH₄-HF scatterplots fall onto a compact curve for a given latitude band. The tropical correlation curve and the high-latitude correlation curve define the envelope of all the possible correlations. Figures 1a, 1b and 1c show the CH₄-HF scatterplots for the tropical region for the entire year of 1992, mid-February to mid-March 1992 southern polar region and mid-August to mid-September 1992 northern polar region. The two available polar region measurements were taken during the late summer in each hemisphere, before the polar vortices formed.

Methane and HF are indeed observed to have simple relationships. In the tropical and high southern latitude regions the correlation curves seem slightly bent compared to the curve in high northern latitudes which is nearly linear. Since most chemical activity (removal of CH₄ and formation of HF) occurs in the tropical-low latitude region, the slope of the CH₄-HF curve is mostly determined by the relative effects of CH₄ re-

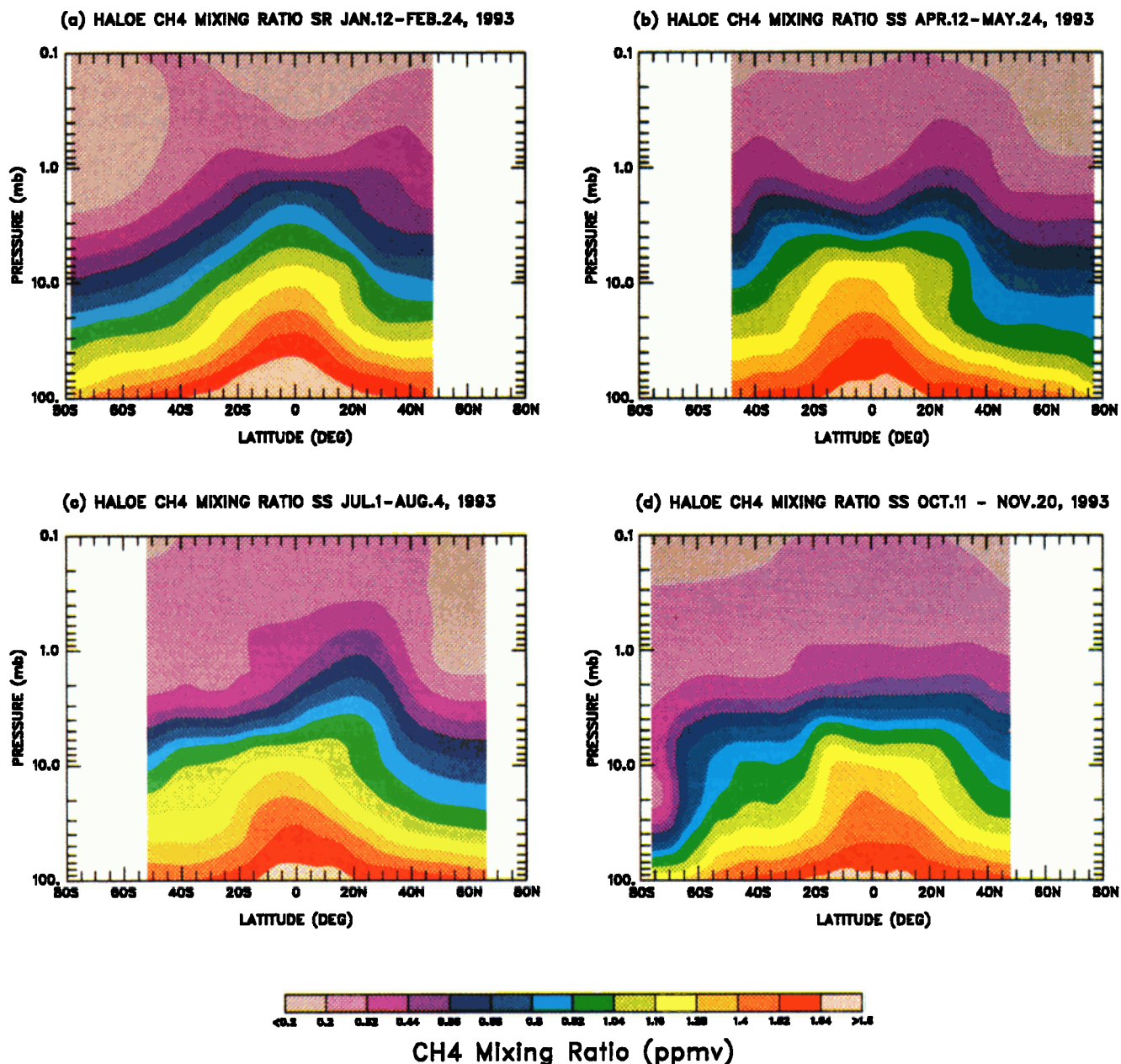
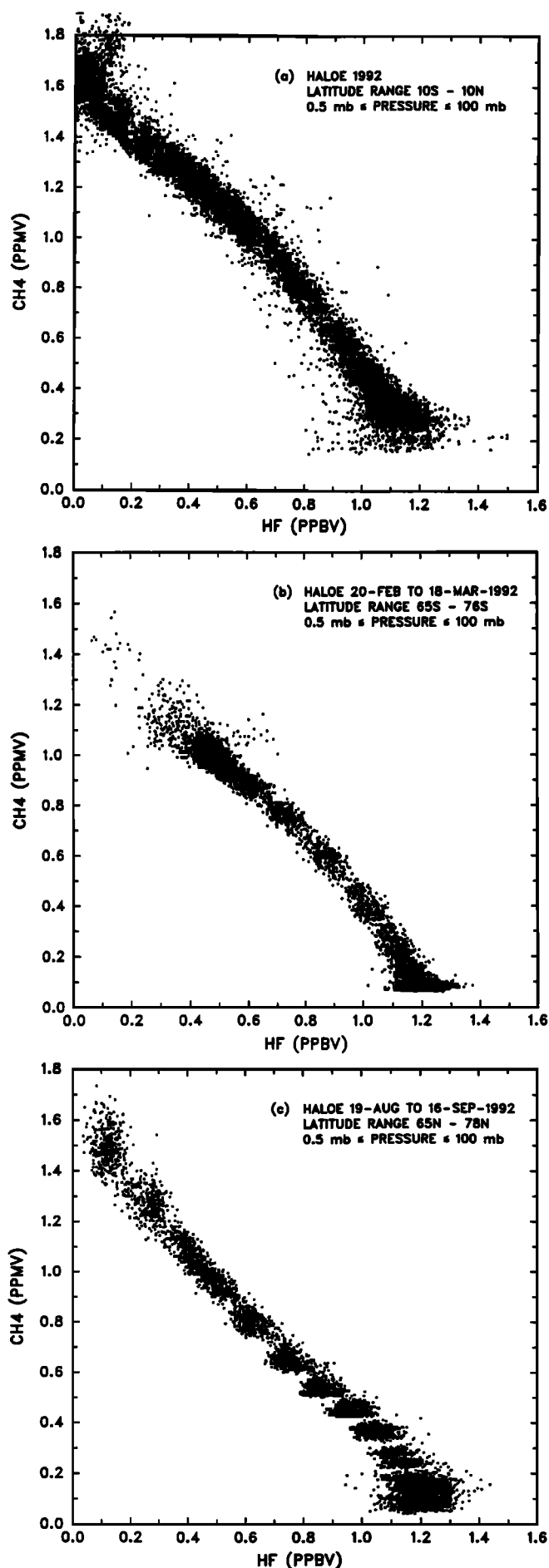


Plate 1. Pressure versus latitude cross sections for CH₄ volume mixing ratio measured by Halogen Occultation Experiment (HALOE) in 1993: (a) January 12 to February 24, sunrise; (b) April 12 to May 24, sunset; (c) July 1 to August 4, sunset; and (d) October 11 to November 20, sunset.

moval rate and HF production rate as functions of altitude. Figure 1a shows that CH₄ and HF data follow correlations with slightly different slopes above and below the corresponding pressure level where CH₄ = ~1.0 ppm, which might imply (see discussions of Figure 4) the ratio of CH₄ removal to HF production changes at about 6 mbar (CH₄ = ~ 1.0 ppm from Plate 1). The observed CH₄-HF correlations globally are found to lie in between the tropical bent curve and high-latitude curves depending on the competitive effects of seasonal mixing processes and advection. For example, the CH₄-HF correlation for CH₄ < 0.8 ppm in the February to March southern polar region (Figure 1b; also see Fig-

ure 2) is found to bend slightly toward and merge to the tropical curve (Figure 1a) compared to that in August to September northern polar region (Figure 1c). During the 1992 southern late summer, relatively larger variability in HALOE-observed tracer profiles at southern high latitudes is found than that shown in data of northern late summer high latitudes (Figures 1b versus 1c), implying differences in wave mixing processes which would draw tracer correlations at high latitudes to near that of tropics.

It is worth mentioning that at the top and bottom pressure levels defined in Figure 1, measurements in the tropical region and at high latitudes show differ-



ent values of CH₄ (and HF). For instance, tropical CH₄ at 100 mbar is found to be greater than 1.6 ppm, while 100 mbar CH₄ at polar latitudes is observed to be less than 1.6 ppm. At 0.5 mbar, data in polar regions show smaller CH₄ values than those in the tropics. Figure 1c also indicates that when CH₄ is $< \sim 0.2$ ppm, HF becomes constant at ~ 1.2 ppb in the 1992 mesosphere, which was perhaps nearly the total inorganic fluorine amount at that level. Note that atmospheric concentrations of HF and CH₄ are increasing with time [World Meteorological Organization (WMO), 1992; Gunson *et al.*, 1994], so that future measurements of these species will presumably reveal higher VMRs.

Figure 2 shows the averaged CH₄-HF correlation curves for data in Figure 1. The high-latitude curves for the two hemispheres are shown in Figures 1a and 1b with the tropical curve plotted for comparison. It is found that in the very low (near 100 mbar) and very high stratosphere (near 0.5 mbar) the scattered points of CH₄-HF for tropical and polar regions nearly coincide. In the middle stratosphere the ranges of CH₄ - HF points for tropics and polar regions are clearly separated. For example, a constant CH₄ mixing ratio surface (e.g., CH₄ = 1.0 ppm) would correspond to a larger value of HF in the tropics (e.g., HF = 0.65 ± 0.05 ppb) but a lower value of HF in polar regions (e.g., HF = 0.45 ± 0.05 ppb); this is more than a 35% change in HF. Figure 2 and the above statement indicate that in the stratosphere, CH₄ constant VMR surfaces (its isopleths or contour lines) have steeper slopes than HF although this is not easily seen by visually comparing the pressure versus latitude cross sections for CH₄ (Plate 1) and HF [Luo *et al.*, 1994, Plate 1]. HALOE results of global CH₄-HF correlations agree with theoretical analyses which state that the vertically stratified tracer having the longer chemical lifetime will have steeper VMR isopleths than the tracer with the shorter chemical timescale [Mahlman *et al.*, 1986].

A model simulation of CH₄-HF correlations is shown in Figure 3. The NCAR two-dimensional model treats stratospheric radiative, dynamical, and chemical processes interactively. More detailed descriptions about the model can be found in the work of Brasseur *et al.* [1990], and the fluorine chemistry employed is described by Luo *et al.* [1994]. Qualitatively, model CH₄-HF correlations agree very well with HALOE observations in Figure 2. Model CH₄-HF correlations at high latitudes

Figure 1. Scatterplots of simultaneously measured volume mixing ratios of CH₄ and HF (data version 17). The pressure range is between 100 mbar and 0.5 mbar. (a) All the data for the entire year 1992 for latitudes between 10°S and 10°N; (b) data between February 20 and March 18, 1992, in latitudes 65°S - 76°S, and (c) data between August 19 and September 16, 1992 in latitudes 65°N - 78°N. (b) and (c) The only HALOE data available in the polar region before the formation of the polar vortices. (b) Includes only very few data points at 100 mbar (between CH₄ = 1.5 ppm and 1.6 ppm) due to a dense aerosol layer affecting instrument pointer tracker.

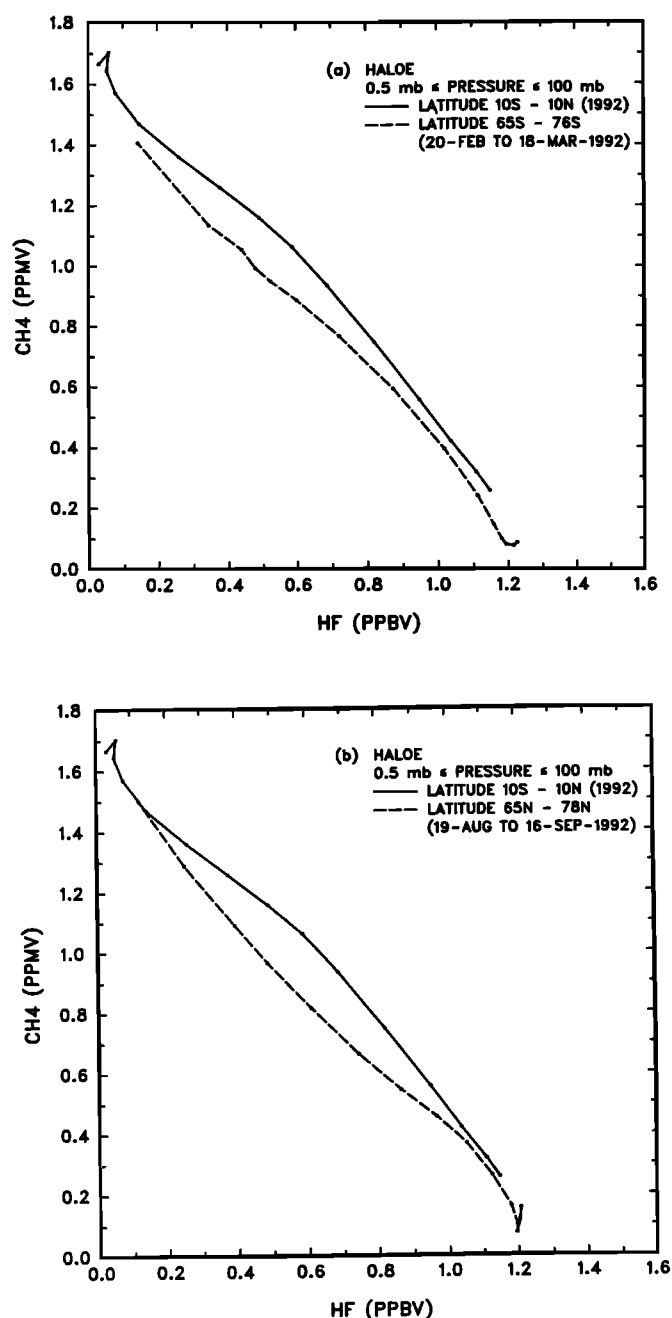


Figure 2. Averaged CH₄-HF correlations shown in Figure 1. The pressure range is between 100 mbar and 0.5 mbar. (a) Solid curve is for latitudes 10°S - 10°N, entire year 1992, and dashed curve is from data taken between February 20 and March 18, 1992, in latitudes 65°S - 76°S; and (b) solid curve is for latitudes 10°S - 10°N, entire year 1992 (same as in Figure 2a), and dashed curve is from data taken between Aug.19 and Sep.16, 1992 in latitudes 65°N - 78°N.

also show a shift from that of the tropics as we discussed for HALOE data. The model tropical CH₄-HF correlation curve bends in a similar way as HALOE data showed. To get a feeling for the role of the chemistry in determining their relationships, Figure 4 shows NCAR model CH₄ removal rate ($\text{cm}^{-3} \text{s}^{-1}$) versus HF production rate ($\text{cm}^{-3} \text{s}^{-1}$) in the tropics and polar region.

It is obvious that compared to tropical rates, the CH₄ removal rate and HF production rate at high latitudes are insignificant. The two species therefore could serve as very good dynamical tracers at high latitudes. In Figure 4 the maximum production rate for HF occurs at about 32 km and the maximum removal rate for CH₄ occurs at about 38 km. For altitudes below and above these two levels the CH₄ removal rates and the HF production rates gradually decrease.

The different slopes of the model tropical rate correlation curve for altitudes below and above 32-38 km in Figure 4 can be used to explain the bend in CH₄-HF VMR relationships. For example, Figure 4 shows that relative to HF production the tropical CH₄ removal is slower in the lower stratosphere (altitudes less than 32-38 km) than in the upper stratosphere (altitudes greater than 32-38 km). The tropical CH₄ mixing ratios (Figures 2 and 3) are therefore reduced at a slower rate in the lower stratosphere relative to the increasing rate of HF VMR with altitude.

In summary, the high-quality HALOE data allow us to examine the latitudinal dependences of CH₄-HF correlations. The observed global CH₄-HF distributions and their relationships agree well with theoretical analysis and model simulations. The results show that because horizontal mixing is not infinitely fast compared to tropical production and loss, the latitudinal pattern of the tracer interrelationship cannot be ignored. The assumption of a universal relationship needs to be evaluated by global satellite data and model simulations for any specific pair of tracers.

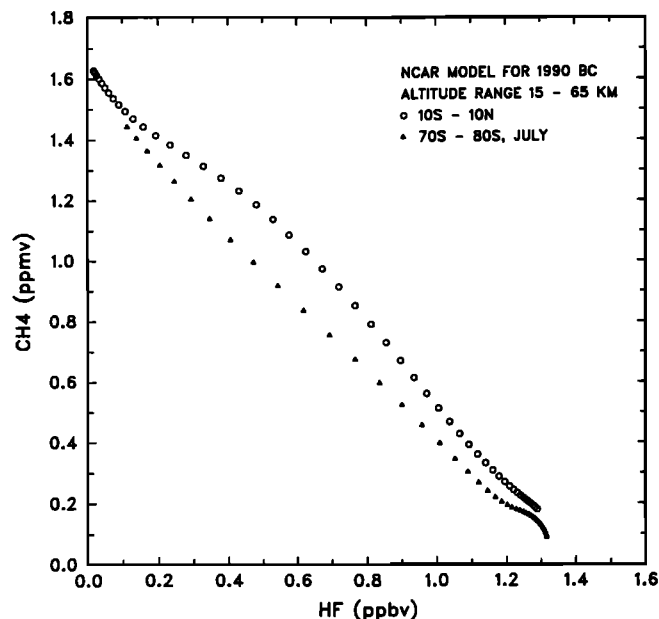


Figure 3. NCAR model simulations of CH₄ versus HF using 1990 CFC boundary condition (the quantum yield for CF₂O photolysis was unity in the model run; see discussions by Luo *et al.* [1994]). The circles are the average for the entire year in the tropics (10°S - 10°N) and the triangles are the average for July in the south polar region (70°S - 80°S) when the removal and production rates for CH₄ and HF are found to be the lowest.

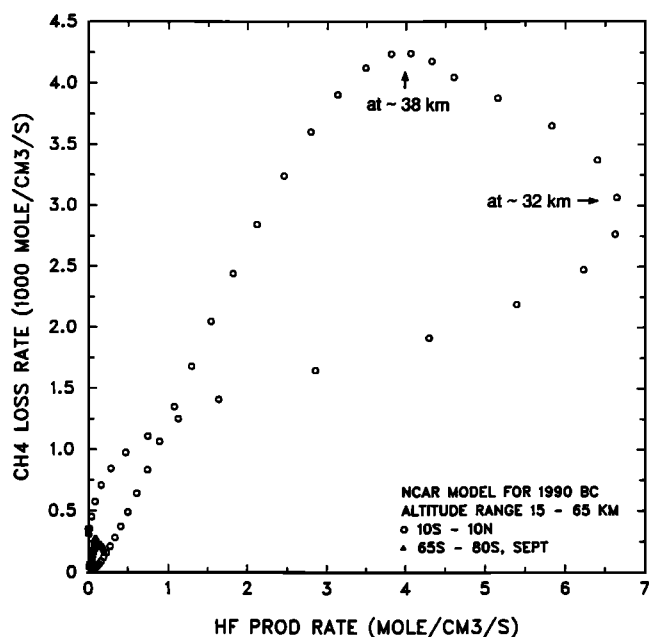


Figure 4. NCAR-model-calculated averaged CH₄ removal rate ($\text{cm}^{-3} \text{s}^{-1}$) versus HF production rate ($\text{cm}^{-3} \text{s}^{-1}$) in the tropics ($10^{\circ}\text{S} - 10^{\circ}\text{N}$; circles) and polar region ($65^{\circ}\text{S} - 80^{\circ}\text{S}$; triangles) between 15 and 65 km. The HF production rate reaches a maximum at 32 km and the CH₄ loss rate reaches a maximum at about 38 km.

Measurements in the Polar Vortex

In this section we will describe HALOE observed CH₄ and HF in the region of the Antarctic polar vortex. Two papers [Russell *et al.*, 1993a; Luo *et al.*, 1994] reported that on an isentropic surface the polar vortex was associated with observed low CH₄ and high HF compared to outside the vortex, an indication of diabatic descent, and this feature extends vertically throughout the stratosphere. HALOE data show a sharp gradient near the vortex boundary in the tracer field on an isentropic surface. It is also found that the CH₄ constant VMR surfaces in the 0.4-0.8 ppm range were displaced downward by 12-13 km between February-March and September-October 1992 within the Antarctic vortex, and the HF surfaces in the same altitude range were displaced downward by 7-8 km during the same time period [Schoeberl *et al.*, 1995]. This indicates that the volume mixing ratios of CH₄ and HF are not truly conserved following air motions within the vortex during a long season. The combination of chemical processes, the different vertical and meridional gradient of the two tracers, and eddy mixing processes result in different observed downward shifts of their VMR surfaces.

The scatterplot of CH₄ versus HF in and out of the polar vortex is of interest. Figure 5 shows all HALOE simultaneously measured CH₄ versus HF for the latitude band 65°S and poleward in September-October 1992. The 1992 averaged tropical CH₄-HF correlation curve and the late-summer averaged high-latitude curve (Figure 2a) are also overlaid on the CH₄-HF scatterplot.

Since the 1992 Antarctic vortex was not symmetric over the pole at the time when the HALOE data were taken [Schoeberl *et al.*, 1995] a large portion of the profiles were taken outside the vortex and near its boundary, in addition to many profiles within the vortex for the latitude range in Figure 5. Compared to the CH₄ - HF scatterplot for February-March in the same latitude region (Figure 1b), their relationships for the spring vortex in Figure 5 are not so compact. This is an indication that the CH₄-HF pairs in Figure 5 include data for different dynamical regions. Compared to the February-March initial correlation, the CH₄ - HF correlation for inside the vortex became more linear, while the correlations for outside the vortex appear to be drawn toward the curve near the tropics due to strong eddy mixing. The following example will illustrate the observed shift of CH₄-HF correlation inside the vortex from that of outside.

We examine here one day of HALOE observations in which profiles for both inside and outside the vortex are available. Figure 6 shows HALOE tangent point locations for October 10, 1992. It also shows the maximum wind line on the 500 K potential temperature surface. There were 12 sunset measurements for the day (odd event numbers 1, 3, ..., 23). Using the maximum wind line on 500 K as a rough indicator of the vortex boundary in the lower stratosphere, we found that five sunset measurements were made outside the vortex (event 1,3,5,7, and 9) and seven measurements were made inside the vortex (event 11, 13, ..., and 23).

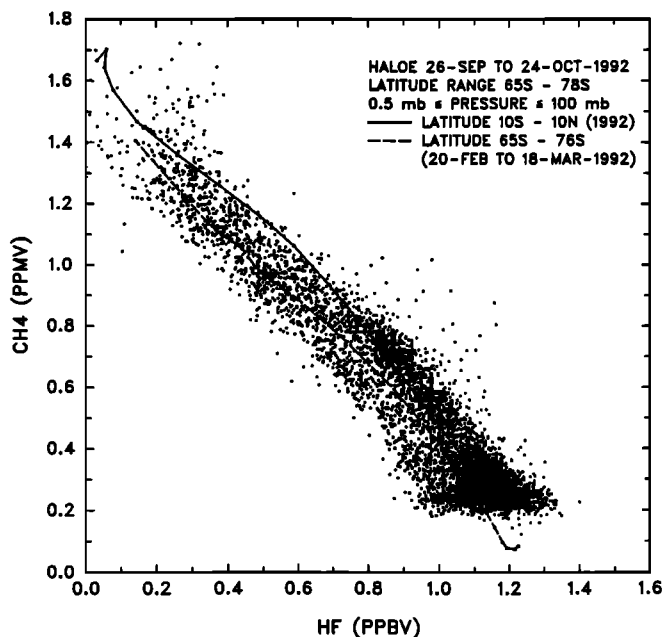


Figure 5. Scatter diagram for HALOE CH₄ versus HF points from HALOE simultaneously measured volume mixing ratios of CH₄ and HF for latitudes 65°S and poleward in the time period September 26 to October 24 1992 (data version 17). The pressure range is between 100 mbar and 0.5 mbar. The two curves are from Figure 2a, the averaged tropical CH₄-HF correlation, and the averaged polar region correlation observed in February-March 1992.

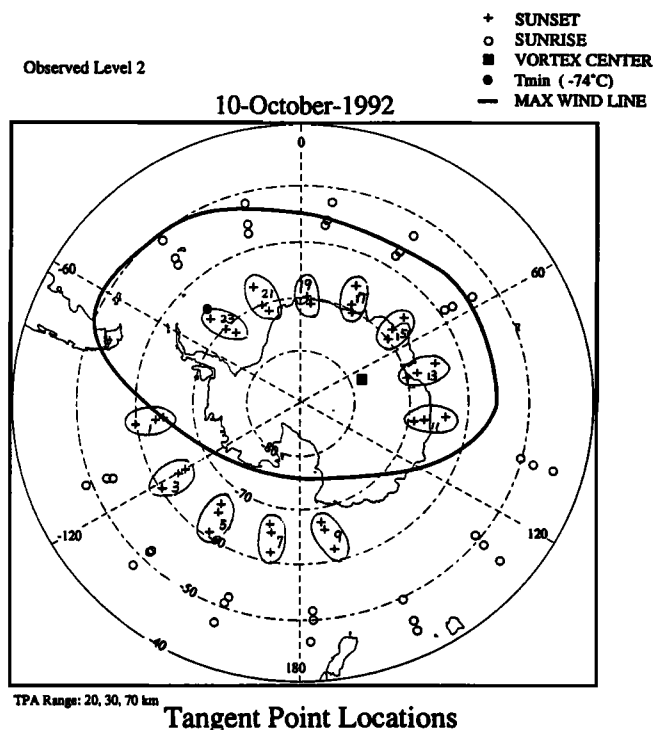


Figure 6. HALOE tangent point locations for October 10, 1992 (provided by A. Tuck and HALOE science team). The maximum wind line on 500 K potential temperature surface is used to identify sunset measurements made inside or outside the polar vortex. The 12 sunset events for the day are marked by event numbers 1, 3, ..., and 23.

Plate 2 shows CH₄ and HF profiles for all 12 sunset events on October 10 and their correlations. It is clear that in the 20 to 30 km range the vortex is well isolated from the region outside the maximum wind line. Inside the vortex, CH₄ and HF show distinct low and high values compared to their outside values, an indication of strong air descent over the past seasons. Above ~30 km the vortex seems to be quite disturbed in the late September to October time period. We find many profiles of CH₄ and HF folded (*i.e.*, reached a maximum or minimum value) to follow values measured outside the vortex as represented by the two red profiles in Plate 2.

HALOE observations in September-October 1992 show, in general, not only was the low CH₄ (high HF) area in the upper stratosphere (e.g., 5 mbar) much smaller than the area in the lower stratosphere (e.g., 20 mbar) but also the tracer VMR gradient on an isentropic surface in the upper stratosphere was smaller [Schoeberl *et al.*, 1995]. HALOE observations of CH₄ or HF profiles at a fixed location could therefore be composed of data inside the vortex in the lower stratosphere and data outside the vortex in the upper stratosphere, as the two red curves in Plate 2 show.

The CH₄-HF correlations in Plate 2 bottom are typical for HALOE measurements in October 1992 and in the 65°S-78°S latitude band. Note that CH₄ = 0.2 ppm and HF = 0.95 ppb pairs were found near 25 km, and

for altitudes below this level, the CH₄-HF correlations inside the vortex are clearly shifted from those of outside. For example, on the CH₄ = 0.5 ppm surface, HF is found to be ~0.8 ppb inside the vortex, while it was ~1.0 ppb outside the vortex, over 20% difference in HF. We found a similar relative amount change for CH₄ in and out the vortex on a constant HF surface.

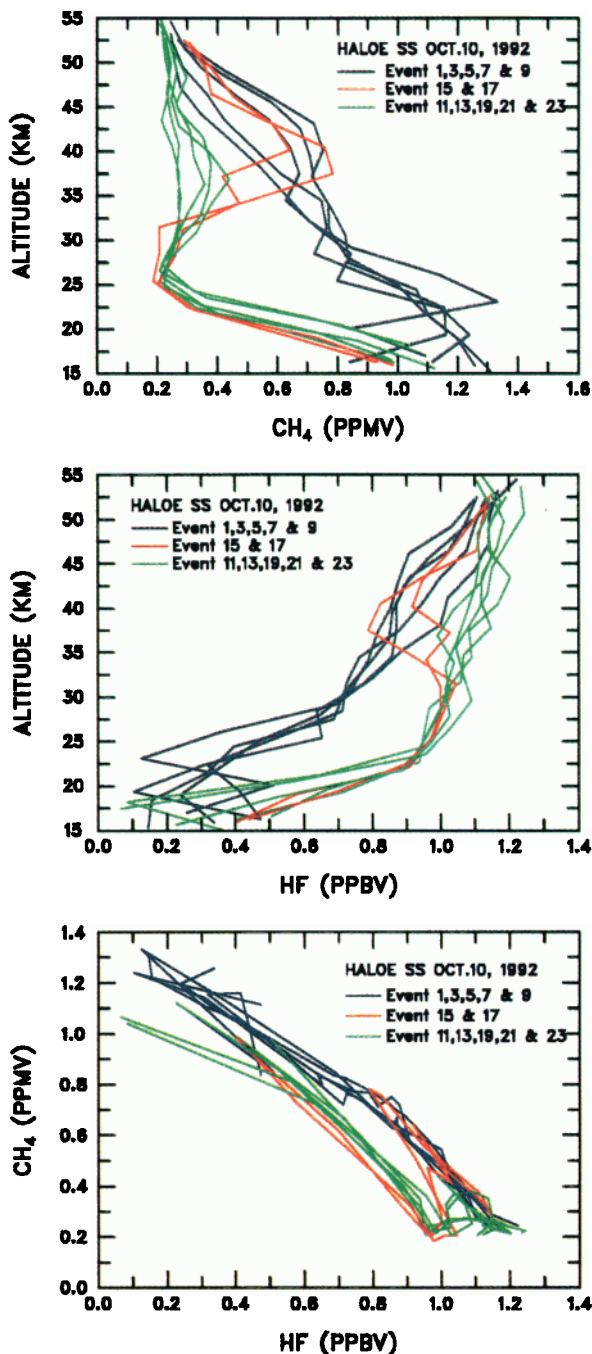


Plate 2. HALOE sunset CH₄ and HF profiles and their correlations for October 10, 1992, at latitudes ~63°S. The tangent point locations for the 12 events are shown in Figure 6. According to the maximum wind line, the red and green profiles were taken inside the polar vortex and the blue profiles were taken outside the vortex on the 500 K surface. See text for more discussions.

The CH₄-HF correlations for inside and outside the vortex are found that both shifted relative to their initial correlation in February-March. Considering the CH₄ = 0.5 ppm surface again, we found that averaged values of HF = ~0.92 ppb in February-March. HF = ~0.8 ppb well inside the vortex and HF = ~1.0 ppb outside the vortex in late September to October. As we discussed in this paper, this 10-15% change in HF for a constant CH₄ value mainly resulted from the isolation of the vortex which apparently prevents remote tropical production of HF and loss of CH₄ from being communicated to high latitudes. The poleward-downward transport during the winter season and the quasi-horizontal mixing processes (especially at levels above 20 mbar in spring) brought air with different mixtures of CH₄ and HF into the polar vortex. If there were no latitudinal dependences of CH₄ removal, HF production, and mixing processes, the CH₄-HF relation would not shift from their initial correlation in February-March. This is only a qualitative description. Model simulations are needed to understand the changing processes from the CH₄-HF state in Figure 1b to that in Figure 5 and Plate 2 (bottom).

The usage of tracer correlation curves to infer the unavailable measurements (e.g., O₃ versus N₂O) or to identify any chemical perturbations should be based on full knowledge of the latitudinal and seasonal dependences of the correlation curves. Most stratospheric models are not able to simulate realistic polar vortices and several other observed phenomena, such as the winter subtropical transport barrier. Global satellite observations provide simultaneously measured multilong-lived tracer fields as well as active chemical tracer fields. It would be necessary to examine the correlations between any interesting pair of tracers globally before applying their correlations under a special condition, such as outside the spring vortex, to any other region. During the Antarctic and Arctic aircraft campaigns, most data were taken along a constant potential temperature surface (isentropic surface) across latitude lines between midlatitudes and the polar regions. The change in tracer compositions on a given isentropic surface indicates the existence of diabatic processes. If there is a "universal" correlation curve between two tracers under consideration, the tracer combination would fall somewhere on that curve no matter what sampling method is used (e.g., along an isentropic surface, along an isobaric surface, or the vertical profiles of one against the other), and any shift from the "universal" correlation would imply a chemical perturbation. However, our examinations of global and polar vortex HALOE CH₄ and HF relationships indicate that the CH₄-HF correlations shift with latitude, suggesting that they are not in an ideal "slope equilibrium" or "gradient equilibrium" state globally.

Figure 7 shows HALOE-observed CH₄ versus HF in September-November 1992 for the southern hemisphere on the 650 K potential temperature surface. We found that the data seem to follow a compact curve. However, comparing to our collections of global CH₄-HF curves,

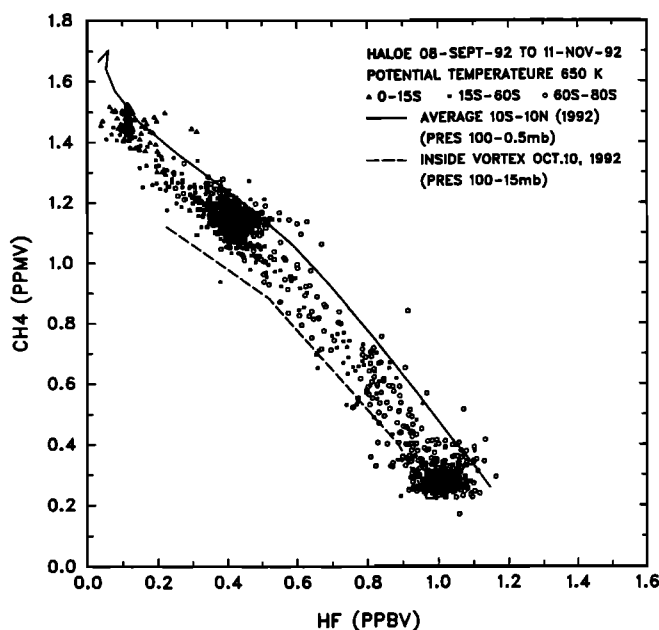


Figure 7. HALOE-measured CH₄-HF scatter diagram for data sampled on the 650 K potential temperature surface in the southern hemisphere between September 8 and November 11, 1992. The solid curve is the averaged CH₄-HF correlation for entire year 1992 between 10°S and 10°N latitudes (Figure 2). The dashed curve is CH₄-HF for event 19 (green in Plate 2) inside the vortex on October 10, 1992 (pressure levels 100-15 mbar).

we found the CH₄-HF combination actually switches from one curve to the other. On the 650 K surface, CH₄ values greater than ~0.5 ppm (HF <~0.8 ppb) were found outside the vortex and equatorward, and these measured CH₄ and HF pairs should fall on the curves that correspond to outside the vortex. The measurements having CH₄ = 0.2-0.4 ppm were well inside the vortex at 650 K and the CH₄-HF correlation should fall on a shifted curve relative to that of the tropics. We included in Figure 7 the two extreme fitted correlation curves from HALOE observations, the solid curve for the yearly averaged tropical CH₄-HF pairs, and the dashed curve for the October 10, event 19 inside the vortex. The relative shift of these two curves represents the maximum shift for CH₄-HF correlations from HALOE data. Any fitted correlation curve would depend on the sampling strategy and it should fall inside the CH₄-HF area defined by the two extreme curves in Figure 7. If one assumes that the CH₄-HF correlation curve for outside the vortex is the "universal" correlation curve, the measurements inside the vortex would indicate a HF loss if CH₄ is considered to be a conserved tracer, or a CH₄ loss if HF is assumed to be a conserved tracer.

In the lower stratosphere, where aircraft fly, the correlation curves for CH₄-HF in and out the vortex are found to gradually merge together, but they are still shifted from that of the tropics (Figure 2) which is somewhat isolated from midlatitudes by an observed subtropical barrier. Figure 7 is a good example to illus-

trate the relatively isolated regions in the stratosphere, namely, the tropics, the midlatitude "surf zone" and the polar vortex. The mixing of air masses between the regions seems to be inhibited, as demonstrated by the three groups of tracer mixtures on the 650 K surface in Figure 7.

4. Conclusion

In this paper we discussed the interrelationship between two stratospheric long-lived tracers, CH₄ and HF, using a year of global HALOE observations. This study allows us to quantitatively examine the roles of chemical and dynamical processes on the distributions of stratospheric tracers. In general, the meridional structures of CH₄ and HF for different seasons are nearly identical, which indicates that in most parts of the stratosphere the chemical timescales of these two species are usually longer than the timescale for dynamical processes. Several distinct features in their VMR zonal mean pressure versus latitude cross sections that have been predicted theoretically or observed in tracer measurements by other satellite instruments are clearly shown in HALOE data: namely, the equinox "double-peak" in tracer isopleths associated with the semiannual oscillation, the tilting in the tracer equatorial vertical axis during solstice conditions, the relative flat VMR surfaces, the "surf zone," in winter midlatitudes bounded by polar vortices and a subtropical barrier, and the distinct downward displacement of tracer VMR in the polar vortex.

Global simultaneously measured CH₄-HF scatterplots indicate that the correlation curves of the two species shift with latitude. The bent tropical curve and the nearly linear high-latitude curve define the envelope of all possible correlation curves globally and seasonally. As the NCAR two-dimensional model simulation shows, the altitude-dependent chemical removal of CH₄ and formation of HF have the largest influence on their correlations in the tropical region, which causes the bend in their correlation curve. The high-latitude CH₄ versus HF, in particular during the winter, is determined by transport processes and their mixing ratios display a nearly linear relationship. HALOE-observed CH₄-HF correlations indicate that the constant mixing ratio surfaces for the two tracers do not quite coincide; the CH₄ contour lines have steeper slopes than that of HF, supporting the model simulations of a longer chemical lifetime for CH₄ compared to the chemical timescale for HF or CFCs. The relatively steeper CH₄ and flatter HF surfaces of constant mixing ratio are found also to occur in the polar vortex [Schoeberl *et al.*, 1995]. The global correlations between CH₄ and HF observed by HALOE agree well with the results of NCAR model calculations, though the model does not simulate the polar vortices.

The CH₄-HF correlation curves observed in the Antarctic vortex are found to be shifted from their correlations in the late summer before the vortex is formed and from that of outside the vortex in spring. Com-

pared to the February-March polar region, the correlation between CH₄ and HF within the vortex became linear while that outside the vortex appears to move closer to the correlation for the tropics. The two distinct CH₄-HF relationships inside and outside the vortex indicate the long-season isolation of the vortex. In September-October a large number of observed CH₄-HF pairs above ~ 20 mbar are found to have mixing ratios characteristic of outside values, in agreement with the occurrence of spring vortex breakup and shrinking.

A major point we want to emphasize is the importance of a global survey of the relationship between a tracer pair of interest. It is found that a universal correlation curve of CH₄ versus HF does not exist although their meridional structures look very similar. In other words, HALOE data are able to be used to reveal that CH₄ and HF are not in an ideal global "slope equilibrium" state. A constant CH₄ VMR contour will meet with some lower values of HF at high latitudes compared to the HF value in the tropics. The amount of change in HF for a constant CH₄ could be as large as 10-35% depending on altitude and latitude. The largest change is found across the dynamical "barriers," such as the polar vortex and the winter subtropical barrier. HALOE-observed CH₄-HF pairs in the whole hemisphere on a potential temperature surface, analogous to the available aircraft sampling path for multitracers, were used to demonstrate that measurements inside and outside the vortex actually follow different correlation curves although those limited data with a large range of CH₄-HF mixture due to diabatic effects also appear to follow a compact correlation curve.

Our demonstration of CH₄-HF correlation inside and outside the vortex implies that there is an "intrinsic" missing amount of HF associated with the vortex for a constant CH₄ compared to the HF outside, or alternatively, a different CH₄ value on a constant HF surface. Similarly, in a model vortex study by Hall and Prather [1995], less O₃ on a given N₂O surface is found at high latitudes than at midlatitudes. We conclude that the usage of universal correlation curves between tracers has to be examined carefully, especially for some stratospheric tracers which have even a shorter chemical lifetime than the CFCs, such as O₃ and HCl.

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