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Partitioning Between Chlorine Reservoir Species Deduced from Observations in the Arctic Winter Stratosphere

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Abstract. Simultaneous observations of several chlorine source gases, as well as HCl and ClO, have been performed in the Arctic stratosphere on 1 and 9 February 1994, using balloon-borne instrumentation as a contribution to SESAME (Second European Stratospheric Arctic and Mid latitude Experiment). The observed mixing ratios of HCl and N_2O show a clear anticorrelation. No severe loss of HCl was observed inside the vortex during our measurement. These measurements showed that during this period at 20 km and above, HCl was either in excess, or at least as abundant, as $ClONO_2$ and comprised between 50 and 70% of the available chlorine, Cl_y. On 1 February, measurements were made inside the polar vortex. The air mass sampled on this day showed a clear signature of diabatic descent, and also enhanced levels of ClO with a maximum of 230 pptv at 22.5 km. A 10 day backward trajectory analysis showed that these air masses had passed a large region of low temperatures a few hours prior to the measurement. Temperatures along the back trajectory at the 475 K and 550 K levels (20.1 and 23.7 km respectively) were cold enough for heterogeneous chlorine activation to occur, in agreement with the observed elevated ClO mixing ratios.

Key words: stratosphere, polar processes, chlorine partitioning.

1. Introduction

It is by now well established that stratospheric ozone depletion, which has been observed over the Antarctic (e.g., Farman *et al.*, 1985; Proffitt *et al.*, 1989) and over the Arctic (e.g., v.d. Gathen *et al.*, 1995; Manney *et al.*, 1994; Müller *et al.*, 1996) is related to man-made emissions of long-lived halogenated compounds (e.g., Solomon, 1990; Anderson *et al.*, 1991). Ozone losses observed at mid latitudes of the Northern Hemisphere during spring time (Stolarski *et al.*, 1991; McCormick *et al.*, 1992; Wege and Claude, 1994) may also be related to chlorine chemistry (e.g., Toumi *et al.*, 1993). The most abundant of the long-lived halogenated compounds are the chlorofluorocarbons (CFCs). These long-lived compounds are the source of the more reactive chlorine compounds found in the stratosphere. The amount

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of chlorine contained in these more reactive compounds is referred to as available chlorine or inorganic chlorine, Cl_y. In the unperturbed stratosphere at mid latitudes, the most abundant compounds in the Cl_y family are the so-called reservoir species, $ClONO_2$ and HCl.

The partitioning between $ClONO_2$ and HCl prior to the onset of heterogeneous reactions, which convert these two species into more reactive chlorine compounds is a matter of controversy. Webster *et al.* (1993) measured HCl concentrations between 120 and 50 hPa in the mid and high latitude northern stratosphere that represented less than 50% of the available chlorine Cl_y, leading to the hypothesis that $ClONO_2$ may be in excess of HCl in the Arctic, prior to the onset of heterogeneous reactions. These low HCl abundances observed by Webster *et al.* (1994) can not be reconciled with model calculations (Webster *et al.*, 1994; Salawitch *et al.*, 1994). From measurements of ClO, NO, NO_2, O_3 and N_2O on board the ER-2, Stimpfle *et al.* (1994) inferred that only 12% of the Cl_y could be in the form of $ClONO_2$ in the mid latitudes lower stratosphere. Together with the simultaneously observed relatively low measured HCl mixing ratios by Webster *et al.* (1993) they concluded that the budget of Cl_y could not be balanced, indicating a remaining gap in the understanding of the chlorine partitioning. Rinsland *et al.* (1995) find HCl to be in excess of $ClONO_2$ outside of the vortex throughout the stratosphere at latitudes north of 60° N in April 1993. Zander *et al.* (1990) have also shown that there was more HCl than $ClONO_2$ in the mid latitude stratosphere of the northern hemisphere above 15 km altitude in April and May 1985 based on ATMOS data. Dessler *et al.* (1995) compare $ClONO_2$ and HCl mixing ratios observed by UARS (Upper Atmosphere Research Satellite) between 60° N and 60° S and conclude that HCl is the slightly more abundant reservoir species, but that the Goddard 2D model (e.g., Considine *et al.*, 1994) they used, tended to overpredict HCl at lower altitudes and to underpredict it at higher altitudes. Altogether, discrepancies between the model calculations and some of the measurements continue to exist, concerning the partitioning between $ClONO_2$ and HCl.

We have performed several simultaneous observations of chlorine source gases and reactive chlorine compounds using balloon-borne instrumentation during the three phases of the SESAME campaign in 1994 and 1995. Results from two flights launched from the SSC (Swedish Space Corporation) ESRANGE research facility (68° N, 21° E) near Kiruna, in Northern Sweden, during phase I of SESAME in February 1994 are presented here. The implications with regard to the partitioning of the reservoir gases are discussed by using correlations between the observed species and by comparing the observed mixing ratios of HCl to the mixing ratio of available chlorine.

2. Experimental

The two profile observations were made on 1 February and 9 February 1994. The scientific payload used in this study consisted mainly of two types of instruments

Table I. Instruments incorporated in the scientific payload of balloon flights launched from ESRANGE near Kiruna on 1 and 9 February 1994

1 February 1994	
Cryogenic whole air sampler (15 samples)	CF_2Cl_2, $CFCl_3$, $C_2F_3Cl_3$, CCl_4, CH_3Cl, CH_3CCl_3, H_2, CH_4, CO_2, N_2O
SLS	ClO, HCl, HNO_3, O_3, N_2O
ECC ozone sonde	O_3
9 February 1994	
Grab sampler (16 samples)	CF_2Cl_2, $CFCl_3$, $C_2F_3Cl_3$, N_2O
SLS	ClO, HCl, HNO_3, O_3, N_2O
ECC ozone sonde	O_3
UV O_3 photometer	O_3

measuring chlorine, nitrogen and hydrogen species: Whole air samplers operated by the Forschungszentrum Jülich (KFA) and a submillimeterwave limb sounding spectrometer (SLS) developed at the Jet Propulsion Laboratory (JPL) in Pasadena, California. The instruments which were accommodated on the gondola are listed along with the target species in Table I.

Two different types of whole air samplers have been used in this investigation: a cryogenic whole air sampler (Schmidt *et al.*, 1987), which collected large air sample at different altitudes in the stratosphere during the controlled slow descent of the balloon on 1 February 1994, and a grab sampler (Bauer *et al.*, 1994), which collected ambient pressure whole air samples during the descent of the gondola beneath the parachute on 9 February. The analysis of the whole air samples was carried out in the KFA laboratory using gas chromatography (GC) with electron capture detection (ECD) and flame ionisation detection (FID). The cryo-samples were analysed using several GC systems (cf. Engel and Schmidt, 1994), for CH_4, N_2O, CO_2, and CFCs, including the 6 most abundant chlorine containing source gases CF_2Cl_2, $CFCl_3$, $C_2F_3Cl_3$, CCl_4, CH_3Cl and CH_3CCl_3 that constitute over 95% of the organic chlorine species (cf. WMO, 1991; Kaye *et al.*, 1994) and is later referred to as total organic chlorine ΣCl_{org}. The quantity of air available from the grabsamples is too small to allow for as complete a determination and, therefore, only CF_2Cl_2, $CFCl_3$ and $C_2F_3Cl_3$ as well as N_2O were measured.

The Submillimeterwave Limb Sounder (SLS) is a heterodyne radiometer measuring thermal emission spectra near 640 GHz (for detection of ClO, HCl, and O_3) and 604 GHz, (for detection of HNO_3 and N_2O) designed for use on high altitude balloons and aircraft (Stachnik *et al.*, 1992a,b). In order to view a well defined air mass, the gondola is stabilised and oriented using a pointing system.

When the balloon reaches ceiling altitudes, a limb scanning sequence is started. Limb scanning is accomplished by a flat mirror ($\sim$ 20 cm diameter) connected to a stepper motor. The limb scan sequence consists of observations at elevation angles ranging from 0 to –6° in steps corresponding to approximately 2 km tangent

height intervals. Additional observations at slight upward angles (1–3°) are made to measure species abundance above the balloon height. Limb scans are alternated with calibration measurements of 'cold' sky at +47° elevation angle and the on-board blackbody target.

During both flights a global positioning system (GPS) was included in the payload, providing a measurement of the geometric altitude. Accurate information about the location of the balloon was thus available at all times. Pressure and temperature were measured by a PTU (Pressure, Temperature, Humidity) sonde on the payload as well as with separate temperature and pressure sensors. A standard ECC ozonesonde was also incorporated in the payload for the two flights as well as an ozone photometer during the flight on 9 February.

3. Data Evaluation

3.1. ORGANIC SOURCE GASES AND TOTAL AVAILABLE CHLORINE

The source gases analysed in the cryogenically collected samples represent more than 95% of the organic chlorine, allowing us to determine ΣCl_{org} directly. For the calculation of ΣCl_{org} each molecule is weighted by its respective number of chlorine atoms.

$$\begin{aligned}\Sigma Cl_{org} = {} & 2 * CF_2Cl_2 + 3 * CFCl_3 + 3 * C_2F_3Cl_3 + 4 * CCl_4 + \\ & + CH_3Cl + 3 * CH_3CCl_3 \,. \end{aligned} \tag{1}$$

For the grabsamples taken on 9 February ΣCl_{org} could not be determined directly and was therefore calculated using a correlation function between CF_2Cl_2 and the total organic chlorine derived from measurements with the cryosampler (see Schmidt *et al.*, 1994). These correlation functions have to be updated regularly in order to account for the different tropospheric trends of the chlorine source gases. Figure 1 shows the correlation between CF_2Cl_2 and the total organic chlorine observed during 5 flights of the cryosamplers in 1993, 1994 and 1995. In a similar approach, a correlation between N_2O and the total organic chlorine can be derived (not shown). The correlation functions obtained from the fit calculations are (updated from Schmidt *et al.*, 1994):

$$\Sigma Cl_{org}[\text{pptv}] = 0.030 * CF_2Cl_2^{1.884}[\text{pptv}] + 53.2[\text{pptv}] \,, \tag{2a}$$

$$\Sigma Cl_{org}[\text{pptv}] = 0.00365 * N_2O^{2.37}[\text{ppbv}] + 13.4[\text{pptv}] \,. \tag{2b}$$

Available chlorine, Cl_y, is the sum of chlorine which has already been released from the organic source gases. In the absence of heterogeneous reactions, the bulk of the Cl_y will exist as either HCl or $ClONO_2$. Usually only a small fraction of the Cl_y is present in the active forms which can destroy ozone. However, this situation can change dramatically if surface reactions become important and HCl and $ClONO_2$ can undergo heterogeneous conversion. Cl_y is calculated as the

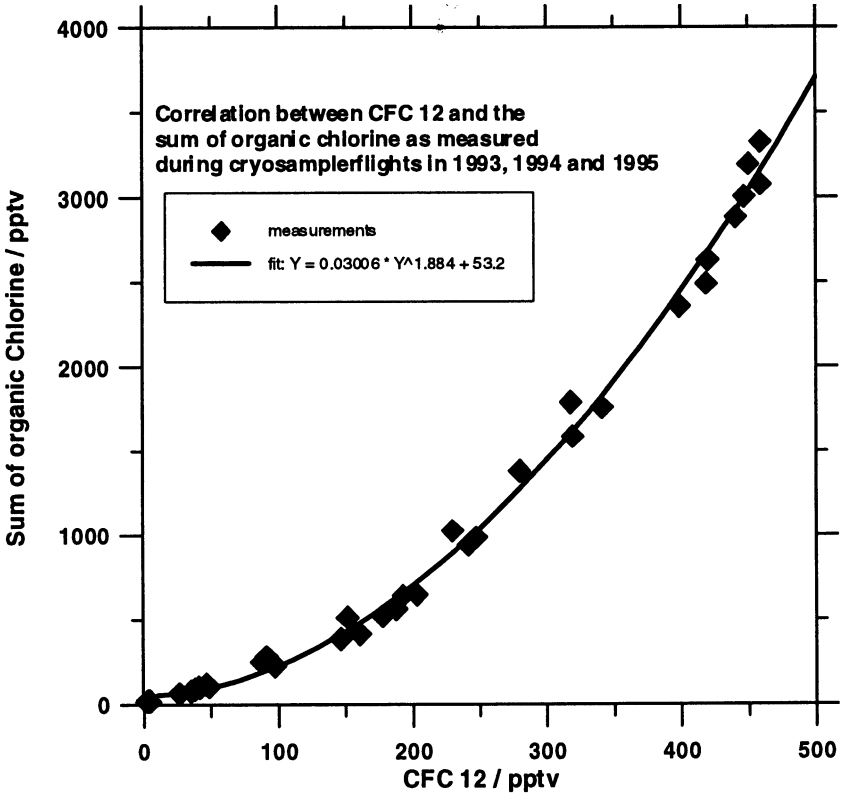

Figure 1. Correlation between CF_2Cl_2 and ΣCl_{org} observed during the flights of the cryosamplers in 1993, 1994 and 1995. The flights were performed at different latitudes (44° N and 68° N), during different seasons and under different meteorological situations.

difference between the total chlorine, defined as ΣCl, and the organic chlorine ΣCl_{org}. In order to calculate Cl_y the total chlorine has to be known. Total chlorine can be estimated from the tropospheric chlorine burden taking into account the age of the air at different altitudes of the stratosphere (Schmidt *et al.*, 1994). The age of stratospheric air can be inferred from measurements of CO_2, as CO_2 increases with time in the troposphere, but has no significant sources or sinks in the stratosphere (Schmidt and Khedim, 1991). This age increases with altitude until it reaches a constant level above a certain altitude (Schmidt and Khedim, 1991). The region of changing age is called the transition layer. Due to a technical problem, no measurements of CO_2 could be obtained during the cryosampler flight on 1 February. We therefore used the mean age of 4 years found above this transition layer during our cryosampler flights in 1993, 1994 and 1995 (Schmidt and Engel, unpublished results, see Schmidt and Khedim (1991), for the calculation of age). The top of the transition layer is generally observed at about 80 hPa in the Arctic. We have therefore fitted a curve to the age deduced from previous flights. The best

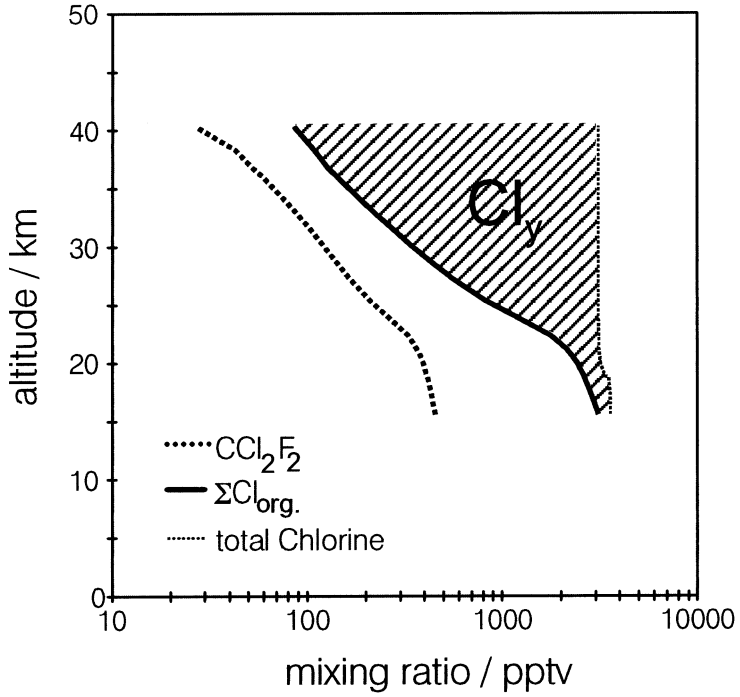

Figure 2. Schematic representation of the relation between different compounds in the chlorine family (adapted from Schmidt *et al.*, 1994).

fit was achieved using a sigmoid function, which assumes a smooth increase of the age between 200 and 80 hPa and a constant age of 4 years above that. From this a similar sigmoid curve (3) approximating the vertical distribution of total chlorine, ΣCl, can be derived:

$$\Sigma\mathrm{Cl}[\mathrm{pptv}] = \mathrm{Cl}_{\mathrm{early}}[\mathrm{pptv}] + (\mathrm{Cl}_{\mathrm{late}}[\mathrm{pptv}] - \mathrm{Cl}_{\mathrm{early}}[\mathrm{pptv}])/ (1 + (p[\mathrm{hPa}]/10^{2.102})^{-7.807}) . \quad (3)$$

$\mathrm{Cl}_{\mathrm{early}}$ and $\mathrm{Cl}_{\mathrm{late}}$ represent the tropospheric chlorine loadings at the early date (corresponding to the age found above the transition layer, i.e., 4 years on the average) and at the later date, i.e., the year of the measurement. Total chlorine is approximated as the sum of the 6 above mentioned chlorine source gases (CF_2Cl_2, $CFCl_3$, $C_2F_3Cl_3$, CCl_4, CH3Cl and CH_3CCl_3) in the troposphere in the respective year (WMO, 1991, 1994; Kaye *et al.*, 1994), again weighted by the respective number of chlorine atoms. The relationship between these different chlorine species and families is explained graphically in Figure 2. The error in the determination of Cl_y is largely due to errors in the assumptions about the total chlorine (e.g., uncertainties in the age of the air) and is estimated to be of the order of 300 pptv, independent of altitude.

3.2. HCL, CLO, N_2O AND HNO_3 FROM THE SLS INSTRUMENT

The raw data of the SLS instrument consit of a series of atmospheric emission spectra at different elevation angles, corresponding to different tangent altitudes. Due to interference problems, which probably originated from the emitter of the ECC ozonesonde flown on the same balloon on 1 February 1994, part of the spectra had to be rejected for the retrieval of the mixing ratios. Each spectrum is the sum of atmospheric signals emitted along the observation path weighted by the path length through each atmospheric layer. The path length and weighting are largest for the layer at the tangent height. Vertical profiles of the mixing ratios are inferred from the limb scan spectral data as follows: An atmospheric radiance is developed using line positions and intensities from the JPL Submillimeter, millimetre and microwave spectral line catalogue (Poynter and Pickett, 1985), National Meteorological Centre temperature profiles, measured instrument field of view, and detailed spectrometer filter shapes. In this simulation, the vertical mixing ratio profiles of constituent species are modelled using triangular basis functions (linear segments). The radiance model is linearized by evaluating finite difference partial derivatives of radiance with respect to constituent abundance, initially using climatological mixing ratio profiles as the linearization point. The linearized model is fitted to the observed spectra using a linear least-squares algorithm. This procedure yields profiles of ClO, HCl, O_3, HNO_3 and N_2O with a vertical resolution of about 2.5 km. A more detailed description of the SLs instrument and the data retrieval is given in Stachnik *et al.* (1992a,b).

After calculating the available chlorine from the whole air sampler measurements, the values were interpolated linearly to the tangent altitudes of the SLS instrument.

4. Meteorological Situation and Measurements

The distribution of trace gases in the stratosphere is strongly influenced by transport processes, e.g., by vertical descent inside the polar wintertime vortices. Potential vorticity (PV) is a measure of the position with respect to the polar vortex, with high values of PV found inside the polar vortex and lower levels outside. Figures 3a, b show the analysed distribution of PV over the northern hemisphere on the 550 K potential temperature surface for the two flight days. While the launching site ESRANGE near Kiruna (black dot; 68° N, 21° E) was outside of the polar vortex on 9 February, it was inside of the polar vortex on 1 February on this level.

Due to the strong vertical gradient in PV it is difficult to compare PV values from different days at different altitudes in one Figure. We have therefore plotted the vertical profiles of modified PV (Lait, 1994) in Figure 4. Modified PV is calculated from the standard PV by scaling with a factor which contains a reference potential temperature, in order to remove much of the altitudinal dependence of standard

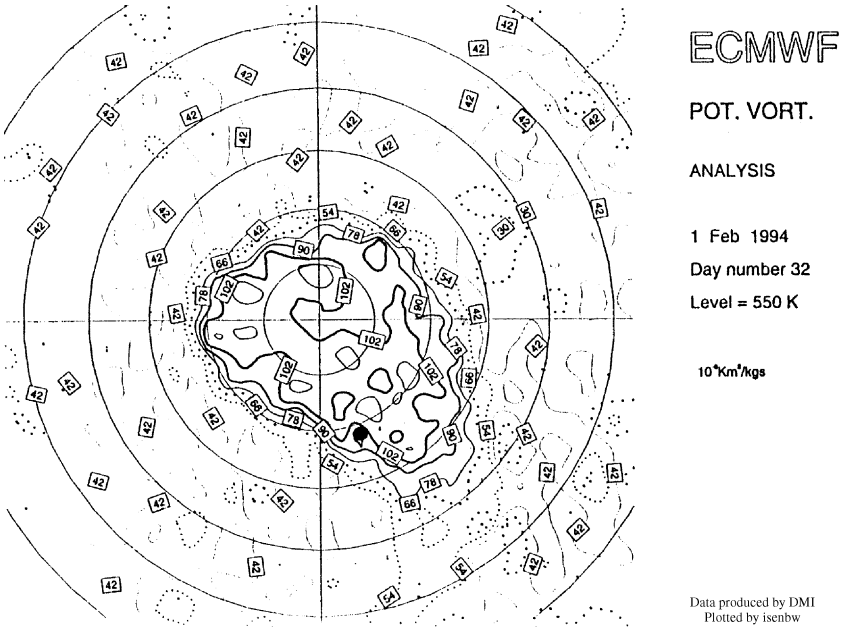

Figure 3a. Distribution of potential vorticity over the northern hemisphere for 1 February 1994 on 550 K potential temperature. The PV was calculated by the Danish Meteorological Institute (DMI) based on data of the European Centre for Medium Range Weather Forecast (ECMWF). The launch station Kiruna is marked by the black dot.

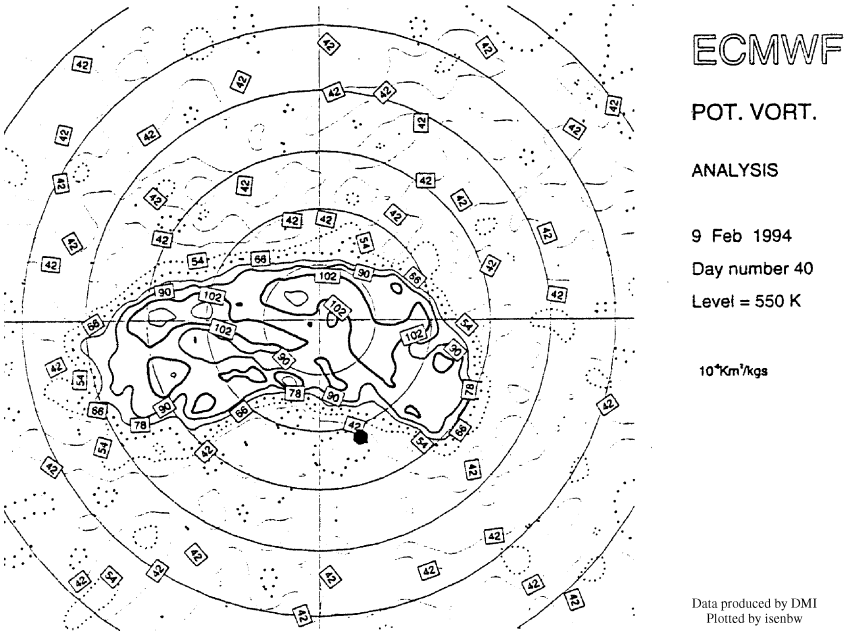

Figure 3b. As Figure 3a for 9 February 1994.

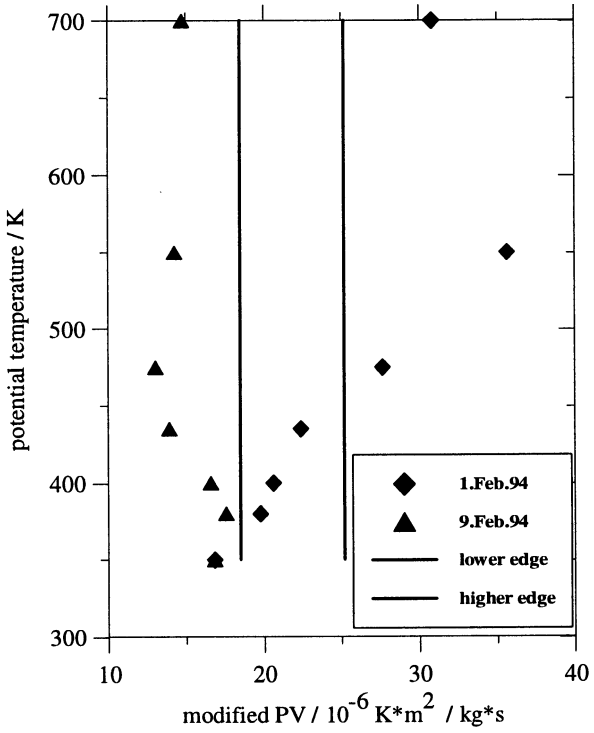

Figure 4. Vertical distribution of modified PV over Kiruna and vortex boundary values for the two flight days. The higher and lower edge values are those values of modified PV which are assigned to the inner and outer boundary of the vortex edge, based on the PV values given by Bauer *et al.* (1994). Values in between these two boundaries can not be characterized unambiguously as inside or outside of the vortex.

PV. We used a reference potential temperature of 420 K as in Lait (1994) for the calculation of modified PV.

$$\text{mod PV} = \text{PV}(\theta/\theta_{\text{ref}})^{-9/2} \tag{4}$$

In order to find values of modified PV which can be assigned to the inner and outer vortex edges we used the standard PV edge values given by Bauer *et al.* (1994) and calculated boundary values of modified PV for the inner and outer edges of the vortex using the reference temperature of 420 K again. According to this modified PV, values below 18.5 [10^{-6} km^2/(kg s^{-1})] represent outside vortex air masses, values above 25.2 [10^{-6} km^2/(kg s^{-1})] are typical of vortex air. Values between these two boundaries are classified as edge of the polar vortex. Based on this classification, the balloon was inside of the polar vortex above a potential temperature of about 450 K on 1 February, whereas it was in the vortex edge region at lower potential temperatures. On 9 February it was outside of the polar vortex during the whole flight.

The viewing direction of the SLS instrument was roughly towards wet south west on both occasions with tangent altitudes at a distance of about 100 to 200 km from the balloon. The N_2O profiles measured on the respective days by the two instruments are compared to our updated mid latitude reference profile, derived from many flights in mid latitudes in early winter (Schmidt *et al.*, 1991) in Figures 5a, b. Some disagreement between the instruments can be seen with the remote sensing instrument, generally showing higher mixing ratios in the altitude region between 15 and 25 km. This may be partly due to uncertainties in the pressure broadening coefficients which are used for the retrieval of the SLS profiles. The same feature is observed during both flights. As the SLS instrument was looking away from the centre of the vortex on both occasions, it can not be excluded that the effect is also partly due to different airmasses observed by the two instruments, containing different amounts of N_2O. A detailed analysis of the meteorological situation using data from U.K. Meteorological office and a domain filling back trajectory technique (not shown), yielded no information that would suggest that different air masses were sampled by the two techniques on 9 February. On 1 February the situation is somewhat ambiguous and the SLS instrument could have been viewing a filament of mid latitude air at the 475 K potential temperature level not sampled by the cryosampler.

Figures 6, 7, 8 and 9 show the vertical profiles of CF_2Cl_2, Cl_y, ClO and HCl, the first two being measurements or derived quantities fromt the *in-situ* instrument, the latter two being remotely sensed profiled from the SLS instrument. The remotely sensed profiles have rather large error bars. This is caused by the short integration times which had to be used, since the meteorological conditions did not allow for long duration balloon flights during early February 1994. The profiles of N_2O, CF_2Cl_2 and Cl_y clearly indicate that the air observed on 1 February, inside of the polar vortex, had descended from higher altitudes due to diabatic cooling. This effect is observed in all profiles of long lived trace species inside the polar vortex (e.g., Schmidt *et al.*, 1991; Bauer *et al.*, 1994; Loewenstein *et al.*, 1990; Schoeberl *et al.*, 1992; McIntyre, 1992; Müller *et al.*, 1996). The maximum descent is inferred at the highest altitudes (i.e., about 25 km) and corresponds to more than 10 km when compared to mid latitudes in early winter. Diabatic descent is also indicated by the HCl profiles (Figure 9), where on a given altitude, higher HCl is observed inside of the polar vortex (1 February), than outside (9 February).

Between 20 and 25 km higher mixing ratios of ClO are observed inside the vortex than outside although both measurements were taken at similar solar zenith angles ranging between 81 and 83°. The time scale for sequestration of ClO into $ClONO_2$ via the reaction of ClO with NO_2 is much shorter (about 3 days at 10 hPa and 10 pptv of NO_2) than that of diabatic descent (about 1 km per week, depending on altitude, cf. Bauer *et al.*, 1994). Therefore, the enhanced ClO usually observed at higher altitudes would not persist over timescales involved in diabatic descent and the enhanced ClO can thus not be caused by transport. The amount of Cl_y observed on 1 February was higher than on 9 February by up to 30%, which could explain

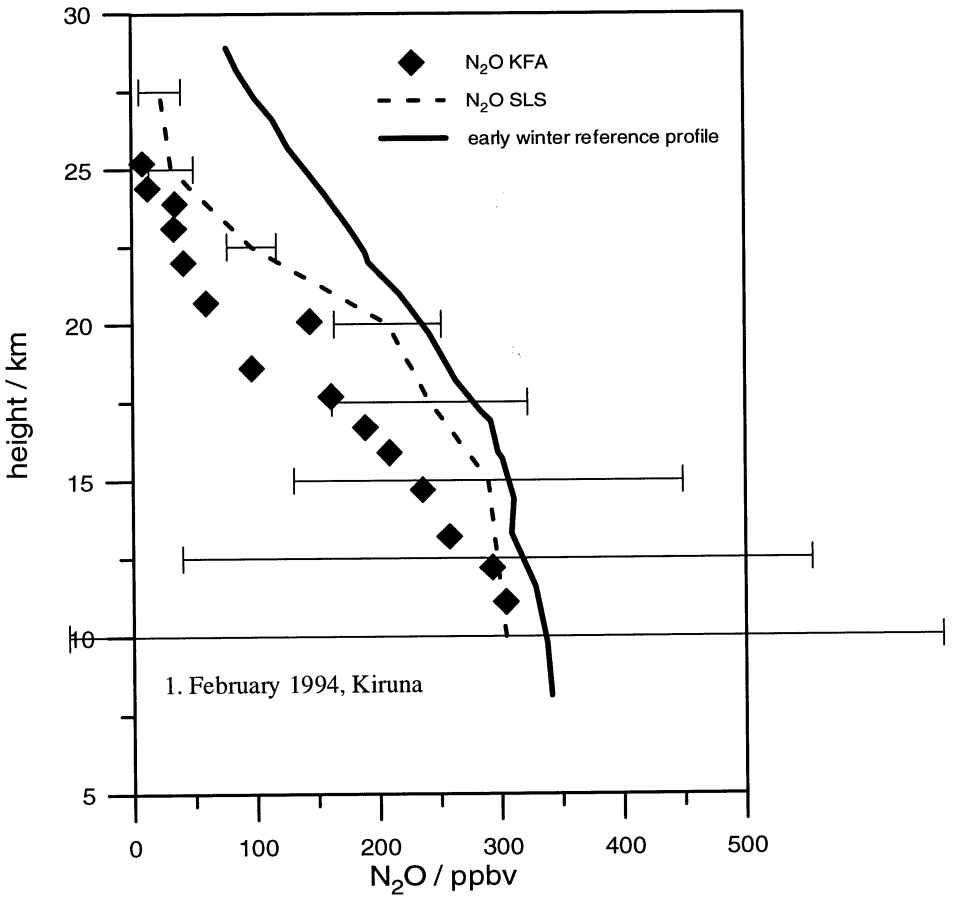

Figure 5a. N_2O profiles observed by the two instruments on 1 February 1994 compared to a mid latitude reference profile (updated from Schmidt *et al.*, 1991). The meteorological data showed the balloon to be inside of the vortex above 475 K (about 20 km) and in the edge of the polar vortex below that.

a proportional enhancement in ClO due to gas phase chemistry when compared to 9 February. At 22.5 km the ClO observed on 1 February is however 2.3 times higher than on 9 February. Based on ER-2 measurements during the AASE-II experiment in the Arctic in the winter of 1991/92 Toohey *et al.* (1993) showed that elevated ClO was observed when low temperatures occurred somewhere along the calculated back trajectory. The temperature threshold for enhanced levels of ClO found by Toohey *et al.* (1993) was about 195 K at typical ER-2 flight altitudes of about 20 km. This behaviour is attributed to heterogeneous reactions which convert chlorine reservoir species to active forms of chlorine. Backward trajectories were calculated using ECMWF data for the endpoint Kiruna. The trajectories ending on 1 February are more confined to the Arctic region than those ending on 9 February. This is in agreement with the higher PV values found on 1 February. The temperature

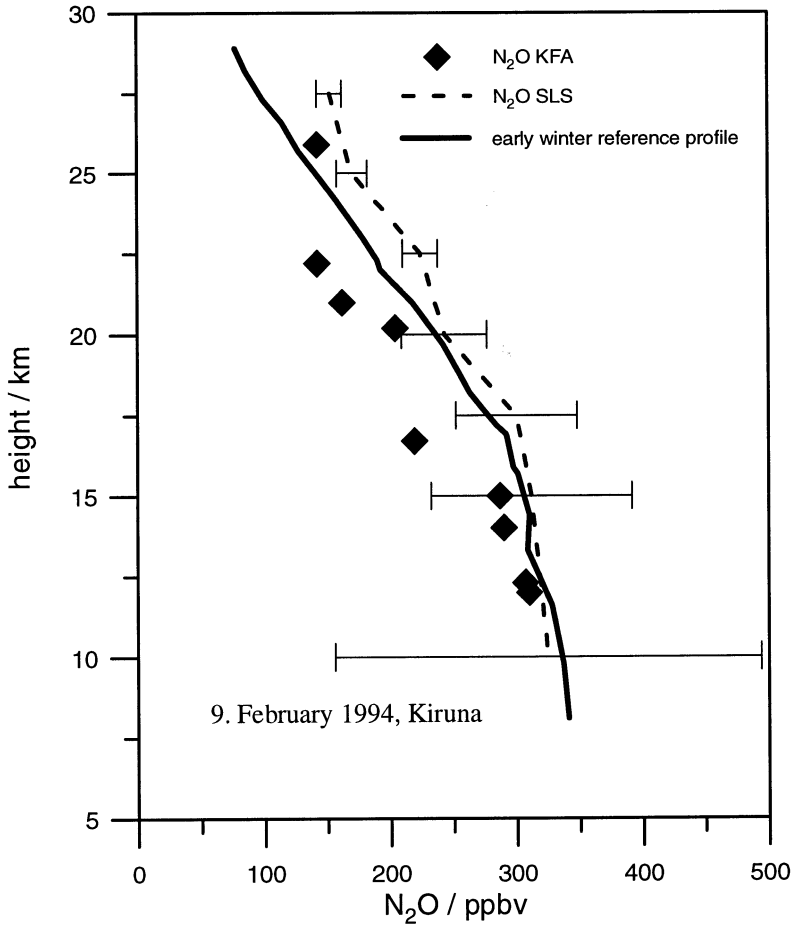

Figure 5b. As Figure 5a but for 9 February.

distribution on the 550 K (about 23.5 km) surface for 1 February shows that the air parcels travelled through a region of cold temperatures ($T < 193$ K), situated between northern Scandinavia and Greenland, a short time prior to the measurement (about 10 hours). This is consistent with the picture given by Toohey *et al.* (1993), indicating that heterogeneous processing may have occurred shortly before the measurement.

5. The HCl Fraction of the Available Chlorine

In the absence of heterogeneous processing of stratospheric air, the mixing ratios of N_2O (and other long lived tracers) and HCl are inversely correlated (Webster *et al.*, 1993; Müller *et al.*, 1996). Figure 10 shows the anticorrelatio between the N_2O measured in-situ and the HCl observed from the remote sensing instrument on the

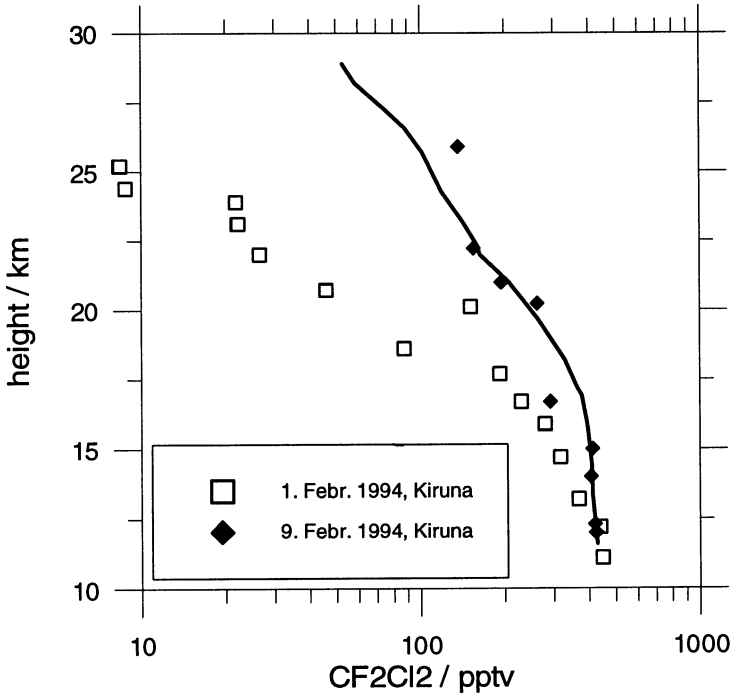

Figure 6. Vertical profiles of CF_2Cl_2 observed on 1 and 9 February 1994 over northern Scandinavia. Also included is a reference profile from mid latitudes for early winter (updated from Schmidt *et al.*, 1991.

two flight days. While the HCl values on a given N_2O level are lower on 1 February inside the vortex, when compared to those observed on 9 February outside of the vortex, no significant difference in the correlations observed on the two days can be derived within the combined error bars. If the N_2O data from the SLS instrument are used, a different correlation between N_2O and HCl is derived, with higher HCl values on the same N_2O level (not shown). Also plotted in Figure 10 is the correlation observed by Webster *et al.* (1994) in the northern hemisphere (15° N–60° N) during the SPADE campaign in 1993 and photochemical box model calculations (Salawitch *et al.*, 1994) for 34° N (Webster *et al.*, 1994). In the absence of heterogeneous reactions, a similar correlation should be expected between these two compounds at 68° N as observed at 34° N, due to the long lifetimes of HCl and N_2O under these conditions (cf. Plumb and Ko, 1992). Our data from 9 February agree with these model calculations but we find significantly higher amounts of HCl on the same N_2O level than observed by Webster *et al.* (1994). It should be noted that the measurements of Webster *et al.* (1993, 1994) were conducted in other years than our study. Year to year variability caused e.g. by different aerosol loadings, can thus not be excluded as the cause for this difference.

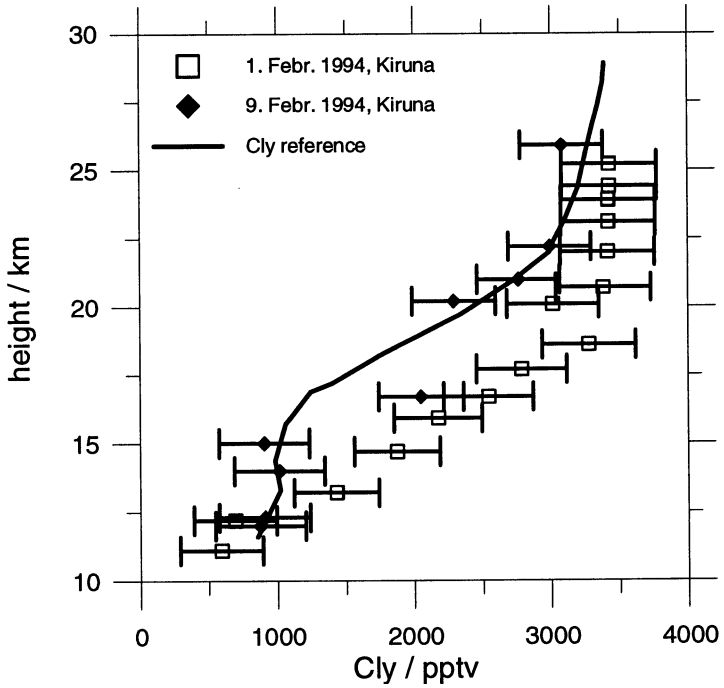

Figure 7. As Figure 6 for available chlorine, Cl_y. The mid latitude reference profile is updated from Schmidt *et al.* (1994).

The correlation observed on 1 February shows slightly lower HCl values than the model. As no significant difference between the anticorrelation of HCl and N_2O inside and outside of the vortex is observed, it can be concluded that little HCl loss had occurred in the air mass observed on 1 February 1994 inside the Arctic polar vortex. This is in good agreement with observations by Naujokat *et al.* (1994) showing that the temperatures in the winter of 1993/1994 were near average temperatures during the early winter, but unusually low in March 1994.

The HCl fraction of Cl_y (based on the CF_2Cl_2 and N_2O measurements obtained by the whole air sampler) observed on 1 February increases with altitude (Figure 11), as expected from photochemical models (Webster *et al.*, 1994; Salawitch *et al.*, 1994). No such increase can be derived inside the errors of the measurements during the flight on 9 February. No minimum in the HCl fraction can be detected in our data as suggested by the models. This may, however, be due to the large experimental error in the lower part of the stratosphere, which is caused both by errors in the determination of the available chlorine, Cl_y, as well as experimental errors in the HCl data, which increase in the lower part of the stratosphere. In the upper part of the stratosphere the HCl fraction is larger on 1 February compared to 9 February, whereas in the lower stratosphere the largest HCl fraction occurs on 9 February. On both days, HCl accounts for more than 50% of the available chlorine

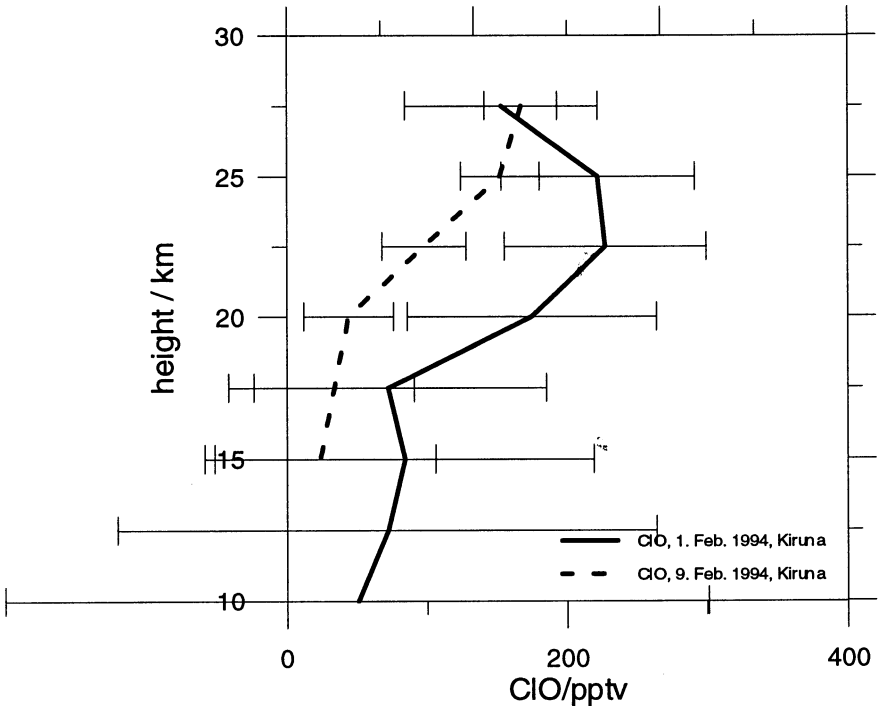

Figure 8. Vertical profiles of ClO observed on 1 and 9 February 1994 over northern Scandinavia.

at all levels above 20 km ($\approx$ 50 hPa). Even on the 20 km level on 1 February, 50% of the Cl_y were found to be in the form of HCl. As noted above, elevated ClO was found at this level, indicating that some HCl had probably been removed through heterogeneous chlorine activation. However, HCl was still calculated to be more abundant than $ClONO_2$ (the fractional abundances being 50 and 44% respectively). The average values of the observed HCl fraction were 53% at 20 km, 54% at 22.5 km and 66% at 25 km based on the N_2O values observed by the *in situ* instrument. If the N_2O observations by the SLS instrument are used for the calculation of the available chlorine, a higher fraction of the Cl_y is calculated to be in the form of HCl mainly at the lower altitudes. The average values are between 66 and 68% of the Cl_y for the altitude region between 20 and 27.5 km. Taking into account the discrepancies between the observed N_2O values it can be concluded that the HCl fraction was between 50 and 66% (up to 70% if the SLS N_2O data are used) during our measurements between 20 and 27.5 km. As one flight was inside of the vortex and the other one outside, this suggests that during the winter of 1994, HCl was at least as abundant, or in excess of $ClONO_2$ in the northern hemisphere Arctic stratosphere above 20 km, before the onset of heterogeneous chlorine activation.

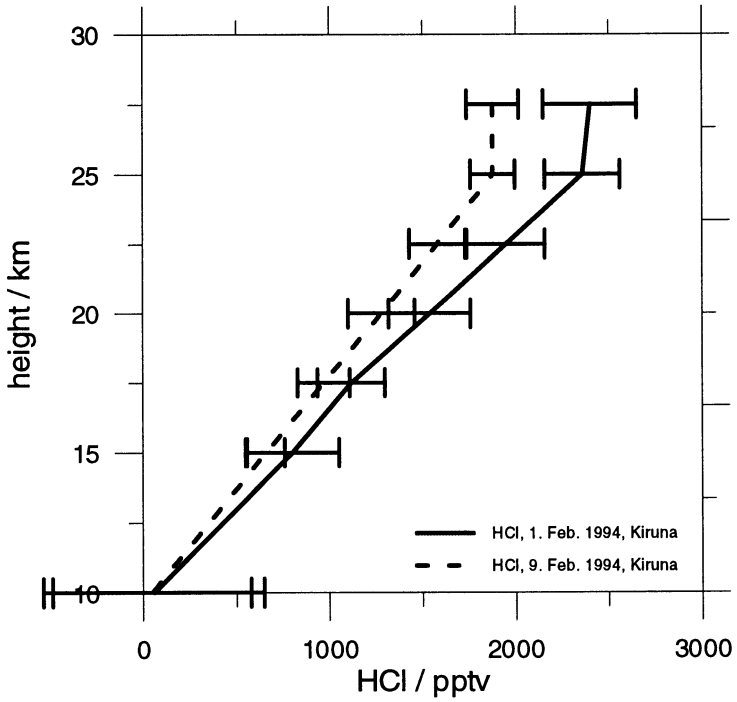

Figure 9. As Figure 8 for HCl.

6. Summary and Conclusions

We have performed simultaneous balloonborne measurements of chlorine source gases and reactive chlorine compounds on 1 and 9 February 1994 from ESRANGE near Kiruna in Northern Sweden (68° N), in the frame of the SESAME campaign. The flight on 1 February took place inside the Arctic polar vortex, whereas outside vortex air masses were probed on 9 February. The measurements of the long lived trace gases on 1 February show that the air masses had descended from much higher altitudes. A similar correlation between N_2O and HCl was observed on both days. As one flight took place outside of the vortex and the other one inside, it can be concluded that only little heterogeneous HCl loss had occurred up to early February, in the winter of 1993/1994, inside the Arctic polar vortex. On both occasions HCl was found to be at least as abundant, or in excess of, $ClONO_2$ at 20 km altitude and above. Its fractional abundance of the available chlorine being between 50 and 66% (66 to 70% based on the N_2O measurements by the SLS instrument), for the altitude region between 20 and 27.5 km. As the distribution of the available chlorine amongst the reservoir species is very important in the quantitative investigation of chlorine activation processes, more and accurate simultaneous measurements of HCl, $CONO_2$ and Cl_y are necessary in order to determine the ratio of HCl to $ClONO_2$ more precisely. On 1 February, somewhat enhanced mixing ratios of ClO

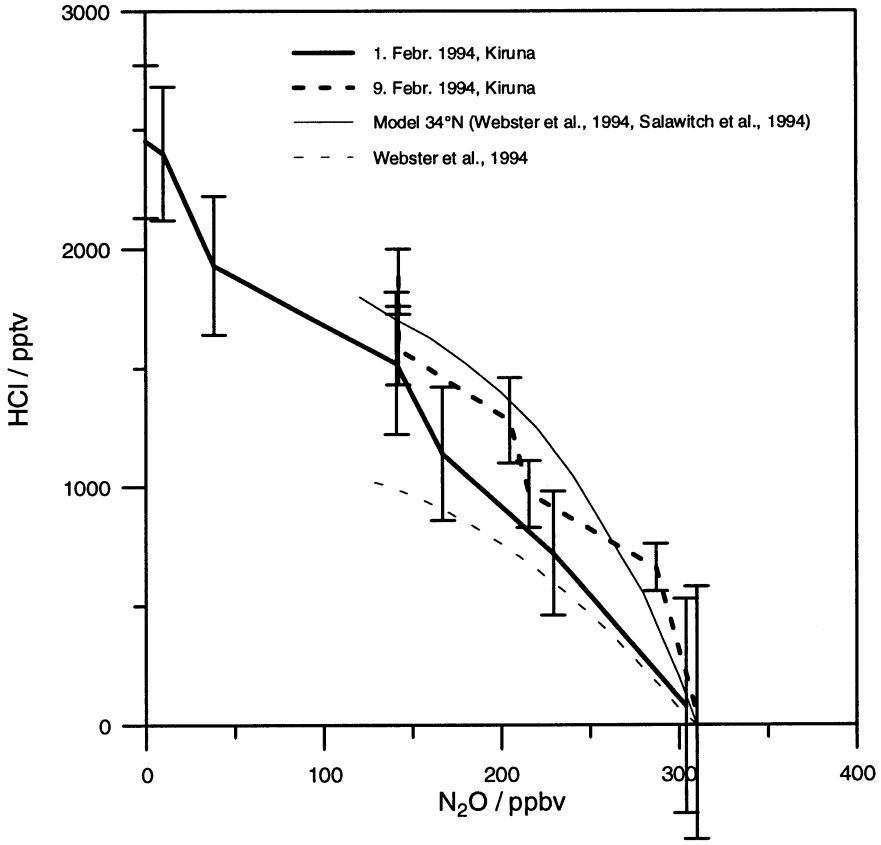

Figure 10. Anticorrelation between N_2O and HCl observed on the two flight days compared to measurements made by Webster *et al.* (1994) and model calculations for 34° N (see text) or discussion. The N_2O data f rom the *in situ* instrument have been used. If the N_2O data from the SLS instrument are used, a good anticorrelation is also observed, but higher values of HCl are found on the same level of N_2O.

were observed inside the polar vortex. The backward trajectories for this day, show that the airmass had passed through a region of very cold temperatures, only a few hours prior to the measurement. As only small differences in the HCl to N_2O correlation are observed between the two days, the somewhat enhanced ClO levels were probably the result of recent and moderate chlorine processing.

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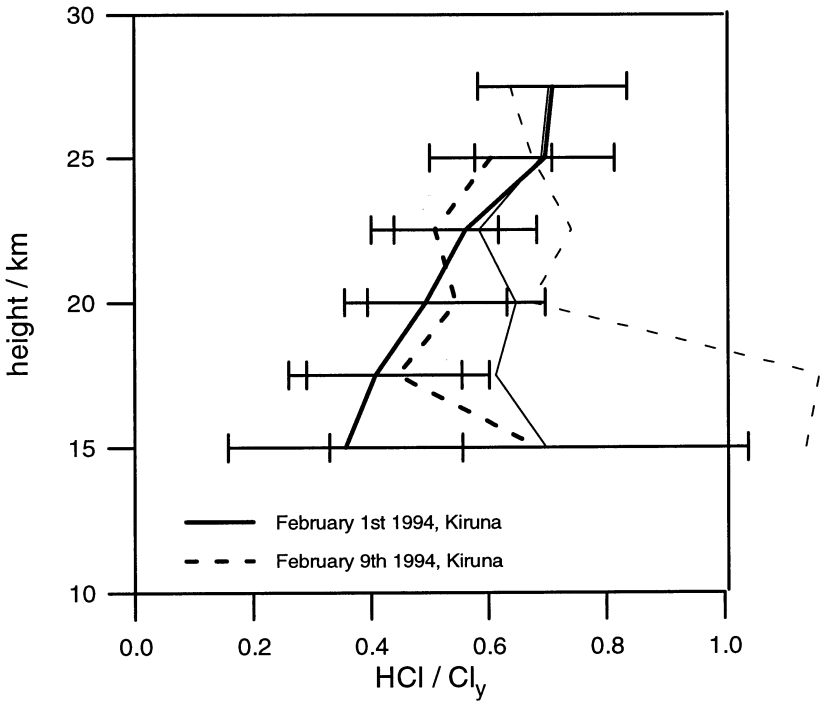

Figure 11. Ratio of HCl to Cl_y at different altitudes derived for the two flight days. While the bold lines represent the ratio calculated based on the *in situ* measurements the thin lines indicate the ratio based on the SLS N_2O data.

campaigns. Reimar Bauer has performed most of the gas chromatographic measurements at KFA. Discussions with Cornelius Schiller, Daniel McKenna, Rolf Müller and Kenneth Carslaw are gratefully acknowledged. Meteorological data were supplied by the Danish Meteorological Institute (DMI) via the Norsk Intitutt for Luftforskning (NILU) based on the data of the European Centre for Medium Range Weather Forecast (ECMWF). Thanks go to both reviewers for helpful comments and suggestions.

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