

**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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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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1. 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 minimum temperatures below the threshold for type 1 polar stratospheric cloud (PSC) formation occurring 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 column amounts for HCl, ClONO₂, HF and HNO₃ 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 O₃ and ClO available from some of the sites. All of these sites are equipped with high-resolution Bruker 120HR or 120M Fourier transform 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 analyses can be found in other publications [Bell et al, 1997; Galle et al, 1996; Blumenstock et al, 1997; Notholt et al, 1997; Zander et al, 1993]. Estimates of the levels of uncertainty inherent in these measurements is reported in Paton-Walsh et al, 1997.

2. MEASUREMENTS

Figure 1 shows the evolution of the vertical column amounts of the chlorine reservoirs HCl and ClONO₂ and also of the ratio of (HCl + ClONO₂)/HF which were measured from mid January to the end of March 1996 at the five sites. The ratio result is important because it removes much of the natural dynamic variability in column Cl, and so can be used as an indicator of chlorine activation, [Chipperfield et al, (1997)]. The normal scatter in the measured time series of this ratio, in the absence of stratospheric chemistry, will be determined by the combination of residual dynamic effects and the measurement uncertainties. The residual dynamic effects were estimated at each site using the SLIMCAT 3D CTM with all the species initiated as inactive tracers. Estimates of the 2σ (95% confidence) limits for the variations of the (HCl + ClONO₂)/HF ratio, in the absence of heterogeneous chemistry, are by this method determined to be 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. These estimates were made by calculating the mean measured values of the ratio only when the site was located outside the polar vortex (PV < 36 × 10⁶ Km²/kgs). Therefore any measurements of the (HCl + ClONO₂)/HF ratio which fall below the lower 2σ limit are therefore good indicators of chlorine activation.

A diagram of the ratio of (HCl + ClONO₂)/HF columns measured at the network of sites (Figure 1a) indicates an interesting episode in mid February. [It should be noted that the HCl columns from Kiruna, 67°N, are presented as stratospheric columns only and so are ~15% lower than the total vertical columns.]. On February 14th, day 45, extremely low (HCl + ClONO₂)/HF ratios (< 2) were measured at both Kiruna and

Harestua. The ECMWF potential vorticity (PV) analysis for the 475 K level at 1200 hours UT February 14th, shown in figure 2a, confirms that both Kiruna and Harestua are well inside the polar vortex ($PV > 48 \times 10^6 \text{ Km}^2/\text{kgs}$). This suggests that there was large scale chlorine activation within the polar vortex at this time. Interestingly the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratio measured at London, 51°N is also significantly low, (2.6) although the PV at 1200 hours UT is only $28 \times 10^6 \text{ Km}^2/\text{kgs}$, and the stratospheric temperature is above the threshold for PSC formation. These UK measurements were made just two hours earlier between 09.30 hours and 10.30 hours UT thereby suggesting that there was either chlorine activation occurring outside of the vortex or that there was substantial mixing of air from the edge of the polar vortex down to latitudes of 51°N . This event did not, however, extend as far south as the Jungfraujoch, where the value of the measured ratio was normal. By day 49, February 18th, the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratio at Harestua had increased to 3.5 despite the fact that the station was still situated within the vortex - although not very far from its edge, with a PV value of $46 \times 10^6 \text{ Km}^2/\text{kgs}$. (See Figure 2b). The value of the ratio obtained at London was 4.0 with a PV of $27 \times 10^6 \text{ Km}^2/\text{kgs}$. The following day (50) the polar vortex had moved south, resulting in London being at a similar position at the edge of the vortex as Harestua had been the previous day, with a PV value of $46 \times 10^6 \text{ Km}^2/\text{kgs}$ (See Figure 2c). However, the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratio at this time at London was 1.8, and at Kiruna and Harestua, which were both deep inside the vortex ($PV > 53 \times 10^6 \text{ Km}^2/\text{kgs}$), the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratios were 1.6 and 2.0 respectively. Thus the three sets of measurements on day 50 suggest that the vortex is highly activated and well mixed, even out to the edges of the vortex. In contrast, the evidence from the comparison of the measurements made at London on day 50 with those made at Harestua on day 49 suggests that the vortex edge itself is not well mixed but is very variable in composition.

On day 89 the same three sites are well within the polar vortex again with $PV > 44 \times 10^6 \text{ Km}^2/\text{kgs}$, (see Figure 3d), but the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratios obtained are all approximately 4, thereby showing that no significant chlorine activation is present in the vortex this late in the spring. Further details of how this temporal recovery of activated chlorine occurs back to its normal reservoirs can be seen in Figures 1b and 1c. These show that the ClONO_2 values are highly variable during February and March, especially at the higher latitudes of 60°N and 67°N where the ClONO_2 columns range from less than $2 \times 10^{15} \text{ molecules cm}^{-2}$ to more than $6 \times 10^{15} \text{ molecules cm}^{-2}$. The very high ClONO_2 columns (above $7 \times 10^{15} \text{ molecules cm}^{-2}$) measured around day 85 are indicative of deactivation of chlorine from ClO and Cl_2O_2 through transformation into ClONO_2 . The marked decrease in ClONO_2 columns after day 85, accompanied by an increase in HCl columns, show that much of the chlorine is converted into the main chlorine reservoir (HCl) as recovery continues during spring.

Figure 1d shows a diagram of the ratio of O_3/HF columns measured at the sites at 67°N , 51°N and 47°N . This ratio of O_3 against HF highlights chemical changes by removing much of the effects of natural dynamical variability column - as with the $(\text{HCl} + \text{ClONO}_2)/\text{HF}$ ratio. However the dynamic variability of this O_3/HF ratio is greater because of the substantial differences in the shapes of the HF and O_3 concentration profiles. The 2σ variations of this ratio outside the polar vortex 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 obtained 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 of 3.1 calculated for the site. However, statistically-significant low values of the O_3/HF column ratio were measured during the occasional excursions of the polar vortex over London (days 50, 88, 89 & 92) and over the Jungfraujoch (days 89,91,105,106,107 & 109). These provide evidence that regions 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 at these times.

3. COMPARISONS WITH A 3D MODEL

The vertical column measurements of HCl, ClONO₂ and HNO₃ at all of the sites have been compared to the outputs 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 ClONO₂ 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, however, is not so good at the other sites (where the tropospheric HCl contribution is included in the measurements but not in the model). This agreement also generally worsens as the winter progresses, suggesting a divergence of the modelled values from the measured results.

The modelled ClONO₂ columns are generally significantly lower than the measured values, especially at the higher latitude sites. The model also fails to reproduce the very large fluctuations in the springtime ClONO₂ columns which are 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 chemical ozone depletion which arises from in-situ photolysis of ClONO₂ that has been eroded from the vortex.

4. CONCLUSIONS

FTIR measurements have been carried out at a series of European ground-based sites during the Northern hemisphere winter of 1995/96. These have been used to provide evidence of substantial activation within large areas of the polar vortex and of consequential subsequent ozone depletion. The measurements suggest a well-mixed central vortex area surrounded by a vortex edge which can 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. Comparisons with the SLIMCAT 3D CTM highlight an underestimation of ClONO₂ concentrations in the model, with subsequent implications for the model's predicted underestimate of O₃ loss.

5. ACKNOWLEDGEMENTS

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FIGURES

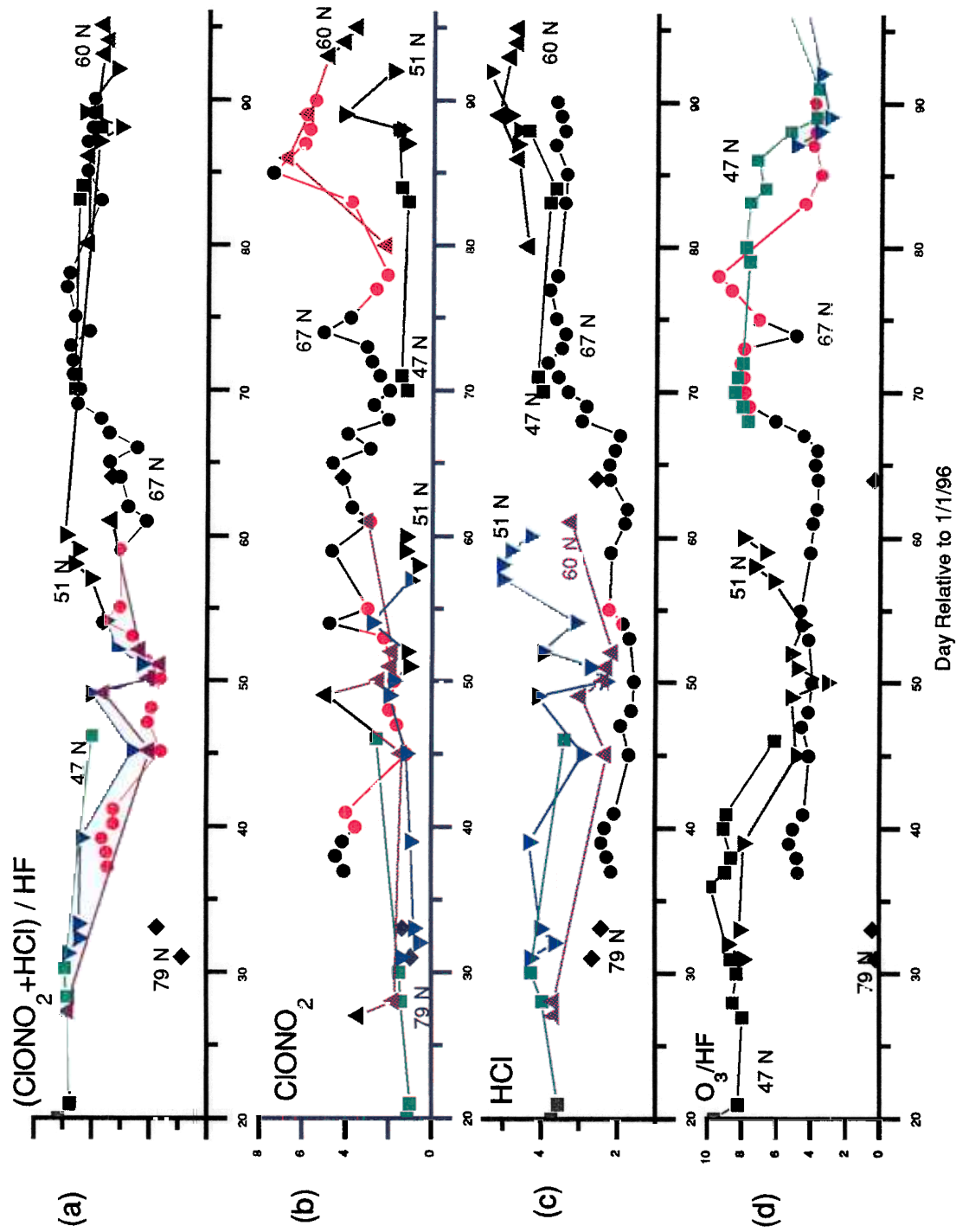


Figure 1: (a) $(\text{HCl} + \text{ClONO}_2) / \text{HF}$ ratios; (b) ClONO_2 columns; (c) HCl columns and (d) O_3 / HF ratios from sites at 79°N, 67°N, 60°N, 51°N, and 47°N from mid-January to mid-April 1996.

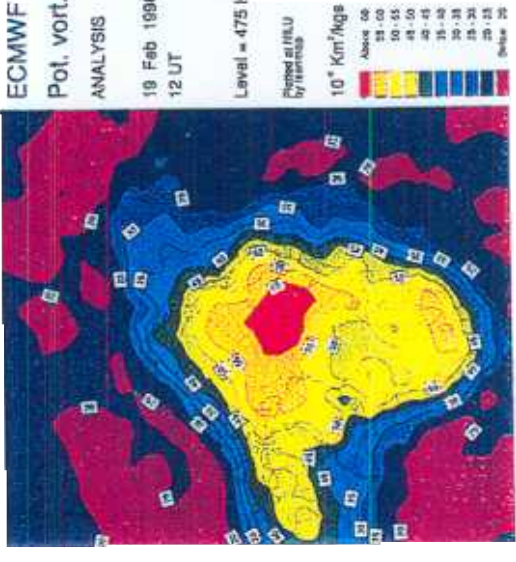
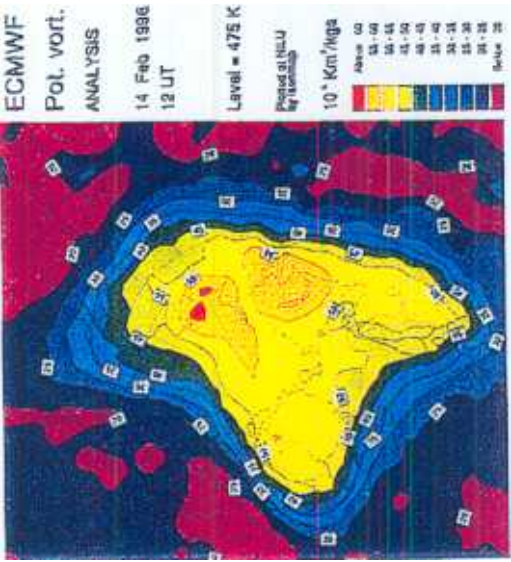
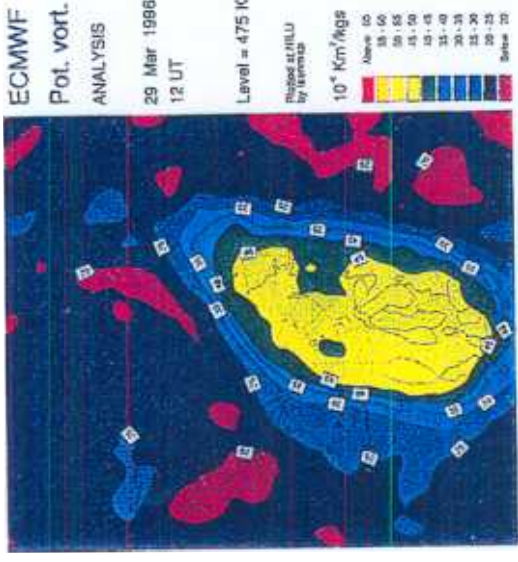
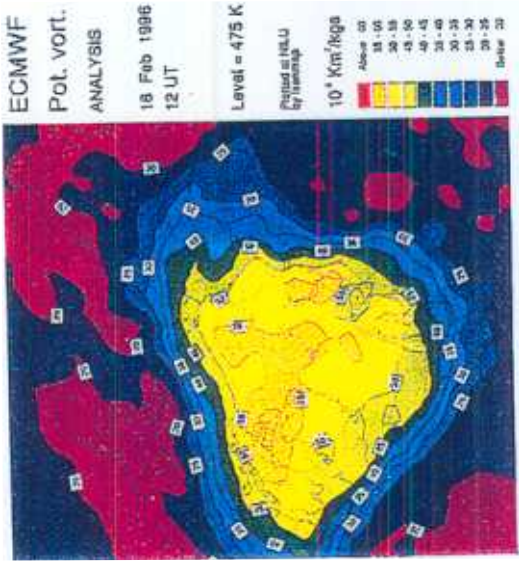


Figure 2: ECMWF potential vorticity analysis from 12 UT on (a.) 14 Feb 1996; (b.) 18 Feb 1996 and (d.) 29 Mar 1996

HCl

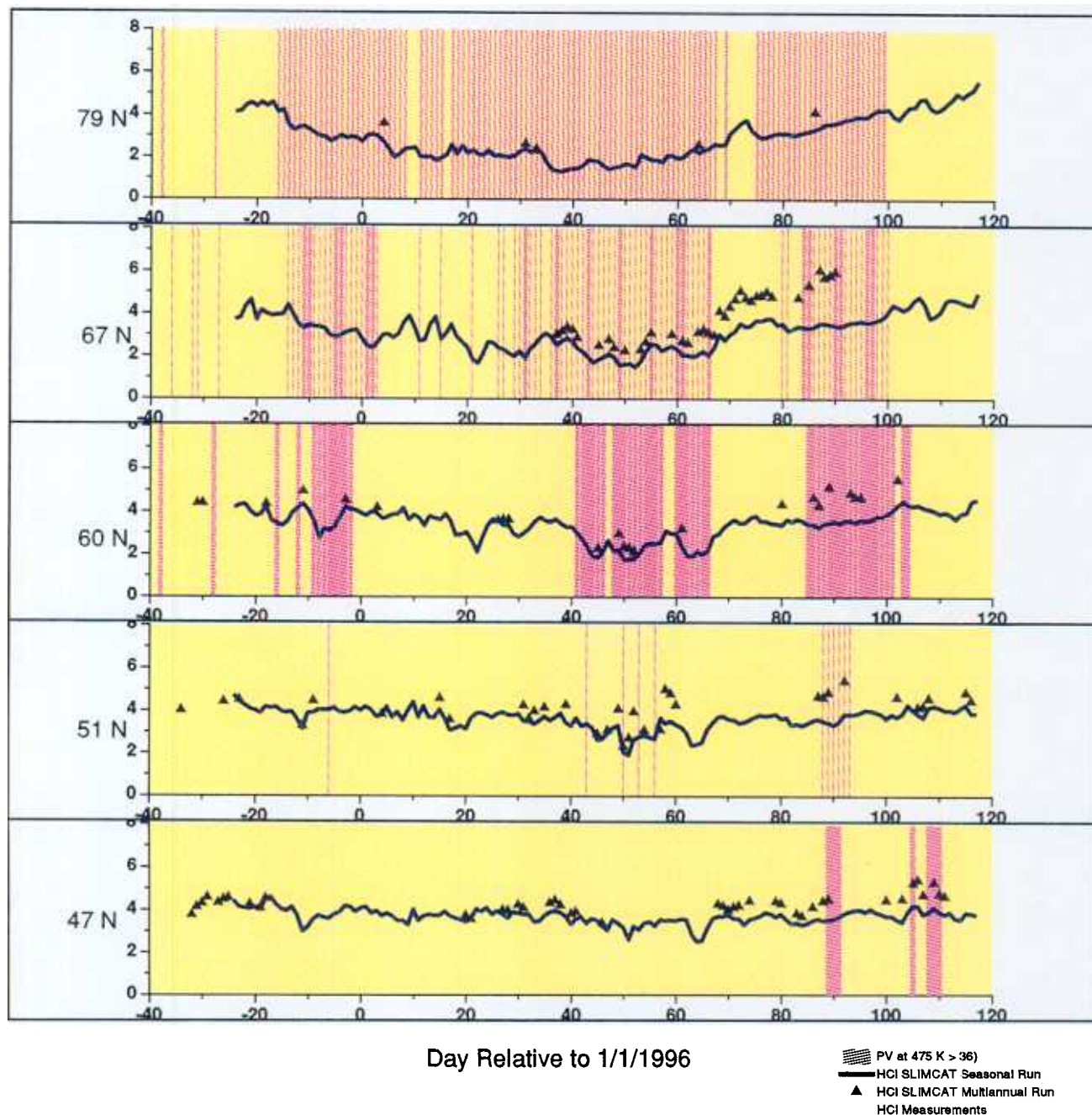


Figure 3a: Comparison of SLIMCAT modelled columns of HCl with measurements at 79°N, 67°N, 60°N, 51°N and 47°N from mid-January to mid-April 1996

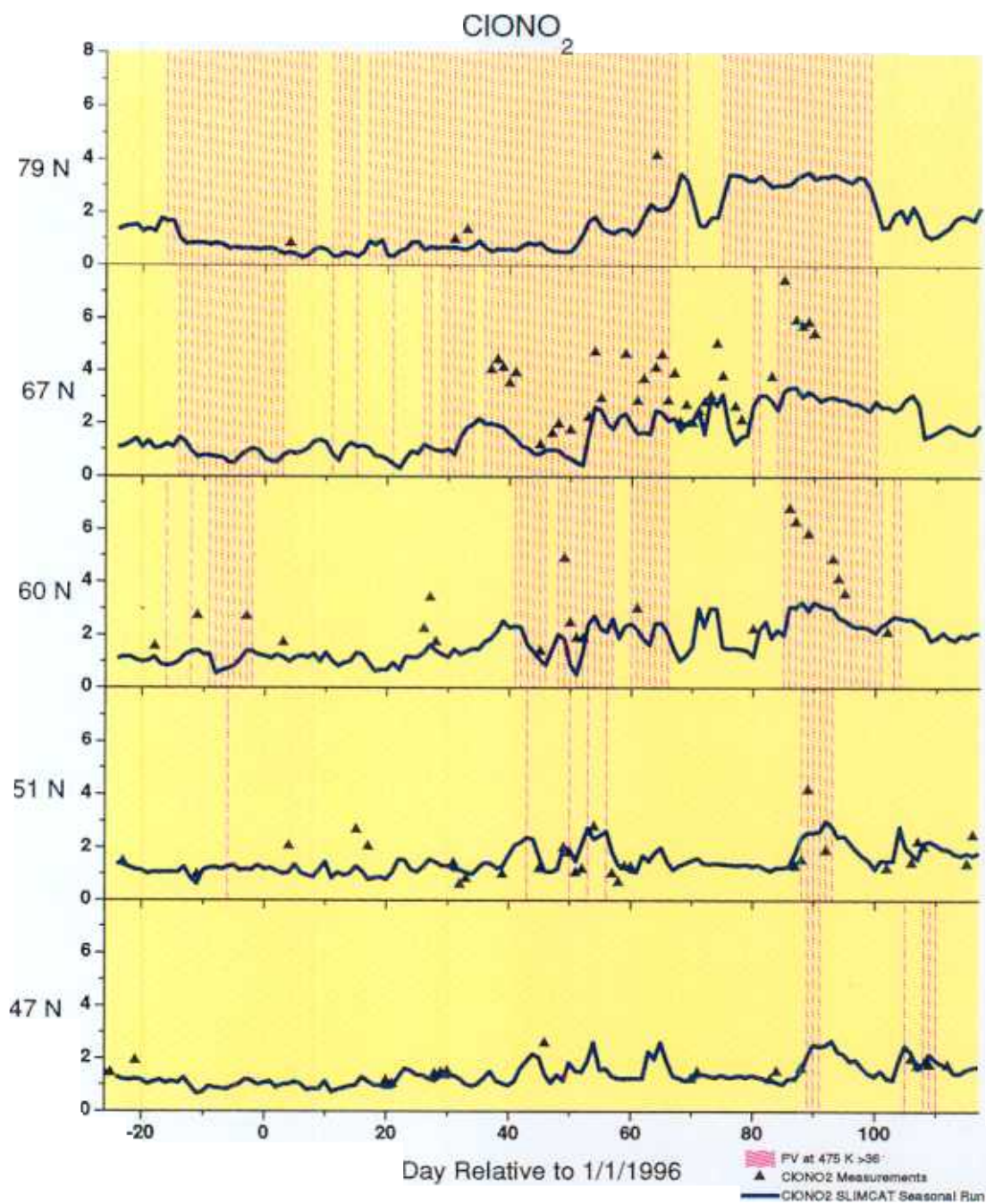


Figure 3b: Comparison of SLIMCAT modelled columns of ClONO_2 with measurements at 79°N, 67°N, 60°N, 51°N and 47°N from mid-January to mid-April 1996