Correlated millimeter wave measurements of ClO, N₂O, and HNO₃ from McMurdo, Antarctica, during polar spring 1994

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Abstract. Ground-based observations of stratospheric ClO, N_2O, and HNO_3 were made almost continuously at McMurdo Station, Antarctica (77.9°S, 166.6°E), during the austral spring of 1994, using two separate microwave receivers. Vertical profiles of these trace gases have been retrieved from the pressure broadened emission spectra between September 4 and October 8, 1994. In early September, McMurdo was located well inside the polar vortex, and high mixing ratios of chlorine monoxide (up to 1.8 ppbv) were measured in the lower stratosphere. Because of vortex movement, later measurements were taken in edge regions, where ClO was found to be quite variable. This vortex movement also provided an opportunity to study relative changes between all three species. Almost no HNO_3 was seen below 20 km during the measurement period, indicating that stratospheric air had been efficiently denitrified by polar stratospheric cloud formation. A significant increase of the nitric acid column was observed only around September 20, when McMurdo was closer to the outer edge of the vortex. At the beginning of the measurements, the vertical profiles of the inert tracer N_2O had already descended so far that very little N_2O was present above 20 km. During the observation period, the N_2O distribution did not show strong changes except for a slight downward trend which increased with altitude. This indicates, as noted in previous years, that subsidence continued in the stratosphere over McMurdo Station until at least early October, when measurements were stopped. The temporal correlations between the behavior of ClO, N_2O, HNO_3, altitude, and temperature at the 50-hPa level, and of ozone measured by local ozonesondes show that changes in the atmospheric composition were partly due to dynamic effects. A backward trajectory analysis was performed to interpret the ClO data in an attempt to clarify some irregularities.

1. Introduction

Since the first discovery of the seasonal ozone hole over Antarctica [*Farman et al.*, 1985], extensive trace gas measurements have been made which have clearly identified the essential role of chlorine chemistry in the Antarctic springtime depletion of ozone [*Solomon*, 1990]. High concentrations of chlorine monoxide were first measured by ground-based remote sensing techniques in 1986 and 1987 from McMurdo Station (77.9°S, 166.6°E) [*de Zafra et al.*, 1987; *Solomon et al.*, 1987; *de Zafra et al.*, 1989], and by in situ aircraft measurements in 1987 [*Anderson et al.*, 1989]. Satellite measurements of ClO [*Waters et al.*, 1993] have been carried out by the Microwave Limb Sounder (MLS) on board the Upper Atmosphere Research Satellite (UARS) launched in September 1991. Because of satellite geometry and instrument limitations, these measurements are restricted to latitudes ≤ 80° South in observing the Antarctic vortex and alternate between hemispheres at intervals of ~36 days. UARS observed the deep southern hemisphere only until September 10 in 1994, resuming

on October 17, which provided a small overlap in early September with the measurements presented in this work. Additionally, the horizontal resolution of the MLS is quite coarse (~2° x 2°), and therefore a large smoothing is applied to regions of strong gradients (e.g., the vortex edge). In agreement with our measurements, however, the MLS data show enhanced ClO values during the 1994 overlap period, compared to measurements taken earlier in the season.

The long-term evolution of ClO during a major ozone hole event was observed from our chlorine monoxide measurements taken in the spring of 1993 at McMurdo Station, which was located well inside the polar vortex during that time [*de Zafra et al.*, 1995]. In that series of observations, measurements of the diurnal cycle of ClO with 1- to 2-hour temporal resolution were obtained and compared with predictions of a photochemical model [*Shindell and de Zafra*, 1996a]. For the set of measurements discussed here, during spring 1994, the use of two separate millimeter wave receivers enabled us to measure for the first time ClO, HNO_3, and N_2O nearly simultaneously within the same air over a region of Antarctica.

Nitrous oxide (N_2O), which only has tropospheric sources, has a relatively long lifetime in the stratosphere (1 year at 33 km altitude and significantly longer at lower altitudes and during polar winter). It has been used as a tracer in a number of studies of atmospheric transport processes, especially subsidence inside the polar vortex [*Wofsy et al.*, 1994, *Crewell et al.*, 1995, and references therein]. Nitric acid (HNO_3) plays an important role in ozone destruction by condensing from the gaseous phase under very cold (T≤195 K) conditions in the lower stratosphere to participate in the formation of polar stratospheric clouds (PSC). On the basis of measurements in the Antarctic early winter [*Van Allen et al.*, 1995; *de Zafra et al.*, 1996] the HNO_3

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Table 1. Millimeter-wave Receiver Specifications

	SIS Receiver	Schottky Receiver
Spectral lines	ClO: 278.6 GHz	HNO₃: 269.2 GHz
		N₂O: 276.3 GHz
Bandwidth, MHz	600	512
Resolution,MHz	1.18	1
Receiver type	single sideband	double sideband
Noise temp.,K	≤350	~700
Physical temp.,K	4.5	~20

column shows a rapid decrease, by a factor of 5 to 10 in column density, beginning as soon as the temperature drops below ~195 K. The recovery when the temperature rises again at the end of winter is very slow, indicating that a significant amount of HNO₃ has gravitationally settled with the particles of stratospheric clouds.

In this paper ground-based millimeter-wave measurements will be used to describe the temporal development of ClO, HNO₃, and N₂O near the edge of the vortex during the time of ozone hole formation in 1994. The main emphasis will be put on the correlation between these trace gases and the local meteorological parameters as well as with ozonesonde data taken by the University of Wyoming.

2. Measurement Technique and Data Retrieval

During the field measurements, two separate millimeter-wave receivers were employed to measure spectral lines in the 260-280 GHz range: (1) a high-sensitivity SIS (superconductor-insulator-superconductor) receiver [*de Zafra et al.*, 1994] together with an acousto-optical spectrometer for continuous measurements of ClO, and (2) a conventional Schottky diode receiver [*Parrish et al.*, 1988] with a filter bank spectrometer for the HNO₃ and N₂O measurements. Instrument specifications are listed in Table 1.

The stronger lines of HNO₃ and N₂O were each measured for about 4 hours a day and integrated to obtain daily averages. A background correction for the emission of ozone and sinusoidal standing wave features was applied using a multiple fit program. The amplitude of the sine wave fitted to the spectra was typically a factor of 10 lower than the HNO₃ or N₂O line

amplitude. Chlorine monoxide spectra were recorded continuously whenever weather conditions allowed. The need for continuous measurement arises not only from the long integration times required for this weak line amplitude (< 0.2 K), but also from the strong diurnal cycle for ClO [*Shindell and de Zafra*, 1996a]. In the lower stratosphere (< 30 km), ClO almost vanishes during the night. This allows us to remove nearby ozone lines and weaker baseline artifacts in the spectra by subtracting predawn spectra from the midday spectra without losing significant information on the midday lower stratospheric ClO, which is most relevant to ozone depletion chemistry. Here we define midday as the time between 2 hours after sunrise and 2 hours before sunset, when the time averaged ClO is at least 90 % of its noon value [*Shindell and de Zafra*, 1996a].

Sample spectra after the background corrections, together with theoretical spectra (offset by -0.05 K), are shown in Figure 1 for all measured molecules. Here the spectral intensity is expressed in degrees Kelvin, using the linear Rayleigh-Jeans approximation to relate emission intensity to an equivalent blackbody temperature at millimeter wavelengths. HNO₃ has a large number of closely spaced emission lines in the millimeter-wave region. The spectrum shown in Figure 1 includes eight major lines (plus several very weak lines) which contribute to the emission in both receiver sidebands . This explains the asymmetric line shape, while the spectra of N₂O and ClO contain only one symmetric emission line.

The vertical mixing ratio profiles of ClO and N₂O were retrieved from the pressure-broadened line shapes using the Chahine-Twomey inversion technique. In the retrieval process, combinations of different vertical starting profiles and sets of weighting functions were used to minimize any bias induced by these. The deconvolution process is described in more detail by *de Zafra et al.* [1995a] for ClO and by *Crewell et al.* [1995] for N₂O. Owing to the presence of a number of lines, vertical HNO₃ profiles can not be retrieved by using the Chahine-Twomey inversion technique. Instead, a constrained matrix method was used [*Twomey*, 1977]. An iterative procedure was incorporated into this method to obtain the solution with the best possible fit to the spectral data.

Vertical profiles retrieved from the spectra shown in Figure 1 are presented in Figure 2. They are the basis for the theoretical spectra shown in Figure 1. An error analysis for N₂O and ClO deconvolutions [*Emmons and de Zafra*, 1994] including
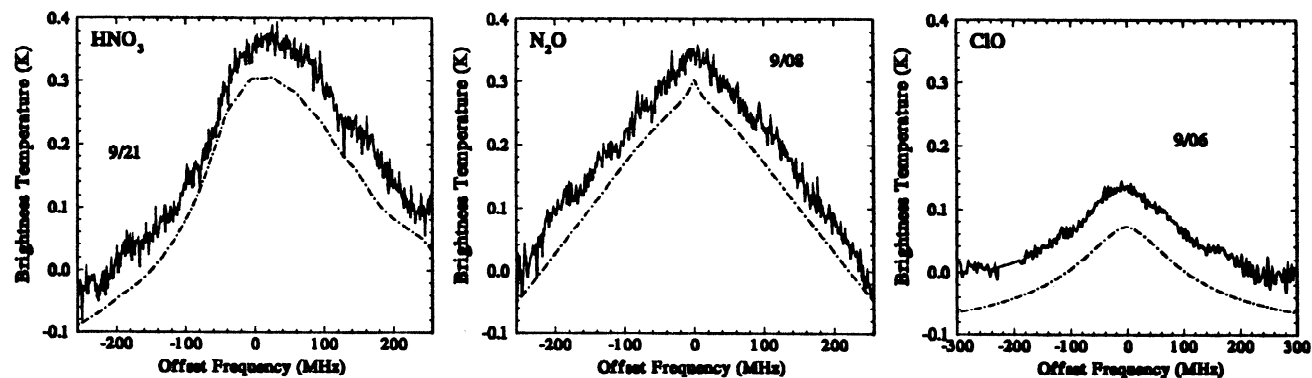

Figure 1. Observed emission spectra of HNO₃, N₂O, and ClO measured in September 1994 at McMurdo station (solid lines). Intensity, as equivalent blackbody radiation temperature in degrees Kelvin, is plotted versus relative frequency in megahertz. All spectra have been arbitrarily normalized to zero offset at the edges of the spectral window. Theoretical spectra derived from the altitude profiles shown in Figure 2 are offset by −0.05 K (dash-dotted lines).
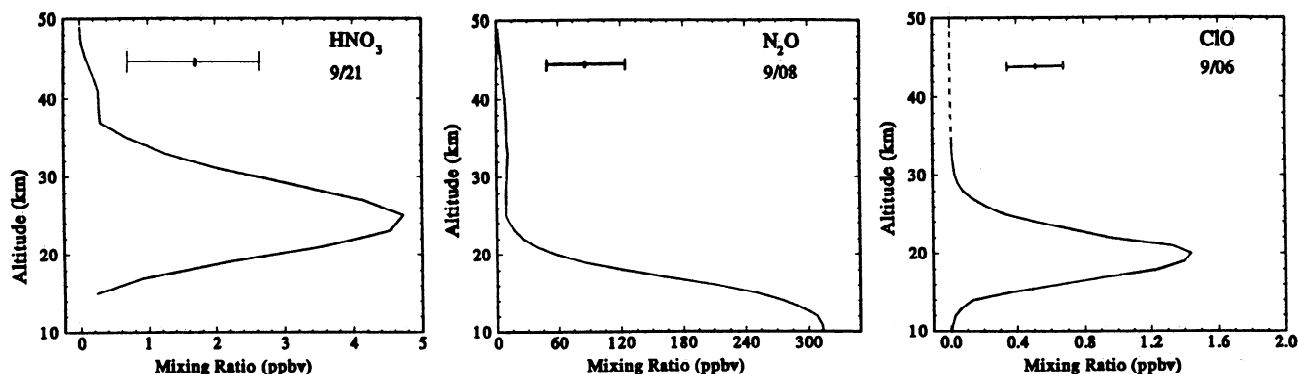
Figure 2. Retrieved vertical profiles for HNO_3, N_2O, and ClO derived from the spectra shown in Figure 1. The error bars shown in each frame represent the maximum estimated error over the covered altitude range.

uncertainties from spectral noise and calibration parameters, as well as temperature, pressure, and pressure-broadening coefficient uncertainties, yields an overall uncertainty in the region around 20 km altitude of about ±20% for N_2O and of about ±13% for ClO. The difference in the errors is due to the different shape of the vertical profiles for these two molecules. The overall uncertainty in the HNO_3 profiles is estimated to be about 1 ppbv in the regions from 16 and 20 km and 35 to 50 km, reducing to 0.8 ppbv between 20 and 35 km. The bars in each frame represent the maximum estimated error.

3. Observations

Figure 3 presents contour plots of ClO, HNO_3, and N_2O for the observation period from September 4 (day 247) until October 8 (day 281), 1994, along with temperatures provided by the National Meteorological Center (NMC). For self-consistency, NMC temperatures were used throughout, although local ozonesonde and meteorological balloon temperature data

were available. The reason for that is the infrequency of the ozonesonde launches (typically 2-3 days) and the low bursting altitude (~200 hPa) of the standard meteorological balloons. Unfortunately, a comparison shows that the NMC temperatures at some altitudes sometimes differ by up to 5 K from local balloon measurements, which may in part be due to the coarse spatial gridding of the former. For our purposes, which include back trajectory analysis, we want to work with the same data set for all applications, rather than with two different temperature fields.

Figure 4 presents a contour plot of Ertel's potential vorticity (PV) versus time on the 475 K potential temperature level along the 166.7°E meridian (McMurdo Station), provided by NASA Goddard Space Flight Center (GSFC). The solid line indicates 78°S, the latitude of McMurdo. The intrusion of air with lower absolute PV (|PV|) over McMurdo can be seen around day 262, and again after ~day 278, marking a shift of the vortex away from McMurdo toward eastern Antarctica.
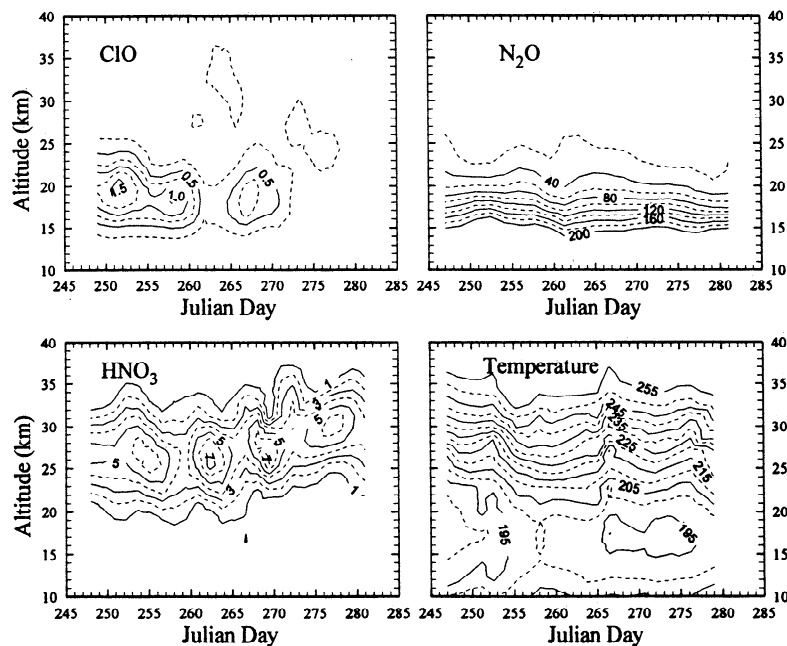

Figure 3. Vertical distributions of ClO, N_2O, HNO_3, and NMC temperature during the observation period from September 4 (day 247) to October 8 (day 281) over McMurdo. Numbers on the ClO, N_2O and HNO_3 plots signify mixing ratio in parts per billion by volume. Temperature data are in degrees Kelvin. In all plots, labels are attached to solid line contours.
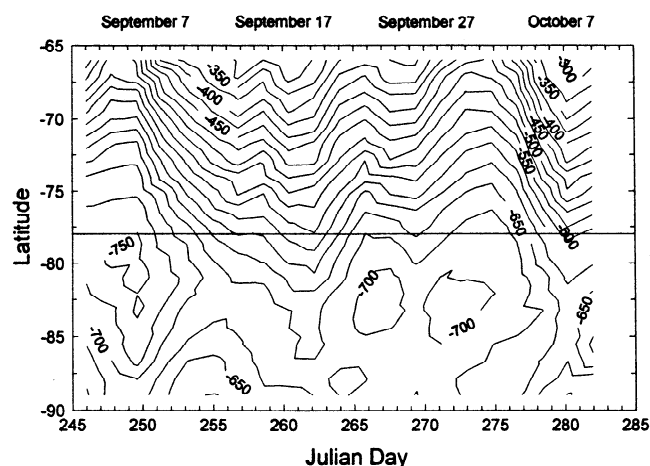
Figure 4. Ertel's potential vorticity (PV) in 10^{-7} (K m²)/(kg s) on the 475 K potential temperature level along the McMurdo station meridian (166.7°E) as a function of latitude and time. The solid line marks the latitude of McMurdo Station.

ClO

The ClO contour map in Figure 3 shows a layer of enhanced ClO in the lower stratosphere with a peak value initially at about 19 km in early September (day 249), when our observations started, lasting until mid-September (day 260), and exhibiting a descent rate of ~1 km in agreement with the descent measured in 1993. A second period of enhanced ClO occurred in late September (days 265 to 268). The peak value of about 1.8 ppbv reaced within the earlier maximum can not be seen due to the contour spacing. This peak value agrees well with peak values observed in 1993 [*de Zafra et al.*, 1995], when McMurdo was located well inside the polar vortex. The ClO maximum in the upper stratosphere is not evident due to the day-minus-night subtraction process described earlier. This upper layer exhibits a relatively small diurnal change in the Antarctic early spring and much of it is subtracted away. We believe that the intermittent 0.25 ppbv contours at higher altitudes are not real, but arise from the day-minus-night subtraction process because of the variable quality and duration of the nighttime measurements, and the inherently poorer signal to noise ratio for upper stratospheric ClO emission. In agreement with our enhanced ClO values, the MLS observed large ClO mixing ratios close to McMurdo for the overlap period from September 4 to 10 (J. Waters, NASA-JPL, personal communication, 1995).

HNO₃

Until September 24 (day 267), little HNO₃ was seen below 20 km, similar to vertical profiles obtained over the South Pole in 1993 [*de Zafra et al.*, 1996], indicating that lower stratospheric air had been denitrified by polar stratospheric clouds (PSCs), in agreement with the high ClO abundance at 19 km for this period. After September 24, HNO₃ completely disappeared between 20 km and our lower limit of observability at ~16 km. In early September (day 247) the maximum HNO₃ concentration, about 5.6 ppbv, was found at about 27 km. Later the altitude of the maximum layer rose to ~30 km. The apparent differences in the peak amounts (~1 ppbv) over the observation period are within the statistical uncertainties of the data. The evident upward movement of the peak mixing ratio after day 272 might be attributed to intrusion of extra-vortex air containing

more HNO₃ at higher altitudes. Back trajectories and PV maps indeed indicate that the vortex over McMurdo shifted poleward more at higher altitudes (~30 km) than at lower altitudes (~19 km) in late September to early October, although a study by *Roche et al.* [1994] would seem to indicate that exterior vortex air does not necessarily contain more HNO₃ than air from inside the vortex at this altitude, in contrast to a strong gradient exhibited at lower altitudes.

N₂O

The contour map presented in Figure 3 shows that compared to pre-winter values [*Crewell et al.*, 1995], a strong descent had occurred prior to the time our measurements started and there was scarcely any N₂O left above 20 km. However, according to a linear fit applied to surfaces of constant mixing ratio, a further descent of about 1 to 2 km, depending on altitude, took place during the observation period. This would be consistent with other data for the vortex core [*Crewell et al.*, 1995] and model predictions [*Manney et al.*, 1994], and also with the downward trend seen in the altitude of peak ClO in both 1993 and 1994. We caution against attempting to derive a quantitative descent rate during the whole observation period from these data because movement of the vortex edge near McMurdo complicates the issue.

4. Interspecies Correlations

Column densities above 16 km have been calculated for the three measured trace gases on all days of measurements. The altitude limitation arises from the limited bandwidth of our receivers, which can not detect the strongly pressure-broadened emission lines below ~16 km altitude (e.g., a typical pressure broadening coefficient of 2.5 MHz/hPa results in a half width at half maximum of 250 MHz at about 15 km). For ClO the column density is based on day-minus-night spectra and therefore comes essentially from the lower stratospheric layer. Inclusion of the upper layer would contribute very little to the total column density, however. In Figure 5 the column densities of the observed molecules, as well as the results of ozonesonde measurements by the University of Wyoming (T. Deshler, personal communication, 1994) and NMC data on the 50-hPa level are illustrated. A comparison with Figure 4 shows that the altitude of this pressure surface, which is close to the 475 K surface, provides a good measure of position relative to the vortex edge, while the temperature indicates the possibility of PSC formation. Every dot marks a measuring event; the gaps in between are due to bad weather or occasional instrumental problems.

Temperature and Altitude of the 50-hPa Layer

In early September, temperatures (T_{50hPa}) were very low (< 190 K), as was the 50-hPa surface height (A_{50hPa}) indicating that McMurdo was located well inside the polar vortex. Sunrise had already occurred over McMurdo, giving approximately 10 hours of sunlight on September 5 (day 247) at 18 km altitude. Both A_{50hPa} and T_{50hPa} increased until day 263 and then decreased to a second minimum before the vortex moved away from McMurdo in early October.

Ozone

The ozone volume mixing ratio at 19 km decreased almost linearly to 0.2 ppmv over the observation period, due to catalytic
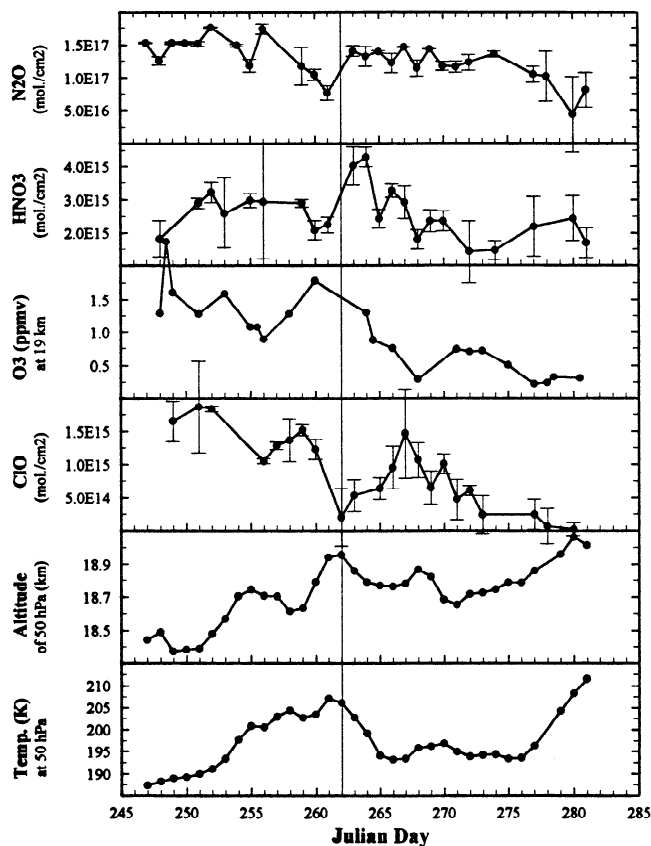
Figure 5. Column densities of ClO (day minus night), N₂O, and HNO₃ above 16 km during the observation period from September 4 (day 247) to October 8 (day 281) over McMurdo. The error bars represent the uncertainty due to the least squares sum in the retrieval process. Additionally, NMC data (geopotential altitude and temperature of the 50-hPa surface) and ozonesonde data (University of Wyoming) are shown. In each case, dots indicate days when data were available. The vertical line marks September 19.

destruction by chlorine. The major exception was a peak around day 262 (note the gap in ozonesonde data) coincident with maxima in both A_{50hPa} and T_{50hPa} which indicates that McMurdo was in the vortex wall at this time. The apparent lack of correlation between ozone, A_{50hPa}, and T_{50hPa} evident toward the end of the observation period will be discussed later.

ClO

The ClO column density started with enhanced values which decreased over time. A first local minimum occurred near day 256 followed by a second minimum around day 262. At the latter minimum, A_{50hPa}, T_{50hPa}, and ozone all had large values, again coincident with the shift of the vortex towards eastern Antarctica (see Figure 4). After recovery to 1.5×10^{15} molecules/cm² on day 267, ClO fades away toward the end of the measurements. The data show a good anticorrelation with HCl data taken at the same location (K. Kreher, personal communication, 1995), indicating repartitioning of Cl occurred during this time period. In general, high ClO values coincide with low temperatures and low ozone values. We shall discuss the apparent lack of correlation between temperature and ClO starting about day 271 in section 5 when back trajectories are analyzed.

HNO₃

The nitric acid column density showed very low values (2 to 3×10^{15} molecules/cm²) which increased to about 4.5×10^{15} molecules/cm² on days 263 and 264 when McMurdo was in the vortex wall. A comparison with the South Pole values of de Zafra et al. [1996] shows good agreement in magnitude. Van Allen et al. [1995] have also measured HNO₃ column densities over the South Pole, obtaining somewhat larger values. The difference can be attributed to the different altitude range which has been covered for column measurements. Van Allen et al. assumed that 17% of the HNO₃ lies below 12 km and get 5.3×10^{15} molecules/cm² for the column above 12 km for late winter. Data from the cryogenic limb array etalon spectrometer (CLAES) from September 1992 show zonal mean profiles averaged over 4° latitude similar to our profiles, but with peak values only two thirds as high as those presented here [Roche et al., 1994]. In the CLAES data a strong gradient in the HNO₃ mixing ratio close to 75°S at ~22 km is evident, which supports the assumption that the increase in the HNO₃ column density around day 263 was caused by vortex movement.

N₂O

The N₂O column density above 16 km decreased slightly over the observation period, consistent with the continued subsidence of vortex air. It showed a local minimum at about day 261 correlated with the movement of the vortex edge over McMurdo. The model of Manney et al., [1994] predicts a stronger descent at the vortex edge relative to the core region, which offers a reason for this decrease. The magnitude of the column densities agrees very well with data taken at South Pole in 1993 [Crewell et al., 1995].

Summary

The measurements presented in Figure 5 disclose some interesting correlations with each other. Note particularly that the intrusion of air masses from the edge region of the vortex around day 262, also illustrated in the PV map of Figure 4, shows up clearly in every panel. Later, toward the end of the observation period in early October (~day 278), the temperature and altitude of the 50-hPa surface and the PV in Figure 4 indicate that McMurdo was again in the edge region of the vortex, but the ozone mixing ratio at 19 km and the HNO₃ column density as well as the N₂O column density now do not follow the previous trend. It appears that the values of temperature and altitude which define the vortex core on the 50-hPa level early in the season should perhaps be shifted to larger values by the end of September or early October. This could be necessitated by increasing solar heating due to higher solar zenith angles and longer daylight periods in early October.

Table 2 presents a correlation matrix of the measured quantities. They all show a negative correlation coefficient with time and with the altitude of the 50 hPa surface. The weak correlation between the HNO₃ column density and the temperature at 50 hPa is due to the fact that nearly all HNO₃ had already been removed from this altitude. The correlation coefficient between the ClO column density and the ozone volume mixing ratio is calculated directly from the data shown in Figure 5. The positive correlation of 0.74 is caused by the same time correlation coefficient for both molecules. After the removal of this linear time trend from the ozone data a more reasonable negative correlation of − 0.51 remains.

Table 2. Correlations Between Different Trace Gases and Meteorological Parameters

	Time	Altitude at 50 hPa	Temp. at 50 hPa	ClO column
ClO column	-0.82	-0.76	-0.42	1
N₂O column	-0.61	-0.71	-0.68	0.68
HNO₃ column	-0.42	-0.15	0.01	0.42
Ozone (19 km)	-0.79	-0.60	0.07	0.74(-0.51)*

* after removal of linear ozone time trend.

5. ClO - Temperature Correlations

It is been known for several years that heterogeneous chemical processes on PSCs are a necessary precursor to ozone loss during ozone hole events [e.g., *Solomon*, 1988]. The relations between ClO abundance, temperature at PSC altitudes, and position relative to the polar vortex are of great interest in determining the time and temperature relationships between PSC events and chlorine activation. As a contribution to this question, the ClO volume mixing ratio at 19 km altitude and T_{50hPa} are plotted versus A_{50hPa} in Figure 6. Note that the 50 hPa surface in Figure 6 oscillates only between 18.3 and 19.1 km altitude, which allows us to compare pressure altitude and geometrical altitude with negligible inconsistency. The error bars represent the one-sigma spread of the different results from retrievals using different starting profiles and weighting functions. This graph provides an indication of the observing position relative to the vortex, and it relates ClO abundance and temperature in the altitude range of interest. The graph is divided into three different regions based on A_{50hPa}: namely, A_{50hPa} < 18.5 km, inside the vortex, with large amounts of ClO and low temperatures; 18.5 km < A_{50hPa} < 18.9 km, a transition region with no obvious relation between the two quantities; and A_{50hPa} > 18.9 km, in the vortex wall, where ClO was less and the temperature greater. A relatively sharp border between the three regions is evident. Both within the inner vortex and the vortex wall, one finds a strong anticorrelation between ClO

abundance and temperature, but in the transition region high temperatures could be observed together with high ClO, and low temperatures were observed with low ClO. For further classification, the history of the observed air parcels has to be taken into account.

As *Shindell and de Zafra* [1996b] have pointed out, there is a relationship between ClO abundance and temperature in the lower Antarctic stratosphere, based on the strong inverse dependence of heterogeneous reaction on temperature, as well as the evaporation temperature of PSCs. Without heterogeneous chemistry high levels of ClO can not be maintained for long because active chlorine shifts to the reservoir HCl via the reactions

$$ClO + OH \rightarrow HCL + O_2$$
$$ClO + CH_4 \rightarrow HCL + CH_3$$
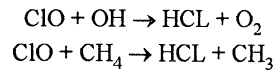
The time constant for this process is highly dependent on solar exposure. Under typical Antarctic conditions an 80% reduction of ClO has been calculated to occur within ~12 days if the process is started on September 21, and within ~5 days if the process is started on September 29 [*Shindell and de Zafra*, 1996b]. These results show that the renitrification of the lower stratosphere is not necessary for the deactivation of chlorine.

Isentropic back trajectories on the 475 K (~19 km) level were obtained from NASA GSFC. In Figure 7 the minimum, maximum, and average temperature that the different air parcels experienced within the previous 7 days are plotted against the ClO volume mixing ratio at 19 km altitude observed on the final day of the trajectory. A similar analysis was done by *Schoeberl et al.* [1993] for a variety of air parcels from Arctic and Antarctic airborne measurements during 1987-1992, which showed a strong anticorrelation between temperature and ClO abundance. In Figure 7 the minimum, maximum, and average temperatures belonging to a given air parcel are displayed directly above each other along with the Julian day number when the ClO-measurement was taken. In general, low prior temperatures coincide with enhanced ClO values, but on days 271-273 the
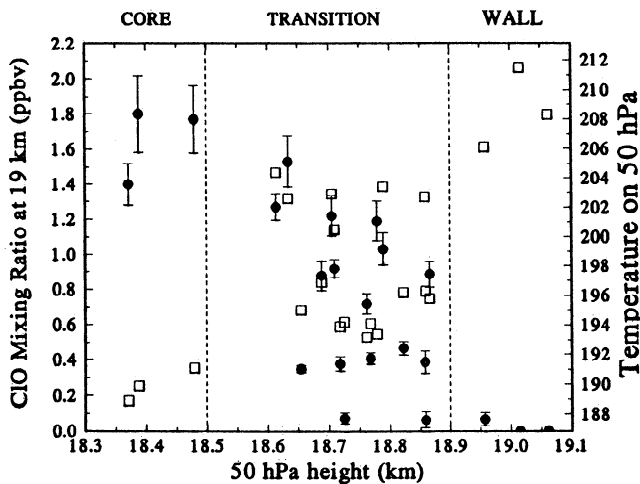

Figure 6. ClO volume mixing ratio at 19 km altitude (solid circles) and the temperature at 50 hPa (open squares) versus the altitude of the 50-hPa layer. Three different regions can be distinguished: inside the vortex (high ClO, low temperatures), a transition region where ClO and temperature show a poor correlation, and the vortex wall (low ClO, high temperatures),.
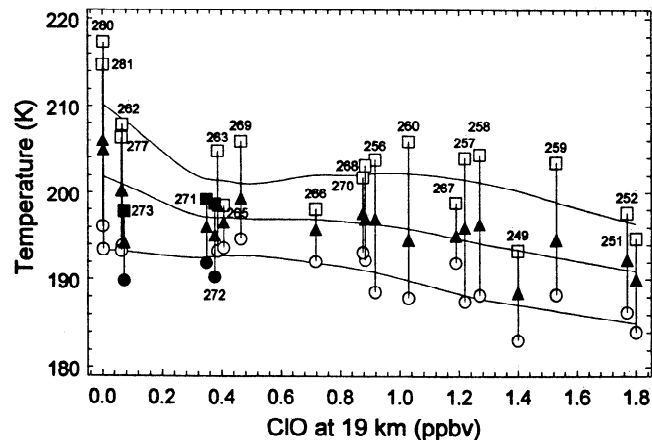

Figure 7. Minimum (circles), average (triangles), and maximum (squares) temperature that a given air parcel experienced within the previous 7 days versus ClO volume mixing ratio at 19 km altitude. The error bars are the same as in Figure 6 but are not plotted for clarity. The numbers within the frame belong to the empty boxes and indicate the Julian day when the measurement was carried out. The anomalous cases of days 271-273 are marked with solid symbols.

lowest temperature previously encountered by the air parcels was near 190 K and yet no enhanced ClO could be observed. Assuming the accuracy of both the ClO and temperature data we suggest two ways to explain this. (1) These events represent anomalous cases during which very little Cl was free from its inactive reservoirs. This could be caused by air too recently from outside the vortex to have been pre-processed to remove NO_X, for instance. (2) No PSCs were in fact present on the trajectories to convert Cl from its reservoirs into chemically active forms. We elaborate on these possibilities in the following paragraphs.

If the ClO mixing ratios of 1.5 ppbv on day 259 (September 16) and 0.07 ppbv on day 273 (September 30) are picked as examples, the minimum temperatures are nearly the same for both days. This extreme difference in mixing ratios together with the almost identical minimum temperatures and even colder average and maximum temperatures on day 273 appears to be an ideal case to check whether the intrusion of extra-vortex air over McMurdo was observed on days 271-273. We note first that if extra-vortex air was observed, the air must have had time to cool down to ~190 K without being denitrified, keeping the NO_2 content high enough to prevent chlorine activation. In Figure 8 the maximum northern excursion and the minimum |PV| achieved during the previous 7 days are plotted against the ClO volume mixing ratio at 19 km. The tendency for high southern latitudes and large |PV| to go together with enhanced ClO mixing ratios is obvious if the three data points in the lower left corner are omitted. These are specifically days 271-273, the anomalous cases already noted in Figure 7. If the back trajectory data are accurate, Figure 8 gives no evidence that air observed on these days had been outside the vortex core in the preceding 7 days. This is supported by the almost identical HNO_3 and N_2O column densities for the compared days.

It is well known that the temperature at which NAT-PSCs are formed strongly depends on the amount of HNO_3 available [e.g., *Hanson and Mauersberger*, 1988]. Our data show almost no HNO_3 at this altitude (Figure 3) for the complete observation period, which would have lowered the condensation temperature for NAT particles to ~190 K, depending on the H_2O concentration [*Marti and Mauersberger*, 1993]. Within the experimental uncertainties, we did not observe any significant

change in the HNO_3 content at 19 km altitude over the complete measurement period. Therefore we should assume that the temperature at which PSCs formed did not change significantly either. The temperatures experienced by air parcels that were observed over McMurdo on days 271-273 were lower than those of air parcels that contained enhanced ClO mixing ratios (e.g. days 267, 268, 270). LIDAR measurements taken by the Istituto di Fisica dell' Atmosfera, Frascati, Italy, show no PSCs over McMurdo after September 15 (G. DiDonfrancesco, personal communication, 1995), which is consistent with the NMC temperature at McMurdo on the 50-hPa pressure surface (see Figure 5). No direct information on PSC occurrence is available for the air parcels before their arrival over McMurdo, however. The 1994 back trajectories (Figure 7) do not show a final rise in temperature above 190 K until some time between day 273 (September 30) and day 277 (October 4). In contrast to local measurements at McMurdo (see Figure 5), the back trajectories indicate that the air parcels observed over McMurdo on days 271-273 should have encountered PSC temperatures, although only marginally reaching the PSC formation temperature for air highly depleted of HNO_3.

If we accept the validity of the back trajectories, we must still deal with the accuracies of the NMC temperatures. We have noted above that at times NMC temperatures and local ozonesonde temperatures can differ by as much as 5 K at 19 km altitude, although this is rare. A positive bias of 1-3 K is more common in the NMC data, however, and perhaps partly reflects temperature averaging over a standard grid. In any case, it is probable that the minimum temperatures from gridded NMC data are a little too large, thus increasing the likelihood that PSCs were encountered within the previous week by air observed on days 271-273. This would confirm the discrepant nature of the data for these three days. On the other hand, we point out that back trajectory calculations starting in or near the vortex wall are a delicate matter, especially toward the latter phases of vortex development. This could lead to incorrect values for latitude, temperature and PV for days 271-273, and reduce or eliminate the apparent discrepancy of low temperature and low ClO for these days.

6. Conclusions

For the first time, nearly simultaneous ground-based measurements of vertical distributions for ClO, HNO₃, and N₂O were carried out in conjunction with direct ozonesonde measurements during a major Antarctic ozone hole event. In contrast to one year before, when McMurdo was clearly located well inside the polar vortex through nearly all the September to October observation period, this was the case only in the beginning of the observation period in 1994. The trace gases observed therefore showed variations due to both the ongoing chemistry and the shifting vortex position. Since the observation site lay frequently in the wall region of the vortex in 1994, a more complex mixture of chemical and dynamical effects could be seen in the observed trace gases. We have identified a transition region near the inner vortex boundary where we observed both large amounts of ClO together with high stratospheric temperatures and low ClO with low temperatures, in contrast to strong anticorrelations between ClO and temperature in the vortex core and the vortex wall. Backward trajectory analyses on the 475 K level were conducted to determine the temperatures, potential vorticities, and geographical positions which the different observed air parcels
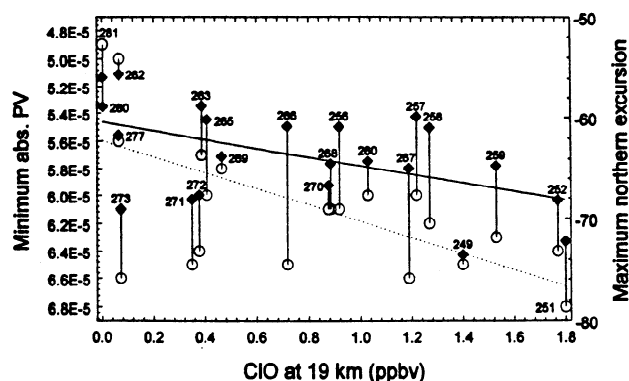

Figure 8. Maximum northern excursion (solid diamonds) and minimum |PV| (open circles) that a given air parcel experienced within the previous 7 days versus ClO volume mixing ratio at 19 km altitude. The error bars are the same as in Figure 6 but are not plotted for clarity. The solid line represents a linear fit to the maximum latitude; the dashed line represents a linear fit to the minimum |PV|.

had recently experienced. This generally showed a good correlation between the observed ClO mixing ratios and PV, maximum northern excursion and temperature, respectively. The correlation between local meteorological parameters at McMurdo (altitude of the 50-Pa pressure surface and temperature at the 50-Pa pressure level) and our data along with the ozonesonde data is generally good, but exceptions in late September could not be readily explained, except by an assumption of erroneous back trajectory calculations.

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