CHAPTER 9

Trends in Stratospheric Minor Constituents

Panel Members
R. S. Stolarski, Chair
W. P. Chu
M. T. Coffey
W. S. Heaps
J. A. Kaye
M. P. McCormick
R. Zander
Chapter 9

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9.1 INTRODUCTION

The evidence for increasing concentrations of the source gases (CFC's for Cl and F, N₂O for N, and CH₄ for H, among others) has been summarized in Chapter 8 of this report. Photochemical models predict that increasing source gas concentrations are also expected to lead to changes in the concentrations of both catalytically active radical species (such as NO₂, ClO, and OH) and inactive reservoir species (such as HNO₃, HCl, and H₂O). For simplicity, we will refer to all these as trace species. This chapter addresses the question of long-term trends in these trace species.

In particular, we consider two questions associated with trace species concentrations. First, are those species whose concentrations are expected to be increasing actually doing so? Second, are there observed changes in any trace species not expected on the basis of the measured increase in source gases?

The consideration of these questions is difficult because of the limited data base of measurements of stratospheric trace species. In situ measurements are made only infrequently, and there are few satelliteborne measurements, most over a short time span insufficient for trend determination. Instead, ground-based measurements of column content must be used for many species, and interpretation is complicated by contributions from the troposphere or mesosphere or both. In this chapter, we examine existing measurements as published or tabulated; they have not been subjected to the rigorous review that has been applied to the ozone data examined in the bulk of this report.

9.2 ODD NITROGEN

The odd nitrogen compounds (N, NO, NO₂, HNO₃, N₂O₅, ClONO₂, and HO₂NO₂) are important to the chemical balance that determines stratospheric ozone concentrations. They participate in catalytic reactions and can interfere with catalysis by chlorine, hydrogen, and bromine compounds. Because their principal source is nitrous oxide—N₂O—which is known to be increasing at about 0.2 percent per year (see Chapter 8 of this report), a slow increase in the concentration of odd nitrogen compounds should be expected. This increase is sufficiently slow that no currently measurable changes in stratospheric odd nitrogen compounds are expected to result from it. Superimposed on this should be variations caused by interannual variability of the dynamics that transport odd nitrogen from its source in the middle stratosphere to its sinks, either in the mesosphere or troposphere.

Larger changes or long-term cyclical variations, if they are to occur, would likely have to arise from changes in the amount of odd nitrogen generated elsewhere in the atmosphere. In the upper mesosphere and lower thermosphere, processes involving ions and electrons lead to production of NO, which is then transported down to the stratosphere. This problem has been discussed extensively by Solomon and Garcia (1984b), Jackman et al. (1980), and Callis and Natarajan (1986). It has also been suggested (Ko et al., 1986, and references therein) that lightning may be an important source of odd nitrogen production, especially in the tropical upper troposphere. This odd nitrogen might then be transported into the stratosphere. Thus, changes in the rate of troposphere–stratosphere transport in the Tropics might also lead to changes in stratospheric odd nitrogen content. The rest of this section reviews the measurement evidence for changes in the odd nitrogen compounds.
9.2.1 Nitrogen Dioxide—NO₂

Callis and Natarajan (1986) used differences between data from the Stratospheric Aerosol and Gas Experiment (SAGE-I and SAGE-II) experiments to deduce a dramatic change in odd nitrogen species between 1979 and 1984. They found 60 to 70 percent larger stratospheric NO₂ concentrations at midlatitudes in 1984 as compared to 1979. Data taken in 1979 by the Limb Infrared Monitor of the Stratosphere (LIMS) instrument on Nimbus-7 indicate low NO₂ values consistent with SAGE-I, while data taken in 1982 by the Solar Mesosphere Explorer (SME) satellite are consistent with the higher values measured by SAGE-II in 1984. Figure 9.1 from Callis and Natarajan (1986), shows 1 day of data from each of the SAGE instruments. Figure 9.1a shows SAGE-I data for November 25, 1979, at approximately 66°S latitude, as a function of altitude and longitude. Peak values of slightly over 6 ppbv occur between 30 and 35 km altitude. Figure 9.1b shows the same type of plot from SAGE-II for December 4, 1984. Peak mixing ratios are greater than 10 ppbv. Although the figure shows data from 2 particular days, Callis and Natarajan state that these are consistent with the results obtained over larger periods. They showed data averaged over several days (3 days of SAGE-I data, 7 days of SAGE-II data), indicating that the SAGE-II-determined profile was greater than that of SAGE-I by an amount in excess of the maximum difference attributed to the error bars in the measurements.

The detailed comparison of SAGE-I and -II data is complicated by the fact that different wavelength channels were used in the measurements of NO₂ by the two instruments. In SAGE-I, NO₂ amounts were obtained largely by consideration of the difference in absorption strength of NO₂ between two relatively broad-band channels at 385 and 450 nm, with bandwidths of 30 and 20 nm, respectively (Chu and McCormick, 1986). In SAGE-II, two narrow-band channels at 452.4 and 447.5 nm, with bandwidths of 1.9 and 3.2 nm, respectively, were used (McMaster, 1986; Chu, 1986).

![Figure 9.1](image)

Figure 9.1. Solar occultation measurements of daytime mixing ratios of NO₂ in ppbv by the SAGE and SAGE-II (preliminary data) instruments. Positive longitudes are those east of Greenwich. (a) Longitude-altitude plot of 1979 SAGE data for November 25, 1979, using data over a latitude range from 65.3°S to 66.9°S. (b) Similar plot for SAGE-II data for December 4, 1984, for the latitude range 63.6°S to 66.0°S. Contour interval for both plots is 1 ppbv. Figure taken from Callis and Natarajan (1986).
The reality of these changes is critically dependent upon the absolute calibration of each satellite instrument. In particular, the SAGE-II information was based on a preliminary calibration obtained as a personal communication from McCormick and Chu. The SAGE-II data are being validated by the SAGE-II Science Team for release. Thus, any final statements concerning NO₂ changes cannot be made as of this writing.

Another way to test the relative calibration of satellite measurements is to compare them to ground-based measurements that can be continually checked for the maintenance of their calibration. For NO₂, the principal available ground-based measurements are of the column amount during the daytime. These are made by visible absorption spectroscopy (Noxon et al., 1979; McKenzie and Johnston, 1984; Elansky et al., 1985; Shibasaki et al., 1986, and references therein). The ground-based measurements have been discussed in detail in WMO (1986). These measurements have been made sporadically since the mid-1970's. Figure 9.2, from Coffey (1988), shows sunset measurements of the total column of NO₂ by various experimenters plotted as a function of time from 1975 through 1986. The figure is broken into four panels based on the latitude of the measurements. Figure 9.2a shows the high northern latitude measurements (60°N to 80°N). The solid curve is a sinusoid with a frequency of one per year and a minimum on January 1 chosen to represent the expected seasonal variation of stratospheric NO₂ (annual cycle, winter minimum). The amplitude of the sinusoid is chosen to include approximately the full range of the values measured. The high northern latitude data clearly are too sparse to draw any significant conclusions concerning trends in NO₂.

Figure 9.2b shows the northern midlatitude (35°N to 45°N) measurements with a sinusoidal curve determined as above. Although a number of interpretations are possible for the data shown, it is clear that there is no large trend in the data. The minimum in the winter of 1979 to 1980 seems to be a bit lower than those of the early 1980's by some 20 percent, but there is no obvious upward trend in the maxima. The data during the rapid spring increase and fall decrease are very difficult to evaluate in terms of trend because of the possibility of small shifts in the seasonal phase. Figures 9.2c and 9.2d show the data for NO₂ column amount for the mid-southern latitudes and high-southern latitudes, respectively. In both cases, insufficient data exist to make any statements about trends.

Coffey (1988) has performed a similar comparison with satellite data for NO₂ from the LIMS, SAGE-I, SAGE-II, and SME instruments. Because the satellite measurements are not made below about 24 km, the integrals shown are above 24 to 25 km altitude for each instrument, and only sunset data are used for the SAGE instruments. About half of the NO₂ column is included in an integral above 24 km. Figure 9.3 shows the comparisons in the same format as in Figure 9.2. Figure 9.3a is for 60°N to 80°N with LIMS, SAGE-I, SME, and SAGE-II data. The peak values seen in 1979 are certainly lower than in 1983 to 1985, but it is not entirely clear from the data in the figure that this is representative of any long-term change. It is clear that careful examination of an entire seasonal cycle is important in assessing the meaning of any observed changes. Figure 9.3b shows the same comparison for 35°N to 45°N. Again, no clear picture of long-term change emerges. The data for 35°S to 45°S and for 60°S to 80°S are shown in Figures 9.3c and 9.3d, respectively. Here the seasonal peak is clearly defined, indicating a somewhat lower concentration of NO₂ in 1979 than in the mid-1980's. The difference is about 20 percent. Figure 9.4, from Johnston and McKenzie (1989), shows an update through early 1988 of the monthly average NO₂ slant column amounts measured at Lauder, New Zealand. The record is dominated by a seasonal cycle, shows some interannual variability, but contains no large trend.
The problem of changes in NO₂ remains interesting and largely unsolved. More definitive statements await the formal release of the SAGE-II data. The data shown indicate the possibility of some relatively large changes and cannot rule out an increase of 10 to 20 percent in the Southern Hemisphere from 1979 to 1986. They do not appear to support the 60 to 70 percent changes reported by Callis and Natarajan (1986), however. The smaller changes of order 10 to 20 percent would still give rise to significant variations in the balance of the stratospheric ozone photochemistry. The data record is still insufficient to determine whether any observed changes are long-term trends, solar cycle variations, or just dynamically induced interannual variability.

9.2.2 Nitric Oxide—NO

There are not nearly as many measurements of NO as there are of NO₂. A number of in situ altitude profile measurements have been made from balloons and some latitude surveys have
been made from aircraft. These measurements are described in WMO (1986) in some detail. While they are very important in examining the stratospheric chemical mechanism and in testing some ideas about transport, they do not form a long-term data base suitable for determining stratospheric odd nitrogen trends.

McPeters (1989) has deduced NO concentrations near and above 1 mb from the 255.5-nm albedos measured by the SBUV instrument. This is a wavelength that was originally used to measure ozone near the stratopause but was found to be contaminated by the nitric oxide gamma bands resulting from resonant-fluorescent scattering of sunlight by NO. The region at or above 1 mb is one in which the NO concentration might be expected to be quite variable because of the influence of mesospheric and lower thermospheric sources of odd nitrogen from particle precipitation.

Figure 9.3. NO2 column amounts above 24 km from indicated satellitborne experiments. Curve is a sine function as in Figure 9.2. Arrangement and labeling of panels is as in Figure 9.2. Figure taken from Coffey (1988).
Figure 9.4. Monthly averaged NO$_2$ slant column amounts at Lauder, New Zealand (45°S, 170°E). Figure taken from Johnston and McKenzie (1989).

Figure 9.5 shows the variation of cumulative NO above 1 mb (48 km) between 1979 and 1986 for five latitude zones. A clear decreasing trend of about a factor of 2 is seen at equatorial latitudes. This decrease occurs during a period of decreasing solar activity (Lean, 1987), but without a longer data period it is impossible to determine whether there is any connection to solar activity. The measurement of cumulative NO above 1 mb includes a large contribution from NO in the upper mesosphere and thermosphere; much of the variation may be due to changes in these regions. Because the NO measurement depends on the relative strengths of individual NO gamma bands, it is little affected by possible changes in instrument calibration (McPeters, 1989). The annual variation of NO at high latitudes is of much larger amplitude than in the Tropics, making long-term changes more difficult to detect. There is not any clear trend in NO above 1 mb outside of the Tropics. There is, however, a large degree of interannual variability at high latitudes. For example, the large increase in NO from 60°S to 80°S in July 1982 is known to be related to the solar proton event of July 13, 1982 (McPeters, 1986).

9.2.3 Nitric Acid—HNO$_3$

There are not enough column or in situ measurements of HNO$_3$ to deduce any significant changes. The only satellite-based data—those from the LIMS experiment on Nimbus–7—cover only a short (7 month) time period and, thus, are not useful in trend determination. One pair of relevant measurements is that recently reported by Murcray et al. (1987) for HNO$_3$ column measurements made at the South Pole on December 5, 1980, and November 26, 1986. Within their respective error bars, the two amounts were equal—$(1.6 \pm 0.3) \times 10^{16}$ molecules per cm$^2$ in 1980, $(1.4 \pm 0.4) \times 10^{16}$ in 1986.
Figure 9.5. SBUV NO data showing column amount of NO above 1 mb in molecules per cm² as a function of time for the period 1979 to 1986 in the indicated latitude ranges. Figure obtained from McPeters (1989).
9.2.4 Other Odd Nitrogen Compounds

Only recently have unambiguous measurements of the remaining stratospheric odd nitrogen compounds $\text{N}_2\text{O}_5$, $\text{ClONO}_2$, and $\text{HO}_2\text{NO}_2$ become available. All were observed by the shuttleborne Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument, which flew as part of Spacelab 3 in 1985 (Russell et al., 1988). Measurements of $\text{ClONO}_2$ have also been made using the balloonborne Stratospheric Infrared Interferometer Spectrometer (SIRIS) instrument (Massie et al., 1987), as well as from the ground by Zander and De Moulin, 1988. These data, together with what little data existed before (WMO, 1986), are inadequate for trend determination.

9.2.5 Trends in Total Odd Nitrogen

Each of the above species can show trends with time either because of a variation in the total odd nitrogen or because of a change in the balance of the chemistry within the nitrogen family. The two effects could also counteract one another somewhat by being of opposite sign for the particular constituent. The only way to uniquely separate the effects is to measure the total odd nitrogen concentration. This is an especially important quantity, as the efficiency with which chlorine catalyzes ozone destruction is nonlinearly dependent on the total amount of stratospheric odd nitrogen.

Determination of total odd nitrogen has been done only once, using measurements of all important odd nitrogen constituents ($\text{NO}$, $\text{NO}_2$, $\text{HNO}_3$, $\text{HNO}_4$, $\text{N}_2\text{O}_5$, and $\text{ClONO}_2$) made with the ATMOS spectrometer. Measurements were made for two latitudes (30°N, 48°S) on May 1, 1985. Maximum values of approximately 17 ppbv were obtained at approximately 43 km (2 mb) (Russell et al., 1988).

Estimates of total odd nitrogen were also inferred previously from LIMS measurements of nighttime $\text{NO}_2$ and $\text{HNO}_3$. These two constituents make up most of the total odd nitrogen at night, the remainder being in the form of $\text{N}_2\text{O}_5$, $\text{ClONO}_2$, and $\text{HNO}_4$. Maximum values of 24.4 to 27.7 ppbv were inferred, with maximum zonal and meridional monthly averages ranging between 22.8 and 23.8 ppbv in the 35 to 37 km range (Callis et al., 1986). Substantially smaller values (maximum of 21 ppbv) were calculated by Solomon et al., as described in WMO (1986), using LIMS daytime measurements and a photochemical model. The difference in these two inferred values emphasizes the uncertainties in the precise interpretation of total odd nitrogen from limited data.

A comparison of the total odd nitrogen inferred from the LIMS data and that directly measured by ATMOS for May 1 at 30°N is shown in Figure 9.6. The two results are in agreement within their respective error bars below 42 km, differing by a maximum of about 15 percent, with larger differences above that altitude. The differences are within the extremes of the error limits of the two instruments, but also may be related to real atmospheric variability. Thus, the data are insufficient to discriminate among models that predict different total odd nitrogen amounts. Additional measurements using the surface-catalyzed reduction technique (Fahey et al., 1985), which was used most recently as part of the Airborne Antarctic Ozone Experiment, should make in situ measurement of total odd nitrogen easier in the near future.

9.3 HALOGENS—CHLORINE, FLUORINE, BROMINE (Cl, F, Br)

The major source molecules for halogens are known to be increasing by amounts corresponding to 5.4 percent per year for fluorine, 3.4 percent per year for chlorine, and 2 to 4 percent per
year for bromine, based on measurements of halogenated organics in the troposphere (see Chapter 8, Table 8.1). The rate of increase for bromine is caused entirely by growth in halons and does not include possible growth in CH$_3$Br. It is considered an inevitable consequence of these increases that the concentrations of the resulting stratospheric gases (Cl, CIO, HCl, ClONO$_2$, HOCI, HF, etc.) should increase. The evidence for actual increases in these gases is unclear with the exception of HF and, to a lesser extent, HCl.

9.3.1 Hydrogen Chloride—HCl

Two sets of long-term column measurements of HCl seem to show contrasting results. In a series of aircraft-based measurements, Mankin and Coffey (1983) found evidence for an annual increase of the HCl column above 12 km of 5 percent per year from 1978 to 1982. This estimate was obtained by considering all data taken between the latitudes of 35°N and 55°N, and converting them to 45°N based on the observed latitude dependence, and then fitting a linear temporal trend to the converted data. Data of Mankin and Coffey (1983) taken between 35°N and 55°N and normalized to 45° are shown in Figure 9.7. This increase has been confirmed with
additional measurements made through 1987 (Coffey, personal communication, 1988), also normalized to 45°; these also are shown in Figure 9.7.

In a series of ground-based measurements from the Jungfraujoch Observatory in Switzerland (3.58 km, 46.55°N) since 1977, also shown in Figure 9.7, Zander et al. (1987a) found evidence of an apparent small increase in the total HCl column. A trend of 0.75 ± 0.2 percent per year or about $2 \times 10^{13}$ molecules per cm$^2$ per year increase in HCl was deduced by Zander et al. (1987a). This trend was calculated by determining the mean of the 1977 to 1980 observations and that of the 1983 to 1986 observations and assuming a constant rate of increase between these mean points. The weak linear trend is superimposed on significant short-term variability, which may be partially a result of variability in the tropospheric HCl column (see below), although analysis
of the line shape indicates that much of this variability is caused by changes in the HCl amount above 8 km (Zander et al., 1987a). There is also a seasonal variation, in which the HCl column maximizes in the spring and minimizes in late summer to early winter. The amplitude of the seasonal variation is approximately 10 percent (Zander et al., 1987a).

A trend analysis of these data shows that the total HCl column has been increasing at about two to three times the rate deduced by Zander et al. (1987a) over the time of the measurements. There are two major reasons for this difference: the extension of the data through 1987 and the deseasonalization of the pre-1982 data, which are biased in favor of high HCl months. The large seasonal variation and the uneven sampling in the 1977 to 1981 data cause the mean value to be above what it would be if the seasonal variation had been removed before taking the mean. A simple deseasonalized recalculation of the means of 1977 to 1980 and 1983 to 1986 data using the seasonal cycle as given in Zander et al. (1987a) more than doubled the derived slope in the HCl data ($4.5 \times 10^{13}$ molecules HCl per year). In a more detailed analysis (Wofsy, personal communication), the data were deseasonalized by separately averaging for each year the months of seasonal high (February to June) and seasonal low (July to November) values, omitting the December values, which are frequently lower than the other fall month values. The values for the seasonal high group were corrected to those of the seasonal lows by subtracting an amount of $4.5 \times 10^{14}$ molecules per cm$^2$. A plot of these 17 deseasonalized values vs. time is well fit, with the exception of one value, by a straight line with a slope equivalent to an annual increase of $(6.0 \pm 1.3) \times 10^{13}$ molecules cm$^{-2}$ yr$^{-1}$, which corresponds to an annual increase of between 2 and 3 percent per year over the 1976 to 1987 time period. The scatter of the pre-1982 data about this line is substantially greater than for the post-1982 data.

There is also an unexplained difference between the rate of increase in the post-1982 seasonal high (February to March) and seasonal low values. The annual rate of increase in the former appears to be at least a factor of 2 larger than in the latter. Further data over the next few years will be necessary to quantify any changes in the seasonal cycle. One should interpret annual rates of increase that are seasonally dependent with some caution.

Several additional measurements of the HCl column are also presented in Figure 9.7. These include the ground-based measurements of Marche et al. (1980) made from Reims, France (83 m altitude, 49°N) in 1979, and of Marche and Meunier (1983) and Zander et al. (1987c) from the Observatoire de Haute-Provence (OHP) Mt. Chiran station (1.905 km altitude, 43.88°N) in June 1981 and September 1983, respectively. Also plotted are an aircraft-based measurement made from 11.9 km altitude at 45°N in September 1983 (Zander et al., 1987c) and a shuttle-based measurement made with the ATMOS instrument in May 1985 covering the altitude range of 15 to 55 km (Raper et al., 1987). Finally, two measurements of the total HCl column above Denver made in October 1985 by Goldman et al. (1986) are also shown. These additional data shed no direct light on trends, but do support the magnitude of the total HCl column ($2-3 \times 10^{15}$ molecules per cm$^2$, the important contribution of tropospheric HCl, and the existence of important short-term variability in the HCl column (the data of Marche and Meunier, 1983, showed a 25-percent change in the HCl column over a period of 1 week).

The difference in magnitude between the aircraft results of Mankin and Coffey (1983) and the ground-based results of Zander et al. (1987a) should be related to the tropospheric HCl content. This is known to be highly variable, both in total amount and in vertical dependence (Vierkorn–Rudolph et al., 1984). In an aircraft flight made off Tromso, Norway, on September 8, 1981, under conditions of heavy clouds and rain, during which HCl is expected to be efficiently
scavenged, a well-mixed profile with a mixing ratio of approximately 70 pptv was obtained from 0.5 to 7 km. This suggests that 70 pptv is a reasonable value for the “clean” troposphere. Such a mixing ratio would lead to an expected HCl column from 3.5 to 12 km (the approximate altitudes of the Jungfraujoch and aircraft observations, respectively) of \(0.7 \times 10^{15}\) molecule per cm\(^2\). Larger tropospheric columns were obtained in other measurements, but in most of these the highly elevated HCl values observed (as large as nearly 500 pptv) were confined to altitudes near and below 1 km, and thus may not strongly influence the Jungfraujoch data, which are obtained at 3.58 km altitude; they will be more important for lower altitude stations, such as OHP.

The differences between HCl columns measured from the ground on September 8, 1983, at Jungfraujoch (\(2.43 \times 10^{15}\) molecules per cm\(^2\)) and OHP (\(2.67 \times 10^{15}\) molecules per cm\(^2\)) and that measured on the same day from an aircraft (\(1.65 \times 10^{15}\) molecules per cm\(^2\)) at 11.9 km (Zander et al., 1987c) are somewhat larger than the expected tropospheric values based on a mixing ratio of 70 pptv, but the differences are within the uncertainties of the measurements plus meteorological variability.

There is also evidence that stratospheric HCl amounts may be strongly affected by large volcanic eruptions, such as those of El Chichón in March and April 1982 (Mankin and Coffey, 1984); this has been discussed in WMO (1986). No additional evidence has become available since publication of that report. Given the apparent increase in the column HCl amounts in the post-1982 measurements of Zander et al. (1987a), it is important that the effects of volcanic eruptions on stratospheric HCl amounts be better understood.

### 9.3.2 Hydrogen Fluoride—HF

Measurements of a substantial increase in the HF column have been made from both ground-based (Zander et al., 1987b) and aircraft-based (Mankin and Coffey, 1983) techniques. Zander et al. (1987b) reported evidence of a cumulative annual increase since 1976 of 8.5 ± 1 percent in the total HF column above the Jungfraujoch station (see Figure 9.8). Mankin and Coffey (1983) found evidence for an annual increase of 12 percent in the HF column above the 12-km cruising altitude of their aircraft for the period 1978 to 1982. Zander et al. (1987b) also found a strong seasonal variation in the total HF column, very similar in amplitude and phase to that of HCl described above. Since the chemistries of stratospheric HCl and HF are quite different (HCl is converted to C10 and, thus, the other chlorine-containing species by reaction with OH, while HF is nearly completely unreactive), this suggests that much of this seasonal variation is dynamical in origin.

A statistical analysis of the Zander et al. (1987b) HF data, similar to the one for HCl, yielded a trend line with a slope of \((3.62 \pm 0.24) \times 10^{13}\) molecules cm\(^{-2}\) yr\(^{-1}\), corresponding to an increase of between 5 and 10 percent per year over the 11 years of data.

The ratio of HF to HCl given by the total column measurements provides an indication of the contribution of chlorofluorocarbon decomposition to the total stratospheric chlorine burden, as naturally occurring sources of stratospheric chlorine do not contain fluorine. The measurements of Zander et al. (1987b) show that this ratio has increased substantially from the 1977 to 1979 time period, when it was 0.15, to the 1983 to 1985 time period, when it was 0.24.

Mankin and Coffey (1983) similarly found a ratio of 0.19 for 1978 to 1979 and 0.23 for 1983 to 1985 (Mankin and Coffey, personal communication). The ATMOS value obtained in May 1985 was 0.25 (Raper et al., 1987). The large increase in the HF–HCl ratio provides important
confirmation of the breakdown of fluorocarbons in the stratosphere. In Wofsy’s analysis, the annual increase in the HCl column is 1.7 times that of the HF column, which is consistent with that based on industrial emissions.

9.3.3 Chlorine Monoxide—ClO

While there are a number of in situ measurements of stratospheric ClO content, made primarily by Anderson and coworkers (see WMO, 1986), the large variation obtained in these measurements and their limited number precludes their use in determination of long-term trends of stratospheric ClO. There are, however, 5 years of ground-based microwave column
measurements taken over Hawaii (deZafra et al., 1985; P.M. Solomon, personal communication), as well as several data points taken earlier elsewhere. These measurements determine the total CIO column density above a pressure level corresponding to approximately 30 km altitude. The results of this period of measurement, summarized in Figure 9.9, do not yet show any clear indication of an increase in upper stratospheric CIO. Accurate trend determination will require substantially increased sampling frequency and a longer data record.

9.3.4 Inorganic Bromine—Brx

Increasing concentrations of bromine-containing molecules in the stratosphere, primarily BrO, are expected based on the 3 percent per year observed increase in the concentrations of several brominated source gases (see source gas chapter of this report), especially CBrClF₂ and CBrF₃. Only very limited data of stratospheric Brx compounds exist, however, and these data are not sufficient for trend determination.

Figure 9.9. Time series of midday CIO column abundances above 30 km measured by ground-based millimeter wave spectrometry taken from Hawaii (from deZafra et al., 1985, with data since 1984 provided by P. Solomon, personal communication, 1987).
9.4 \textit{H}_2\textit{O}/\textit{HO}_x

9.4.1 Water—\textit{H}_2\textit{O}

Upper stratospheric water vapor should be changing as a result of its production from oxidation of methane (\textit{CH}_4), which in the troposphere is known to be increasing at the rate of approximately 1 percent per year (see Chapter 8 of this report). The data on upper stratospheric water vapor are too sparse and variable to discern any trend.

Substantially more data exist on the water content of the lower stratosphere, however, where methane oxidation is not expected to be a significant source of water. Most of these have been made with a balloonborne frost-point hygrometer. Lower stratospheric water vapor is thought to most strongly reflect temperatures near the tropopause and may thus be a better diagnostic of changing tropopause meteorology and of troposphere–stratosphere exchange than of changing methane oxidation amounts.

In a series of balloon flights from Washington, D.C. (1963 to 1980), and Boulder, Colorado (since 1980), Mastenbrook and Oltmans (1983) have shown evidence for both a quasi-biennial oscillation and a nonlinear long-term trend in the \textit{H}_2\textit{O} mass-mixing ratio at 60 mb. This may be seen in Figure 9.10a (Oltmans, personal communication, 1987), which shows that \textit{H}_2\textit{O} amounts tended to increase over the first third of the data set, to decrease over the middle third, and to be relatively constant over the final third. Trend determination from these measurements is difficult because of the shorter term variability. This is removed in the calculation of a 12-month running mean, which is the solid line shown in Figure 9.10a. Some differences between the Washington, D.C., data and the Boulder data are also possible, as the balloons launched from Washington, D.C., ascended through the relatively humid boundary layer, while those launched from Boulder encountered much drier air during the early portion of their ascent.

Examination of measurements made at higher altitudes (up to 20 mb, or approximately 27 km) over Boulder from 1980 to 1987 shows no clear evidence of any long-term trend (Oltmans, 1986; Oltmans, private communication, 1987). All time series (plots of mixing ratio vs. measurement time) in the 20 to 60 mb range are well represented by lines of zero slope with small scatter. Data down to lower altitudes (120 mb, or approximately 15 km) are also well represented by lines of zero slope, but the scatter of the points increases substantially with increasing pressure.

Additional measurements of lower stratospheric water vapor were made with an aircraftborne frost-point hygrometer over southern England during 1972 to 1980. These data, plotted in the form of representative stratospheric humidity (r.s.h), defined as the average of the humidity mixing ratios at 180, 160, and 147 mb when they were within 20 percent of each other, show an apparent decrease in \textit{H}_2\textit{O} mixing ratio from 1972 to 1976 and an increase from 1977 to 1980. Trend determination from these data, taken from Foot (1984) and shown in Figure 9.10b, is clearly complicated by their large variability. Because these data were taken so low in the stratosphere, the air masses sampled may contain a nonnegligible tropospheric component.

Several years of measurements of stratospheric water vapor over Mildura and Alice Springs, Australia, have also been reported (Hyson, 1983). These data, made by an aircraftborne far infrared radiometer, give mean-mixing ratios over 1-km altitude increments up to 21 km. The mean 15 to 21 km mass-mixing ratios, shown in Figure 9.10c for the period 1973 to 1979, show clear evidence of a quasi-biennial oscillation and some indication of a decrease from approximately 3.0
Figure 9.10. Time series of stratospheric H$_2$O vapor measurements made by frost-point hygrometer measurements. (a) 60 mb mixing ratios obtained from balloon flights launched at Washington, D.C. (1963 to 1980), and Boulder, Colorado (since 1980). Solid line is 12-month running mean through the data. Figure obtained from S. Oltmans (private communication, 1987). (b) Representative stratospheric humidity measured on aircraft flights over southern England near 50°N from 1972 to 1980. Figure taken from Foot (1984). (c) Mean 15 to 21 km water vapor mixing ratio (ppmm) over Mildura and Alice Springs, Australia, from 1973 to 1979. Curve is cubic spline fit to data. Figure taken from Hyson (1983).
ppmm during 1973 to 1976 to 2.3 ppmm during 1976 to 1979. The limited number of data and the large quasi-biennial oscillation make quantitative trend determination difficult, however.

Evidence against very large changes in stratospheric H2O amounts was obtained by comparison of monthly zonal means in the lower stratosphere of LIMS (November 1978) and SAGE-II (November 1985) data. The two satellite instruments, using very different techniques, obtained H2O amounts within 20 percent at all latitudes studied outside of the hygropause region (Larsen et al., 1986). Because of the preliminary nature of the SAGE-II analysis, it is impossible at this time to offer a more definitive conclusion about any change in stratospheric water vapor.

![Graph](image-url)

**Figure 9.11.** Time series of normalized monthly OH column amounts from indicated groundstations. Normalization procedure is described in Burnett et al. (1988). (a) Fritz Peak, Colorado. Figure obtained from E. Burnett (private communication, 1987). (b) Boca Raton, Florida. Figure obtained from Burnett et al. (1988).
9.4.2 Hydroxyl—OH

The only data set of upper atmospheric OH amounts potentially suitable for determining long-term trends is the total column measurements made by Burnett and coworkers with a Pepsios spectrometer. The longest running data set is that taken from the NOAA Fritz Peak Observatory, dating back to 1977 (Figure 9.11a). Additional data recently have become available from Boca Raton, Florida (Figure 9.11b), and Poker Flat, Alaska (Burnett et al., 1988). Interpretation of these measurements is complicated because they are of the total OH column, which includes a small tropospheric and a large mesospheric contribution, so that stratospheric OH may make up only some 40 percent of the observed amount. Also, the measured OH column reflects the strong diurnal variation of OH, which needs to be accounted for in any comparison of data. Finally, OH is expected to have a strong seasonal variation, associated mainly with the seasonal variation in the solar zenith angle.

The data from the Fritz Peak and Boca Raton stations are summarized in Figure 9.11 (Burnett et al., 1988; Burnett, personal communication, 1987). These data have been normalized to remove the dependence that can be directly related to solar zenith angle, thus removing diurnal and some seasonal dependence. Variation remaining reflects other seasonal processes (those not directly related to solar zenith angle) and any long-term variation. The Fritz Peak data show a substantial increase from 1977 to 1980, which has been suggested but not demonstrated to be associated with the solar cycle (WMO, 1986), but little or no evidence for long-term changes since that time. The Boca Raton data might be interpreted as showing a net decrease over the 1980 to 1982 period, with evidence for strong variability after 1984. The limited number of data, the large error bars, and the complicating seasonal variations make it impossible to determine whether there is any long-term variation in these measurements.

9.5 SUMMARY

An unambiguous long-term increase of between 5 and 10 percent per year in the total column amount of atmospheric HF has been observed over the last decade in measurements from the ground and from aircraft. This is consistent, within error bars, with predictions based on the measured increase of organic fluorine in the troposphere. An increase of the column amount of atmospheric HCl has now also been observed. Aircraft data that measure the column amount in the stratosphere show a large increase (5 percent per year). Ground-based data from the observatory at Jungfraujoch of the total column above the station, which includes both tropospheric and stratospheric components, indicate a smaller change (2 to 3 percent per year). These data now extend into 1987, and have been reanalyzed to account for seasonal variations in the trend estimates. Trend measurements of HCl are especially difficult to make because a large and variable contribution of tropospheric HCl to the total column, a large seasonal variation, and a possible interference from volcanically injected HCl all are superimposed on the small annual increase expected. It should be noted that any differences between the absolute values or trends determined from ground-based and aircraft measurements should, in general, be attributable to a tropospheric column contribution in the former. In the present case, this comparison leads to a tropospheric HCl column above Jungfraujoch that is somewhat larger than reported in a limited set of independently measured tropospheric HCl concentrations, but the differences are within the uncertainties of the measurements plus meteorological variability.

There is not yet a clear indication of an increase in the column amount of upper stratospheric ClO (also expected to be increasing at the same rate as HCl). There are insufficient data to study the long-term trends of stratospheric bromine compounds.
Satellite-based measurements of NO$_2$ have been interpreted as showing large (60 to 70 percent) increases during 1979 to 1984, but such increases are not supported by ground-based and aircraft measurements over that time. Subsequent analyses of SAGE data also do not support the large increases originally suggested, but do not rule out the possibility of smaller changes (10 to 20 percent) during the 1979 to 1984 period, especially in the Southern Hemisphere. Such increases, if real, must be due to changing inputs of odd nitrogen from either the mesosphere (NO produced from ionic processes in the thermosphere) or troposphere (NO produced in lightning discharges), as they are much larger than the very small (1 percent) increases expected over that time from increasing concentrations of stratospheric N$_2$O. SBUV data of NO at and above the stratopause region seem to imply some long-term decrease in the Tropics over 1979 to 1986, but no clear trends were seen at high latitudes. No definitive changes in the total amount of stratospheric odd nitrogen, which includes NO, NO$_2$, HNO$_3$, N$_2$O$_5$, ClONO$_2$, and HNO$_4$, can be deduced at this time.

Balloonborne frost-point hygrometer measurements of water vapor made over Boulder 1980 show no evidence of a trend in middle and lower stratospheric (20 to 120 mb) water vapor. Analysis of data obtained previously over Washington, D.C., appeared to show some unexplained cyclical variation over 1963 to 1980, but these data are complicated by substantial short-term variability and a quasi-biennial oscillation. There is also no evidence of a trend in the total OH column over Fritz Peak over 1980 to 1987, although some unexplained variation prior to 1980 was obtained. Neither of these unexplained variations is related to the expected increase in stratospheric hydrogen species associated with the oxidation of the increasing amounts of stratospheric methane.

In order to determine unambiguously what the long-term trends of these species are, a campaign of frequent measurements of these constituents must be carried out. In the long term, the Network for the Detection of Stratospheric Change (NDSC) will be very useful for trend determination. Plans have already begun for setting up stations in both the United States and Europe. This network must evolve into a set of worldwide stations that measure the concentrations of key atmospheric molecules on a continuing basis. In the short term, measurements need to be made on a continuing basis by existing instruments at their current locations (e.g., HCl and HF from Jungfraujoch, ClO from Hawaii, OH from Fritz Peak, H$_2$O from balloon measurements in Boulder, etc.). In addition, the SAGE-I and -II NO$_2$ and H$_2$O data should be fully exploited after release by their science team. Periodic measurements of trace constituent concentrations by aircraft instruments and the shuttleborne ATMOS instrument could also play an important role in determining their long-term trends. When the UARS satellite is launched, additional information concerning trends should be available from several instruments on that satellite. A coordinated plan for determining trends in the species considered here has been presented in the U.S. National Plan for Stratospheric Monitoring 1987 to 1997 (Federal Coordinator, 1988).