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Journal
Journal of Geophysical Research, 99(D8)

ISSN
0148-0227

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Publication Date
1994-08-20

DOI
10.1029/94jd01246

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. D8, PAGES 16,691–16,705, AUGUST 20, 1994

Observations of stratospheric hydrogen fluoride by halogen occultation experiment (HALOE)

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Abstract. The Halogen Occultation Experiment (HALOE) Hydrogen Fluoride (HF) channel on the Upper Atmospheric Research Satellite is providing the first global measurements of stratospheric HF, the dominant fluorine reservoir in the atmosphere. This paper describes the latitudinal and seasonal variations of HALOE-observed HF in terms of vertical profiles, altitude/latitude cross sections, and column abundances. The HF global distribution shows a "tracerlike" structure and its column amount increases with latitude, in agreement with previous aircraft measurements of the HF column amount. A comparison between the HALOE HF column above 20 km and the ATMOS 1985 measurements is used to estimate the annual rate of increase of stratospheric HF. Exponential rates of 4.9-6.6% yr^{-1} and linear growth rates of 6-8.6% yr^{-1} in 1985 and 4.3-5.5% yr^{-1} in 1992-1993 are found. HALOE HF measurements during the 1993 Antarctic spring are briefly described. This species behaves like a conserved tracer and its distribution shows an area of enhanced mixing ratios correlated with the polar vortex that has a clear latitude boundary. Finally, simulated HF distributions by the National Center for Atmospheric Research two-dimensional model are used to compare with HALOE observations of HF. Reasonable agreements in the global structure and the absolute amount of HF are found. The differences between the model and the observed results indicate the need for improving treatment of atmospheric dynamics and fluorine-related chemical parameters in the model simulations.

1. Introduction

Stratospheric hydrogen fluoride (HF) is believed to be the dominant stable reservoir of free fluorine atoms released from the photochemical breakdown of the man-made chlorofluorocarbons (CFCs) [*Stolarski and Rundel*, 1975; *Sze*, 1978]. The measurement of HF is therefore recognized to be important in investigating the changing effects of anthropogenic products on the global ozone layer as well as on the chemical and dynamical processes in the upper atmosphere. The tropospheric source gases that contain fluorine atoms are mainly CF_2Cl_2 (CFC-12), $CFCl_3$ (CFC-11), $C_2F_3Cl_3$ (CFC-113), and CHF_2Cl (HCFC-22). Figure 1 shows a plot of the historical record and projection of the tropospheric total fluorine volume mixing ratio (parts per billion by volume) as a function of time between 1970 and 1995. Data were adopted from World Meteorological Organization report 25 [WMO, 1992] which assembles the measurements and the best projected CFC releases to the atmosphere. Tropospheric total fluorine has annual increase rates of greater than 10% yr^{-1} in the mid-1970s to about 4% yr^{-1} in the early 1990s. In the stratosphere, similar growth trends for HF, which is essentially the difference between the total fluorine and the fluorine amount in the CFCs [*Zander et al.*, 1992], are expected. The possibility that fluorine species (CF_3 in particular) could influence stratospheric ozone amounts was suggested by *Ko et al.* [1994], but laboratory studies and analysis by *Ravishankara et al.* [1994] predict little if any impact of CF_3 on O_3. Although fluorine-containing species are not actively involved in the catalytic destruction of ozone, they are tightly linked with the more reactive chlorine-containing species through their common anthropogenic sources. Natural sources of organofluorine chemicals are thought to be negligi-

Paper number 94JD01246.
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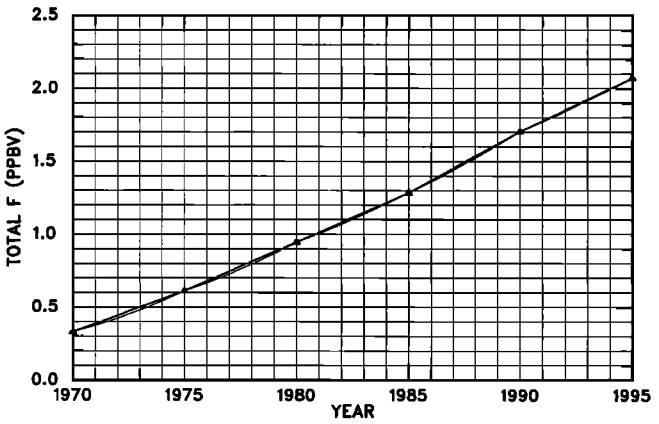

Figure 1. Historical record and projections of total fluorine concentration in the troposphere. Data (triangles) are taken from WMO report 25 (1992) with total F defined as $[CFCl_3] + 2[CF_2Cl_2] + 3[C_2F_3Cl_3] + 4[C_2F_4Cl_2] + 5[C_2F_5Cl] + 2[CF_2BrCl] + 3[CF_3Br] + 2[CHF_2Cl]$. The thick solid lines are the connections between two adjacent data points (separated by 5 years); the thin solid curves are calculated by $F = F_o(1+\alpha\%)^{(x-x_o)}$ between any two points, where $\alpha\%$ is the fixed annual increase rate within the 5 years and x and F represent year and total fluorine, respectively (see more discussions on the definitions of annual increasing rate in section 4).

ble; very few chemicals containing C-F bonds have been found in nature [*Cicerone*, 1981]. An additional anthropogenic chemical, CF_4, is usually not considered as a HF source because of its very long lifetime; see discussion in section 6.

The variation of observed HF, a dominant fluorine reservoir species, and HCl, a more reactive chlorine reservoir species, have already been used in studies of the polar ozone hole [*Coffey et al.*, 1989; *Toon et al.*, 1989; *Toon et al.*, 1992a, 1992b; *Kaye et al.*, 1990]. Stratospheric HF is also considered to be a conserved tracer in studying atmospheric transport processes. Its formation rate is similar to the destruction rate of the CFCs as a function of altitude and its only sink path in the stratosphere is to diffuse downward to the troposphere where it is removed by rain. HF therefore has a long lifetime in the stratosphere.

Global observations of HF in the stratosphere have been obtained by the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) since its launch over two and one-half years ago [*Russell et al.*, 1993a]. The HALOE HF data set provides us information for the first time on the global distributions and temporal variations of this poorly known species in the stratosphere. It is the aim of this paper to report and analyze HALOE-measured HF, which no doubt will enhance our knowledge of this important fluorine-containing species.

Two long-term measurements of HF column abundances at ground sites were reported previously: the Jungfraujoch International Scientific Station in Switzerland (46.6°N) between 1977 and 1986 [*Zander et al.*, 1987a] and Kitt Peak in Arizona (32°N) between 1978 and 1990 [*Rinsland et al.*, 1991; *Wallace and Livingston*, 1991]. Both measurements were used to study the trend of HF column, and ~ 8.5 and $\sim 9\%$ yr^{-1} increases in HF column were found at the two locations. These two ground measurements show complicated seasonal variations in column HF. A maximum in February to March and a minimum between September and November with about $\pm 10\%$ seasonal variations were observed at both locations.

The vertical distributions and the column amount of stratospheric HF have been measured by a number of balloon-aircraft-borne instruments [*Zander*, 1981; *Mankin and Coffey*, 1983; *Park et al.*, 1984; *Zander et al.*, 1987b; *Coffey et al.*, 1989; *Toon et al.*, 1989; *Mankin et al.*, 1990] as well as by a space-borne instrument, the atmospheric trace molecule spectroscopy (ATMOS) Fourier transform spectrometer [*Zander et al.*, 1990]. During its flight in orbit from late April to early May 1985, ATMOS provided two zonally averaged HF volume mixing ratio profiles, for sunset at 29°N and sunrise at 48°S. The second and third flights of ATMOS in April 1992 and 1993 covered larger latitude bands and these unpublished data sets should provide information on the latitudinal distributions of several fluorine-containing species in the stratosphere. *Mankin and Coffey* [1983] reported 34 aircraft HF column observations made from January 1978 to July 1982. Their measurements cover the latitude range 5°-70°N and were mainly made in the summer and winter. They were the first to show the latitudinal dependence of the HF column and its increases with latitude. They also made a least squares fit to their HF data using a form $a + b\cos(\text{latitude})$ with b being a negative number. A 12% yr^{-1} rate of increase for HF was determined from their 5 years of airborne measurements (1978-1982).

Several model studies and comparisons to the limited observations of the three fluorine reservoir species have been reported. *Kaye et al.* [1991] presented and discussed calculations of the global distributions of HF, CF_2O, and CFClO using a two-dimensional model. The simulated latitudinal variation of column HF roughly agrees with the measurements by *Mankin and Coffey* [1983] although model results show that the linear dependence of the HF column on the cosine of the latitude is not valid year-round. The model study of the phase of the HF column seasonal cycle also agrees with ground observations at Jungfraujoch and Kitt Peak with maximum column occurring in late March and early April. The model calculation showed that the amplitude of the annual cycle is larger at high latitudes than low latitudes. Comparisons of model simulations with *Mankin and Coffey* [1983] latitudinal HF column measurements and Kitt Peak 1980 HF column seasonal measurements were reported in the NASA 1992 models and measurement workshop report [*Prather and Remsberg*, 1993]. Four modeling groups (AER, GSFC, NCAR and WASH) provided their results. AER model-Kitt Peak comparisons have also been described in more detail by *Rinsland et al.* [1991]. In general, models are all able to simulate latitudinal and seasonal variations of HF column from observations, but there are

large differences in the absolute values among models. A crucial parameter, the quantum yield of CF_2O photolysis, is suggested to be near unity rather than 0.25 from the studies of *Kaye et al.* [1991] and *Rinsland et al.* [1991]. This parameter would greatly change the theoretical partitioning of the fluorine reservoir species HF and CF_2O and, consequently, the absolute value of the modeled HF column. The possible loss of CF_2O on stratospheric ice, HNO_3-treated ice, and on sulfuric acid solution coatings has been investigated in the laboratory by *Hanson and Ravishankara* [1991]. They found that the loss of CF_2O on these materials was very slow or nonexistent; their upperlimit rates imply that this loss "will be insignificant on timescales of a year, such as the annual polar chlorine activation phenomenon."

In this paper we describe HALOE-measured stratospheric HF, including its global distribution and seasonal variations. We will also compare the measurements of the spatial and temporal variations of HF column amount observed prior to UARS with HALOE observations. HALOE measurements of HF profiles during the 1993 Antarctic spring near the southern polar region will be discussed briefly. Finally, a comparison between the model simulations of global HF by the National Center for Atmospheric Research two-dimensional model and the HALOE observed HF will also be described.

2. Observations of Halogen Occultation Experiment (HALOE)

HALOE is the only instrument on UARS measuring hydrogen fluoride in the stratosphere. Detailed descriptions of HALOE and its HF channel can be found in a paper by *Russell et al.* [1993a]. The measurement of HF volume mixing ratio profiles is made by one of the four gas filter channels in the HALOE instrument. HALOE, which uses the solar occultation approach, observes solar radiation absorbed by atmospheric gases along the Earth limb for one sunrise and one sunset event on every satellite orbit. For the HF channel, after passing through a broadband filter centered at 2.45 μm, the sunlight is split into two paths, a HF gas cell path and a vacuum path. The HF gas cell functions as a narrow band filter. The ratio of the difference signal obtained from the two paths divided by the vacuum path signal along with other information (e.g., the temperature versus pressure profile determined from the CO_2 channel) is used to retrieve HF volume mixing ratios.

The Upper Atmosphere Research Satellite launched on September 12, 1991, has a nearcircular orbit at 585 km altitude with a 57° inclination. It orbits the Earth about 15 times each day. It therefore provides $\sim$ 15 pairs of spacecraft sunrise and sunset observation opportunities daily. Figure 2 shows the HALOE daily averaged 30-km tangent point latitude coverage in 1993. Each latitude position for a day in the graph is the averaged latitude over $\sim$ 15 sunrise or sunset events along a narrow latitude circle. Because of the rate at which the latitude of occultation events progress, the accumulation of approximately 1-month data provides a nearly global three-dimensional data set. Because HALOE uses the Sun as its radiation source, the measurements during the winter months are limited to the areas with latitudes less than $\sim$ 55° in the winter hemisphere, which can be clearly seen in Figure 2.

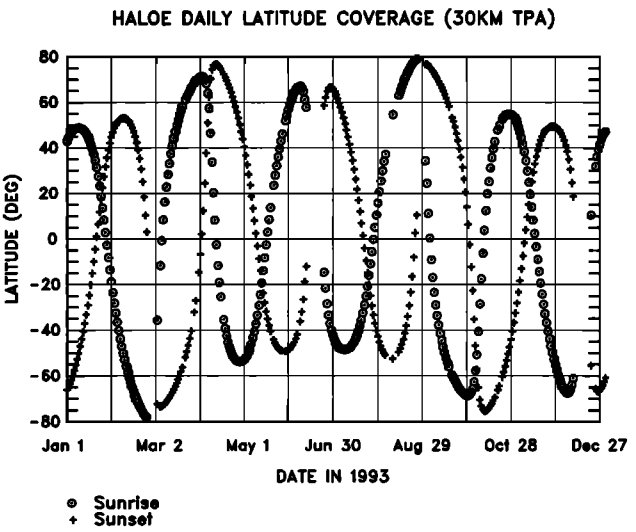

Figure 2. Halogen occultation experiment (HALOE) daily averaged latitude coverage in 1993. The latitude locations are for 30-km tangent point altitude (TPA) and they are calculated by averaging $\sim$15 events along the latitude circle band for each day. These events in a same day are separated by $\sim$ 24° in longitude with slightly different latitudes ($\leq \pm 5°$).

The HALOE instrument has made excellent measurements in all eight channels since it started to take scientific data on October 11, 1991. There is one time period of 37 days, between June 3 and July 10, 1992, when UARS experienced a solar array anomaly which forced HALOE and the other UARS instruments to be powered off. Figure 2 also shows about 3 to 4 time periods (a few days) during which HALOE does not take data either because spacecraft sunrise or sunset does not occur or the eclipse period is lengthened causing elevated instrument temperatures. When the temperature of the instrument exceeds a predetermined threshold defined to protect the detectors at high solar illumination angles, HALOE is turned off by ground command.

A HF validation paper is in preparation by the HALOE science team. We will discuss that among the HALOE's eight channels, sunspots have the largest effects on the retrievals of the HF channel, and efforts have been made to remove this effect. Our experiences with HALOE HF data indicate that in the current version data set, there are only relatively few profiles that have been contaminated by sunspot effects with very short duration (2 or 3 time periods in a year). Those profiles can easily be identified and eliminated from the data set used for scientific studies.

The lowest altitudes of HALOE-retrieved vertical profiles are lower for the higher-latitude measurements than they are for the tropical regions mainly because of volcanic/sulfate aerosol effects on the pointer/tracker.

The Mount Pinatubo volcanic eruption in June 1991 had a large effect on HALOE observations in its first few months in orbit [*Russell et al.*, 1993a], but as the years went by, the volcanic aerosol effects gradually reduced. The typical lowest altitude in the 1991 and early 1992 data at midlatitudes for the HF channel is near 25 km, while in the current data set (late 1993), the lowest altitude is about 12 km.

3. Global Distribution of Hydrogen Fluoride (HF)

Prior to HALOE, there were no observations available on the global distributions of stratospheric HF. Theoretical studies and some very limited measurements however indicate that HF is of stratospheric origin and it does not have chemical sink paths in the stratosphere so that the vertical mixing ratio increases with altitude. The HF distribution should anticorrelate with the source gas CFCs. The photodissociation of CFCs in the tropics and stratospheric transport together determine the latitudinal distribution of HF and its column abundances which are characterized by a positive latitudinal gradient in the HF mixing ratio and an increase with latitude in its column as seen by *Mankin and Coffey* [1983].

Although HALOE does not provide daily measurements of global HF (see Figure 2), a latitude sweep in $\sim$ 20-30 days would provide a seasonal representation of the HF morphology since the timescale of the stratospheric circulation is of the order of several months. In fact, we have checked many possible latitude sweep data sets (sunrises, sunsets only, or the combinations of sunrises and sunsets) and found that the HF pattern shown in its latitude versus pressure cross sections are quite similar among 2-4 possible latitude sweeps in a season (2-3 months). This can also be demonstrated by comparing Plate 1c and Plate 3 for HF zonal distributions in July and September, respectively, which will be discussed below.

Figure 3 indicates the four data blocks we used to illustrate the latitudinal distributions of HALOE observed HF. These four time periods were selected to be representative of the seasons, data quality, and data availability. The general patterns of HF shown in a

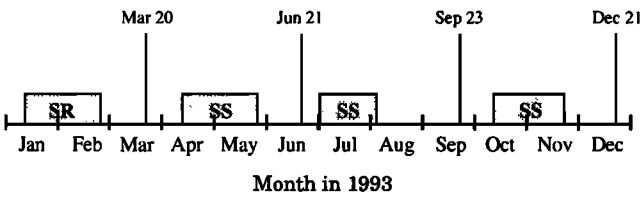

Figure 3. Four time periods (shaded areas) selected for the plots of latitude versus pressure cross sections of HF mixing ratios. The dates are listed in Plate 1. The equinox and solstice dates for 1993 are marked. SR or SS represent that data for sunrise or sunset events are selected.

same season of 1992 and 1993 are similar (except slight increases in absolute values from 1992 to 1993), but there are more data available in the 1993 northern summer (see discussion in section 2).

Plates 1a-1d show HALOE HF latitude versus pressure cross sections for the four time periods in 1993, which are essentially for winter, spring, summer, and fall seasons. The HF mixing ratio profiles of a selected time period are binned to latitude boxes having $\pm 5°$ width and centered at latitude grids with 1° steps. A normalized Gaussian function is applied to the profiles in a latitude bin to weight the profiles differently according to their distances to the latitude grid of the bin [*Luo et al.*, 1994]. The pressure levels included in the plots are between 100 and 0.32 mbar. HALOE HF retrievals above 0.32 mbar are noisy, but the mean values there, at high latitudes in particular, tend to stay constant through the lower mesosphere until HALOE loses its sensitivity in the middle to upper mesosphere. The great similarity between HALOE-observed global patterns of CH_4 and HF [*Russell et al.*, 1993a] indicates the internal consistency of the instrument.

As expected, the HALOE observations of HF latitude versus pressure cross sections (Plate 1) show an increase of HF mixing ratio with altitude. Since the source gases of stratospheric fluorine (CFCs) enter the stratosphere mainly in the tropical region and experience photolysis in the middle to upper stratosphere, HF decreases lower down into the troposphere as it is washed out. The stratospheric transport circulation that consists of upwelling in the tropics and downwelling at high latitudes produces the HF minimum over the tropics and maximum over the high latitudes.

The gross pattern of HF mentioned above is generally consistent with theoretical estimates. But as seen in Plate 1, it also has some unique seasonal characteristics. In particular, the HF pattern in April to May 1993 (Plate 1b) shows a "double-peak" feature of equatorial maximum and subtropical minimum, while during the second equinox season of October to November 1993 (Plate 1d), the double-peak structure is not quite so pronounced. These characteristics are also evident from the stratospheric and mesospheric sounder (SAMS) observations of CH_4 and N_2O in 1979 [*Jones and Pyle* 1984]. The double-peak structure of atmospheric tracers is believed to be the result of sinking motion over the tropics and rising motion over the subtropics induced by the semiannual oscillation (SAO) of the equatorial zonal wind during its westerly phase [*Gray and Pyle*, 1986, 1987]. The weaker double-peak structure of HF for the second equinox season of the year is consistent with observations of seasonal asymmetry in the equatorial SAOs, with stronger westerly phase in the first semiannual cycle (beginning in the northern hemispheric winter) than the second semiannual cycle (beginning in the southern hemisphere winter) [*Delisi and Dunkerton*, 1988a]. *Delisi and Dunkerton* [1988a, b] proposed the "self-enhancing" effect as a possible mechanism for producing the asymmetry, namely, that a stronger easterly in the tropics during northern hemispheric winter (due

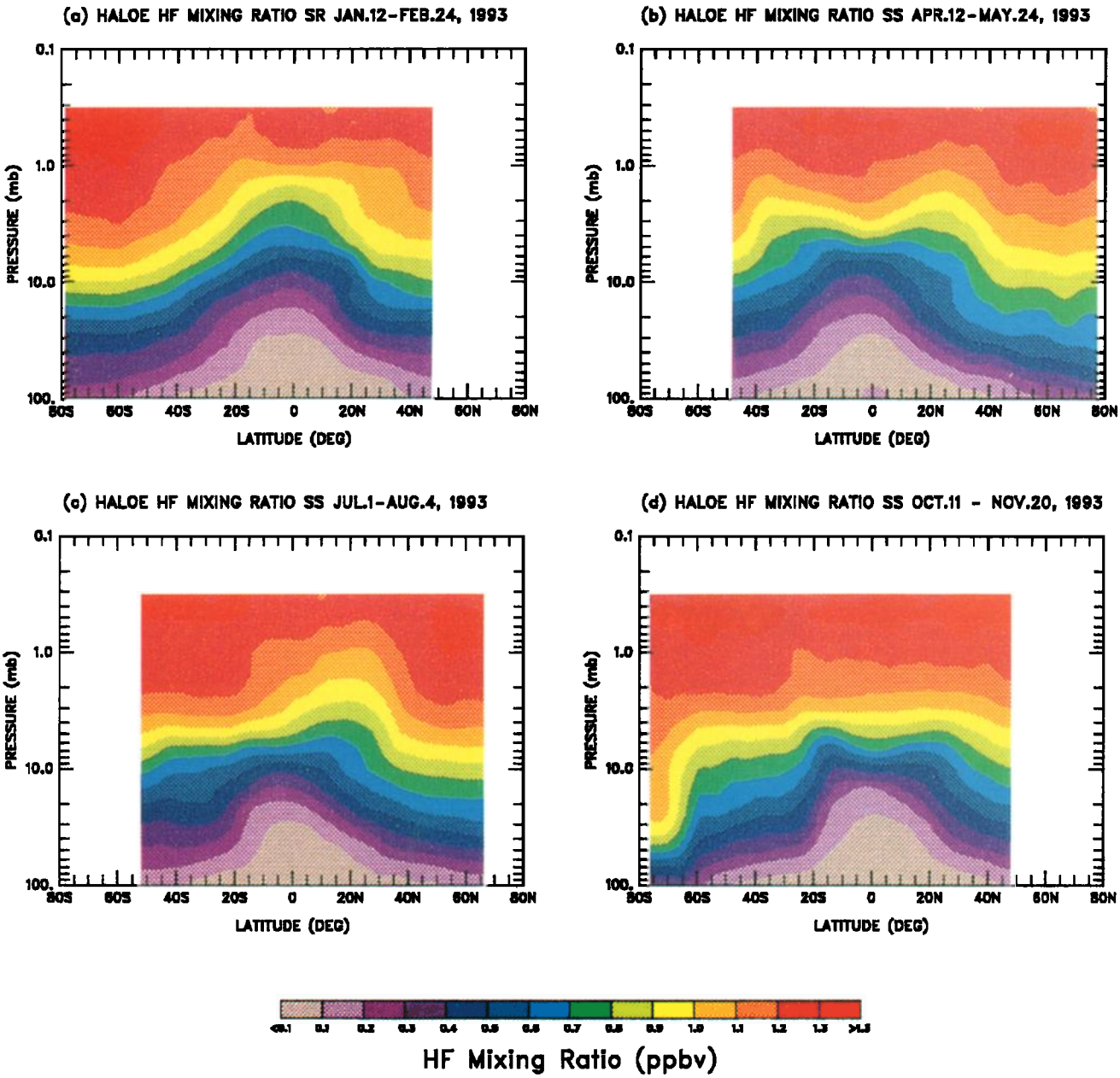

Plate 1. HALOE-measured HF latitude versus pressure cross sections for the time periods in 1993: (a) January 12 to February 24, sunrise; (b) April 12 to May 24, sunset; (c) July 1 - August 4, sunset; and (d) October 11 - November 20, sunset. The latitude progressing as a function of time refers to Figure 2.

to stronger wave driving) will be followed by stronger westerly as a consequence of enhanced wave momentum deposition during its easterly phase.

Another HF pattern that is characteristic of stratospheric tracers is seen during the solstice season (Plate 1a and 1c). Below around 10 mbar, the region of minimum HF tilts toward the winter hemisphere, while above 10 mbar, it tilts toward the summer hemisphere. This is especially obvious in Plate 1c. The tilting of the minimum axis toward the winter hemisphere in the lower to middle stratosphere can be attributed to the stronger circulation in the winter stratosphere from planetary wave driving. In the upper stratosphere and lower mesosphere the effect of the summer to winter circulation begins to become important, therefore tilting the axis toward the summer pole. Also noticeable, below 10 mbar in the lower to middle stratospheric region, is the strong latitudinal gradient of HF in the winter hemisphere near 20° latitude and a region of weak latitudinal gradient beyond the tropics. This pattern is consistent with other tracer observations [*Trepte and Hitchman*, 1992; *Randel et al.*, 1993]. Strong mixing by planetary waves in the so-called "surf zone" results in a region of weak gradients of HF , while the inhibition of this mixing activity into the tropics contribute to the barrierlike structure of sharp HF gradients seen

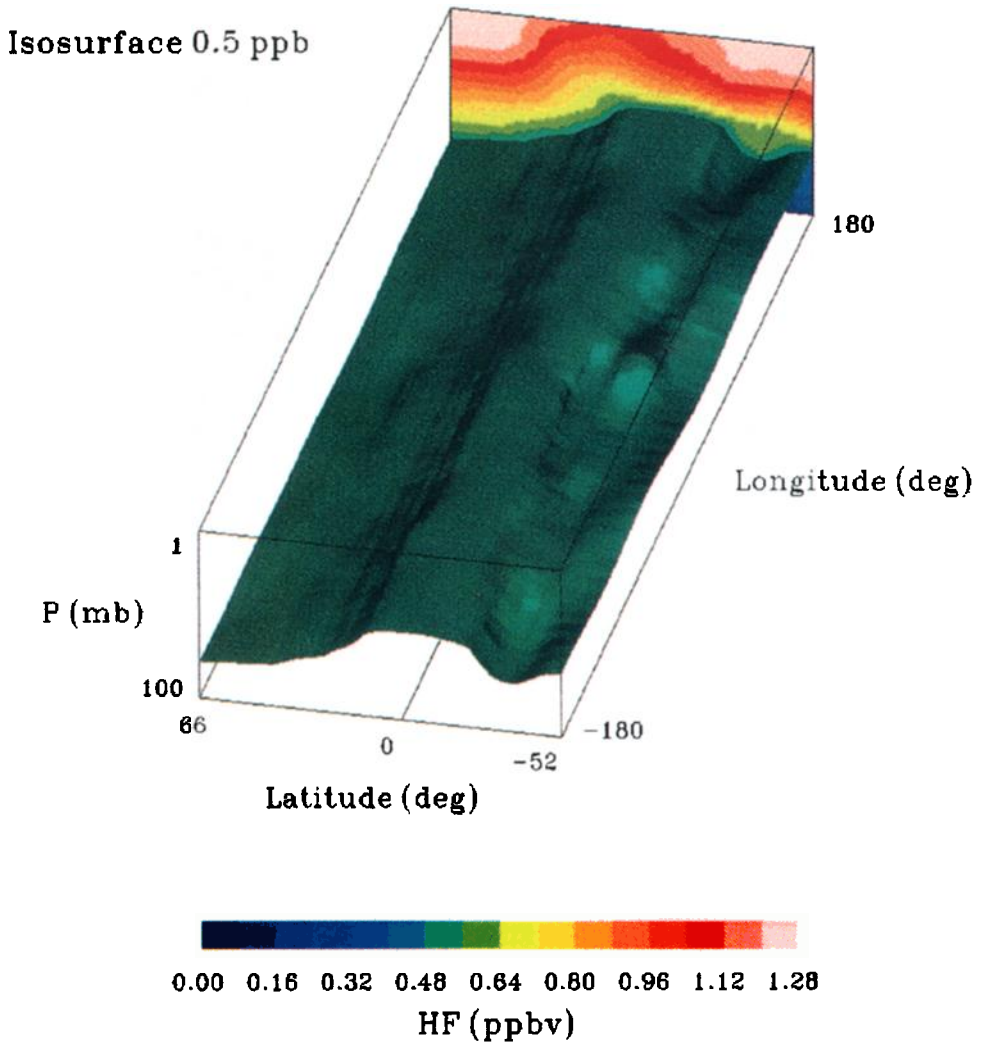

Plate 2. HALOE-measured HF isosurface as functions of longitude and latitude for July 1 to August 4, 1993, at 0.5 ppb. The HF cross sections of latitude versus pressure at 180° longitude is also shown.

near 15° to 20° latitude. It is worth mentioning that in Plate 1a and 1c, above 10 mbar, the HF cross section in the winter season is not a mirror pattern between the northern and the southern hemispheres. Instead, it appears that in the January to February season (Plate 1a) the upwelling in the tropical region in the upper stratosphere is much more intense than the July to August season (Plate 1c). The tilting of the minimum axis toward the winter hemisphere also extends up much higher (to above 1 mbar) in the January to February season in Plate 1a, to the point that it blurs the tilt of the axis toward the summer hemisphere at these altitudes. This may very well be a manifestation of the stronger wave forcing in the northern hemisphere compared to the southern hemisphere.

An isosurface of HALOE-measured HF in the July to August period is shown in Plate 2. The smoothness of the HF constant mixing ratio surface in the northern hemisphere indicates a relatively quiet atmospheric condition in summer. A much more "bumpy" HF isosurface in the southern winter hemisphere demonstrates a large atmospheric variability due to strong wave activities.

It is worthwhile to point out that the HALOE-observed HF mixing ratios are of the order of 1.3-1.4 parts per billion in volume (ppbv) in the lower mesosphere during the year 1993. Observations and photochemical results suggest that in the lower mesosphere the bulk of fluorine is contained in HF [*Zander et al.*, 1992; *Kaye et al.*, 1991]. Assuming that 95% of fluorine is in the form of HF and then comparing the fluorine level in this case (1.37-1.47 ppbv) with the fluorine loading in the troposphere shown in Figure 1, we see that the fluorine was close to ~1.4 ppbv at around 1986 to 1987 in the troposphere. This suggests that the air, on average, took 6 to 7 years to move from the troposphere to the mesosphere.

4. Column Amount of HF

HF total column abundances have been used in the past to study the seasonal and latitudinal variations of this species and to record the increasing trend of the man-made fluorine amount in the atmosphere. In this section we will describe the HF column amount above the lowest altitude measured by the HALOE instrument. As stated before (section 2), the lowest altitudes of HALOE HF profiles gradually decrease with the reduction of Pinatubo aerosol loading in the lower stratosphere. We will therefore mostly use data taken in 1993, the second year of UARS in orbit. This will be compared to the HF column measurements by the ATMOS experiment in early May 1985 to examine the HF loading trend in the stratosphere.

4.1 Latitudinal Dependence of the HF Column

In section 3, four time periods in 1993 are used to describe HALOE observed HF vertical mixing ratio profiles as a function of latitude. The data for these four periods are believed to be suitable to demonstrate the latitudinal and seasonal dependences of global stratospheric HF measured by HALOE even if it does not provide an instant global coverage because of solar occultation coverage limitations. Shown in figures 4a-4d are plots of HF column amount (above 15 km) as a function of latitude for the same four periods. The general features shown in the global HF columns above 15 km are a minimum column in the tropical region (0.3-0.4 $\times 10^{15}$ cm^{-2}), and an increase of HF column with increasing latitude, to $\sim$1 $\times 10^{15}$ cm^{-2} in the summer polar regions (about 3 times larger than the tropical values). There is no obvious shift of the tropical minimum HF columns to either side of the equator.

The differences between the HF column at high latitudes among the four seasons are interesting. The downward displacement of air parcels relative to those in the tropics results in a larger HF column amount, and the amount of displacement seems to make a big difference in the HF column amount values near the polar regions. The typical HF column in the summer polar region is about 1 $\times 10^{15}$ cm^{-2} but the HF amount

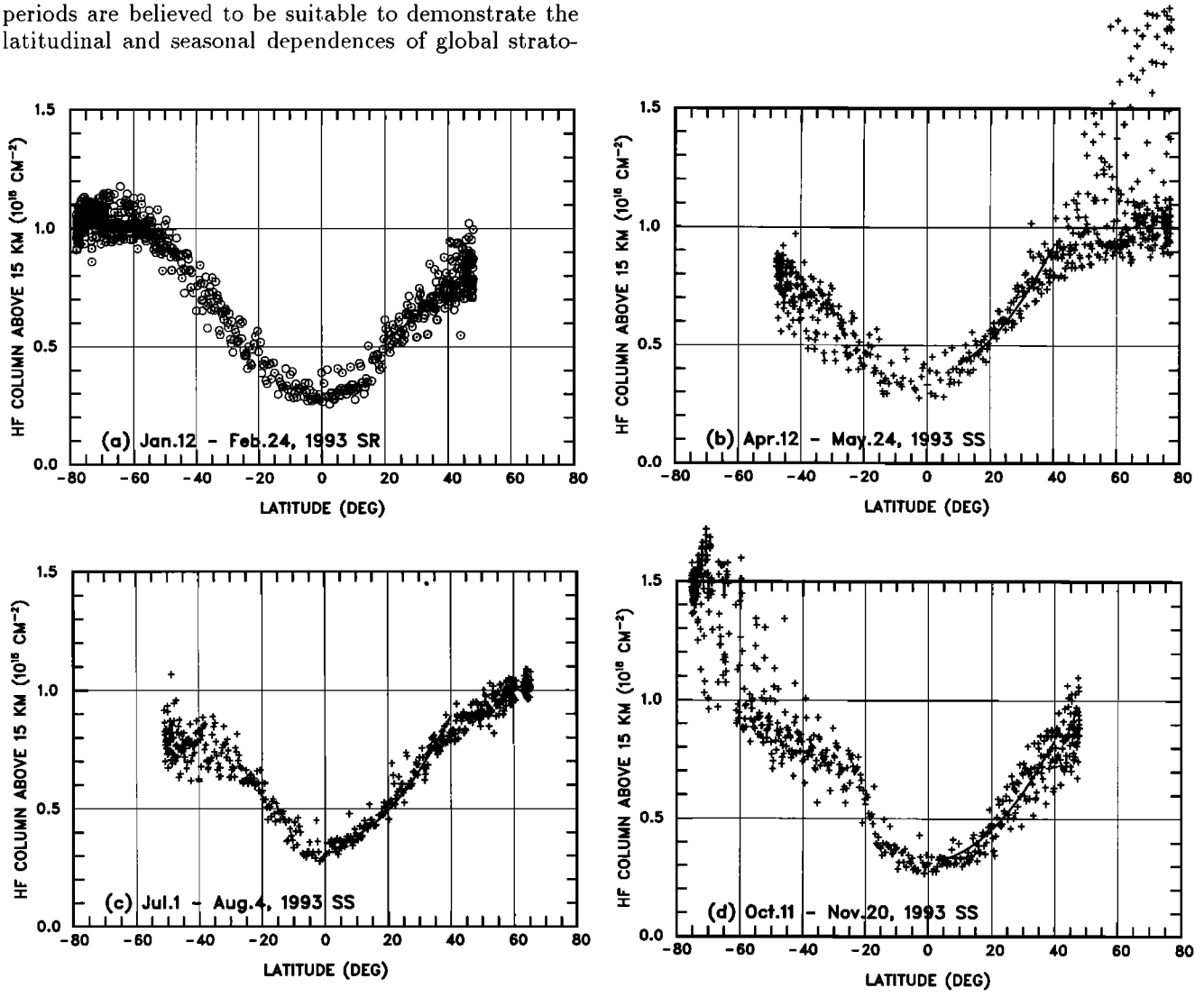

Figure 4. HF column above 15 km measured by HALOE as a function of latitude for the same four time periods in Plate 1 (a, b, c, and d). The solid curves are fitted $a + b\cos$(latitude) for limited latitude ranges.

measured in the winter/spring polar region could reach 1.5-2.0 $\times 10^{15}$ cm^{-2}, or about 50%-100% more (see Figures 4b, 4c, and 4d, and Figure 8). A discussion of HALOE-observed HF profiles and their columns during the Antarctic spring is given in section 6.

In the midlatitudes (40°- 60° latitudes), a relatively "flat" area in the HF column versus latitude diagram is found equatorward of the winter/spring polar region (Figures 4c and 4d, and Figure 8). This feature is not quite so obvious in the HF column amount observed outside the northern winter/spring polar region (Figures 4a and 4b). This feature is consistent with the weak gradient region shown in the HF latitude versus pressure cross sections discussed in section 3. The degree of isolation of the two polar regions could contribute to the differences in the "flatness" of the HF column in the midlatitude winter/spring. Some large HF amounts in the 40° - 60° latitude band in April to May and October to November indicate that the polar air had been mixed into the midlatitudes following the breakup of the winter vortices.

Mankin and Coffey [1983] observed that HF column abundances above 12 km increase with latitudes and they describe this latitudinal dependence by fitting their data to $a + b\cos(\text{latitude})$, where a and b are constants. Model simulations are also able to predict similar latitudinal dependences of the HF column but argue that the above formula is not always valid [*Kaye et al.*, 1991]. HALOE measurements indicate that the Mankin and Coffey proposed relationship between latitudes and HF column is not suitable for high latitudes (~50° and higher), where the column gradient is relatively flat in summer. HALOE measurements also indicate that in the middle/low latitudes, especially in the northern hemisphere, $a + b\cos(\text{latitude})$ can be a good approximation describing the latitudinal dependences for HF columns. We use the formula $a + b\cos(\text{latitude})$ to fit HALOE HF column - latitude data for limited latitude regions in the northern hemisphere (the solid curves in Figure 4). Figure 5 shows the comparisons between these fitted curves for HALOE and the Mankin and Coffey result. The value $a + b$, which is the HF column at the equator, is about 0.35 $\times 10^{15}$ cm^{-2} for HALOE, whereas it is 0.135 $\times 10^{15}$ cm^{-2} from the Mankin and Coffey aircraft data. The large difference between the aircraft and the HALOE results is due to over 10 years time interval which separate the observations coupled with the annual increase of HF. It appears from Figure 5 that the latitudinal gradient of the HF column becomes steeper in recent HALOE's measurements compared to the 1978-1982 aircraft measurements. This could be caused by the increasing stratospheric fluorine loading which will affect the HF altitude dependence or possibly by the differences of atmospheric motions in the two time periods. The altitudes of 15 km for HALOE and 12 km for the Mankin/Coffey HF columns could also contribute to the differences in the different latitudinal gradients since the tropopause at high latitudes is lower in height than that of the tropics.

The $a + b\cos(\text{latitude})$ curve fitted for the January to February period also has a different latitudinal gradient than those for other seasons (Figure 5). As discussed earlier, strong mixing from waves in the winter midlatitudes has the effect of flattening the HF isopleths.

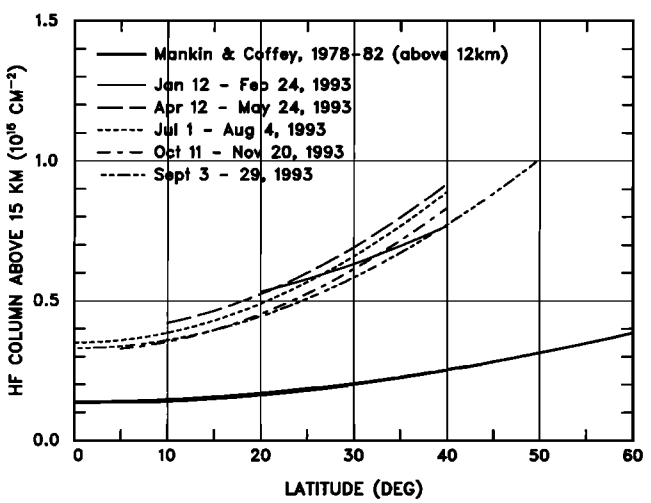

Figure 5. The HALOE HF (above 15 km) latitude curves taken from Figures 4 and 8 in comparing with *Mankin and Coffey*'s [1983] $a + b\cos(\text{latitude})$ curve fitted from their aircraft measurements of HF columns above 12 km in 1979-1982. The $a + b$ of HALOE is ~0.35$\times 10^{15}$ cm^{-2} and that of Mankin and Coffey is 0.135 $\times 10^{15}$ cm^{-2}.

4.2 Seasonal Variation of the HF Column Amount

The HALOE tangent point passes a fixed latitude less than 20 times during a year (Figure 2). We use the limited data set from one latitude region to study the seasonal variations of the HF columns. The HF column as a function of altitude is provided in the HALOE level 2 files. We interpolate the HF column data at a fixed altitude, such as 15 km, and then plot them against time (Figure 6a and 6b) for a narrow latitude band.

Examination of ground-based HF column observations at Kitt Peak at 32°N [*Rinsland et al.*, 1991; *Wallace and Livingston*, 1991] and at Jungfraujoch at 47°N [*Zander et al.*, 1987a] indicate a seasonal variation of about ±10% with the maximum occurring in spring and a minimum occurring in fall. Model simulations are able to predict similar seasonal behavior [*Kaye et al.*, 1991; *Rinsland et al.*, 1991; *Prather and Remsberg*, 1993]. *Mankin and Coffey* [1983], however, did not find obvious seasonal variations in their aircraft measurements of the HF column above 12 km (mostly in the summers and winters of 1978-1982).

The HALOE HF column in Figures 6a and 6b shows a seasonal variation of about ±10% at midlatitudes in both hemispheres. The data suggest a maximum in the HF column in May 1993 for 45°N - 50°N and a relatively flat minimum of HF between the months of June and mid-October. The averaged values for the above two seasons give a rough estimation of approximately 10% seasonal variation in the HF column. The data in 45°S - 50°S (Figure 6b) also show a seasonal trend

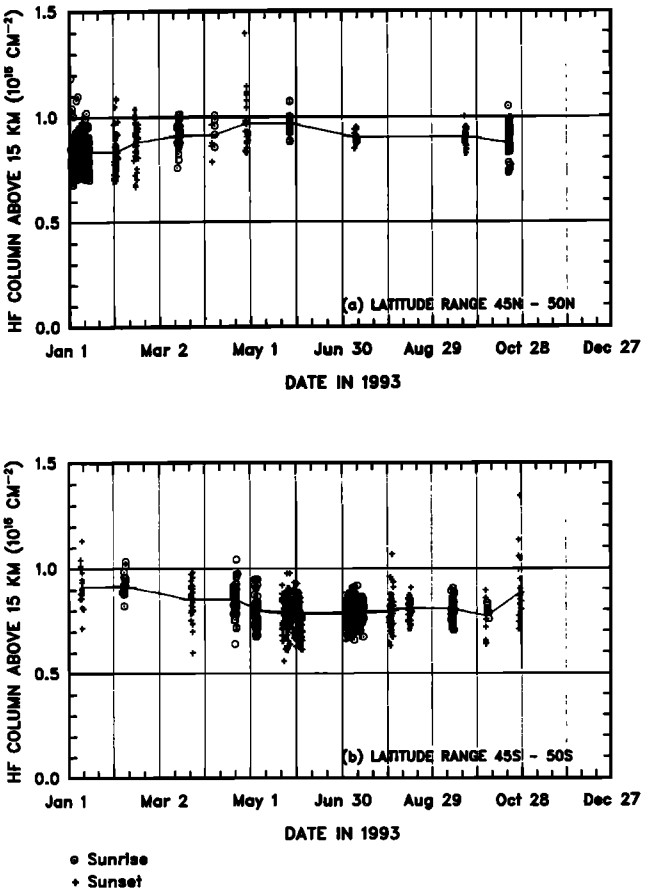

Figure 6. Time dependences of HALOE HF columns above 15 km in 1993 for the latitudes of (a) 45°N - 50°N and (b) 45°S - 50°S. The curves connect averaged HF column of each time group.

with similar magnitude but different phase. Both figures show quite large variations in the HF columns for some very close measurements (in latitude and time) and they are estimated to be about ±10%. This local short-term variation in the HF column is believed to be mostly due to the atmospheric variability (see discussions on the precision of the measurements in the work of *Russell et al.*, 1993a).

4.3 Comparison With the Atmospheric Trace Molecule Spectroscopy (ATMOS) 1985 Measurements

HF vertical mixing ratio profiles were also obtained from another solar occultation experiment, ATMOS, during its three flights on board the space shuttles: eight days in April to May 1985, nine days in April 1992, and nine days in April 1993 [*Zander et al.*, 1990; *Gunson et al.*, 1993). In the HALOE HF validation paper (in preparation), a comparison between the HF profiles from HALOE and ATMOS 1992 and 1993 is given and the agreement is found to be good. Here we examine the differences of the HF column profiles between ATMOS 1985 and HALOE observations in the coincident latitudes and the season. An increase in the stratospheric HF loading should be seen from the two measurements separated by 7-8 years (from 1985 to 1992-1993), and we estimate this trend.

Figures 7a and 7b show the HALOE-measured HF column amount as a function of altitude at the two ATMOS 1985 latitudes in early May 1992 and 1993. The ATMOS-observed HF columns provided in the paper by *Zander et al.* [1990] are also shown which are significantly lower than the recent HALOE measurements. HALOE HF values in 1993 are larger than these in 1992 throughout most column profiles. However, we cannot exclude the fact that the difference in HF columns for these two years may be a result of different dynamical conditions. Nevertheless, the comparison between the values of HF columns in 1985 and 1992-1993 can reveal changes in stratospheric HF loading. The ATMOS zonal mean HF column abundances above 20 km are 3.52×10^{14} cm^{-2} for sunset events at 29°N and 3.77×10^{14} cm^{-2} for sunrise events at 48°S. The averaged vertical columns of HF determined from the HALOE coincident measurments in 1992-1993 are 5.1×10^{14} cm^{-2} (sunsets at ~29°N) and 6.2×10^{14} cm^{-2} (sunrises at ~49°S), respectively. We find a factor of 1.45 (at 30°N) and 1.64 (at 49°S) increase in the HF column above 20

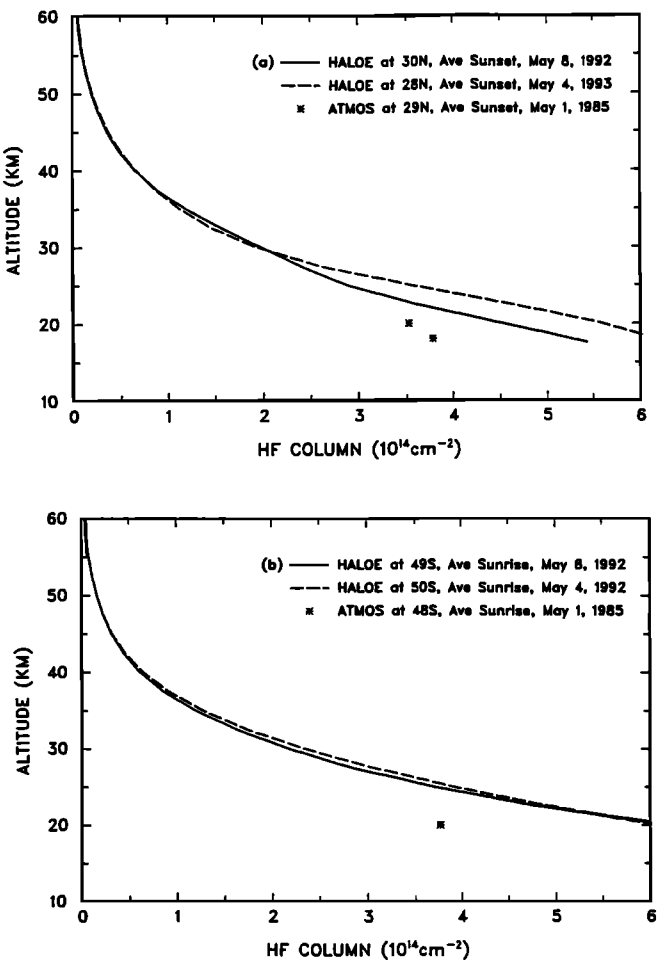

Figure 7. Comparisons between HALOE 1992-1993 and ATMOS 1985 measurements of HF columns. The ATMOS HF columns are above (a) 18 and 20 km and (b) 20 km respectively [*Zander et al.*, 1990].

km during the 7-8 years between May 1985 and 1992-1993.

Two kinds of definitions describing the increasing trend (neglecting seasonal variations) in the stratospheric HF have been used in the past: the exponential increase (assuming a fixed annual percentage rate) and the linear increase (assuming a fixed annual amount of increase) [*Rinsland et al.*, 1991; *Prather and Remsberg*, 1993]. If the annual increase percentage is assumed to be fixed over some time period ($\alpha\%$), the HF amount y_n in year x_n could be expressed as

$$y_n = y_1(1 + \alpha\%)^{x_n - x_1} \quad (1a)$$

or equivalently,

$$y_n = y_1 \exp[\beta(x_n - x_1)] \quad (1b)$$

where x_1 represents a reference year and y_1 is the HF amount in that year. β in (1b), the exponential rate of increase can be related to $\alpha\%$ by $\alpha\% = \exp(\beta) - 1$, so that these two parameters that are both used to describe the trend with time are different in concept but could be very close in value since they are of the order of $\sim$ 10%. The linearly increasing assumption, that is to assume the amount of annual increasing HF column is a constant over a long-time measurement, has also been used to describe the HF column as a function of time [*Rinsland et al.*, 1991; *Wallace and Livingston*, 1991]:

$$y_n = y_1 + \gamma(x_n - x_1) \quad (2)$$

where γ is the increasing amount in HF per year and γ/y_{n-1} is the linear increase rate in year x_n. In the cases of long-term ground-based observations of HF columns (Kitt Peak between 1977 and 1986 and Jungfraujoch between 1978 and 1990), data are fitted to both (1b) and (2) to estimate the annual increase rates, β and γ/y_n. *Rinsland et al.* [1991] found that the linear assumption (equation (2)) has a better fit to the data of Kitt Peak than the exponential increasing assumption (equation (1b)). It is therefore suggested that the atmospheric loading of the HF amount increases by a nearly fixed amount each year rather than by a constant percentage every year, which implies that the annual rate of growth in the total HF amount decreases with time.

We use the HALOE 1992-1993 and ATMOS 1985 HF columns above 20 km to calculate the exponential increase rate b and the the linear increase rates, γ/y_{84} and γ/y_{91-92} for years 1985 and 1992-1993 respectively. For the sunset case at 29°N in May, β = 4.9% yr^{-1}, γ/y_{84} = 6% yr^{-1}, and γ/y_{91-92} = 4.3% yr^{-1}. For the sunrise case at 48°S in May, β= 6.6% yr^{-1}, γ/y_{84}= 8.6% yr^{-1}, and γ/y_{91-92} = 5.5% yr^{-1}. These values reasonably agree with the HF annual increase rates estimated from previous ground measurements [see *Rinsland et al.*, 1991, Table 1] if we consider that the amount of man-made CFCs released to the atmosphere is reduced since 1988.

5. HF Measurements During the Antarctic Spring

HALOE observations for the three consecutive Antarctic springs (1991-1993) provide valuable information on studying the unique chemical and dynamical processes that are associated with the southern ozone hole. All HALOE channels for the long-lived species (CH_4, HF, and H_2O) show strong evidence of a downward displacement of the air inside the polar vortex relative to that outside the vortex [*Russell et al.*, 1993a, b].

Plate 3 shows a HALOE HF latitude versus pressure cross section and its column amount as a function of latitude (Figure 8) for the time period of September 3 - 29, 1993. This cross section covers a wider latitude range than that of July 1 to August 4, 1993 (Plate 1c). The two patterns shown in Plate 1c and Plate 3 are very similar, which indicates that the usage of data in a latitude sweep for some 20-30 days is reasonable in demonstrating the latitudinal dependence of HF profiles. The HF cross section in Plate 3 shows an area with strong downward displacement of the HF mixing ratios at latitudes ~60°S and higher and a large latitudinal gradient near the boundary of this area. This vortex-descent feature is also seen in the HF column plot with an enhanced column inside the polar vortex compared to that outside of the vortex. HALOE three-dimensional data indicate that the polar vortexes in the three Antarctic springs are not quite symmetric over the south pole, especially in 1992. The HALOE measurements of HF profiles along a latitude circle in a day could therefore include measurements both inside and outside of the polar vortex. The HALOE HF column plot in Figure 8 shows a large range of values for latitudes higher than ~55°S. These measurements are believed to occur inside (corresponding to large HF column), outside (with the relatively unchanged column amount of 0.8-0.9 $\times 10^{15}$ cm^{-2} at the latitudes north of 50°S), or near the boundary of the vortex.

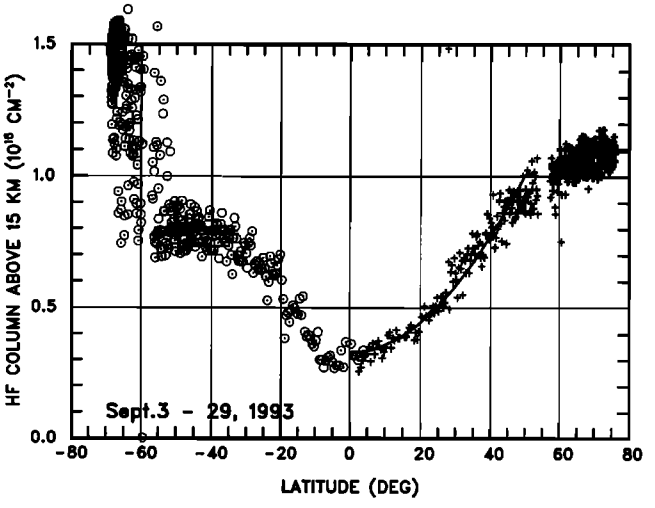

Figure 8. HF columns as a function of latitude during September 3 - 29, 1993.

Like other tracers, the global distribution of stratospheric HF is shaped by the coupling among atmospheric radiative, dynamical, and chemical processes. The fact that those long-lived species have a similar pattern in their cross sections of latitude versus height provides a useful tool in studying atmospheric transport processes. Analysis of the correlations between two tracer species as functions of altitude and latitude should reflect the differences of the chemical- transport coupling effects on these species. During the Antarctic winter-spring, the chemical processes of stratospheric tracers, including HALOE-measured CH_4 and HF, are believed to be slower than any other seasons. Do we expect their mixing ratios to have a similar amount of downward displacement inside the polar vortex? A preliminary analysis of HALOE CH_4 and HF version 16 data in the 1992 Antarctic spring shows that these two species appear to have significant differences in their amount of downward descents inside the vortex compared to that of outside [*Cicerone et al.*, 1993]. Their mixing ratio correlations inside the vortex also show a obvious shift from that of the outside. We will examine the HALOE CH_4-HF correlation in detail in a future paper which we believe is important in understanding the global and polar region transport processes as well as their couplings with the chemical processes of different atmospheric tracers.

6. Comparison With the National Center for Atmospheric Research (NCAR) Two-Dimensional Model

The NCAR two-dimensional model is used to simulate HF global distributions in the current stratosphere based on the best estimates of the tropospheric CFC amount in 1990. This model treats the chemical, dynamical, and radiative processes interactively (***Brasseur et al.***, 1990), and extends from the surface to 85 km and from -85° to 85° latitude. The NCAR model group participated in the 1992 NASA models and measurements workshop [*Prather and Remsberg*, 1993], and along with three other modeling groups, their simulated HF column abundances are used to intercompare among the models and to compare with Mankin and Coffey's observed HF latitudinal dependences as well as with the seasonal variations in the HF column obtained from ground observations at Kitt Peak. Although all four models show similar trends of latitudinal and seasonal variations in the HF column as the observations, their absolute amounts are quite different. As pointed out by *Kaye et al.* [1991] and *Rinsland et al.* [1991], the quantum yield of CF_2O photolysis in the stratospheric fluorine chemical schemes adopted in the model calculations is the key in fluorine partitioning among the stratospheric fluorine reservoirs. We will discuss the values of this quantum yield later in this section. Since HALOE provides measurements of HF profiles in the stratosphere, we will focus on comparisons between vertical profiles in different seasons and latitudes obtained from satellite observations and the NCAR model simulations.

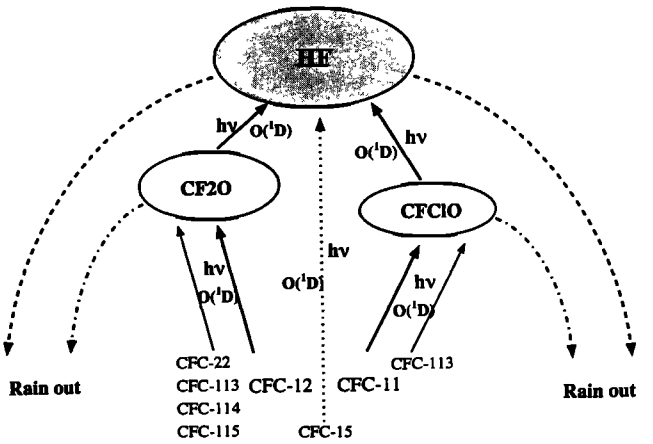

Figure 9. An illustration of the chemical reactions and the removal processes related to the stratospheric fluorine species.

The fluorine chemistry scheme included in the NCAR model is outlined in Figure 9. The CFCs that diffuse upward from the troposphere experience photodissociation in the stratosphere and form two intermediate fluorine-containing reservoirs, CF_2O and CClFO. The main production paths of HF are the photolysis of CF_2O and not so important of CClFO. The HF then is allowed to diffuse down to the troposphere where it is rained out. The ATMOS observations of HF and CF_2O indicate that HF is the dominant fluorine-containing reservoir which is at least 5 times more abundant than CF_2O at altitudes above ~20 km [*Zander et al.*, 1992]. Near the stratopause at least 90% of the fluorine is in the form of HF and it is assumed to stay constant up to and through the mesosphere where both ATMOS and HALOE do not have much sensitivity. However, HALOE HF measurements at high latitudes indeed show that HF mixing ratios tend to stay constant above 45-50 km (see Plate 1).

The NCAR HF model result for early February is shown in Plate 4. To compare with HALOE observations in the same time period, we plot the model HF latitude versus pressure cross section over the HALOE latitude and pressure range for its sunrise measurements between January 12 and February 24, 1993, in Plate 1a. In general, the shapes of the cross-section structure of the model and HALOE HF are similar for the January to February period. The model absolute values also appear to agree well with HALOE observations when a unity CF_2O photodissociation quantum yield and the 1990s tropospheric CFC boundary conditions are used.

The comparisons of the model and HALOE HF cross sections for other seasons are not shown. Tropical dynamics, including the quasi-biennial oscillation (QBO) and semiannual oscillation (SAO), are not yet included in the NCAR two-dimensional model. Therefore the "double-peak" structure in HALOE-observed HF dis-

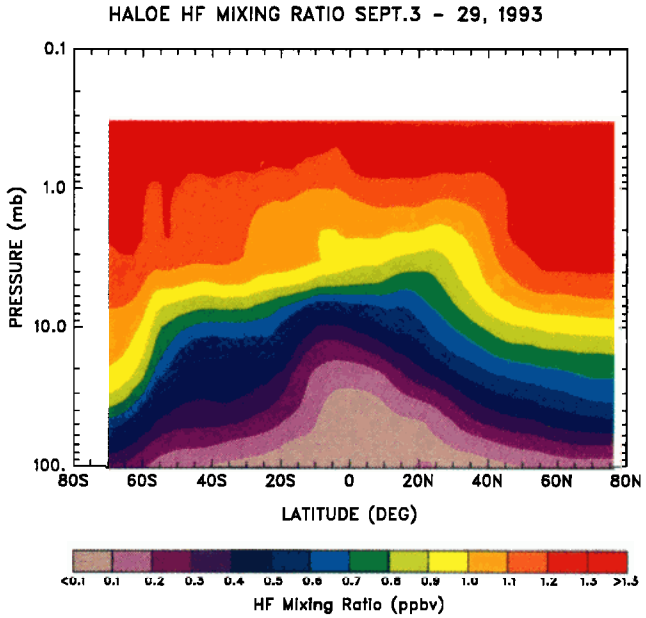

Plate 3. HALOE-measured HF latitude versus pressure cross section, September 3-29, 1993.

tributions during spring cannot be simulated in the present version of the NCAR model. In the northern summer season (July to August), the model HF distribution is almost the mirror image of that in January to February (Plate 4), characterized by a slight tilt of the minimum HF region toward the summer subtropics. However, the tilting of the minimum axis toward the winter hemisphere and the regions of strong latitudinal gradient at 20° winter and weak gradient at the midlatitude, as discussed in section 3, are not well simulated by the model.

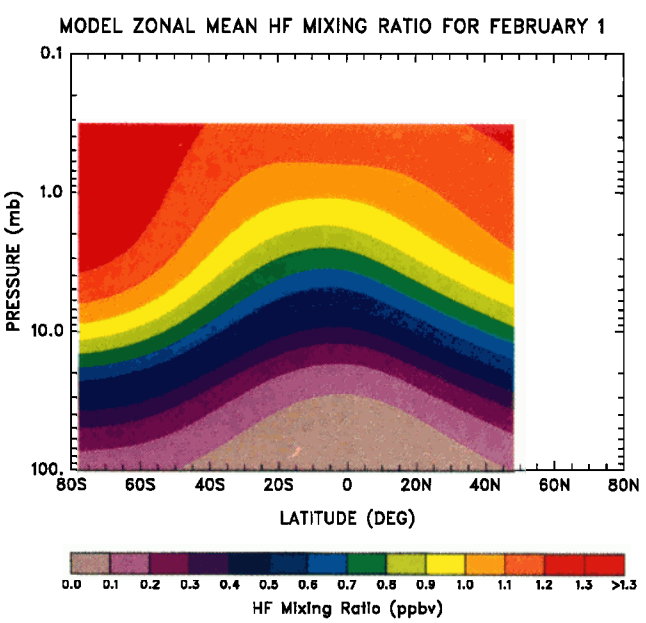

Plate 4. The latitude versus pressure cross section for HF mixing ratio obtained from a National Center for Atmospheric Research (NCAR) two-dimensional model simulation for February with 1990 boundary conditions of tropospheric CFCs. The latitude and pressure ranges are selected to be the same as the HALOE observations in January to February 1993 (Plate 1a). The unit quantum yield for the CF_2O photodissociation is used.

Figures 10a-10d show HALOE-model comparisons of the HF mixing ratio vertical profiles in the latitude bands of 15°S - 15°N and 45°- 55° of the summer hemispheres for the January to February and July time periods. The comparisons for the tropics in January (unit CF_2O photolysis quantum yield case) and July and for the summer midlatitudes in February show good agreement in both profile shapes and the absolute mixing ratios with a slight bias which is probably due to the 3-year difference between model simulations and HALOE observations. Both model and HALOE HF profiles show the tendency for its mixing ratios to stay constant in the stratopause region at higher latitudes, and they both show that in the lower stratosphere HF is produced at higher altitudes in the tropics than in the midlatitudes. Figure 10d shows a different vertical gradient of the HALOE and model HF profiles below 30 km (~10 mbar) for July at summer midlatitudes. This difference is expected because the HALOE-observed HF distribution in July (Plate 1c) shows that the minimum HF region below ~10 mbar is tilted toward the winter subtropics, while the model-simulated HF structure does not show this feature clearly.

There have been some discussions reported on the quantum yield for the photodissociation of CF_2O used in model simulations [*Kaye et al.*, 1990; *Rinsland et al.*, 1991]. Previous model versus measurement comparisons for HF profiles and its column abundances suggest that this quantum yield is closer to unity rather than 0.25 (at 206 nm) listed in the NASA JPL table [*DeMore et al.*, 1992]. Figure 10a includes model-calculated HF profile ranges for both unity and 0.25 quantum yield cases as well as HALOE observations in the tropics. It is obvious that the model HF profiles with the unit quantum yield agree much better with HALOE profiles. The model calculations the with the 0.25 quantum yield of CF_2O photolysis predict a factor of 1.4 lower HF in its mixing ratio near the stratopause than that of HALOE observations. Although the stratospheric HF in 1990 is less than that in 1993, the ratio HF_{93}/HF_{90} should be of the order of 1.16 if a 5% growth rate of stratospheric fluorine is assumed. This also partially explains why the model range of HF mixing ratios in Figure 10 are on the lower side of the HALOE observations in 1993. We conclude from Figure 10 that the quantum yield for CF_2O photodissociation in the stratosphere is unlikely to be 0.25 but closer to unity. It should also be noted that the model calculations did not include HF from atmospheric decomposition of CF_4. If the annual fluorine flux into the stratosphere in the form of CF_4 is of the order of 10^{10} g/yr [*Cicerone*, 1979], it could add 2 to 5% to the absolute HF amounts that arise from the more common CFCs, but the sources and sinks of CF_4 remain unclear [*Cicerone*, 1979; *Ravishankara et al.*, 1993].

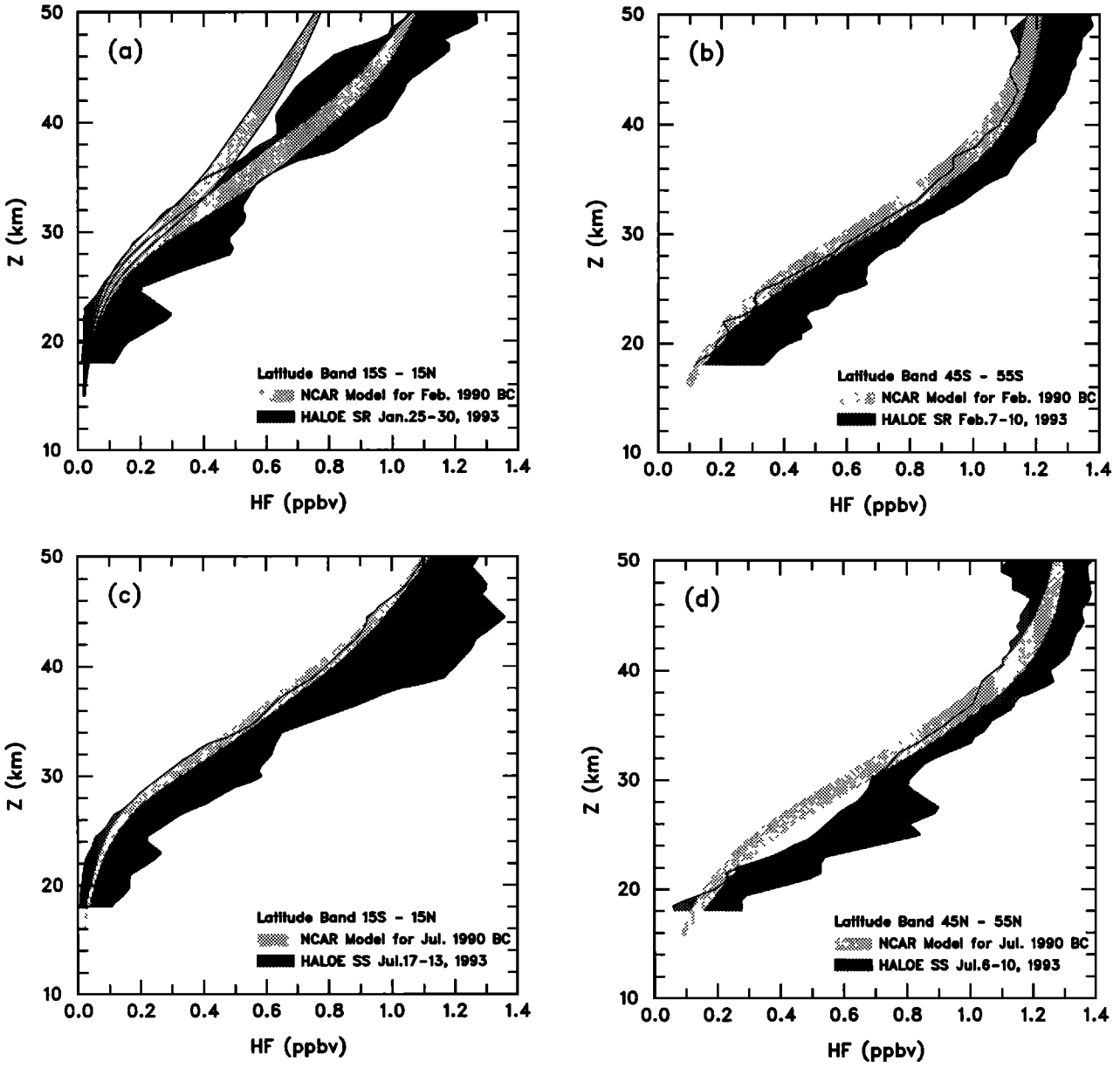

Figure 10. The comparisons between the HF mixing ratio ranges from HALOE observations and NCAR model simulations for selected latitude bands and time periods: (a) tropics (15°S - 15°N) in northern winter, (b) midlatitudes (45°S - 55°S) in January to February summer, (c) tropics in northern summer, and (d) mid latitudes in July to August summer. (a) The model HF include two cases using unit quantum yield (the HF profile group with larger mixing ratios) and 0.25 quantum yield (the HF profile group with less mixing ratios) for the CF_2O photolysis. (b)-(d) The unit quantum yield used in simulations.

7. Conclusion

The HF channel of the HALOE instrument on-board UARS has provided global measurements of stratospheric HF for the first time. This paper describes HF global distributions and its seasonal variations in vertical profiles as well as its column abundances, while another paper [*Russell et al.*, 1994 in preparation] focuses on HF data validation. The behavior of the HF mixing ratio profiles during the 1993 Antarctic spring is also briefly described here. The HF latitude versus pressure cross sections show a familiar general structure seen in other atmospheric tracers, such as N_2O and CH_4, characterized by a "bell-shape" isopleth.

We showed the seasonal variations of the global HF observed by HALOE and found distinctive structures in HF mixing ratios for the four seasons, such as the "double-peak" in northern spring and the HF minimum region tilting in the summer/winter seasons. These features are believed to be controlled by atmospheric dynamical processes. Transport effects on the tracer distributions is coupled with related chemical processes,

depending on altitudes and latitudes. Current models that include fluorine chemistry, represented by the NCAR two-dimensional model discussed in this paper, are able to reasonably simulate the HF global distribution. But more realistic dynamical processes need to be included in the model to simulate the more detailed structure of HF. The theoretical partitioning of stratospheric fluorine (or the absolute amount of HF) is determined by some key photochemical parameters for chemical reactions involving fluorine. As others have suggested, we feel that the quantum yield for CF_2O photodissociation needs to be reexamined.

The accumulation of the stratospheric HF column amount is a result of continuing releases of man-made CFCs into the earth's atmosphere. We made comparisons between HALOE 1992-1993 and ATMOS 1985 measurements of the HF column above 20 km to estimate its annual growth rate. The percentage increase we obtained (exponential rate of 4.9-6.6% yr^{-1} and linear rates of 6-8.6% yr^{-1} in 1985 and 4.3-5.5% yr^{-1} in 1992-1993) agree reasonably with those estimated from long-term ground-based measurements of the HF column amount as well as those from the historical records of tropospheric CFC releases. We did not attempt to make comparisons of the HALOE HF columns with ground-based measurements, because the HF amounts from ground to HALOE lowest levels are unknown and they probably contribute a large amount to the HF columns.

An analysis of the correlations between HALOE-measured halogen species HF and HCl and that of tracers HF and CH_4 is being prepared for future studies. Although prior to HALOE, stratospheric HF is a poorly known species due to lack of experimental data, it has been emphasized that it plays an important role in revealing the effect of anthropogenic activities on the atmospheric chemical compositions. Limited measurements of the columns of HF/HCl prior to HALOE show nearly linear correlations between the two. The question is how this correlation applies to their vertical profiles and how does the relationship change with latitudes and seasons. In the spring polar region this relationship is especially important in determining the roles of dynamical and chemical processes in ozone depletion. This will be the subject of a future paper.

Acknowledgments. We thank the HALOE science and flight operation teams for their outstanding work on data processing and validations L. Gordley, J Park, L. Deaver, and G. Beaver in particular provided us detailed discussions on the HF channel data retrieval and comparisons with UARS collaborative measurements. We are grateful to G. Brasseur, C. Granier, and S. Walters at NCAR for their kind support and help in using the NCAR two-dimensional model. This work is supported by NASA contract NAS1-19155.

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(Received January 24, 1994; revised May 4, 1994; accepted May 9, 1994.)