FTIR and UV-Visible Measurements of Stratospheric Trace Species at Harestua, Norway during Sesame and Comparison with a 3-D Model

D.W. Arlander, J. Mellqvist[1] and B. Galle
Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-40258,
Göteborg, Sweden
M. Van Roozendael, C. Hermans, J.-C. Lambert and P.C. Simon
Belgian Institute for Space Aeronomy (IASB), 3 Avenue Circulaire, B-1180, Brussels,
Belgium
and
M.P. Chipperfield, A.M. Lee
Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge,
CB2 1EW, United Kingdom

INTRODUCTION

Vertical columns of HF, HCl, HNO_3, $ClONO_2$, N_2O, O_3, OClO and NO_2 were retrieved at Harestua, Norway (60.05° N, 10.04° E, Elevation 560 m) beginning on 24' November 1994 and concluding on 1 May 1995 during Phase-III of the recently completed Sesame measurement campaign. FTIR measurements were made with a Bruker 120 M spectrometer (Maximum Resolution = 0.0035 cm^{-1}, (0.9/OPD)). Details regarding the FTIR technique and site are given in (Galle et. al. 1995). The O_3, OClO and NO_2 column measurements were performed with two IASB UV-Visible Spectrometers (Van Roozendael et. al. 1995). The meteorological data implies that the polar vortex passed over the site several times during this period. Time trends in the data set are interpreted in relation to vortex location and chemical processing of the chlorine and nitrogen species and compared with the 3-D Cambridge model SLIMCAT.

The SLIMCAT 3-D model (Chipperfield et. al. 1995) is an off-line chemical transport model (CTM) which uses meteorological analyses to specify the wind and temperature fields. The model uses an isentropic vertical coordinate. The transport model is coupled to a detailed stratospheric chemistry model which integrates the usual Ox, NOy, ClOy, BrOy and HOx species along with some long-lived tracers (e.g. N_2O). The model has 31 chemical tracers and around 100 chemical reactions. The model also has a treatment of heterogeneous reactions on polar stratospheric clouds and sulphate aerosols.

Ground based optical remote sensing techniques such as high resolution FTIR and UV-Visible Spectroscopy enable collection of long term data sets with high time resolution of both stratospheric and tropospheric compounds. A major advantage of measuring at 60° N is the opportunity of recording data inside the polar vortex, at the vortex edge and outside the vortex over relatively short time spans, which may be repeated several times over the course of the arctic winter. Since the vortex can pass over this region several times during the winter, direct comparison of events can lead to a better understanding of the time dependent processes which lead to stratospheric ozone variations. In this presentation we attempt to interpret our vertical column data

---

[1] Also at the Department of Physics, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden.

in relation to major meteorological parameters over Harestua. Conclusions can then be drawn regarding both the chemistry and dynamics over the entire time period.

RESULTS

Time trends are shown in Figures 1-10 for each of the main compounds measured along with meteorological parameters. Modelled values are also given in many of the time trends. The SLIMCAT model starts at 350 K and the lower stratosphere and the troposphere is therefore not included in the vertical columns given. For this reason the model values have in some cases been scaled to the measured values. In general, good agreement is seen between measured and modelled values for the duration of the winter. Some discrepancy is seen for HNO_3 for week 3 (Days 24 - 28), however, due to an initialisation problem in the model which presently does not account for horizontal gradients within the vortex. For $ClONO_2$, however, the underprediction is more persistent and is seen at all sites.

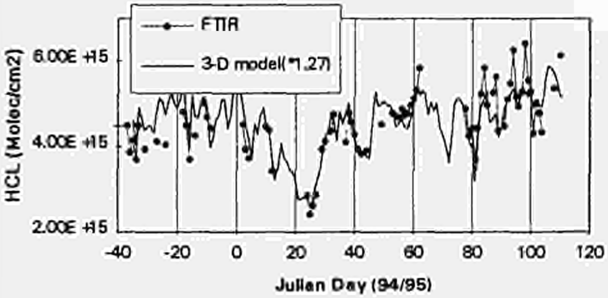

Figure 1. Time trend of HCl as measured by FTIR and predicted by the SLIMCAT model.

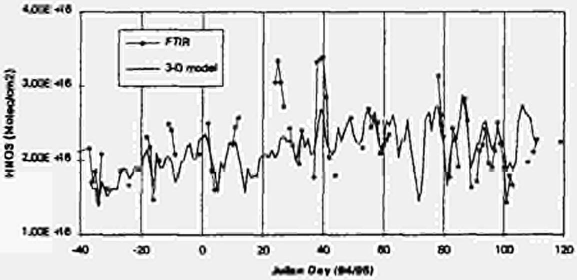

Figure 2. Time trend of HNO_3 as measured by FTIR and predicted by the SLIMCAT model.

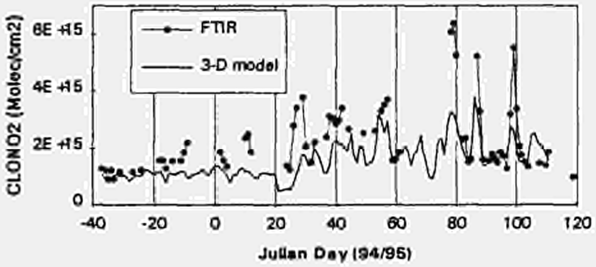

Figure 3. Time trends of $CLONO_2$ as measured by FTIR and predicted by the SLIMCAT model.

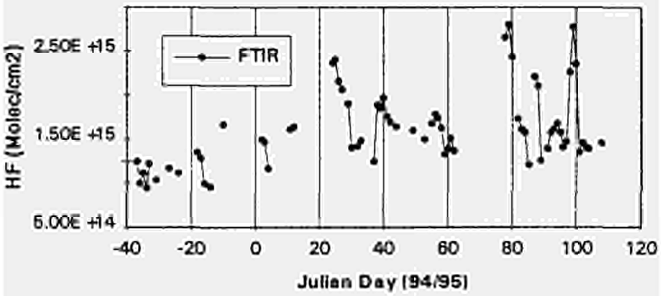

Figure 4. Time trend of HF as measured by FTIR.

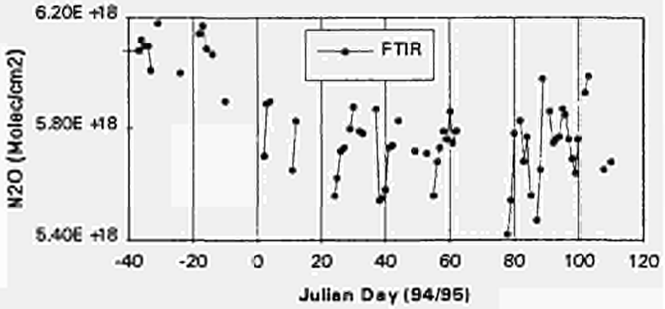

Figure 5. Time trend of N_2O measured by FTIR.

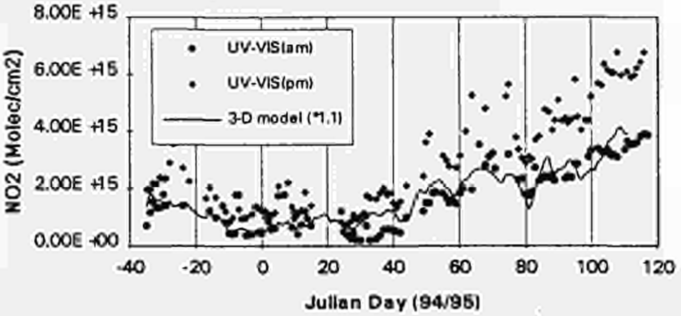

Figure 6. NO_2 time trend (am/pm) by UV-VIS and by the SLIMCAT model (13:00).

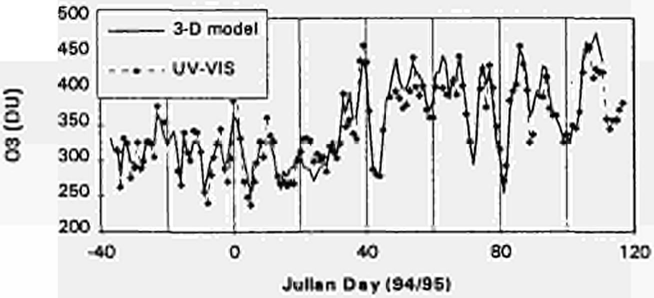

Figure 7. Time trend of O_3 as measured by UV-VIS and predicted by the SLIMCAT model.

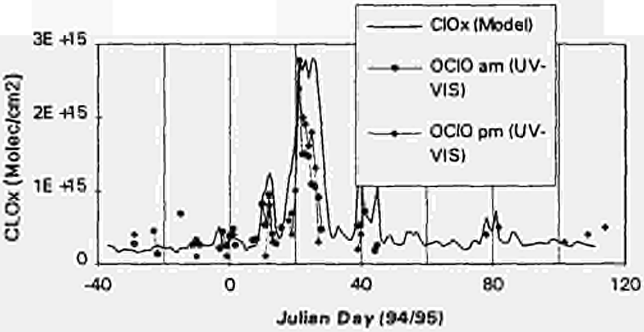

Figure 8. Time trends of CLOx predicted by the SLIMCAT model and difference in measured slant column of OClO between 91° and 82° SZA measured by UV-VIS (*10).

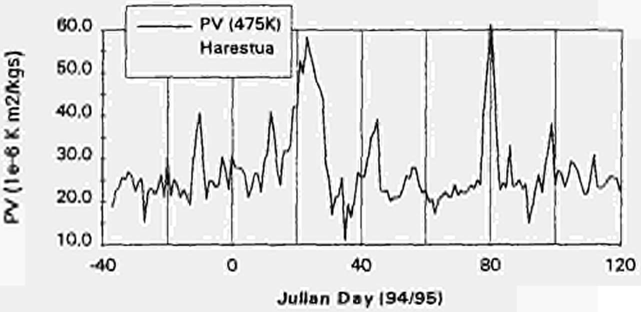

Figure 9. PV at 475 K level above Harestua obtained from ECMWF.

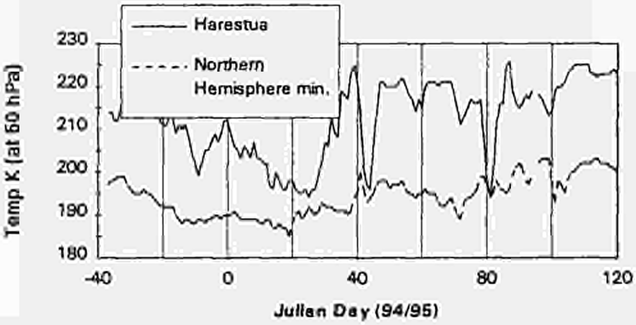

Figure 10. Temperature at 50 hPa level above Harestua and northern hemisphere minimum.

Figure 11 contains further data analyses which assist in pointing out the major chemical and meteorological processes which occurred. Main points of interest include how well the time trends of several of the species track with potential vorticity (PV), stratospheric temperature and tropopause height. The first major vortex episode over Harestua occurred during the third week of January 1995 (Days 24 - 28). This period was characterised by elevated PV values and low stratospheric temperatures. An interesting aspect here is that the ($ClONO_2$ + HCl)/HF and HCl/HF ratios had decreased to their lowest points of the winter, implying that large amounts of active chlorine (ClOx) were present as also seen by the very high OClO values. Our preliminary FTIR results of ClO during this period indicate a three-fold increase above background conditions. The highest value was observed on 25' Jan. 1995, which corresponded with the highest PV value. Vortex conditions persisted for several days. From the 50 hPa temperature plot, we assume that it was sufficiently cold (ca. 195 K) for Type-I PSCs to exist, and chemical processing of the chlorine reservoirs was in an advanced stage. From our preliminary analyses of the measured data, approximately 70% of the chlorine reservoir species were converted to activated chlorine species.

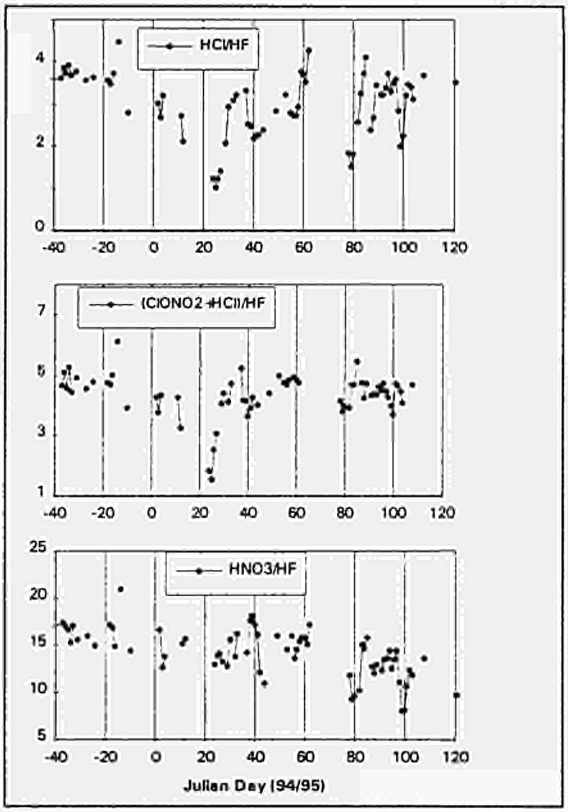

Figure 11. Ratios between several compounds and HF.

The second episode occurred in mid-late March, whereby the highest PV values of the winter, peaking on 21' March 1995 - Day 80, were seen. This event is characterised by different processes as compared to the major January event. It is apparent that the active chlorine (ClOx) which was seen in January, had been effectively converted to $ClONO_2$ by late March. This is seen most easily by comparing the ratios ($ClONO_2$ + HCl)/HF and HCl/HF for both episodes. By Day 80, ($ClONO_2$ + HCl)/HF ratios had greatly increased, whereas HCl/HF remained low. This illustrates the quicker recovery of $ClONO_2$ to that of HCl.

High values of HF and HNO_3 coinciding with high PV on Days 78/79 could imply increased subsidence, however, Days 80-82 were characterised by higher tropopause heights which caused lower HF and HNO_3 values and increased N_2O. Of these two dynamic effects, the tropopause height appears to have a more significant effect. Meteorological changes occurred very rapidly in this period which may need further investigation using high resolution models. Some OClO was observed at this time, but much lower than previously.

Minor episodes occurred on Days: -10 (21' Dec. 1994), 12 (12' Jan. 1995), 45 (14' Feb. 1995) and 99 (09' April 1995) as seen by elevated PV and OClO values which anti-correlate very well with the temperature trend at the 50 hPa level above the site. All of these dates correspond to PV values which imply near-vortex edge conditions. The later episodes show increased OCLO columns and decreased ($ClONO_2$ + HCl)/HF ratios, both of which indicate chlorine activation. The low HCl/HF ratio on Day 99 once again indicates the slow recovery rate of HCl.

The recovery of HCl to background levels by the end of the campaign was apparent, as also indicated from the decrease of $ClONO_2$ to background along with other chlorine species. This is further substantiated by measurements made in July and August of 1995. During the course of the winter, NO_2 is seen to recover slowly as HNO_3 in turn declined.

CONCLUSIONS

From the measurement and model results presented here, it can be implied that some of the processes which lead to stratospheric ozone variations can be explained. Chlorine activation processes which lead to ozone destruction appeared to play a major role during several periods above the site. When interpreting such data, it is important to examine the time trends of meteorological parameters as well as the chemical species. For such measurements, it is necessary to have high resolution data on potential vorticity, subsidence, tropospheric heights, stratospheric temperatures and evidence of the presence and type of PSC. Further modelling efforts will include short-term changes in vertical columns over a day due to vortex laminae passing over the site.

ACKNOWLEDGEMENTS

The authors thank Ole-Peder Sveen and Willy Skoglund of the Solobservatoriet Harestua, Norway for their logistical support, and Kjersti Karlsen of the Norwegian Institute for Air Research (NILU), for assistance with FTIR measurements. The Swedish contribution was supported by the Swedish Environmental Protection Agency and the Swedish Space Corporation.

REFERENCES

1.) B. Galle, J. Mellqvist, D.W. Arlander and K. Karlsen, Ground Based High Resolution FTIR Measurements of Stratospheric Molecules at Harestua Norway, Proceedings of the Third Annual Symposium on Polar Stratospheric Ozone, Schliersee, Bavaria, 1995 (This Publication).

2.) Chipperfield et. al., Three-Dimensional Modelling During Sesame, Proceedings of the Third Annual Symposium on Polar Stratospheric Ozone, Schliersee, Bavaria, 1995 (This Publication).

3.) Van Roozendael, M., C. Hermans, Y. Kabbadj, J.-C. Lambert, A.-C. Vandaele, P.C. Simon, M. Carleer, J.-M. Guilmot and R. Colin, UV-Visible measurements of Stratospheric Trace Constituents at Harestua, Norway During Sesame, Proceedings of the Third Annual Symposium on Polar Stratospheric Ozone, Schliersee, Bavaria, 1995 (This Publication).