

Observations of Chemical Composition

Ulrich Schmidt, lecturer
Institute for Meteorology and Geophysics
Johann Wolfgang Goethe-University
Frankfurt am Main, Germany

Fred Stroh, Céline Phillips, and Kimberly Strong, rapporteurs

Introduction

Observations of chemical composition are crucial to our understanding of the stratosphere. They are needed for the determination of its basic composition and for the characterization of its spatial and temporal variability. Measurements of long-lived chemical species, so-called tracers, provide information about dynamical transport processes. Correlative measurements of families of chemical species provide information on details of chemical processes in the system. Generally, measurements of chemical composition are the only way to validate and improve atmospheric models, such as those developed for predicting the response of the stratosphere to anthropogenic processes, and to test laboratory data relevant to the stratosphere. An example for the validation of model predictions was the detection of ClONO_2 (Murcray *et al.*, 1979) after models suggested that the formation of ClONO_2 from NO_2 and ClO would have a strong effect on Cl_x chemistry.

No unique technique or instrument exists which is able to provide information about the global stratospheric composition with satisfactory temporal and spatial resolution. Instead, a variety of different measurement techniques have been developed, each with its own strengths and weaknesses. Measurement strategies have also evolved as our understanding of stratospheric chemistry has improved. Limited observations of single species are now considered useful only if they successfully demonstrate a new technique, represent the first observation of a species, identify an unknown process, or add information to relevant data sets. For example, the single measurement of the concentration of an iodine species would be of great interest, because iodine has recently been suggested as a possible potential contributor to ozone depletion (Solomon *et al.*, 1994). However, nowadays a single measurement of OH , a very reactive species, is of little use if those species that determine its concentration in local photostationary state (see the previous lectures by Dr. Susan Solomon) are not measured simultaneously.

In recent years, as we try to quantify changes in the chemical composition of the stratosphere, the emphasis has shifted to techniques that provide continuous, global, or simultaneous measurements. Continuous observations are crucial to studies of the temporal variability of a species, ranging from diurnal variations to long-term trends. Global coverage, involving the measurement of a species at many different locations, is needed for the establishment of climatologies of trace species. Simultaneous observations, in which the abundances of many species in a chemical family are measured at the same time, are proving to be highly valuable for investigating the chemical cycles that occur in the stratosphere. The large number and variety of measurement techniques now available make intercalibrations and intercomparisons essential for establishing confidence in the acquired data. They are needed for the validation of new techniques, the improvement of available techniques, error analysis, and for ensuring a meaningful combination of data sets obtained using different methods.

In general, observations of chemical composition are quantified in terms of an abundance as a function of latitude, longitude, and time. Vertically resolved observations are also given as a function of some coordinate describing altitude. The most commonly used quantities to describe the abundance of a trace gas are as follows:

Column density. Defined as the total number of molecules in a vertical column above a unit area. Column densities for ozone are usually given in Dobson units (DU), where 1 DU is defined as 1 milliatmosphere cm. Typical ozone column densities are around 300 DU ($= 9 \times 10^{18}$ molecules/cm²).

Number density. Defined as the number of molecules per unit volume at ambient pressure.

Volume mixing ratio (VMR). Defined as the ratio of the number density of the gas to the number density of air at the given altitude. This is usually expressed in ppmv (parts per million by volume), ppbv (parts per billion by volume), or pptv (parts per trillion by volume).

Concentration. Usually given as a mass per unit volume, but which can have several different definitions; for example, g/cm³, g/m³, moles/m³ (all at STP), and g/g.

Several different variables are also used to specify the altitude. The *geometric altitude*, given in km, is generally used for remote sensing data, because the viewing geometry is based on geometric units. The *pressure altitude*, given in hPa, is preferred for in-situ

observations, as mobile platforms often have a pressure sensor on board. The pressure altitude can be converted into geometric altitude based on tabulated standards (*e.g.*, the US standard atmosphere (1976)) or based on data from an actual radiosonde measurement. The *flight level*, often quoted as the cruising altitude of an aircraft is simply a modified pressure altitude, and is defined as the geometric altitude that corresponds to the pressure, again based on a tabulated standard. *Potential temperature* is a useful measure of altitude, as it is a conserved property for adiabatic processes. It is defined as

$$\Theta = T (p_0/p)^k, \text{ where } k = (1 - c_v/c_p) = 0.286 \text{ (for dry air)}. \quad (1)$$

The mixing ratio of a long-lived gas such as N_2O or CH_4 can also be used to specify altitude. This is referred to as the *tracer concept*. For example, N_2O is particularly useful in labelling measurements for the investigation of trends or distributions because

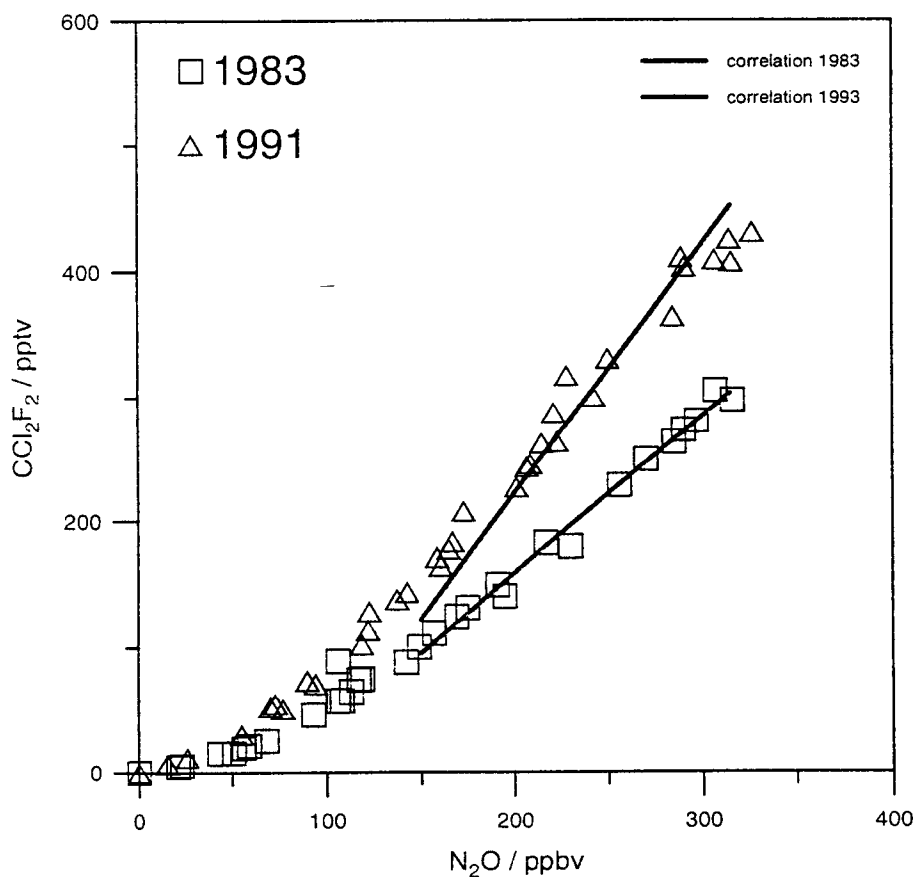


Figure 1. CCl_2F_2 as a function of N_2O , as measured at Aire sur l'Adour (44°N) by cryogenic whole air sampling in 1983 and 1991. The correlation derived for the data measured in 1983 and 1993 is also plotted (figure courtesy of A. Engel).

it has a photochemical lifetime comparable to the lifetime of vertical transport and of advection in the mean meridional circulation which are on the order of years for the lower stratosphere. A second advantage of N_2O is that it only shows a small anthropogenic trend of approximately 0.2% per year. For these reasons air parcels exhibiting similar N_2O mixing ratios have experienced a similar photochemical history. Figure 1 shows an example of how the distribution of CCl_2F_2 behaves as a function of N_2O . At high mixing ratios of N_2O , *i.e.*, low in the atmosphere, CCl_2F_2 increases linearly with N_2O , indicating that its concentration in this region is controlled primarily by transport processes. The nonlinear relation between CCl_2F_2 and N_2O at lower N_2O mixing ratios suggests that the CCl_2F_2 is destroyed photochemically at the corresponding higher altitudes. In addition, Figure 1 clearly shows how the mixing ratio of CCl_2F_2 has increased throughout the lower atmosphere between 1983 and 1991 and 1993, respectively.

In the following two sections techniques and platforms employed in the observation of chemical composition will be classified and selected techniques that have produced valuable quantitative measurements of key species in stratospheric ozone depletion will be introduced and discussed. The reader is referred to Schmidt and Zander (1996) for a comprehensive compilation of observational platforms, techniques and references to the original literature. The fourth and fifth sections will discuss measurement strategies and summarize outstanding issues in stratospheric chemistry that can be studied through new or improved observational techniques.

Observation Techniques and Platforms

Measurements of chemical composition are generally performed using either in-situ or remote sensing techniques. *In-situ techniques* make observations at the location of the instrument. Only direct observations are truly in-situ, but indirect sampling techniques, whereby samples are collected and analyzed later in a laboratory, have also been used with considerable success. In-situ sampling methods need to be verified with respect to the stability and contamination of the collected samples. Generally, in-situ instruments can be designed for highly specific applications by employing the most suitable sensor that offers optimum sensitivity and is adapted to operate at the temporal resolution required to meet the necessary spatial resolution. However, in-situ measurements in the stratosphere can only be made from mobile platforms. This means that their use for long-term observations of the stratosphere (needed to determine climatological trends) is limited by operational costs and the availability of suitable platforms. In addition, the platform and payload of the in-situ measurement may chemically contaminate the

air mass that is probed (*e.g.*, outgassing from balloons, aircraft emission) and thereby lead to erroneous results.

Remote sensing techniques detect and interpret the results of the interaction of electromagnetic waves with the molecules in the atmosphere, through absorption, emission, or scattering. They may be passive techniques, making use of natural light sources (the sun, the moon, stars, or atmospheric emission), or active techniques, making use of artificial light sources. Their principal advantages are their applicability over a broad range of wavelengths (UV, VIS, IR, FIR, MW) and the fact that they provide data based on pure physical information. Remote observations, generally, are least affected by contamination, alteration, or chemical perturbation of the sample volume. However, they provide only limited spatial resolution, require relatively large and heavy instruments, and entail extensive and expensive spectral evaluation (see the previous lecture by Dr. Clive Rodgers).

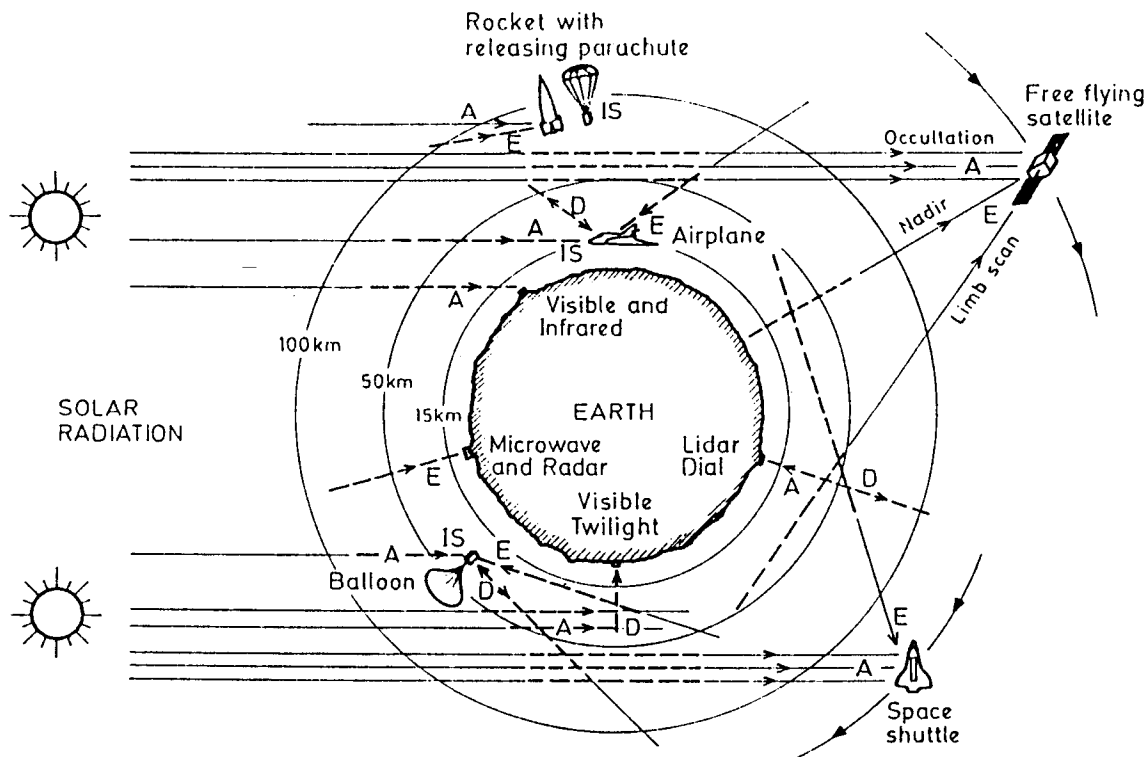


Figure 2. Illustration of the different methods and platforms that can be used to investigate stratospheric composition. In-situ measurements are denoted by "IS", while "A", "D", and "E" indicate techniques that use absorption, diffusion (scattering), and emission of radiation (from Schmidt and Zander, 1996).

Measurements of stratospheric composition can be performed from a number of platforms. These are illustrated schematically in Figure 2. *Ground stations* are the most common location for instruments, generally being used for remote sensing observations of total columns and vertical profiles. To perform reliable long-term measurements ground stations require a location with a clean environment. Therefore preferred sites are either at high altitudes above the often polluted boundary layer (*e.g.*, Jungfrauoch in Switzerland, Kitt Peak in Arizona, Mauna Loa in Hawaii, Hohenpeissenberg in Germany, Haute Provence in France) and/or at remote background locations (*e.g.*, Lauder in New Zealand, Ny Alesund on Spitsbergen, Dumont D'Urville in Antarctica). In principle, ground stations are ideal for long-term monitoring of trace gas concentrations, allowing the evaluation of decadal trends of stratospheric species. In practice, there are only a few long time series (> 10 years) for any gases other than ozone. The Dobson-Brewer network is an example of a highly successful network of ground-based instruments which have been used to monitor stratospheric ozone since the 1920s. Another example, the Network for the Detection of Stratospheric Change (NDSC), will be described in more detail in a later section.

Aircraft can serve as platforms for both remote sensing and in-situ measurements. They offer the advantage of operational flexibility and good spatial coverage. Aircraft are particularly useful for the investigation of chemical processes, because they can carry sets of instruments for the simultaneous observation of many different species. In addition, they can be used to travel to locations of particular interest, obvious examples being Antarctica to observe the "ozone hole", and active volcanoes to monitor volcanic plumes. However, the operational range of available aircraft is limited to the lower stratosphere, with the upper altitude limit being about 21 km. This means that it is not possible to make in-situ observations of the middle stratosphere from aircraft. Operational aircraft being used to investigate the chemical composition of the stratosphere include the NASA ER-2 and DC-8, the WB 57 (all US), the Transall (Germany), the M55-Geophysika (Russia), and the Caravelle (France). Two new aircraft being developed for high altitude missions are Strato2C (Germany) and the unmanned Perseus (US).

Balloons have the advantage of being able to reach altitudes as high as 40 km or more, carrying in-situ or remote sensing payloads ranging from only 1 kg (radiosondes and ozonesondes) up to several tons. They can make observations over many hours or days at high altitudes and have been designed for special tasks such as valve-controlled slow descent, double ascents, and boomerang flights. The major limitation of balloon launches is that they depend on such factors as meteorological conditions at the ground

and at altitude, logistics at the launch site, the telemetry range, and air traffic safety control. Balloon measurements are also at risk of contamination from the balloon and the flight train. A number of balloon launch sites are available for routine operational services. Most of them are located in the northern hemisphere (*e.g.*, Palestine and White Sands (US), Aire sur l'Adour and Gap (France), Kiruna (Sweden), and Andoya (Norway)).

Rockets can achieve even higher altitudes than balloons, carrying instruments well into the mesosphere. They can be launched at almost exactly the time of interest for the investigation of a specific process. However, rockets are less commonly used for stratospheric measurements now than in the past, due to several disadvantages. These include the limited vertical resolution due to the large velocities during both ascent and descent, the need for powerful and expensive multistage rockets for heavier instruments, and the fact that only a few launch sites are available (*e.g.*, White Sands, Wallops Island and Poker Flat (US), Kiruna and Andoya). In addition, instruments must be designed to operate under extreme conditions, such as high accelerations, shock vibration, and shock wave heating. Techniques have been developed to improve the altitude resolution by separating the payload from the rocket prior to apogee (and thereby avoiding the shock wave) and using a parachute to slow the descent.

Satellites are another type of observation platform which can be used to probe the composition of the stratosphere. All measurements made from satellites employ remote sensing techniques, and most involve passive observations of radiation modified through interaction with the atmosphere. Satellite observations have been invaluable in establishing global climatologies for stratospheric trace species. Important examples of satellite observations are UARS (Upper Atmosphere Research Satellite) (see the following lecture by Dr. Joe Waters), TOMS (Total Ozone Mapping Spectrometer), SAGE I and SAGE II (Stratospheric Aerosol and Gas Experiment) (see the following lecture by Dr. Ray Hoff).

Selected Techniques

MEASUREMENT OF OZONE

Ozone is one of the most widely studied atmospheric constituents. Its distribution, variability, long-term evolution, and role in stratospheric chemistry have gradually been determined from a wide range of measurements. Fortunately, this important species

can be measured using a variety of different techniques. These include the following, with R and IS denoting remote sensing and in-situ techniques, respectively:

1. Dobson spectrophotometers (R)
2. Brewer spectrophotometers (R)
3. M-83 and M-124 spectrophotometers (R)
4. LIDAR (LIght Detection and Ranging) and DIAL (Differential Absorption LIDAR) instruments (R)
5. UV and visible photometers and spectrometers (R, IS)
6. optical rocket sondes (R)
7. optical satellite instruments (R)
8. laser heterodyne spectrometers (R)
9. IR and far-IR grating and Fourier transform spectrometers (R)
10. microwave instruments (R)
11. chemiluminescence sondes (IR)
12. electrochemical sondes (Brewer-Mast, EEC) (IS)
13. mass spectrometers (IS)

All of these techniques involve remote sensing, except for the last three which are purely in-situ methods. Descriptions of many of these techniques can be found in Grant (1989).

Measurements of ozone can be roughly grouped into observations of the global distribution of total columns and observations of vertical profiles. Satellite-based instruments and networks of ground-based instruments are generally used to obtain global maps of total ozone over time. These are needed for studies of geographic variations in ozone, and if such measurements are available for a sufficiently long time, they are invaluable for monitoring long-term ozone trends.

The first measurements of the global ozone distribution were made by a network of ground-based Dobson spectrophotometers. These instruments measure the solar radiation at pairs of wavelengths near 300 nm. One of the wavelengths is chosen to be in a region of significant ozone absorption, while the other one is in a region with very low absorption by ozone and is attenuated by an optical wedge which is adjusted to obtain equal signals from both beams. Comparison of the two signals allows the total vertical column of ozone to be deduced. Dobson spectrophotometers were first used in the 1920s (Dobson, 1968), and were subsequently deployed at many sites around the world. More than 56 stations, most of them located in the mid- to high-latitudes of the Northern Hemisphere form the present network (WMO, 1995). Figure 3 presents the

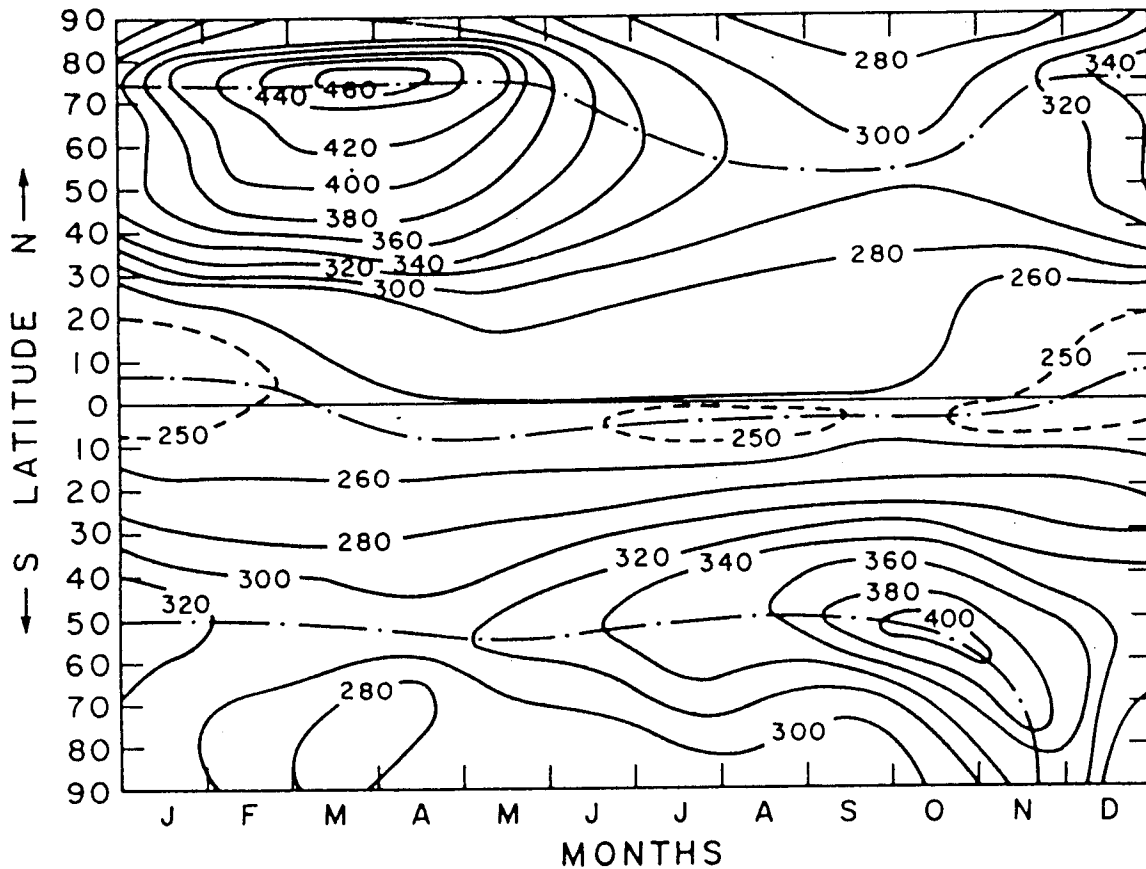


Figure 3. Seasonal variation of zonal averages of total ozone from the Dobson network for the period 1958-1977 (London, 1980). The dashed and dashed-dot lines indicate axes of minimum and maximum columns, respectively (figure from London, 1980).

seasonal variation of zonal averages of total ozone obtained from the Dobson network over the period from 1958 to 1977 (London, 1980), *i.e.*, before the Antarctic “ozone hole” developed regularly in October. It shows the usefulness of such measurements, as the seasonal changes in global ozone are clearly distinguishable over the course of the averaged year. Even with the low spatial resolution of the Dobson network, the minimum at the equator and the winter maxima at high latitudes are obvious.

Higher spatial resolution and greater internal consistency of measurements can be obtained from satellite measurements of total ozone. For example, TOMS was deployed on the Nimbus 7 (1978-1993) and Meteor 3 (1991-1994) satellites. TOMS has been particularly valuable in monitoring the extent and duration of the Antarctic “ozone hole”. However, there is a role for both ground-based and satellite measurements of total ozone, with the former providing a longer term record for studying trends.

Intercomparisons of the data obtained using different techniques are essential for the assessment of the data quality.

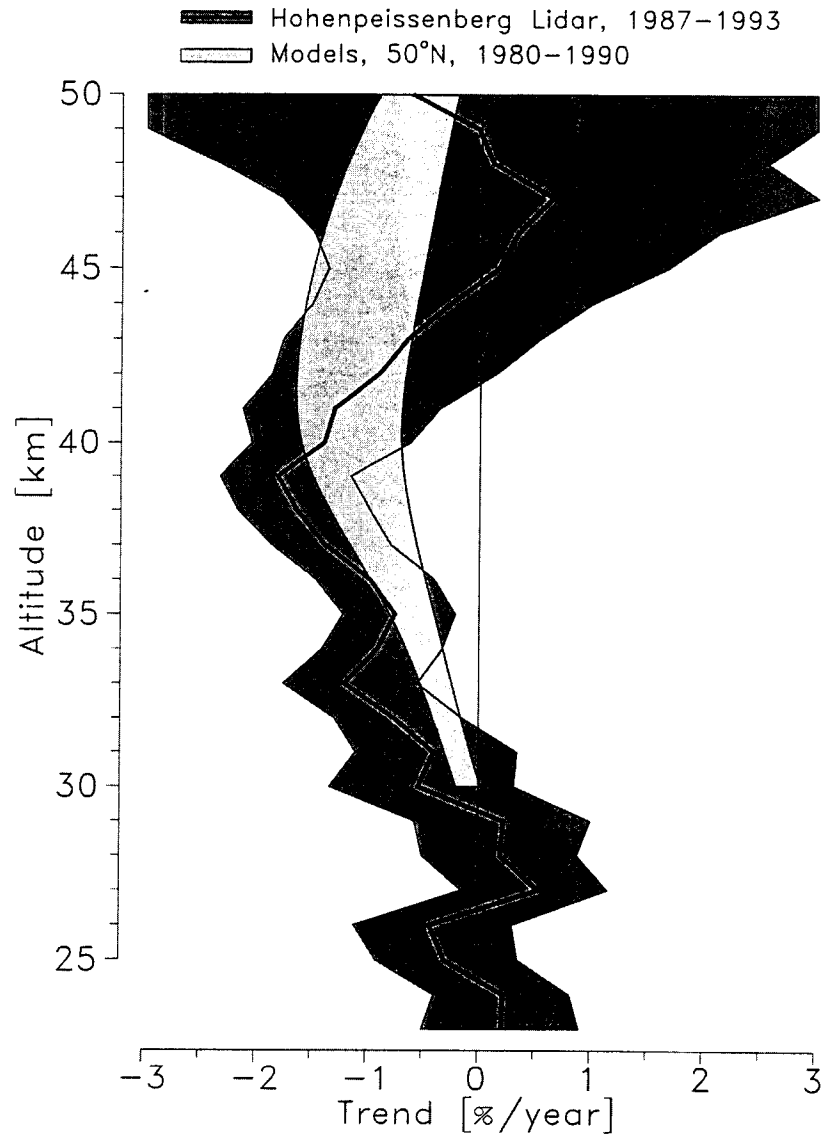


Figure 4. The trend in the vertical profile of ozone derived from DIAL measurements at Hohenpeissenberg between 1987 and 1993 (Claude *et al.*, 1994). The measurements are given as the solid black line while the dark grey area indicates 2σ error bars. The region shaded in light grey represents the ozone trend predicted from model calculations (figure courtesy of W. Steinbrecht).

The second category of ozone measurements is that of vertical profiles.¹ These are frequently obtained by ozonesondes, electrochemical cells sensitive to the ozone concentration, which are carried aloft by small balloons to make in-situ measurements. Vertical profiles can also be derived from Dobson zenith-sky measurements using the Umkehr method, which is based on the fact that the effective scattering altitude

varies with wavelength (Mateer and DeLuisi, 1992). Profiles may also be obtained from satellite measurements of solar occultation (SAGE I and II) and of atmospheric backscatter (Solar Backscatter Ultraviolet Radiometer, SBUV). A comparison of ozone profiles obtained by SAGE II and SBUV can be found in McPeters *et al.* (1994). A recent comparison of ozone trends measured with ground-based and satellite-borne instruments are compiled in WMO (1995).

Since the early 1980s, ground-based DIAL (Differential Absorption LIDAR) systems have been used to measure ozone profiles. With the LIDAR (LIght Detection And Ranging) technique, a pulsed laser beam is directed into the atmosphere and its backscattered component is measured as a function of time, providing information as a function of altitude. For the DIAL technique the laser beam is operated at two wavelengths, one in a region of strong ozone absorption, and one lying outside this region, so that the absorption and hence the concentration of ozone can be determined at each altitude. Because this technique does not require sunlight, unlike most of the other remote sensing techniques for determining profiles, it can be employed day and night, year round. However, daytime measurements may be limited in sensitivity by solar UV radiation that enters the detector. Figure 4 shows trends in the vertical profile of ozone as derived from long-term DIAL measurements (Claude *et al.*, 1994). The observations made at Hohenpeissenberg (Germany) between 1987 and 1993 show a significant decrease in the ozone concentration between 32 and 42 km, by as much as -1.7% per year at around 39 km, roughly consistent with model predictions of ozone destruction by CFCs which are most effective at these altitudes in the mid-latitude stratosphere.

MEASUREMENT OF LONG-LIVED GASES

An understanding of stratospheric chemistry, and particularly stratospheric ozone loss, requires a knowledge of the concentrations and trends of numerous trace species. This in turn requires data on the sources of these species, which are long-lived gases that are of natural or anthropogenic origin. The long-lived source gases for the most important chemical families (see the previous lectures by Dr. Susan Solomon) are shown in Table 1.

Long-lived gases such as CO₂ (important in radiative forcing), SF₆, and CF₄ (both good indicators of the age of stratospheric air) are very valuable tracers. Other long-lived gases that are transported into the lower stratosphere and get involved in chemical processes are CO and non-methane hydrocarbons (both also important in tropospheric

ozone chemistry), and COS and CS₂ (sources of the background stratospheric sulfate aerosol).

Table 1

<i>Family Members</i>	<i>Source Gases</i>
HO _y H, OH, HO ₂ , H ₂ O ₂	CH ₄ , H ₂ O, H ₂
NO _y NO, NO ₂ , NO ₃ , N ₂ O ₅ , HONO, HNO ₃ , HO ₂ NO ₂ , PAN, ClONO ₂ , BrONO ₂ , aerosol nitrate	N ₂ O
Cl _y Cl, Cl ₂ , ClO, Cl ₂ O ₂ , OClO, HOCl, HCl, BrCl, ClONO ₂	CH ₃ Cl, CFCs, HCFCs, and other halocarbons

A variety of techniques can be used for measuring these long-lived gases, some of general applicability, and some better suited for the detection of a particular gas. Most species can be detected by passive remote sensing, either in absorption or emission, at infrared or microwave wavelengths. Many of the long-lived gases (CFCs, N₂O, CH₄, H₂, SF₆, COS, CO₂) can be measured using the indirect in-situ method of whole air sampling followed by laboratory analysis. For these measurements, atmospheric samples can be collected in evaluated sample containers (Schmeltekopf *et al.*, 1976) or in cryogenically-cooled stainless steel bottles (Fabian *et al.*, 1979) that are opened and resealed at a desired altitude. Samples are subsequently returned to the laboratory and analyzed by a method such as gas chromatography. These samples may be collected on aircraft, balloon, or rocket platforms, so that vertical profiles can be derived. In contrast, common techniques to measure H₂O are the in-situ species-specific Lyman-alpha hygrometer, (*e.g.*, Kley and Stone, 1978), or the front-point hygrometer (Mastenbrook, 1968).

N₂O and CH₄ are two source gases well-suited to direct in-situ measurements by tunable diode laser spectroscopy (TDL). With this technique, a narrowband laser emission is scanned across a selected absorption line of the gas of interest. The concentration of this gas can then be determined by passing the last beam through a cell containing an atmospheric sample. TDL provides high spectral resolution and fast time response. A typical example of TDL measurements of N₂O, a gas that is used extensively as a dynamical tracer (see *e.g.*, Figure 1), is the work by Loewenstein *et al.* (1989).

MEASUREMENT OF RESERVOIR SPECIES

Reservoir species are defined as relatively long-lived compounds (compared to the time scales for transport) which are formed from reactions of potentially reactive species and render them in an inactive form. The reactive species are not permanently lost, but can be released through thermal or photochemical processes. The reservoir species of the NO_y family are HNO_3 , ClONO_2 , N_2O_5 , HONO , HO_2NO_2 , BrONO_2 , aerosol nitrate, and PAN (peroxyacetyl nitrate). Those of the Cl_y family are HCl and ClONO_2 (and Cl_2O_2 , HOCl and Cl_2 for perturbed conditions). Most of these species can be measured using passive remote sensing techniques (emission and absorption) in the infrared and microwave regions (see the following lecture by Dr. Joe Waters). HNO_3 and HCl can also be measured during direct in-situ techniques, such as tunable diode laser spectroscopy (Webster *et al.*, 1993) and mass spectrometry (Arnold and Knop, 1987). Indirect in-situ sampling techniques employing impregnated filters have also been used to probe these acidic species. Unfortunately, no in-situ techniques are presently available to measure the other mentioned reservoir species. Such techniques would be extremely valuable to determine the partitioning within the chemical families.

Figure 5 shows vertical profiles of HCl measured by balloon-borne IR spectrometers and HALOE (HALogen Occultation Experiment) aboard UARS in 1993. When compared with an average of profiles measured in 1983 an increasing trend is apparent. This increase in HCl is consistent with the results from balloon-borne measurements performed in 1992 (not shown in Figure 5), and is probably due to the increase in chlorofluorocarbons in the stratosphere from anthropogenic emissions. However, care must be taken when comparing single profiles in this way because the differences between the two flights may be caused by differences in the dynamical situation on the day of the flight. Ideally a larger number of measurements is necessary in order to obtain a statistically significant trend.

MEASUREMENT OF REACTIVE SPECIES

The measurement of radical species is crucial for the understanding of fast chemical processes in the atmosphere. Both in-situ and remote sensing techniques can be used to measure these species. Among the in-situ techniques used are resonance fluorescence, chemiluminescence and indirect in-situ techniques (measurements through collection) such as matrix isolation.

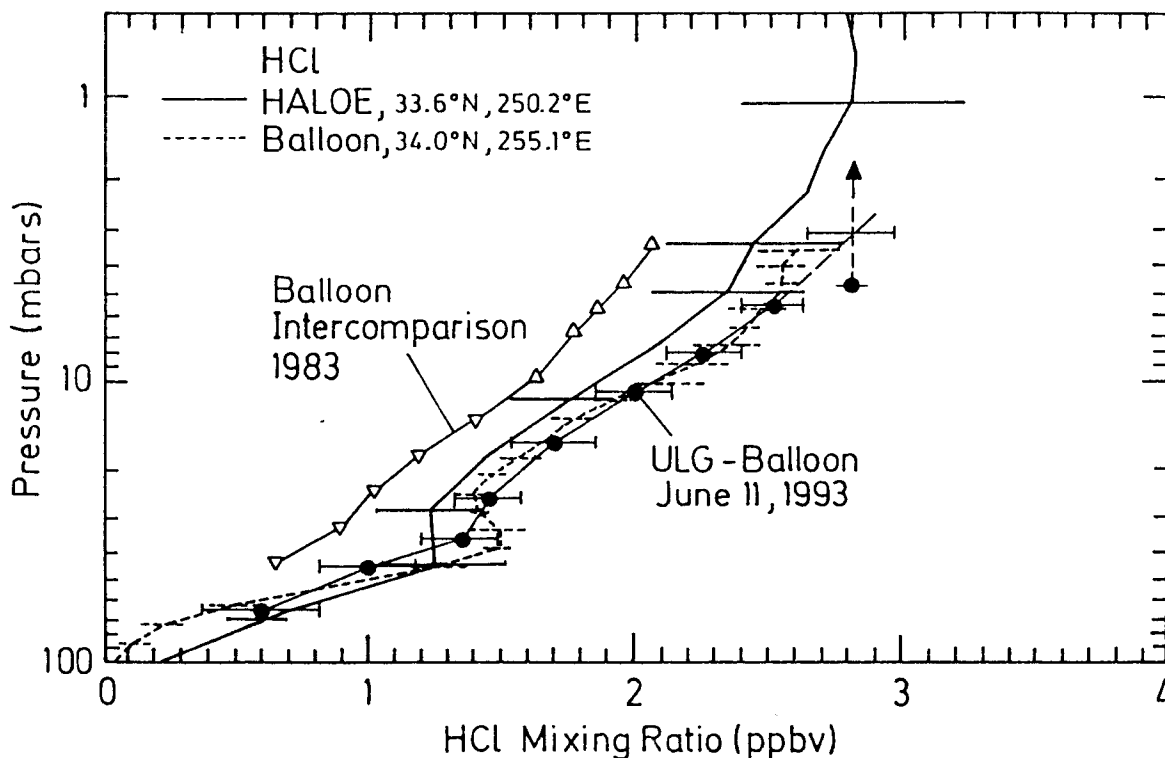


Figure 5. Comparison of HCl vertical profiles. The profile obtained from a balloon-borne IR solar sunset measurement at Fort Sumner on June 11, 1993 is indicated as solid dots. The dashed arrow at the uppermost dot indicates the mean VMR above float altitude of the balloon. (R. Zander, private communication, 1996) A HALOE profile from September 25, 1993 (Russell *et al.*, 1995) is plotted as a solid line while the profile derived from a balloon-borne FTIR absorption experiment launched from Fort Sumner the same day (Russell *et al.*, 1995) is indicated as a dashed line. These profiles are compared to the mean profile obtained from five balloon-borne IR measurements performed during the balloon intercomparison campaign on June 17 and 20, 1983 (from Farmer *et al.*, 1990; figure courtesy of R. Zander).

Resonance fluorescence (fluorescence induced by radiation from a low pressure plasma discharge lamp which is resonant in energy with a preselected electronic transition) has been used to measure OH, Cl and Br. The species HO₂, ClO and BrO can also be measured using this technique after chemical conversion, via the gas phase reaction with NO, to the OH, Cl, and Br radicals, respectively (Brune *et al.*, 1989). Laser induced fluorescence (LIF) can be used to measure HO_x radicals (OH, HO₂, and H).

One way to measure NO is the in-situ chemiluminescence technique. This involves monitoring the photons produced during the chemiluminescent reaction of a radical with a suitable reactant (*e.g.*, ozone). This technique can also be used to measure total reactive nitrogen, NO_y, if all other reactive species within this chemical family can be quantitatively reduced to NO (*e.g.*, by reaction with CO, Fahey *et al.*, 1989).

NO and NO₂ have also been measured in-situ using balloon-borne tunable diode laser spectrometers (*e.g.*, Webster and May, 1987). Above 25 km, where the NO transition lines in the fundamental vibration-rotation band near 5.4 μm do not exhibit pressure broadening, NO columns can also be measured by the Zeeman modulator radiometer (ZMR) technique (McKenzie and Roscoe, 1988).

Reactive species cannot be measured using whole air sampling techniques as they decay or react at the inner surface of the container. A technique which has been developed to stabilize the species immediately after sampling, thereby allowing indirect in-situ measurements, is matrix isolation. This technique involves the cryogenic trapping (at 77K) of free radicals on an inert solid matrix. In the laboratory, the free radicals are detected in the cold samples by electron spin resonance spectrometry (ESR). HO₂, NO₂, and NO₃ have been measured using this technique (Helten *et al.*, 1984). In the case of HO₂, unfortunately, this technique suffered from inherent problems of indirect sampling of such a short-lived species.

Among the common passive remote sensing techniques used to measure radical species are microwave emission and absorption, far infrared emission and UV-visible absorption spectrometry. The infrared absorption of solar radiation is used to measure NO and NO₂ in limb-scan mode from balloons and aircraft. The atmospheric emission of NO and NO₂ in the infrared and of OH and ClO in the far infrared is also used for measurements in limb-scan geometry. ClO has also been measured using infrared laser heterodyne radiometry (Menzies *et al.*, 1981).

HO₂ and ClO can be measured by observing their microwave emission either in limb-scan geometry or from the ground. This involves the measurement of rotational lines at long wavelengths (*i.e.*, millimeter and submillimeter wavelength regions). Due to the pressure broadening of the line shape, these spectral measurements also provide information about the vertical profile distribution (*e.g.*, de Zafra *et al.*, 1984).

UV-visible absorption spectrometry is used to measure NO₂, NO₃, OClO and BrO (OH in the near-UV) by solar occultation from balloons (Pommereau and Piquard, 1994) and by ground-based and air-borne UV-visible spectrometers by observing the solar radiation scattered from the zenith during twilight (see Goutail *et al.* (1994) and references therein). The zenith-sky technique has been used to measure long time series of total column amounts of radical species and ozone with ground-based instruments.

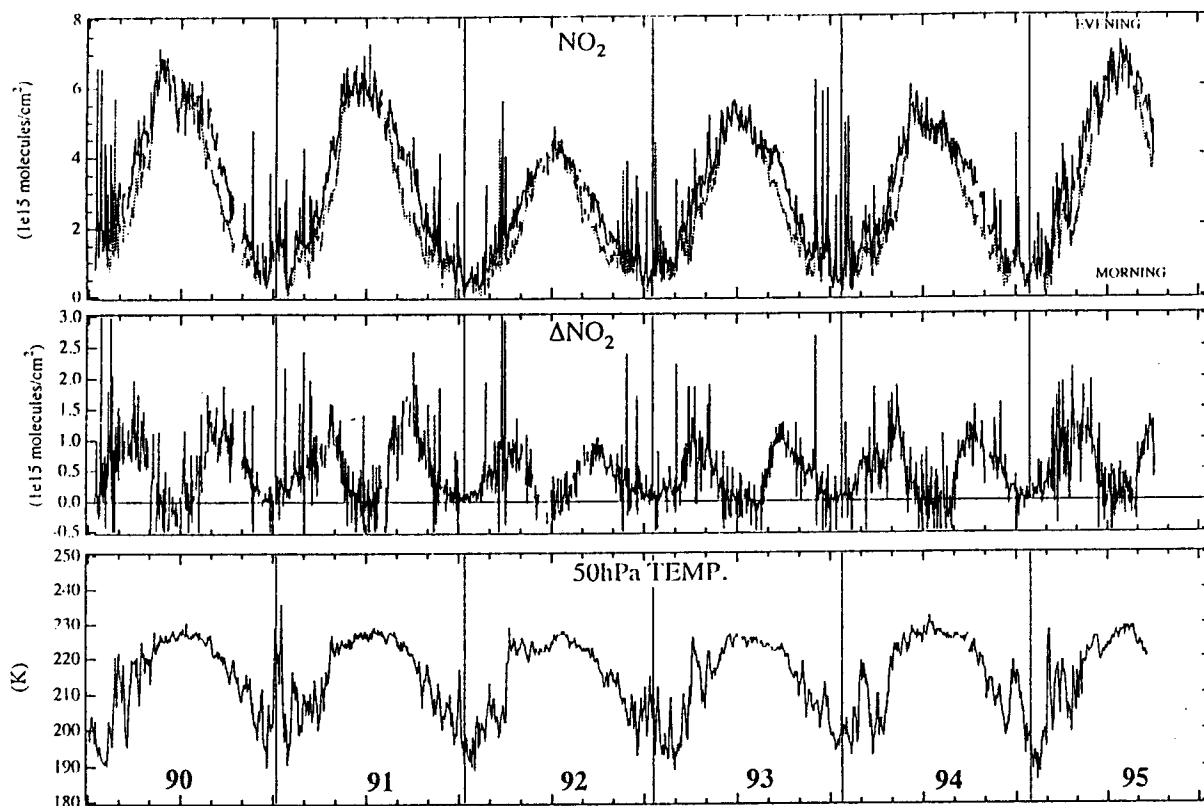


Figure 6. Upper panel: Six year time series of the seasonal variation of NO_2 vertical columns measured twice a day, at sunrise (dotted line) and at sunset (solid line) on the Arctic circle at Sodankyla in Finland. Middle panel: difference between sunset and sunrise columns. Lower panel: temperature as measured from daily radio-soundings from the same station (from Goutail *et al.*, 1994; figure courtesy of F. Goutail).

The upper panel of Figure 6 shows a long time series of the NO_2 column measured twice a day on the Arctic circle. A strong seasonal variation of HO_2 (maximum in summer, minimum in winter), due to the variation of the photolysis of N_2O_5 (absence of sunlight in winter) is immediately apparent. As apparent from the middle panel, the diurnal variation follows a semi-annual cycle, because in summer the formation of N_2O_5 is restricted by the rapid and permanent photolysis of its precursor molecule NO_3 . In 1992 the summer column maximum was reduced by 30% due to the volcanic aerosol emitted by Mount Pinatubo in June 1991. The occasional spikes of NO_2 are due to tropospheric pollution.

Measurement Strategies

Whether attempting to make observations of a new species, fast chemical processes or long-term trends, a measurement strategy needs to be defined. The platform and

technique used and the number of species measured must be carefully chosen depending on the scientific objectives. As mentioned in the introduction, observations of a single species can be of use when making the first observation of a new species or demonstrating the validity of a new observation technique or pointing out a new process. One example is the measurement of profiles of ClO obtained by ground-based microwave observations at McMurdo in Antarctica which showed anomalously high mixing ratios in the lower stratosphere (20 km) during the austral spring of 1986, giving support to the theory of chlorine-catalyzed ozone destruction (de Zafra *et al.*, 1987). Another example is the measurement of the diurnal variation of the NO₂ column abundance and its seasonal variability illustrated in Figure 6, that shed some light on the role of N₂O₅ as an interexchange-point-an of NO_x.

PROCESS STUDIES

When studying chemical processes or long-term trends, a single observation is not sufficient; the simultaneous measurement of a large number of the species involved and, if possible, the total concentration of a family of species (*e.g.*, NO_y or Cl_y) is required. Great effort has been made recently to organize campaigns where as many species as possible are measured simultaneously. One example of campaigns involving the measurement of as many species as possible are those made using the NASA ER-2 aircraft. This aircraft, which has a cruising altitude of 20 km, has been equipped with a large number of in-situ instruments as is shown in Figure 7. The ER-2 platform has been used for several missions, as it can provide high spatial resolution, as well as extensive spatial and temporal coverage and flexibility.

As well as bringing insight into the gas phase chemical processes involved in ozone destruction in the Antarctic, measurements by instruments on board the NASA ER-2 have contributed to the understanding of the role of volcanic aerosol on NO_x chemistry. Comparison of NO_x measurements made by instruments on board the NASA ER-2 before and after the entrainment of Mt. Pinatubo aerosol into the northern hemispheric stratosphere have been used to constrain the role of volcanic aerosol in the chemistry of active nitrogen (Fahey *et al.*, 1993). In Figure 8 the NO_x/NO_y ratios measured in September 1991 and March 1992 are plotted against the measured aerosol surface area. The observations show a reduction of NO_x in the presence of volcanic aerosol, due to the heterogeneous hydrolysis of N₂O₅ on the sulfuric acid droplets. These were the first in-situ measurements to quantify the saturation of the NO_x reduction which had been predicted by theory (see the following lecture by Dr. Guy Brasseur).

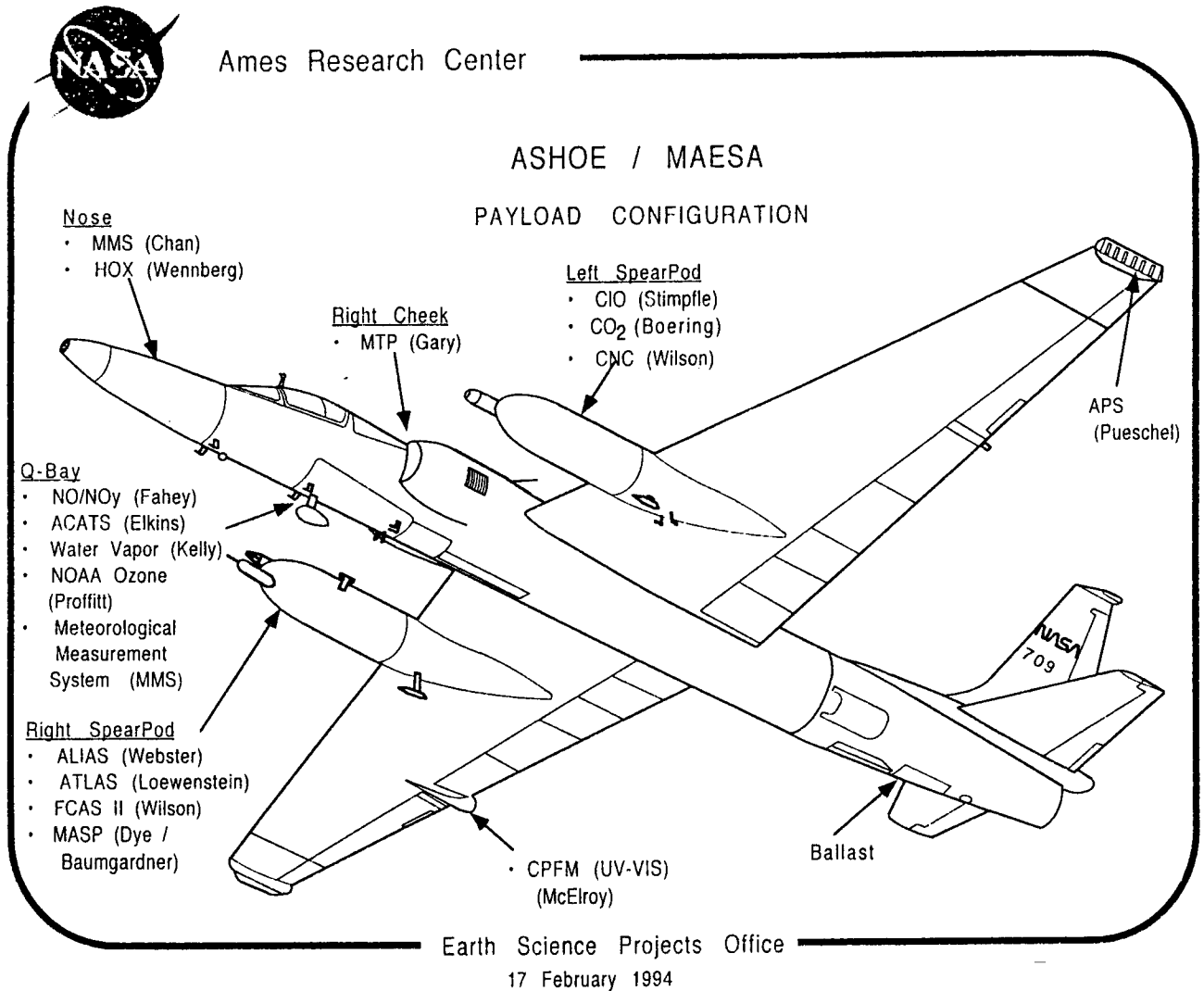


Figure 7. Payload configuration of the NASA ER-2 high altitude research aircraft for the ASHOE/MAESA mission that was carried out in 1994. (For an overview of the experiments see Wofsy *et al.*, 1994; figure courtesy of S. Hipskind).

The estimation of the total reactive nitrogen NO_y and total reactive chlorine Cl_y is extremely useful in quantifying chemical processes, however, their direct measurement is not common. Total reactive NO_y is often estimated from N_2O measurements by exploiting a linear relationship which exists between NO_y and N_2O . This relationship was established by measurements made on board the ER-2 and on balloons where both NO_y and N_2O were measured in-situ (Fahey *et al.*, 1989; Kondo *et al.*, 1994). NO_y is measured by catalytic reduction (by CO) of NO_y compounds to NO on a gold surface at 573K. The NO product is then detected by chemiluminescence after reacting with ozone. N_2O is measured by infrared absorption via tunable diode laser spectroscopy. At constant potential temperature, N_2O decreases with increasing latitude because of

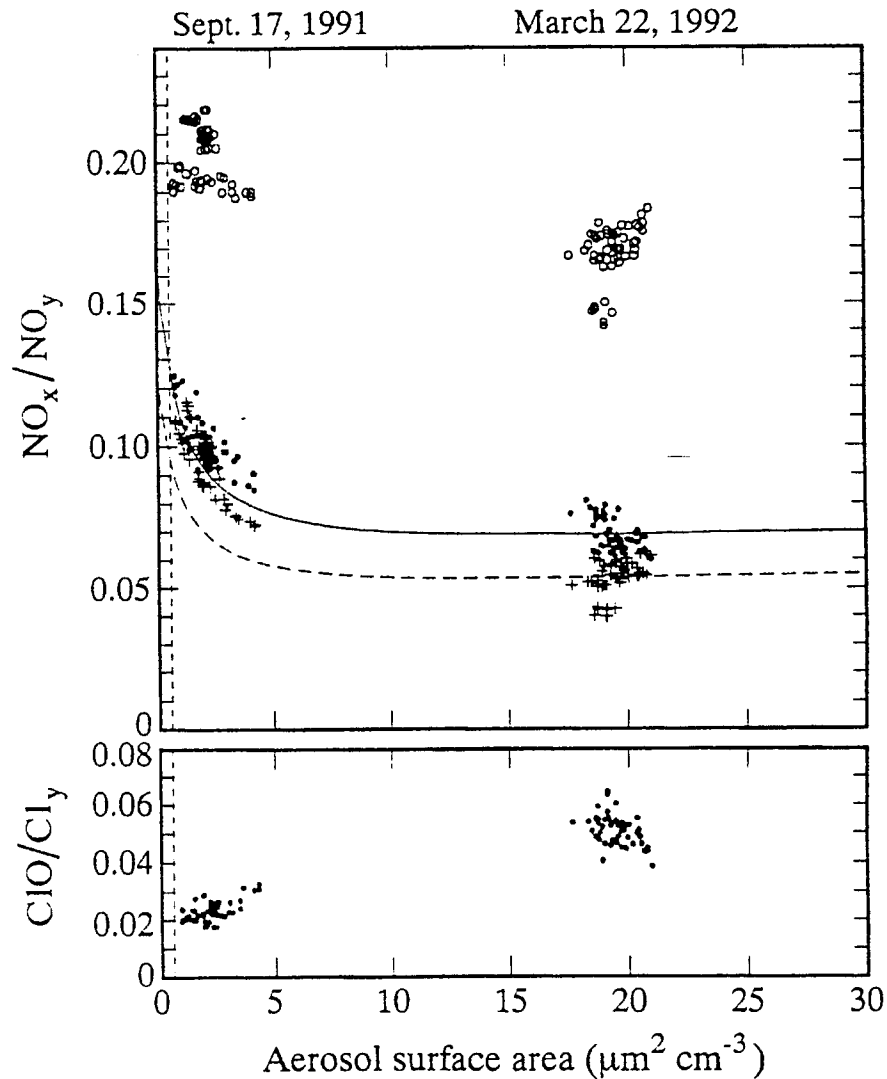


Figure 8. NO_x/NO_y and ClO/Cl_y ratios as measured in-situ on a flight of the NASA ER-2 in mid-latitude air around local noon on 17 September 1991 (left) and 22 March 1992 (right). The data (solid circles) are plotted as a function of aerosol surface area that was simultaneously measured. Also plotted are results from model simulations with gas phase chemistry only (open circles) and heterogeneous chemistry (crosses) included. The dashed line to the left represents the background aerosol surface area ($0.5\mu\text{m}^2\text{cm}^{-3}$) while the curved lines indicate the dependence on the aerosol surface area for the heterogeneous case for September (solid line) and March data (dashed line), respectively (from Fahey *et al.*, 1993; figure courtesy of D. Fahey).

increasing diabatic descent. The correlation of the NO_y data with the N_2O data, as observed on an ER-2 campaign, is shown in Figure 9. If vertical transport of air masses across the isentropes is the only mechanism affecting the N_2O and NO_y mixing ratios, a negative correlation is observed along an isentrope since they decrease and increase with height, respectively. The relationship obtained by fitting the data sets between 140 and

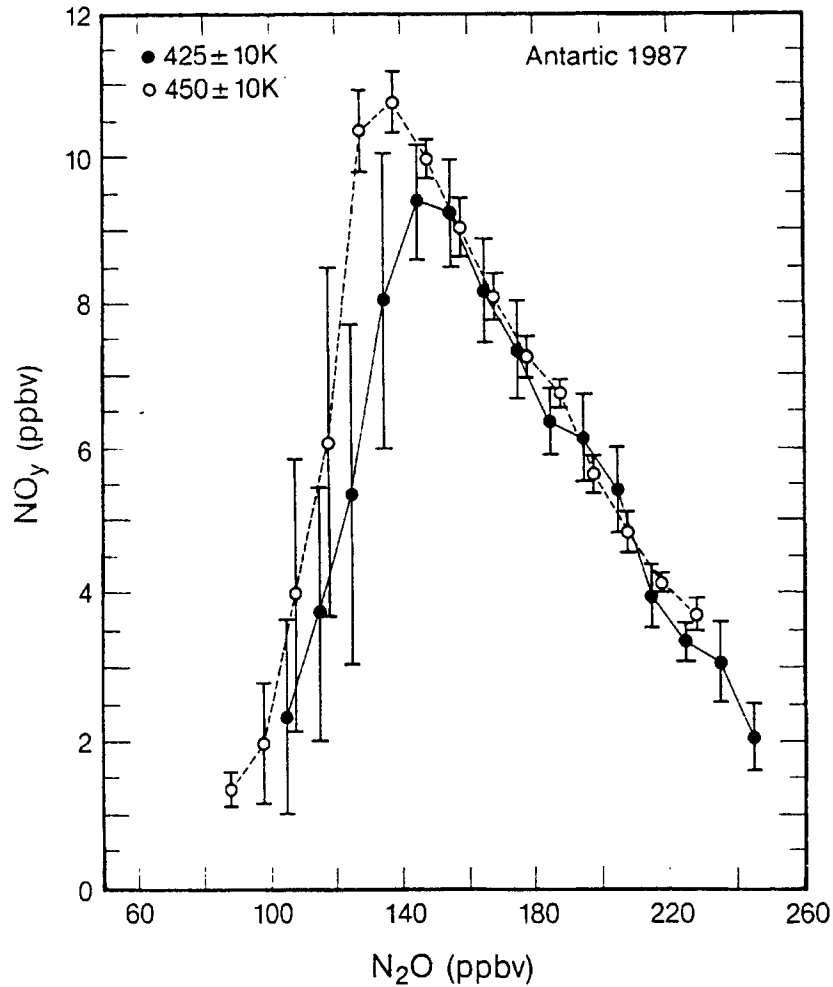


Figure 9. NO_y as a function of N_2O as measured during seven flights of the NASA ER-2 along two nearby isentropic levels into the polar antarctic vortex. Data are averaged over 10 ppbv intervals of N_2O . Only data sampled in regions with an equivalent gas phase mixing ratio of aerosol HNO_3 of smaller 0.3 ppbv were used (from Fahey *et al.*, 1989; figure courtesy of D. Fahey).

220 ppbv of N_2O was used to calculate a surrogate NO_y value, called NO_y^* , from the N_2O measurements. NO_y^* was then used to quantify the denitrification observed inside a chemically perturbed region in the polar vortex where large mixing ratios of ClO were observed. The NO_y values measured were significantly lower than those predicted by the NO_y^* and their comparison showed that 90% of the NO_y had been removed.

An excellent example for the study of the diurnal variation of reactive species from the simultaneous measurement of OH/ HO_2 (LIF technique), NO/ NO_2 (technique described above), and ClO (chemical conversion resonance fluorescence) also performed from the NASA ER-2 is given in Figure 10. Here the sunrise and sunset behavior of the mixing

ratios and the partitioning of five radicals measured in a mid-latitude air mass in May 1993 was compared to model simulations (Salawitch *et al.*, 1994). The variation in NO_x and ClO was explained by taking into account the heterogeneous hydrolysis of N_2O_5 on sulfate aerosol, while the morning spike and slow afternoon decay in HO_x could be satisfactorily reproduced by the model when the heterogeneous hydrolysis of HO_2NO_2 on the aerosol producing HONO was included. HONO can easily be photolyzed to produce HO_x . Although a newer interpretation of the data suggests that the morning spike is actually produced by the photolysis of BrONO_2 rather than from HO_2NO_2 , it becomes obvious that simultaneous measurements of many species are essential to identify processes that are missing in existing models.

Total reactive chlorine, Cl_y , can also be estimated from the measurement of a single long-lived trace gas. Cl_y is simply the difference between the total chlorine loading of the stratosphere (well known because it is due entirely to anthropogenic emissions of CFCs) and the total organic chlorine loading, Cl_{org} ($\approx 2 \times \text{CCl}_2\text{F}_2 + 3 \times \text{CFCl}_3 + 3 \times \text{C}_2\text{Cl}_3\text{F}_3 + 3 \times \text{CH}_3\text{CCl}_3 + \text{CH}_3\text{Cl} + 4 \times \text{CCl}_4$). Since Cl_{org} is correlated with CCl_2F_2 , which is the major chlorine source in the stratosphere, a single measurement of CCl_2F_2 can be used to calculate Cl_y , as is shown in Figure 11. This was done, for example, during the EASOE campaign, when a series of balloon-borne whole air samplers were launched in the Arctic polar vortex from Kiruna, Sweden (Schmidt *et al.*, 1994).

CLIMATOLOGY AND LONG-TERM TRENDS

Measurements for the purpose of climatological studies or to establish long-term trends of chemical species in the Earth's atmosphere face different requirements than measurements for the purpose of process studies. Ideally, the platforms and the instruments deployed for the former purpose should meet the following criteria:

- continuous (year round) operation in latitudinally different zones, often at remote locations,
- capable of long-term field operation,
- capable of high accuracy and long-term stability,
- able to perform measurements with an adequate temporal resolution,
- relatively inexpensive,
- well-defined and documented handling routines and data retrieval algorithms, and
- regularly performed intercomparisons and/or validations.

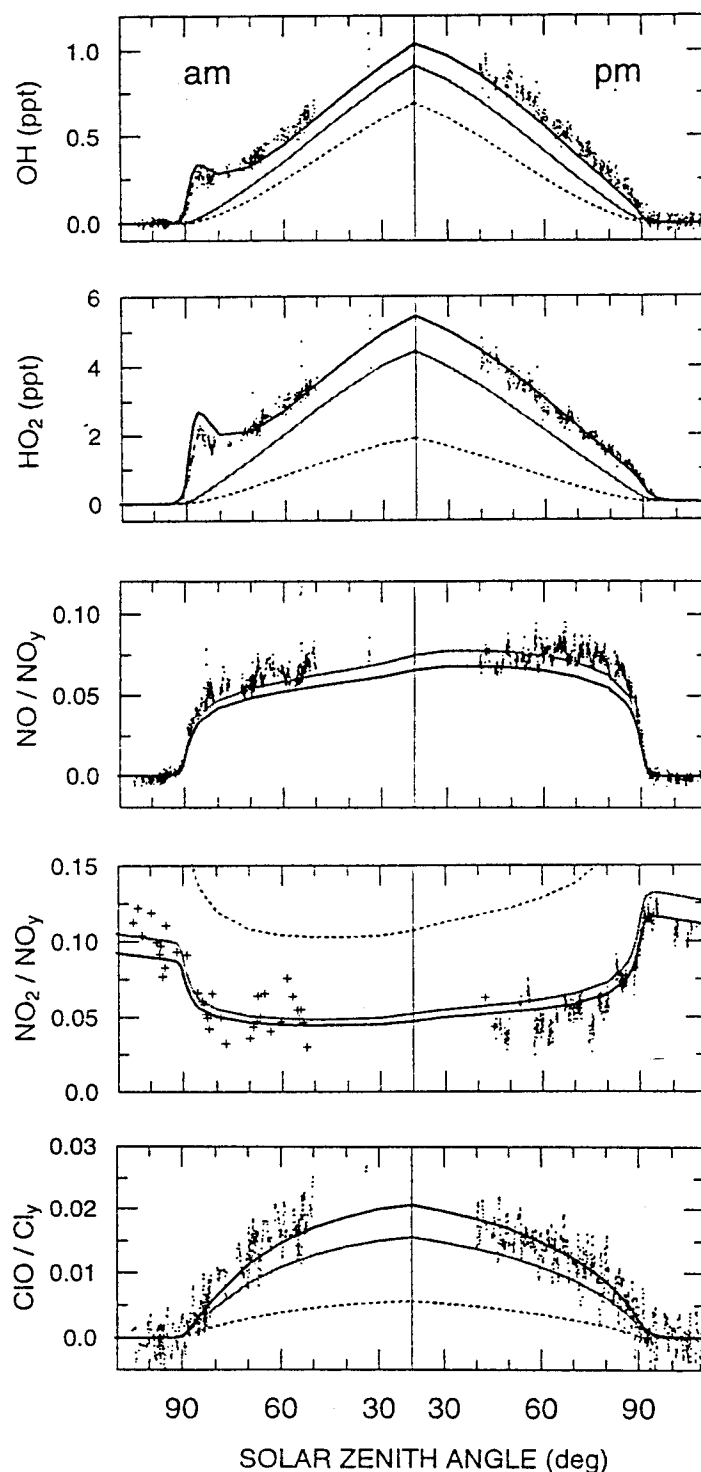


Figure 10. Mixing ratios or partitioning of various radicals as observed by in-situ techniques during two NASA ER-2 flights in May, 1993. Only data within the pressure range 67.0 ± 2.5 hPa and within a N_2O mixing ratio of 250 ± 10 ppbv are plotted. Lines represent model simulations performed with gas phase chemistry only (dotted gray line), heterogeneous chemistry including N_2O_5 hydrolysis (solid gray line), and heterogeneous chemistry also including hydrolysis of HO_2NO_2 to HONO as well as using updated absorption cross sections for HNO_3 (solid black line) (from Salawitch *et al.*, 1994); figure courtesy of R. Salawitch).

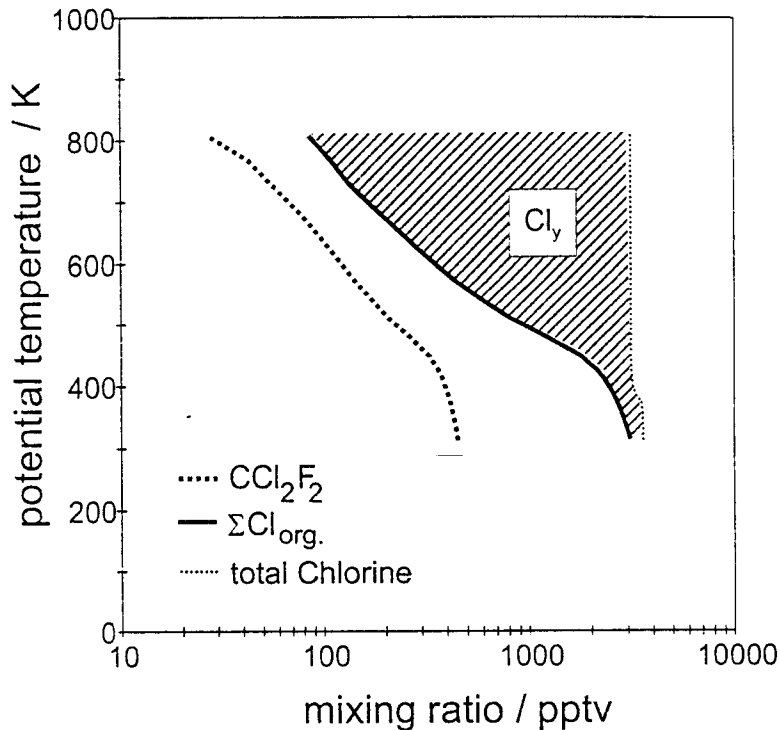


Figure 11. Schematic diagram for the derivation of total reactive chlorine, Cl_y , (hatched area) from the difference of total chlorine and total organic chlorine. The latter is derived from an observed F12 profile (from Schmidt *et al.*, 1994; figure courtesy of U. Schmidt).

These requirements usually limit the measurements to those from ground-based stations, small (weather) balloons, or satellites. However, measurements from other platforms may also be used if they at least partly fulfill the requirements or if no other techniques are available. For building climatologies and studying long-term trends, measurements of single species, whether total column amounts or vertical profiles, are of greatest use if they are conducted over long time periods.

To establish a climatology or a long-term trend, statistical significance must be established either through very accurate single measurements or by an adequate number of less accurate measurements. However, due to financial limitations, the latter is not always possible. The HCl profile measurements performed from balloons in 1983 and 1993 and shown in Figure 5 could be used to derive an overall trend in stratospheric HCl. However, there is no statistical significance to the derived trend because these are too few measurements and a systematic influence by meteorological conditions could not be ruled out.

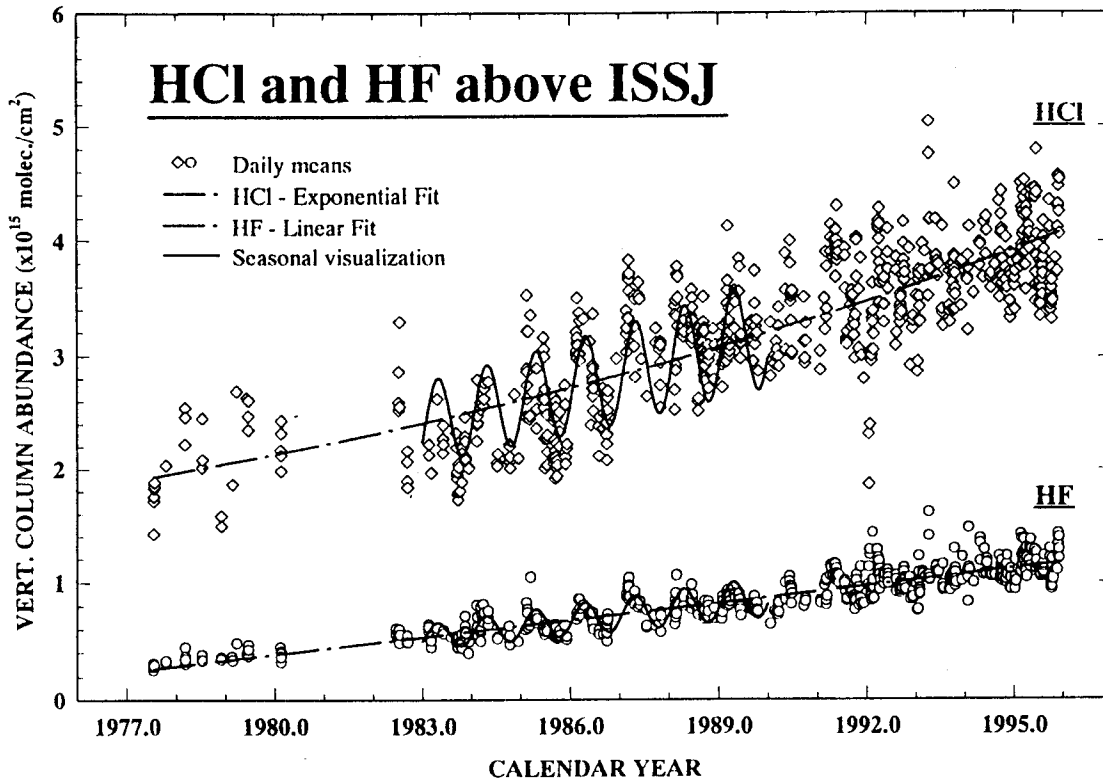


Figure 12. HCl and HF column densities as observed over Jungfraujoch station (Switzerland) by ground based IR spectroscopy from 1977 to 1995 (R. Zander, private communication, 1996; figure courtesy of R. Zander).

Measurements of trace species from ground-based stations can often be done by a variety of techniques and they are usually limited only by tropospheric weather conditions. This means that they can be conducted regularly, and therefore lead to much better continuity in the data sets of ground-based instruments. Figure 12 shows the HCl and HF column densities as measured by ground-based IR spectroscopy above Jungfraujoch station in Switzerland from 1977 to 1992 (R. Zander, private communication, 1996). The data were recorded by grating spectrometers until mid-1989, at which time a FTIR spectrometer was installed at the station. An exponential and linear fit was performed to reproduce the obvious trends in the column densities of HCl and HF, respectively. The main stratospheric sources of both of these trace gases are anthropogenic CFCs. This highly resolved time series of measurements allows a clear identification of the long-term trend, and even shows a smaller periodic variation of the column density with a maximum in spring that is probably due to the seasonal variation in tropopause height and stratospheric OH concentration (OH reacts with HCl reforming active chlorine).

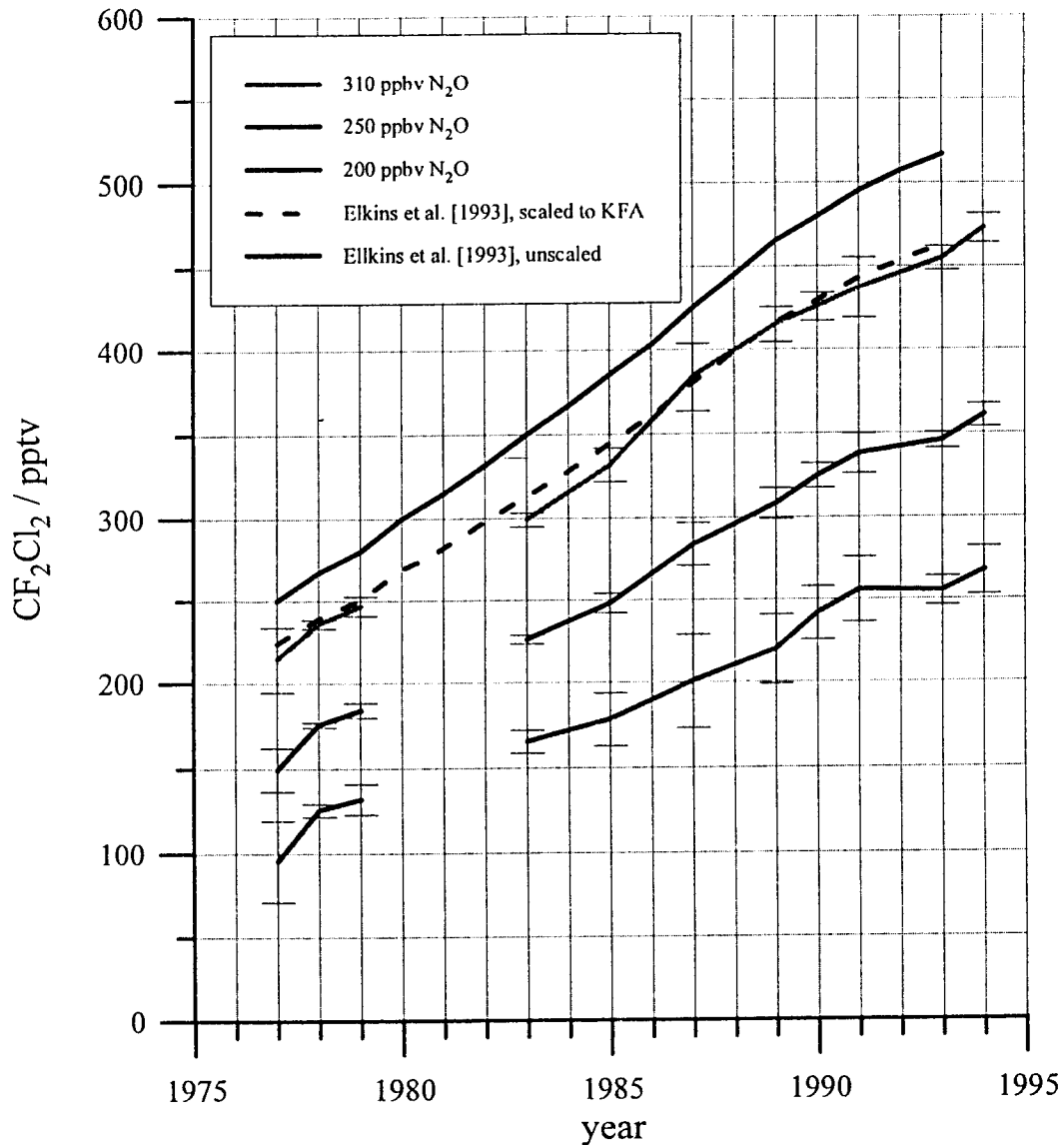


Figure 13. Stratospheric trend of CCl_2F_2 for different mixing ratios of N_2O as measured by in-situ cryo and grab sampling followed by laboratory GC analysis during the years from 1977. Plotted are only mid-latitude data that have been corrected for a tropospheric increase of N_2O of 0.2%/year. For comparison the results of Elkins *et al.* (1993) for the highest level N_2O level are plotted also (figure courtesy of A. Engel).

Measurements of CFCs are very important to check on estimates of future CFC mixing ratios in the stratosphere and to predict their effect on the ozone layer in the polar as well as mid-latitude regions. Figure 13 shows the trend of CCl_2F_2 mixing ratios on different levels of the N_2O mixing ratio as obtained from measurements by in-situ air sampling and gas chromatography (GC) analysis performed by the the group at KFA Jülich (Germany) since 1977. An increase in the mixing ratio of CCl_2F_2 on all three levels is obvious. For comparison, data measured by Elkins *et al.* (1993) from

NOAA at Boulder (US) are plotted for the highest N₂O level. The offset in the two data sets can be explained by the different standards used in the two laboratories. If the measurements by Elkins *et al.* are scaled with the factor found from a laboratory intercomparison, good agreement is achieved as is also obvious from the plot.

THE NETWORK FOR THE DETECTION OF STRATOSPHERIC CHANGE (NDSC)

Much effort has been expended to ensure that global networks monitor the state of the atmosphere continuously on a long-term basis and obtain data of as high a quality as possible. In addition, the availability, continuity, and compatibility of the obtained data sets has to be ensured. Global networks have been established for such purposes as monitoring the incoming solar UV-B radiation and measuring the global ozone column (the Dobson network). Another example of such a network is the Network for the Detection of Stratospheric Change (NDSC).

The planning for NDSC started in 1986, with the objective being the installation of a network of high-quality remote-sounding stations for observing and interpreting the physical and chemical state of the stratosphere. Key species targeted for observation are ozone and ozone-related compounds. The network began operation in January 1991.

The goals of NDSC are:

- to make observations which will allow changes in the physical and chemical state of the stratosphere to be detected as early as possible and which will help to understand the causes of these changes.
- to provide independent calibration of satellite sensors, and
- to obtain data to test and improve multi-dimensional stratospheric chemical and dynamical models.

Table 2 shows a primary set of techniques, able to measure some of the most important stratospheric trace species and physical parameters, that was selected on the basis of being remote sensors which can be continuously operated for long periods at remote locations. Five primary stations, some of which are composite sites, have been selected as shown in Table 3, where the species currently observed within NDSC at the different stations are also listed. Basic requirements for the primary stations were a location at a high enough elevation to minimize tropospheric water and aerosol columns, the ability to operate a certain set of instruments simultaneously, and a global distribution of the geographic locations of the stations. Eventually, the primary stations should be equipped with most of the experiments listed in Table 2, depending on geographical and

Table 2: Primary Techniques for NDSC Stations

<i>Species^a</i>	<i>Technique</i>	<i>Observed Quantity</i>	<i>Alt. Range</i>
Ozone (O ₃)	LIDAR	Vertical Profile	0-45 km ^b
Temperature	LIDAR	Vertical Profile	30-80 km
Aerosol	LIDAR	Vertical Profile ^c	0-30 km
Ozone (O ₃)	Microwave	Vertical Profile	20-70 km
Water Vapor (H ₂ O)	Microwave	Vertical Profile	20-80 km
ClO	Microwave	Vertical Profile	25-45 km ^d
N ₂ O	Microwave and FTIR	Vertical Profile	20-50 km
O ₃ , NO ₂ , OClO, BrO	UV/VIS Spectroscopy	Column Abundance	
O ₃ , HCl, NO, NO ₂ , ClONO ₂ , CH ₄ , HNO ₃	FTIR Spectroscopy	Column Abundance	

^a or physical parameter ^b 0-20 km for YAG, 15-45 km for Excimer-Lidar
^c of aerosol optical density ^d altitude range depending on latitude

Table 3: Primary Stations of NDSC and Operational Measurements

<i>Station Name</i>	<i>Species (Technique)</i>	<i>Composite Sites</i>	<i>Location</i>
Arctic Station	O ₃ (LIDAR) aerosol (LIDAR)	Ny-Ålesund	78.5°N, 11.9°E
		Thule	76.0°N, 69.0°W
		Eureka	80.0°N, 86.4°W
		Sondre Stromfjord	68.7°N, 52.7°W
Alpine Station	O ₃ , T (LIDAR) aerosol (LIDAR)	Observatoire de Haute Provence	43.9°N, 5.7°E
		Plateau de Bure	44.4°N, 5.6°E
		Jungfraujoeh	47.0°N, 8.0°E
		Observatoire de Bordeaux	44.4°N, 1.0°W
Mauna Loa	O ₃ , T (LIDAR) ClO (MW)	Mauna Loa	19.5°N, 155.4°W
		Mauna Kea	19.5°N, 155.4°W
Lauder	O ₃ , T (LIDAR) H ₂ O, O ₃ (MW)	CH ₄ , N ₂ O, HNO ₃ ClONO ₂ , HCl (FTIR)	
			45.0°S, 169.7°E
Antarctic Station	NO ₂ , O ₃ (UV-VIS) aerosol (LIDAR)	Dome Concorde (future site)	74.5°S, 124.0°E
		Arrival Heights	78.0°S, 166.0°E
		Dumont D'Urville	67.0°S, 140.0°E

meteorological characteristics and complementary existing programs. If a co-location of instruments is not possible, composite sites may be established with subsets of the instruments at different locations. In addition, 20 complementary stations have been selected to fill in the geographic gaps of the primary sites.

To ensure the quality of all data, every instrument proposed to NDSC is reviewed by an Instrument Group and has to be approved by the Steering Committee after going through a validation procedure. The validity of the data supplied by an instrument must be continuously monitored by intercomparison measurements. All data and documentation from the instruments, all data handling routines, as well as the validation and calibration history of each instrument must be archived in the NDSC data base at the US National Meteorological Service (NMC) in conformation with a data protocol. All changes in instruments or data processing routines also have to be documented and archived in the data base. To ensure continuity and compatibility of the data base for every single measurement, changes made in the data processing routines have to be applied to the entire data set in the archive. New generic instruments can only be approved for the NDSC after the validity of the technique has been proven and correlative measurements with the established instruments have been performed.

Outstanding Issues

One of the most challenging problems in stratospheric research is the investigation of the causes of ozone depletion in the polar regions and mid-latitudes. To understand the global causes and predict future effects, the important and relevant processes must be investigated. Although great progress has been made, important aspects still need to be investigated. Figure 14 shows an obvious example. The distribution of simultaneously measured ClO and HCl mixing ratios deviates drastically from the one predicted by current models, even when the current understanding of heterogeneous chemistry is incorporated (Webster *et al.*, 1993). Reasons for this discrepancy may be missing chemistry in the model, incorrect rate constants for the modelled reactions, an unresolved instrumental problem, or some combination of these problems. Clearly, more research, and especially new measurement techniques, are required to supply data on missing links in the chemical reactions. The measurement techniques most urgently needed to resolve the open questions of stratospheric ozone depletion are as follows:

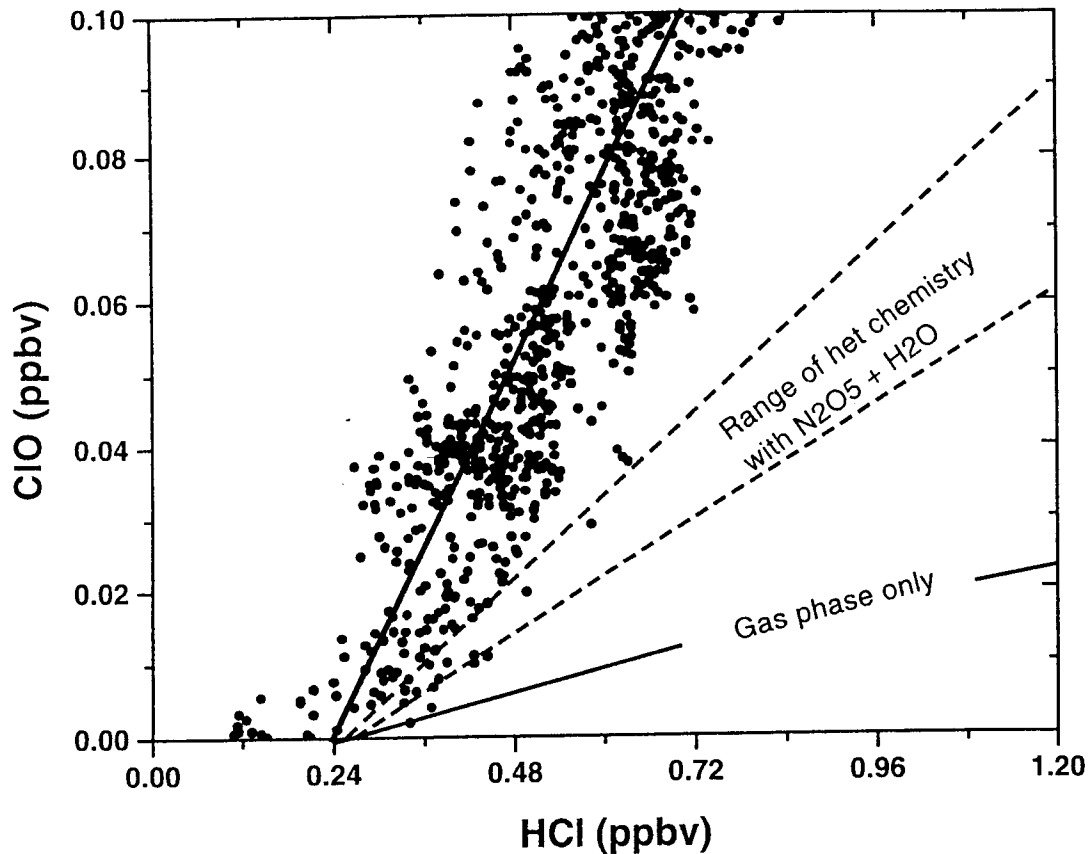


Figure 14. Measured ClO vs. HCl mixing ratios as observed from the ER-2 aircraft in 1991 and 1992 in air masses in the northern hemisphere outside the polar vortex. Data included are limited to ClO mixing ratios ≤ 100 pptv and solar zenith angles $\leq 80^\circ$. Ratios as modelled for gas phase chemistry only and with heterogeneous chemistry included are plotted also Webster *et al.*, (1993) (figure courtesy of C. Webster).

Measurement of aerosol composition. The formation and freezing behavior of stratospheric aerosol particles controlling the heterogeneous chemistry that governs polar ozone loss could be characterized if the composition of the aerosol was known.

In-situ measurement of ClONO₂. The partitioning of chlorine reservoir species which is extremely important for the formation of reactive chlorine species (mainly ClO) could be clarified by this measurement.

In-situ measurement of N₂O₅. This measurement would shed light on a major nitrogen reservoir and could be an alternative to the ClONO₂ measurement because it would simultaneously determine the NO₂ abundance that governs ClONO₂ formation from ClO.

Measurements of more Br species. Br species are contributing to polar ozone destruction and may also play a key role in mid-latitude ozone depletion. Aside from BrO and HBr, no inorganic Br species can currently be measured in the atmosphere, leaving the partitioning of inorganic Br species more or less open to speculation.

Measurements of all I species. I species have the potential to significantly contribute to ozone depletion if they are transported to the stratosphere. Only very limited measurements of I species in the stratosphere setting upper limits to their abundances have been reported up to now.

Additional measurement techniques would also be valuable if they could detect species which have not yet been taken into account but which have a significant effect on stratospheric chemistry, or if they improve currently available techniques to such an extent that new processes involved in stratospheric chemistry can be identified. Also, any new technique supplying a marked improvement in measurement time, accuracy, reliability, or instrument weight will help to provide more or better information on stratospheric composition or dynamics and can contribute to the understanding of the unsolved problems of stratospheric research.

Acknowledgment

We gratefully acknowledge the efforts of all the people who made their figures available to exemplify the various aspects of observational techniques discussed in this chapter. We would like to particularly thank Andreas Engel for proofreading this chapter and Rudolphe Zander for making available several of his unpublished results. Ulrich Schmidt is grateful for travel funds supplied by the DG VII of the European Commission, Brussels, Belgium.

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