Ground-based FTIR Measurements from a Series of European sites during the Winter of 1995/96 and a Comparison with a 3D Chemical Transport Model: Evidence of Chlorine Activation and Ozone Depletion.

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INTRODUCTION

Fourier transform infra-red (FTIR) measurements of stratospheric trace species have been made at a network of five ground-based sites from 79°N to 47°N during the Northern hemisphere winter of 1995/1996. This winter was extremely cold [Naujokat & Pawson, 1996] with temperatures below the threshold for type 1 polar stratospheric cloud (PSC) formation from mid December 1995 until early March 1996 when there was a rapid warming of the stratosphere. Over 25 days experienced temperatures low enough for ice cloud (PSC Type 2) formation.

Vertical columns values for HCl, $ClONO_2$, HF and HNO_3 have been derived from FTIR measurements at the following sites: Ny Alesund, Spitzbergen (79°N, 12° E); Kiruna, Sweden (67°N, 21° E); Harestua, Norway (60°N, 11° E); London, England (51°N 0° E) and the Jungfraujoch, Switzerland (47°N 8° E), with measurements of other stratospheric trace gases, including O_3 and ClO available from some of the sites. All of these sites are equipped with high resolution Bruker 120HR or 120M spectrometers, recording atmospheric spectra in the mid infrared using the Sun as a source. More details of the configuration of the spectrometers and details of the analysis can be found other publications [Bell et al, 1997; Galle et al, 1996; Blumenstock et al, 1997; Notholt et al, 1997; Zander et al, 1993]. Guidance on the levels of uncertainty inherent in these measurements is given in Paton-Walsh et al, 1997.

MEASUREMENTS

Figure 1 shows the evolution of the chlorine reservoirs HCl and $ClONO_2$, and also the ratio (HCl + $ClONO_2$)/HF from mid January to the end of March 1996 at the 5 sites. This ratio removes much of the natural dynamic variability in column Cl_y and so can be used as an indicator of chlorine activation, [see Chipperfield et al,(1997)]. The normal scatter in the measured timeseries of this ratio, in the absence of stratospheric chemistry, will be determined by the combination of residual dynamic effects (which were estimated at each site using the SLIMCAT 3D CTM with all species initiated as inactive tracers) and the measurement uncertainties. Estimates of the 2σ limits for variation of the (HCl +$ClONO_2$)/HF ratio, in the absence of heterogeneous chemistry, of 3.1 to 5.4 at 51°N; 3.1 to 5.9 at 60° N and 2.3 to 6.4 at 67° N were made in this way, taking mean measured values of the ratio when the site was located outside the polar vortex (PV < 36 x 10^{-6} Km^2/kgs). Measurements of the (HCl + $ClONO_2$)/HF ratio which fall below these 2σ limits are therefore good indicators for chlorine activation. [Note that the HCl columns from Kiruna, 67°N, are stratospheric columns only and so are in the range of 15% lower than the total vertical columns.]

The plot of the ratio (HCl + $ClONO_2$)/HF from the network of sites (Figure 1a) shows an interesting episode in mid February. On February 14th, day 45, extremely low (HCl + $ClONO_2$)/HF ratios (< 2) were measured at both Kiruna and Harestua. Figure 2a, the ECMWF potential vorticity (PV) analysis for the 475 K level at 12 UT February 14th, shows both Kiruna and Harestua well inside the polar vortex (PV > 48 10^{-6} Km^2/kgs). This suggests that there was large scale activation within the polar vortex at this time. Interestingly the (HCl + $ClONO_2$)/HF ratio measured at London, 51°N is also significantly low, (2.6) although the PV at 12 UT is only 28 x 10^{-6} Km^2/kgs and the temperature above the threshold for PSC formation. The measurements were made just two hours earlier between 09.30 and 10.30 UT suggesting that there was either activation outside the vortex or substantial mixing of air from the edge of the polar vortex. This event did not extend as far south as the Jungfraujoch, where the measured ratio was normal.

By day 49, February 18th, the (HCl + $ClONO_2$)/HF ratio at Harestua had climbed to 3.5 despite the fact that the station was situated within the vortex towards the vortex edge with a PV

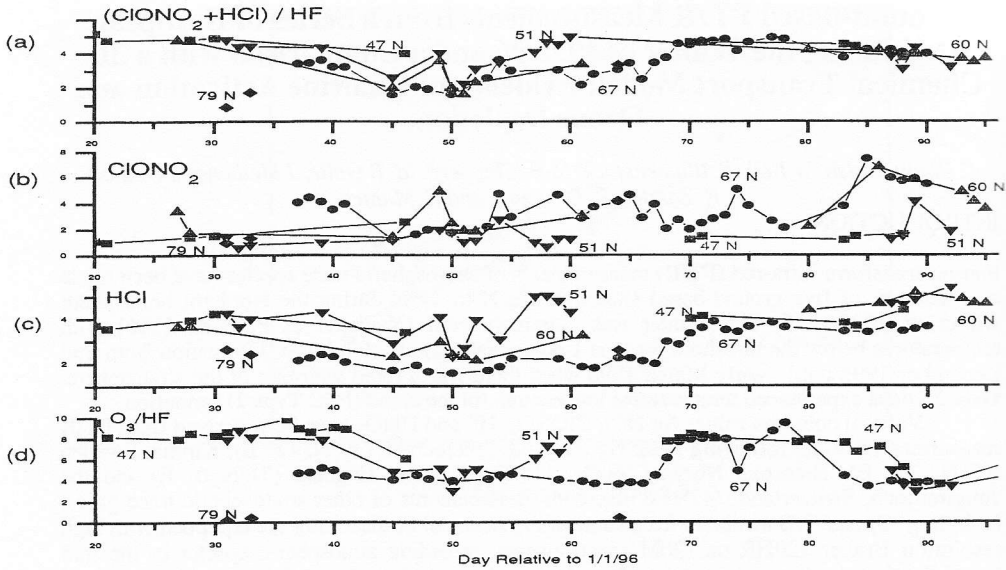

Figure 1: (a) (HCl + $ClONO_2$)/HF ratios; (b) $ClONO_2$ columns; (c) HCl columns and (d) O_3/HF ratios from sites at 79°N, 67°N, 60°N, 51°N, and 47°N from mid-January to mid-April 1996.

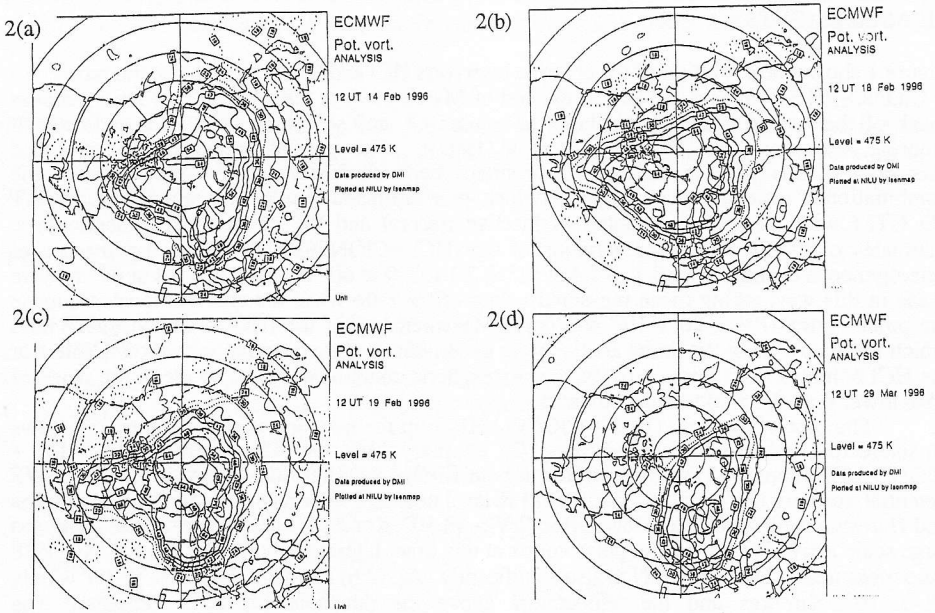

Figure 2: ECMWF potential vorticity analysis from (a) 14 Feb; (b) 18 Feb; (c) 19 Feb & (d) 29 Mar 1996.

value of 46 x 10^{-6} Km^2/kgs. (See Figure 2b). The London value is 4.0 with a PV of 27 10^{-5} Km^2/kgs. The following day (50) the polar vortex has swung south, resulting in London being at a similar position at the edge of the vortex as Harestua was the previous day, with a PV value of 46 x 10^{-6} Km^2/kgs (See Figure 2c). However the (HCl + $ClONO_2$)/HF ratio at London is 1.8, and at Kiruna and Harestua, both deep inside the vortex (PV > 53 x 10^{-6} Km^2/kgs), the (HCl + $ClONO_2$)/HF ratios are 1.6 and 2.0 respectively. Thus the measurements from day 50 suggest that the vortex is highly activated and possibly well mixed even out to the edges of the vortex. In contrast the evidence from the comparison of the measurement made at London on day 50 with

that made at Harestua on day 49 suggests that the vortex edge itself is not well mixed but highly variable in composition.

Much later, on day 89 all these 3 sites are well within the polar vortex again with PV > 44 10^{-6} Km^2/kgs, see Figure 2d, but the $(HCl + ClONO_2)/HF$ ratios are all of the order of 4, showing that there is no significant chlorine activation present in the vortex this late on in the spring. More details of this recovery of activated chlorine into its normal reservoirs can be seen in Figures 1b and 1c. The $ClONO_2$ values are highly variable during February and March, especially in the higher latitudes 60°N and 67°N where columns range from less than 2 x 10^{15} molecules cm^{-2} to more than 6 x 10^{15} molecules cm^{-2}. The very high $ClONO_2$ columns (above 7 x 10^{15} molecules cm^{-2}) around day 85 are indicative of deactivation of chlorine from ClO and Cl_2O_2 and recovery into $ClONO_2$. The marked drop in $ClONO_2$ columns after day 85 is accompanied by an increase in HCl columns as much of the chlorine is converted into the main chlorine reservoir (HCl) as recovery continues.

Figure 1d shows a plot of O_3/HF from 67°N, 51°N and 47°N. Ratioing the O_3 against HF highlights chemical changes by removing much of the natural dynamical variability, as with the $(HCl + ClONO_2)/HF$ ratio, except that the dynamic variability of this ratio is greater because of the substantial differences in the HF and O_3 concentration profiles. The expected 2σ variation of this ratio at Kiruna, London and the Jungfraujoch has been calculated to be 3.1 to 10.9; 3.7 to 9.1 and 4.6 to 9.6 respectively. Measurements of O_3/HF values within the polar vortex from Kiruna (67°N) are consistently low, varying from 4.9 to 3.4 but never falling below the lower 2σ limit for the site of 3.1. However statistically significant low values of O_3/HF were measured during the occasional excursions of the polar vortex over London (days 50, 88, 89 & 92) and the Jungfraujoch (days 89,91,105,106,107 & 109). These provide evidence that areas of chemically depleted O_3 existed in the Northern hemisphere as early as mid February and as late as mid April, and that the effects of chemical ozone depletion extended into the middle latitudes.

COMPARISON WITH A 3D MODEL

The vertical column measurements of HCl, $ClONO_2$ and HNO_3 at all of the sites have been compared to the output of 'SLIMCAT', a three dimensional chemical transport model (3D CTM) described in Chipperfield et al, 1996. Figures 3a and 3b show the measured and the modelled HCl and $ClONO_2$ columns at the five sites from early December until late April. The modelled HCl columns at Kiruna, 67°N agree extremely well with the stratospheric columns measured at this site from day 37 to day 90. The agreement is not so good at the other sites (where the tropospheric HCl contribution is included in the measurements but not in the model), and generally worsens as the winter progresses, suggesting a divergence of the modelled values from the measurements.

The modelled $ClONO_2$ columns are generally significantly lower than the measured values, especially at the higher latitudes. The model also fails to reproduce the very large fluctuations in the springtime $ClONO_2$ columns characteristic of the more northerly sites (especially Harestua, 60°N and Kiruna, 67°N). This is significant because it will cause the model to underestimate the contribution to ozone depletion arising from in situ photolysis of $ClONO_2$ eroded from the vortex.

CONCLUSIONS

FTIR measurements at a series of European ground based sites during the 1996 Northern hemisphere winter have been used to provide both evidence of substantial activation within large areas of the polar vortex and of subsequent O_3 depletion. The measurements suggest a well mixed central vortex area surrounded by a vortex edge that may be highly variable in composition. The measurements also provide evidence of substantial mixing of activated air from the edge of the polar vortex into middle latitudes. Comparison with the SLIMCAT 3D CTM highlights the underestimation of $ClONO_2$ concentrations in the model, with subsequent implications for underestimating O_3 loss.

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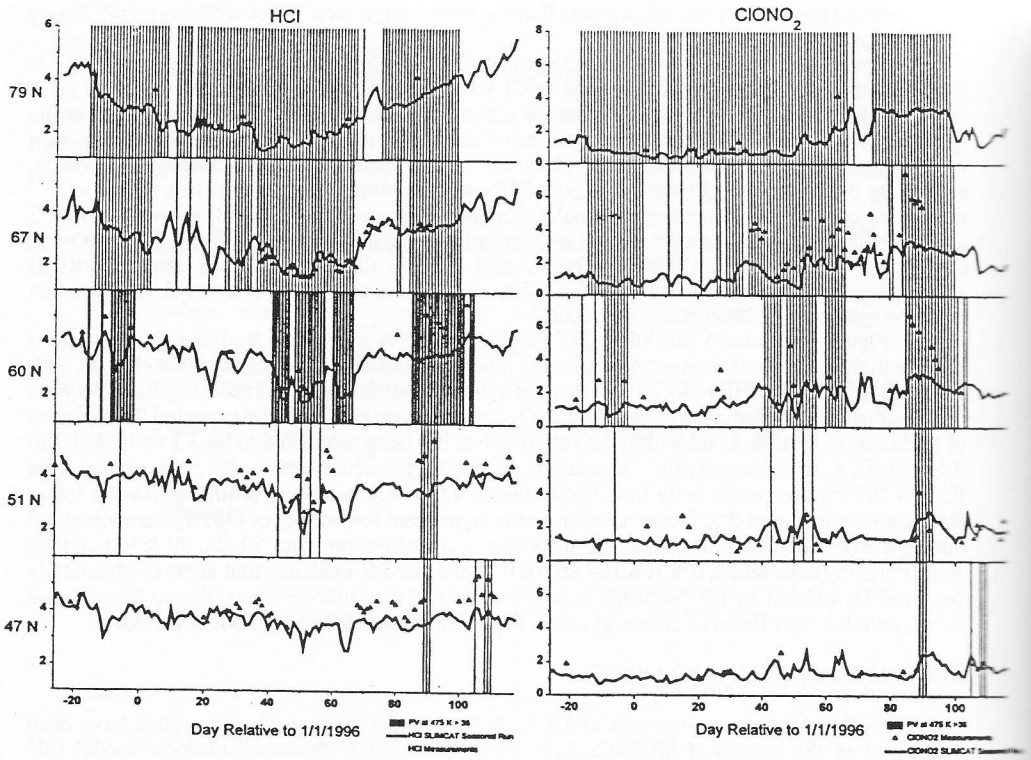

Figure 3: Comparison of SLIMCAT modelled columns of (a) HCl and (b) $CLONO_2$ with measurements at 79°N, 67°N, 60°N, 51°N and 47°N from mid-January to mid-April 1996.

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