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The development and utilisation of advanced remote monitoring techniques for atmospheric measurements

W Bell, P T Woods, N A Martin, T D Gardiner, N R Swann and C Paton-Walsh

Division of Quantum Metrology
National Physical Laboratory
Queens Road, Teddington TW11 0LW

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

Approved on behalf of Chief Executive, NPL,
by Dr J R Gott, Head, Division of Quantum Metrology

CONTENTS

Page

THE DEVELOPMENT AND UTILISATION OF ADVANCED REMOTE MONITORING TECHNIQUES FOR ATMOSPHERIC MEASUREMENTS

by

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1. INTRODUCTION

The Environmental Standards Section of the National Physical Laboratory is currently undertaking a research and development programme for the Department of the Environment under contract no. PECD 7/10/162. This report describes work carried out during the period April 1993 to March 1994. The programme is concerned with the development and utilisation of a number of complementary remote sensing instruments and associated calibration standards.

This report describes progress achieved in all areas covered by the contract. Section 2 includes an overview of the status of advanced techniques being developed at NPL for stratospheric monitoring. Sections 3 and 4 describe NPL's participation in two major European stratospheric measurement projects.

The second phase of the European Stratospheric Monitoring Stations (ESMOS II) project and the subsequent ESMOS/Arctic project.

The Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME).

2. INSTRUMENTS FOR REMOTE SENSING MEASUREMENTS OF STRATOSPHERIC COMPOSITION

2.1 GENERAL PRINCIPLES

Both instruments under development at NPL for remote sensing measurements of stratospheric composition presently operate in solar absorption mode. In this type of measurement the spectrum of sunlight is measured from the ground. The measured spectrum contains absorption features due to tropospheric and stratospheric trace species. By employing instruments capable of high spectral resolution, ($\Delta\nu/\nu < 10^{-5}$) it is possible to identify narrow stratospheric absorption features between broader, pressure broadened features due to tropospheric gases (eg

CH_4, H_2O, CO_2). A simulated transmission spectrum from 500-4000 cm^{-1} (20-2.5 μm) of the atmosphere is shown in Figure 1. Table 1 shows the species measurable by NPL remote sensing instruments and the positions of the absorption features used to derive vertical columns. Figure 2 shows schematically how infrared radiation is absorbed by atmospheric constituents as it passes through the atmosphere.

As can be seen from Figure 2 absorption lines from low-altitude layers are broader than absorption lines at high altitude due to pressure broadening. The lineshape measured from the ground is a superposition of the contributions from each layer in the atmosphere. If the lines can be measured with a high resolution instrument, where the instrument lineshape is narrower than the linewidth of the narrowest component of the absorption line, it is possible to derive information about the vertical distribution of the species being measured.

2.2 THE HIGH RESOLUTION FOURIER-TRANSFORM INFRARED SPECTROMETER (FTIR)

The principles of this technique have been described in a previous report and will not be discussed in detail here. Further details can be found in Bell et al, 1994, Adrian et al, 1994 and Notholt et al, 1994 and references therein. In summary, NPL has developed a high resolution spectrometer giving a maximum optical path difference of 2.57 m (giving $\Delta\nu/\nu < 3.2 \times 10^{-6}$) over the mid infrared region of the spectrum from 2.5-13.5 μm (750-4000 cm^{-1}). A schematic diagram of the instrument is shown in Figure 3. The detection sensitivity of this instrument has been improved during the course of this programme through employing a range of narrow band optical filters. Also, the instrument has been modified to allow measurements in both long wavelength and short wavelength channels simultaneously. These improvements have enabled NPL to measure the vertical column of $ClONO_2$, a very important temporary stratospheric reservoir, involved in chlorine catalysed ozone depletion, from a single high resolution spectrum, which can be obtained in 73 seconds. An example of a spectrum obtained with the FTIR instrument during the first phase of the SESAME campaign is shown in Figure 4. As can be seen from Figure 4, the $ClONO_2$ ν_4 Q-branch absorption is strongly blended with CO_2 and O_3 absorption lines. The retrieval of $ClONO_2$ vertical columns has required significant refinements to the fitting procedure applied to the other molecules with overlapping absorptions. This has entailed a two stage procedure. In the first stage H_2O, CO_2 and O_3 features are fitted over a broad spectral window (779.0-780.7 cm^{-1}). In the second stage the $ClONO_2$ feature is fitted over a narrower window extending from 779.9-780.3 cm^{-1}. The estimated detection limit, expressed as a slant column (slant column = vertical column x airmass factor), is estimated to be 2×10^{15} mol cm^{-2}. It should be noted that

typical vertical columns at mid latitudes during winter/spring are of the order 1-2 x 10^{15} mol cm^{-2}. However, at latitudes of 60°N during winter it is possible to make measurements with zenith angles of greater than 80°, giving airmass factors of 5 or more (ie slant columns of greater than 5 x 10^{15} mol cm^{-2}). It is therefore possible to measure ambient columns of $ClONO_2$ using this technique with an accuracy of about 20%.

THE TUNABLE DIODE-LASER HETERODYNE SPECTROMETER (TDLHS)

General

A brief description of the spectrometer has been given in a previous report. A schematic diagram of the present TDLHS is given in Figure 5. During the EASOE campaign in the winter of 1991-1992 the NPL TDLHS was successfully deployed in Åre, Sweden to measure vertical columns of $ClONO_2$ for the first time together with HNO_3. Previously the TDLHS was shown to be capable of detecting O_3 and HNO_3 from the International Scientific Station of the Jungfraujoch (ISSJ) Switzerland.

Examples of Results

(i) Chlorine nitrate data

An example of high resolution heterodyne data recorded on 24th January 1992 at Åre Sweden is shown in Figure 6. This spectrum covers the ν_4 Q-branch of $ClONO_2$ at 780.2 cm^{-1} and the residuals yield a total column of 1.6 x 10^{15} molecule cm^{-2}. The measurements are from a period when Åre was outside the Artic polar vortex as defined by the dynamic tracer potential vorticity (B Knudsen, private communiation). The $ClONO_2$ total column is close to the typical mid-latitude value reported for the ISSJ of 1.55 x 10^{15} molecule cm^{-2} under unperturbed conditions (Zander et al, 1993). It is also consistent with early winter measurements of Adrian et al (1994) during EASOE. This contrasts with higher burdens that have been observed in late winter (Notholt et al, 1994; Adrian et al, 1994) where there is sufficient NO_2 present from HNO_3 photolysis to react with any available ClO (Toohey et al, 1993).

(ii) Nitric acid data

More recently HNO_3 measurements recorded at Teddington (51.5°N, 0.5°W), have focused on testing the suitability of the TDLHS as a portable instrument for long-term monitoring of stratospheric species at remote sites. The selected local oscillator (LO) has been temperature cycled several times since the EASOE campaign. It remains

capable of single mode operation over the ν_5 HNO_3 P-branch manifold near 870.3 cm^{-1}.

Table 2 gives a summary of the average HNO_3 total columns for the period between 18th January and 15th April 1993 for which solar data could be acquired at Teddington. Figure 7 is a typical fit for this species and was recorded during 2nd April 1993. The total HNO_3 column derived from this single scan is 1.69 x 10^{16} molecules cm^{-2} while the average for the time series is 1.65 (± 0.32) x 10^{16} molecule cm^{-2}. This data represents one of the first regular nitric acid measurement sets at these latitudes.

The columns lie between typical values reported for the ISSJ at 47°N (Zander et al, 1993) and Kiruna, Sweden (67.9°N) (Adrian et al, 1994). This is reasonable since the vertical column of HNO_3 is known to increase with latitude. Variations in the columns reflect atmospheric transport from other latitudes together with the competing processes of HNO_3 photolysis, and reaction of OH with NO_2.

As a result of the Mount Pinatubo eruption of 1991 there are also contributions from the following heterogeneous processes on sulphuric acid aerosols

$$N_2O_5 + H_2O \rightarrow 2HNO_3\ (g) \qquad (2.3.1)$$

$$ClONO_2 + H_2O \rightarrow HNO_3\ (g) + HOCl\ (g) \qquad (2.3.2)$$

These convert NO_x to HNO_3 in the gas phase, and enhance the role played by ClO_x and HO_x families. These processes have been proposed to explain the facts that enhanced burdens of HNO_3 are detected in polar regions, and that of chlorine activation occurs even when temperatures are too high for the formation of PSCs (Rodriguez et al, 1991; Keys et al, 1993; Solomon et al, 1993).

Although laboratory studies have shown that reaction 2.3.1 is efficient at all temperatures, the chemical process rapidly "saturates" if the stratospheric aerosol loading is sufficiently high. The reaction then becomes limited by the nighttime formation of N_2O_5 (Fahey et al, 1993). Also at the temperatures of the mid-latitude stratosphere reaction 2.3.2 may only play a minor role since with its negative temperature coefficient it only becomes comparable to process 2.3.1 at 200K.

During the period of measurements at Teddington the stratospheric aerosol loading is likely to have returned to background levels (Brasseur and Granier, 1992) and thus any heterogenous contribution to the total column is probably small.

TDLHS Measurements during SESAME

Although the main objective of the TDLHS project (Jan 1994-Dec 1996) which is currently supported by the EC is the development of a new portable instrument, based on advanced technology, which can be used at remote sites, it has been used on an opportunity basis to make measurements at Teddington during SESAME Phase I.

In contrast to Aberdeen site logistical problems have up to now prevented measurements from being made at solar zenith angles of greater than 65°. This is just sufficient to detect the ambient unperturbed levels of $ClONO_2$ without a thorough analysis of the data. It is however possible to derive total O_3 columns from the neighbouring spectral transitions. These are summarised in Table 3 for the period 13th January to 14th February 1994.

TDLHS European Collaboration

The current programme includes an EC collaboration between the University of Reims (France), Fraunhofer Institute of Physical Measurement Techniques (IPM) in Freiburg (Germany) and NPL under Contract No. EV5V-CT93-0350 (DG 12SOLS). The main aims of the project are to develop a compact ground based TDLHS which is portable and therefore more suited to field measurements. It is targeted at improving the current monitoring capability of the reservoir species $ClONO_2$ and HNO_3 with a high spectral resolution and high signal to noise ratio (SNR).

Although the selected trace molecules absorb at long wavelengths where the heterodyne efficiency increases the present quality of lasers in this region requires improvement. Efforts are being aimed at developing lasers with low rf noise that will operate at liquid nitrogen temperatures thereby removing the necessity for a closed-cycle helium cooler. In addition, the technique of strong external LO feedback will provide single-mode emission with a narrow linewidth. This is designed to provide an enhanced signal to noise ratio (SNR) when recording solar spectra in the heterodyne mode.

Preliminary tests at 9.4 μm have been carried out at the University of Reims to assess the status of the local oscillator laser package produced by the IPM. These experiments have involved all three of the participating groups. A $^{12}C^{18}O_2$ laser emitting at 1067.35887 cm^{-1} (9P(22) transition) with a linewidth of less than 1 MHz has been heterodyned against a liquid nitrogen cooled laser at the same frequency. Precise wavenumber calibration of the diode was achieved by employing a cell filled

with O_3 and a Fabry-Perot étalon with a free spectral range of 0.01 cm^{-1}. The laser diode was mounted in a new package which allows access to the emitted radiation from both emitting faces of the laser. The output from one face provides the strong optical feedback when coupled to an external resonator. This consists of a diffraction grating with a fine piezo-electric adjustment. However the present resonator package has been found to be extremely sensitive to mechanical vibrations and is being improved.

Figure 8 shows two traces from a spectrum analyser of the $^{12}C^{18}O_2$/TDL heterodyne beat received from the 1.5 GHz photomixer. Without any external feedback, the TDL linewidth was estimated to be of the order of 100 MHz (FWHM). This was reduced to 60 MHz when coupled to the resonator and demonstrates for the first time that line narrowing can be achieved using liquid nitrogen cooled mid-infrared lasers.

Further work is underway to fabricate lasers at the target wavelengths of 12.8 μm and 11.5 μm operated above 77K. A method for tuning the external resonator to provide a typical 1.5 cm^{-1} scan is being implemented.

3. THE SECOND EUROPEAN STRATOSPHERIC MONITORING STATIONS (ESMOS II) PROJECT

The ESMOS project is the European contribution to the global Network for the Detection of Stratospheric Change (NDSC). ESMOS II is the second phase of this project.

Fourier-transform infrared (FTIR) spectroscopy is a powerful measurement technique and has been used widely to conduct remote sensing measurements of stratospheric trace constituents. FTIR instruments are deployed at all the primary sites of the Global Network for the Detection of Stratospheric Change (NDSC) to provide measurements of a wide range of key trace atmospheric species not detectable by other techniques.

The role of NPL involves providing a transfer standard instrument for use at different NDSC sites and organising intercomparison studies. This is recognised as an essential component of the Network by the NDSC Infrared Working Group and by operators of the primary NDSC sites. In this way, NPL, and DoE, maintain a strong presence in the NDSC, and have access to all of the results, without the long-term commitment that is required of an operator of an instrument at a primary site.

FTIR measurements have been carried out throughout the ESMOS II project at a number of sites in Europe:

The International Scientific Station of the Jungfraujoch (ISSJ), Switzerland (46°N, 8°E);

Ny-Ålesund, Spitzbergen (79°N, 12°E). This site represents the main European contribution to the NDSC Arctic Station;

Kiruna, Sweden (68°N, 21°E). Measurements complementary to the NDSC data set are made at Kiruna every winter on a campaign basis by a research group from the Kernforschungzentrum, Karlsruhe (KfK) Germany.

It is important that the column concentration values derived from these measurements are validated so that comparisons can be made between the observed trends in the concentrations of trace species at each site.

It is generally agreed amongst NDSC measurement groups that there are two main components involved in the process of ensuring the results from all NDSC sites are intercomparable:

(i) Verifying that the raw data obtained from the instruments is comparable, and

(ii) Ensuring that this raw data is analysed in a consistent way by all groups.

NPL have been active in both aspects of this process by conducting instrument and algorithm intercomparisons exercises.

The results of the instrument intercomparisons at Denver, Jungfraujoch and Kiruna have been described in the report covering work carried out during the period April 1992 to March 1993.

During the reporting period April 1993 to March 1994 NPL took part in an algorithm intercomparison. In the first phase of this exercise a number of spectra of the species HCl, HF, N_2O and HNO_3 together with appropriate instrument parameters (field of view and resolution) and atmospheric parameters (pressure, temperature and mixing ratio profiles) were circulated to the groups involved in the ESMOS project. The spectra were fitted independently and vertical columns derived for these compounds. Within the specified fitting constraints for this exercise there was still sufficient freedom to allow the assumed volume mixing ratio of the molecule to be changed.

The results were discussed at a workshop in Karlsruhe on 15/16th June 1993. The agreement between the groups is shown in Table 4. As can be seen from Table 4 the 1σ standard deviations for the vertical columns of the species HCl, HF, N_2O and HNO_3 are 4% 6% 2% and 2% respectively. A second phase of the exercise was organised in which the atmospheric and instrument parameters were more rigidly specified. Vertical columns were produced by all groups involved in the operation of all the NDSC sites as well as other important groups involved in FTIR measurements. The results of this exercise were discussed at a workshop in Brussels on April 20th-21st 1994. The vertical columns produced are shown in Table 5. As can be seen from Table 5 the agreement for the species HCl, HF, N_2O and HNO_3 is 1.4% 1.7% 1.1% and 2.2% respectively. Some residual differences remain. These are largely due to the way in which individual groups have interpolated the pressure, temperature and volume mixing ratio profiles to suit their own code grid spacing. A third phase of the exercise is underway to further reduce the residual differences.

A further issue requiring thorough evaluation if the accuracy of the results are to be improved is the accurate characterisation of the FTIR instrument function. NPL are now taking the lead in developing technology to do this on a regular basis. Once developed it is anticipated that this technology will be taken up at all NDSC sites.

4. THE SECOND EUROPEAN STRATOSPHERIC ARCTIC AND MID LATITUDE EXPERIMENT

4.1 BACKGROUND

The European Arctic Stratospheric Ozone Experiment (EASOE) campaign took place in the winter/spring of 1991/92. It was the first coordinated European measurement campaign aimed at understanding ozone loss in the northern hemisphere and involved over 200 scientists from Europe and elsewhere.

The EASOE campaign had a number of specific objectives as part of the overall aim to understand northern hemisphere ozone loss. These included:

(i) Measuring the climatologies of ozone and related species and polar stratospheric clouds, and improving understanding of polar vortex dynamics.

(ii) Carrying out case studies of fast chemistry by measuring simultaneously nitrogen, chlorine and bromine oxides at a range of latitudes and longitudes,

inside and outside the polar vortex from autumn till spring.

Carry out case studies of tropospheric synoptic and orographically forced ozone mini-holes and polar stratospheric clouds in autumn and winter.

Conduct complementary observations from aircraft and balloons for operational forecasting and for post-campaign data interpretation.

The EASOE campaign was successful in a number of key areas:

(a) Chemical Processing

EASOE provided a good picture of the extent of production of active chlorine within the polar vortex. For example, during the EASOE winter, from mid December to late January the polar vortex contained high levels of ClO.

The NPL measurements of the main chlorine reservoir HCl from Åre, Sweden (64°N, 13°E) were negatively correlated with satellite measurements of ClO around this time. The decline of active chlorine into the reservoirs $ClONO_2$ and HCl late in the winter was determined in the EASOE campaign from balloon, aircraft and groundbased measurements.

However, during the campaign there were few simultaneous measurements of all the main inorganic chlorine species (Cl_y) which would have described fully the partitioning within the chlorine family and its temporal evolution as the polar vortex formed and subsequently decayed. In addition there were no high spatial resolution measurements of ClO in the lower stratosphere. The conclusions regarding the extent of processing were largely inferred from column concentration measurements of HCl and $ClONO_2$ from the ground (such as those reported by NPL) and from limited sounding measurements of OClO, HCl and $ClONO_2$, giving some vertical profile information. Microwave measurements obtained from the ground and aircraft provided vertical columns of ClO.

(b) Ozone in Winter and Spring

Ozonesonde measurements of ozone concentration profiles during the autumn-to-spring period provided a detailed picture of the evolution of ozone, and led to an improved understanding of ozone in relation to dynamical processes. This dataset has been used to quantify chemical ozone loss within the polar

vortex.

However from the EASOE ozone data it was not possible to quantify ozone loss outside the vortex.

(c) Sulphate Aerosol

Following the eruption of Mount Pinatubo, the EASOE measurements provided a good dataset for studying the distribution and morphology of sulphate aerosols. Furthermore, the EASOE measurements of NO_x demonstrate the role of their reactions on sulphate aerosols.

However the exact role played by sulphate aerosol in stratospheric chemistry and its radiative impact still remains to be understood in detail.

(d) Polar Stratospheric Clouds (PSCs)

A number of measurements of PSCs were made during EASOE from both aircraft and groundbased platforms, and they have contributed significantly to our knowledge of the extent and type of PSCs present.

However our understanding of physico-chemical processes involving PSCs was hampered by their contamination with sulphate aerosols from the Mount Pintubo eruption. In addition, there were no in-situ measurements of the chemical composition of PSCs.

(e) The Role of the Polar Vortex

The combination of the results of EASOE measurements and meteorological data has been employed to provide a clearer picture of processes occurring in and at the edge of the polar vortex. For example, strong gradients in the tracer concentrations against potential vorticity were found. This implied that the largest concentrations of available (active) chlorine occurred deep inside the vortex.

However more comprehensive measurements of tracers at different positions in the vortex are necessary in order to carry out a full range of studies of vortex dynamics.

(f) Middle-Latitude Ozone Loss

The results obtained during EASOE appear to indicate that stratospheric ozone losses which occur at middle latitudes during early and mid winter were not due in any large extent to mixing of air between the vortex and middle latitudes. However, the displacement of the vortex over middle latitudes probably contributed to middle-latitude ozone loss later during the EASOE winter. Hence the findings of the EASOE campaign highlighted the need for further studies on the issue of middle latitude ozone loss and the following points emerged as central in the planning of a follow-on campaign.

the causes of ozone depletion outside the polar regions remained controversial. Three potential contributing factors to this middle latitude ozone loss are:

production of active chlorine by PSCs outside the polar region;

- heterogeneous reactions on sulphuric acid aerosol;

- transport of ozone poor air from regions of significant ozone depletion.

4.2 THE SESAME CAMPAIGN

In view of the above it is clear that the highest priority objective for the SESAME campaign should be to understand more fully the observed long-term decline in ozone concentrations in latitudes below those where the polar vortex occurred consistently. The specific measurement objectives for SESAME thus include:

(i) the study of chlorine partitioning at high to mid latitudes before, during and after the cold period during winter;

(ii) the study of nitrogen partitioning;

the study of HO_x species;

PSCs and aerosol measurements, in particular in-situ measurements of PSC composition and PSC-induced heterogeneous chemistry;

(v) a network of groundbased and sonde measurements of ozone concentrations;

(vi) targetted measurements at latitudes intermediate between high polar latitudes (>67°N) and mid latitudes (40-50°N) of a wide range of important chemical stratospheric species.

NPL was asked to coordinate an EC project designed specifically to address the requirements outlined in (vi) above.

The project, entitled "Groundbased Measurements of Stratospheric Trace Species Around 60°N as part of SESAME" aims to install and operate high quality infrared and ultraviolet groundbased remote sensing instruments at a number of sites around 60°N in order to measure trends in the column amounts of important trace species. By using the complementary measurement capabilities of UV-visible instruments (O_3, NO_2, OClO, BrO) and infrared instruments (HCl, $ClONO_2$, HNO_3, F-22, N_2O and HF) it is possible to:

1) Determine the partitioning within the Cl_y family (through measurements of $ClONO_2$, HCl and OClO) and thereby determine the extent of heterogeneous processing;

2) Determine to some extent the partitioning within the NO_y family through measurements of HNO_3, NO_2 and N_2O;

3) Determine the dynamical and transport related contributions to the time series of the measured concentrations through measurements of the tracers HF, N_2O and HNO_3.

The sites chosen for this project were:

1) Aberdeen, UK (57°N, 2°W) where NPL conducted measurements using FTIR and the University of Wales conducted UV/visible measurements during Phase I.

2) Southern UK (51°N) where a team from the Rutherford Appleton Laboratory will conduct FTIR measurements during Phase III. In addition, a team from Cambridge University conducted measurements during Phase I from Cambridge.

3) Harestua, Norway (60°N) where a team from the Swedish Environmental Institute will conduct FTIR measurements during Phase III. In addition a group from Belgium conducted UV-visible measurements during Phase I.

4) Keflavik, Iceland (64°N) : where a team from INTA Spain is conducting UV-visible measurements.

5) Jenessai, Siberia (60°N, 90°E) : where a team from MPI Germany will conduct UV-visible measurements.

The location of the sites is shown in Figure 9.

The participants in this project are given in Annex 1. NPL is concerned with the management and organisation of the work of these institutes and with providing an overview of the results obtained.

4.3 MEASUREMENTS FROM ABERDEEN, UK DURING SESAME PHASE I

Introduction

Vertical column amounts of HCl, $ClONO_2$, HF, HNO_3, N_2O and O_3 have been derived from groundbased FTIR measurements from Aberdeen, UK (57°N, 2°W) during the period 13th January 1994-8th May 1994. (Laboratory work is also proceeding to determine which other stratospheric species can be detected). The observed temporal trends in these species are compared in this Report with the dynamical situation in the stratosphere through the use of potential vorticity and trajectory analyses. The partitioning of chlorine between the main reservoir forms, HCl and $ClONO_2$, inside and outside the vortex is also presented in terms of our present understanding of chlorine activation and recovery. Estimates of the extent of stratospheric subsidence within the vortex have been derived from trends in the tracer species HF, N_2O and also HNO_3. These are also summarised below.

Experimental and Data Analysis

The measurements described here were conducted using a Bruker 120M high resolution FTIR spectrometer operating in solar absorption mode. The instrument has been summarsied earlier in this report (Section 2.2) and described in an earlier report.

HCl, HF, N_2O, HNO_3 and O_3 vertical columns were obtained by fitting the observed spectral data using a non-linear least-squares fitting procedure. The fitting procedure involves uniformly scaling an initial guess concentration profile at all altitudes until the simulated absorption feature matches the observed feature. With very high resolution spectra ($\Delta\nu < 0.01$ cm^{-1}), where pressure broadening effects on observed spectral lines are discernible, it is theoretically possible to modify the shape of the

initial concentration profile to optimise the quality of the fit. Work is proceeding to utilise this for future measurements. However, currently the results of all infrared measurements worldwide are processed in this manner. This lack of detailed knowledge of the form of the altitude distribution of the absorber is the dominant source of uncertainty in the vertical columns of HCl, HF, HNO_2 and N_2O and is estimated to be 6% (2σ).

$ClONO_2$ vertical columns are derived from spectroscopic measurements of the ν_4 Q-branch at 780.22 cm^{-1}. This feature is strongly blended with CO_2 and O_3 absorptions. Therefore, in order to optimise the signal-to-noise ratio and to minimise infrared detector non-linearities in this spectral region, a 10 μm long wavelength pass filter was used in conjunction with a liquid nitrogen cooled narrow-band mercury cadmium telluride (MCT) detector, giving an effective optical pass band of 750-1000 cm^{-1}. An example of a chlorine nitrate spectrum obtained using this technique is given in Figure 4. Absorption cross sections at the relevant stratospheric temperatures were obtained from linear interpolation from laboratory measurements at 213K and 296K.

Pressure and Temperature profiles were obtained from ozonesonde measurements made from Lerwick (60°N). These sondes were launched three times per week. The measurement uncertainty arising from the assumed pressure and temperature profile is estimated to be of the order of 5% (2σ).

4.3.3 **Results**

The time series of vertical column amounts is shown in Figure 10. Figure 11 shows as an example, the hemispheric field of Potential Vorticity at 475K, in the period days (74 - 81) when Aberdeen was within the polar vortex. Figure 11 shows the 10 day back trajectories at 475K ending over Aberdeen during the same period, which show that the stratospheric temperature was below the threshold temperatures (T<193K) for type I PSC production.

4.3.4 **Discussion of the Results**

The following represent limited examples of the conclusions which will be derived from the results, once the entire SESAME campaign has been completed, and the results from all the projects discussed and coordinated.

(a) Chlorine reservoirs

During February, Aberdeen was outside the polar vortex. Elsewhere, it has been

noted that northern-hemisphere stratospheric temperatures at 30 hPa pressures were warmer than the long-term monthly means. It is therefore reasonable to assume that the observed HCl and $ClONO_2$ vertical columns were representative of normal values. This assumes that no extensive prior heterogeneous chemical processing of stratosphere has taken place. This assumption is supported by measurements of ClO by the Microwave Limb Sounder during December - February 1994 (Waters, private communication). Outside the vortex, the approximate ratio of HCl and $ClONO_2$ vertical columns was around 2:1 (4.4EI5 : 2.5EI5). This balance is changed during the period days 74-81 when the HCl columns fell to a minimum of 2.72EI5 mol cm^{-2} (day 76). During the same period the $ClONO_2$ columns anticorrelated with the HCl columns with the $ClONO_2$ burden increasing to a maximum of 7.23E15 mol cm^{-2} (day 78). These high $ClONO_2$ values are of the same order as those observed in March 1992 during EASOE at higher latitudes (see Adrian et al, 1994, Notholt et al, 1994 and Oelhaf et al, 1994).

Figure 10 clearly shows Aberdeen to be within the polar vortex during most of this period. Radiosonde measurements from Ny Ålesund, Spitzbergen (79°N) show that for a period of around 10 days in early March (approximately 1st to 10th March) temperatures in the altitude range 18-25 Km were below PSC threshold temperatures. This is supported by the back trajectory analyses shown in Figure 12, which show that air parcels arriving over Aberdeen during days 73-81 had passed through this cold centre and it is thus reasonable that PSC induced chlorine activation occurred during this time.

From the data the total amount of chlorine in reservoir forms (HCl and $ClONO_2$) has been evaluated and this is shown in Figure 13. This total column is in agreement with the total stratospheric inorganic chlorine burdens (Cl_y) where have been estimated from balloon measurements of organic chlorine compounds during EASOE of 5-10E15 mol cm^{-2} (Schmidt et al, 1994).

(b) Stratospheric Dynamics Inferred from Tracer Measurements

The species HF has a stratospheric source, it is inert, and its column is almost entirely stratospheric. The use of measured HF vertical column amounts as a good indicator of stratospheric dynamics has been discussed elsewhere (Toon, 1992). Groundbased measurements of N_2O can also be used as an indicator but are less useful because of the large tropospheric component of the vertical column (~85%).

From Figure 10, it can be seen that when Aberdeen is inside the vortex during days 74-81, the HF column is elevated by comparison to February values of 1.25 E15

mol.cm^{-2} to more that 2.0E15 mol cm^{-2}. Calculations show that this observed increase in the HF column results from a subsidence of 4 km at the 475K potential temperature level (approximately 19km). This value for subsidence within the vortex is consistent with subsidence rates calculated from balloon based in-situ measurements of N_2O inside the polar vortex during EASOE (Schmidt et al, 1994) and groundbased mm-wave measurements of N_2O profiles also obtained during the EASOE campaign (Emmons et al, 1994).

The NPL results obtained have demonstrated the ground-based measurements of HF can be used as a regular indicator of stratospheric dynamics.

The measurements therefore reaffirm that subsidence within the polar vortex greatly enhances the amount of chlorine, normally in reservoir forms, which is available for activation in the lower stratosphere. Furthermore, the results show that these enhanced chlorine burdens can persist until late March at latitudes of 57°N.

4.3.5 **Summary**

The data presented above are examples of measured results which provide a picture of the composition of the Artic polar vortex that is broadly consistent with present understanding of PSC-induced chlorine activation from reservoir forms to active forms (ClO_x). This is followed by a recovery stage in which ClO_x is converted to $ClONO_2$ through the reaction $ClO + NO_2 \rightarrow ClONO_2$. The budget of Cl_y inferred from the measurements is consistent with previous estimates and the peak $ClONO_2$ vertical columns (observed after the recovery stage) are comparable to those observed at a similar phase in the EASOE campaign. The behaviour of the dynamical tracer HF, and to a lesser extent N_2O and HNO_3 indicate subsidence has taken place within the vortex and the estimated extent of this subsidence is consistent with limited less accurate previous estimates.

4.4 COMPARISONS WITH 3D MODELS

One of the fundamental aims of coordinated measurements campaigns such as EASOE and SESAME is to provide an ability to predict future trends in stratospheric ozone. Atmospheric models are potentially very powerful tools for understanding the observed trends in ozone concentrations. However, it is important that any model is compared with a broad range of observational data in order that it can be demonstrated to be consistent with existing data, before any scientific significance is attached to the predictions made by the model. In addition, the model can be used

to provide powerful insights into the physico-chemical processes underlying observational data.

Preliminary comparisons have been made between the NPL dataset obtained during Phase I of SESAME and a three-dimensional atmospheric model currently under development at Cambridge University. The 'Toulouse Off-line Model for Chemistry and Transport' (TOMCAT) uses prescribed wind and temperature fields to advect chemical tracers. Coupled to this transport model is a detailed stratospheric chemistry module containing a comprehensive treatment of gas phase chemistry and heterogeneous chemistry on polar stratospheric clouds and sulphate aerosols. When the wind fields are taken from meteorological analyses, the model is constrained so that direct comparison can be made between the model fields and measured data. This process represents the most powerful technique for constraining and improving three-dimensional predictive models.

A model run, initialised in mid December 1993, was used to generate a time series of vertical columns of HCl, $ClONO_2$, N_2O and HNO_3 over the same period the NPL SESAME Phase I measurements were made. A comparison between observed and modelled columns over Aberdeen is shown in Figures 14(a)-(c). This is the first time that such detailed comparisons have been made in Europe. Several points emerge from this model/data comparison:

(i) The magnitude of the day to day variability is well reproduced for all species.

Qualitatively, the trends observed in the period day 71 - day 82 are reproduced in the model. However:

The modelled HCl columns are systematically higher than the observed columns by 0.5-1.0 x 10^{15} mol cm^{-2} (10%-25%), and modelled $ClONO_2$ columns are systematically low by a similar amount. During the period day 71 - day 82, when Aberdeen was within the polar vortex, the discrepancy between the modelled and observed columns is greater. This indicates that the modelled partitioning within the Cl_y family differs from observations. The time series of modelled and observed (HCl + $ClONO_2$) shows that inside the vortex the modelled (HCl + $ClONO_2$) values are less than the observed value by up to 3 x 10^{15} mol cm^{-2}. The probable cause of this discrepancy is the upper boundary of the model at 10 mb. This results in the model failing to take account of the descent of air from altitudes higher than 10 mb.

This comparison study is ongoing and has already proved important in the process

of refining atmospheric models, and in defining the type and accuracy of field measurements required to constrain models critically.

A study is also underway to compare a set of high spatial-resolution chemical model runs with high time resolution groundbased FTIR measurements of key trace species, in an attempt to identify and measure the composition of filamentary structures which are continually shed from the polar vortex. These structures are considered to play an important role in transporting chemically processed/ozone poor air from high to mid-latitudes.

LIST OF TABLES

LIST OF FIGURES

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Species	Absorption Feature used for Column Retrieval
HCl	2925.9 cm^{-1} (R1)
HF	4038.9 cm^{-1} (P2)
$ClONO_2$	780.2 cm^{-1} (ν_4 Q-branch)
HNO_3	865-870 cm^{-1} (ν_5 P-branch)
N_2O	2480-2485 cm^{-1} (combination band, R-branch)
O_3	779-781 cm^{-1} (ν_2, multiple lines)
CFC22	829.0 cm^{-1} (Q-branch)
CFC12	920-925 (Q-branch)

TABLE 1: Atmospheric trace species measurable by NPL remote sensing instrumentation

Date	Mean Total HNO_3 Column/10^{16} molec.cm^{-2}
18/1/93	1.710
19/1/93	1.680
19/3/93	1.718
23/3/93	1.170
25/3/93	1.350
29/3/93	1.573
2/4/93	1.716
15/4/93	2.260

TABLE 2: HNO_3 columns measured by TDLHS in the period January-April 1993, from Teddington

Date	Total ozone Column/10^{16} molec.cm^{-2}
13/1/94	1.110
14/1/94	1.190
16/1/94	1.150
19/1/94	0.885
26/1/94	0.976
30/1/94	0.829
10/2/94	1.329
12/2/94	1.392
14/2/94	1.251

TABLE 3: O_3 columns measured by TDLHS in the period January-February 1994, from Teddington

	HF		HCl		N_2O		HNO^3	
	SSH961 66.44	SSH152 55.85	SSH958 69.90	SSH970 55.64	SSH966 60.31	SSI149 57.38	SSI013 80.55	SSI054 61.67
Group and Identification	(E15)		(E15)		(E18)		(E16)	
NPL A	1.03	0.94	3.69	3.61	3.79	3.89	1.47	1.45
AWI B	1.08	1.03	3.87	3.95	3.58	3.90	1.41	1.44
IMK C	1.18	1.07	4.06	4.10	3.84	4.00	1.42	1.44
UW+MPIC D	1.11	0.98	3.94	3.98	3.86	4.00	1.40	1.41
ULg E	1.14	1.00	4.12	4.07	3.91	3.97	1.48	1.49
LaRC F		1.01	4.22	4.19			1.48	1.47
UDe G			3.96	3.96			1.45	1.45
URe H	1.22	1.15	3.94	3.98	3.75	3.90	1.49	1.52
ASB I	1.07	0.94	3.96	3.93	3.82	4.04	1.43	1.41
JPL J	1.07	0.99	3.73	3.76	3.81	3.94	1.43	1.46
Mean	1.1	1.01	3.95	3.95	3.80	3.96	1.45	1.45
Std. dev.	0.06	0.06	0.15	0.16	0.09	0.05	0.03	0.03
Std. dev. %	5.4	6.2	3.9	4.0	2.4	1.3	2.1	2.2
Extreme diff. %	16.9	20.1	13.4	14.9	8.8	3.8	6.2	7.5

TABLE 4: **Results of ESMOS II/NDSC algorithms intercomparison exercise - Phase 1**

	HCl		HF		HNO_3		N_2O		CO_2	
	H958	H970	H961	I152	I031	I054	H966	I149	4000	4023
Group and Identification	69.901	55.637	66.444	55.846	80.547	61.666	60.311	57.381	83.480	55.680
	XE15		XE15		XE16		XE18		XE12	
NPL A	4.302	4.376	1.130	1.070	1.474	1.511	3.851	4.001	5.193	5.368
AWI B	4.273	4.346	1.159	1.082	1.504	1.529	3.946	4.098	4.913	5.122
IMK C	4.251	4.324	1.139	1.006	1.488	1.513	3.841	3.986	4.580	4.825
UWO D	4.299	4.327	1.124	1.071	1.483	1.522	3.903	4.073	4.674	5.286
ULG E	4.257	4.333	1.129	1.070	1.461	1.498	3.843	3.992	5.107	5.301
LaRC F	4.277	4.352	1.140	1.064	1.471	1.507	3.844	3.992	5.105	5.338
UDE G	4.255 4.279		1.098 1.131		1.435		3.820		4.950 4.875	5.050 5.089
BISA I	4.225	4.225	1.123	1.070	1.558	1.298	3.832	3.930	5.013	5.013
JPL J	4.255	4.336	1.125	1.069	1.451	1.490	3.831	3.964	4.987	5.089
ENSSA K										
SAO L	4.20	4.27	1.12	1.06	1.47	1.52	3.81	3.95	5.10	5.25
NIWA M	4.27	4.35	1.13	1.07	1.47	1.50	3.86	4.01	5.17	5.33
NCAR N	4.129	4.168	1.068	1.019	1.555	1.520	3.846	4.040	4.875	4.875
AES O	4.309	4.386	1.141	1.082	1.471	1.507	3.852	4.001	4.952	5.063
STEL P	4.27	4.34	1.13	1.07	1.47	1.51	3.24	3.99	5.15	5.30
MPI X	4.23	4.32	1.13	1.06	1.49	1.51	3.87	4.03	4.83	5.48
Mean	4.255	4.321	1.126	1.066	1.483	1.511	3.853	4.004	4.998	5.174
Std. dev.	.040	.058	.013	.014	.033	.010	.033	.043	.156	.179
Std. dev. %	1.0	1.4	1.7	1.4	2.2	0.7	0.8	1.1	3.1	3.5
Extreme diff. %	4.2	5.0	8.1	5.9	8.3	2.6	3.5	4.2	12.3	12.7

TABLE 5: **Results of ESMOS 11/NDSC algorithms intercomparison exercise - Phase 2**

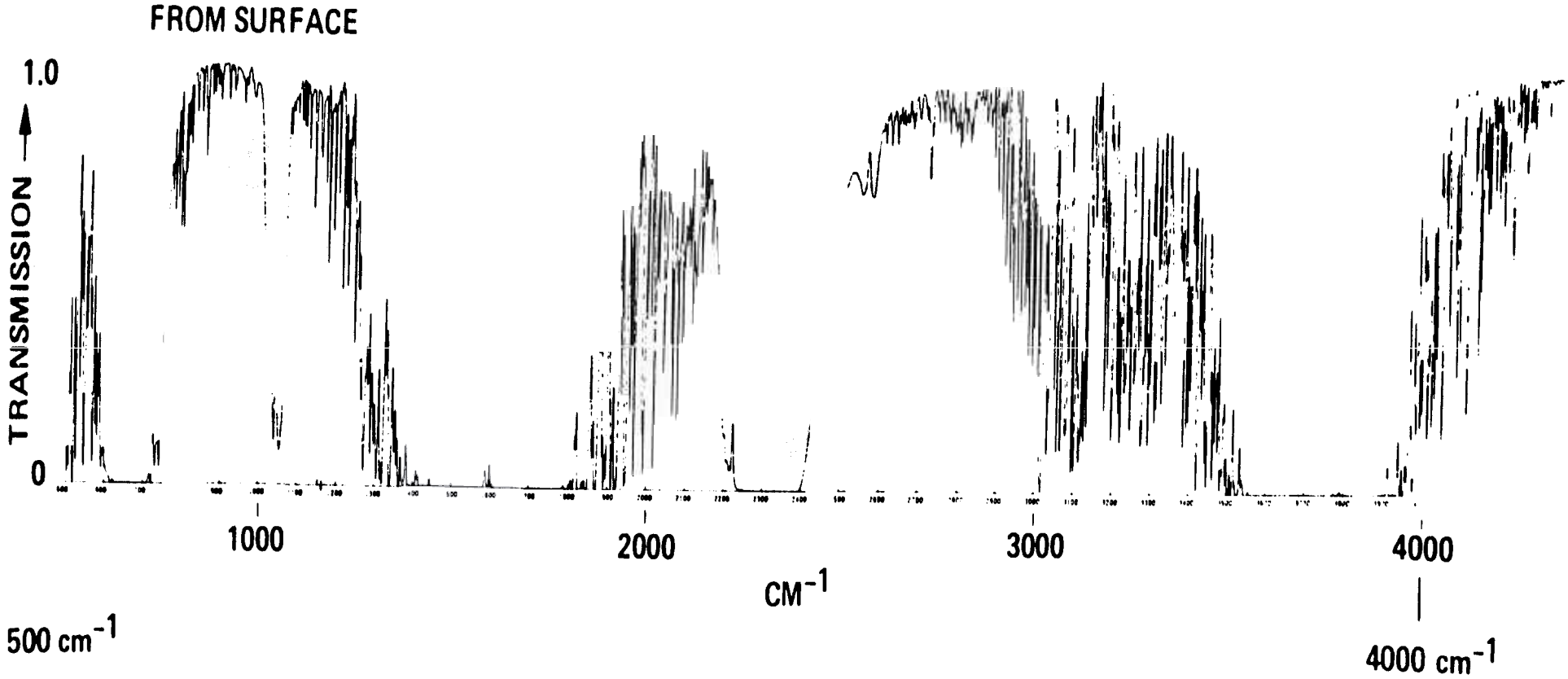
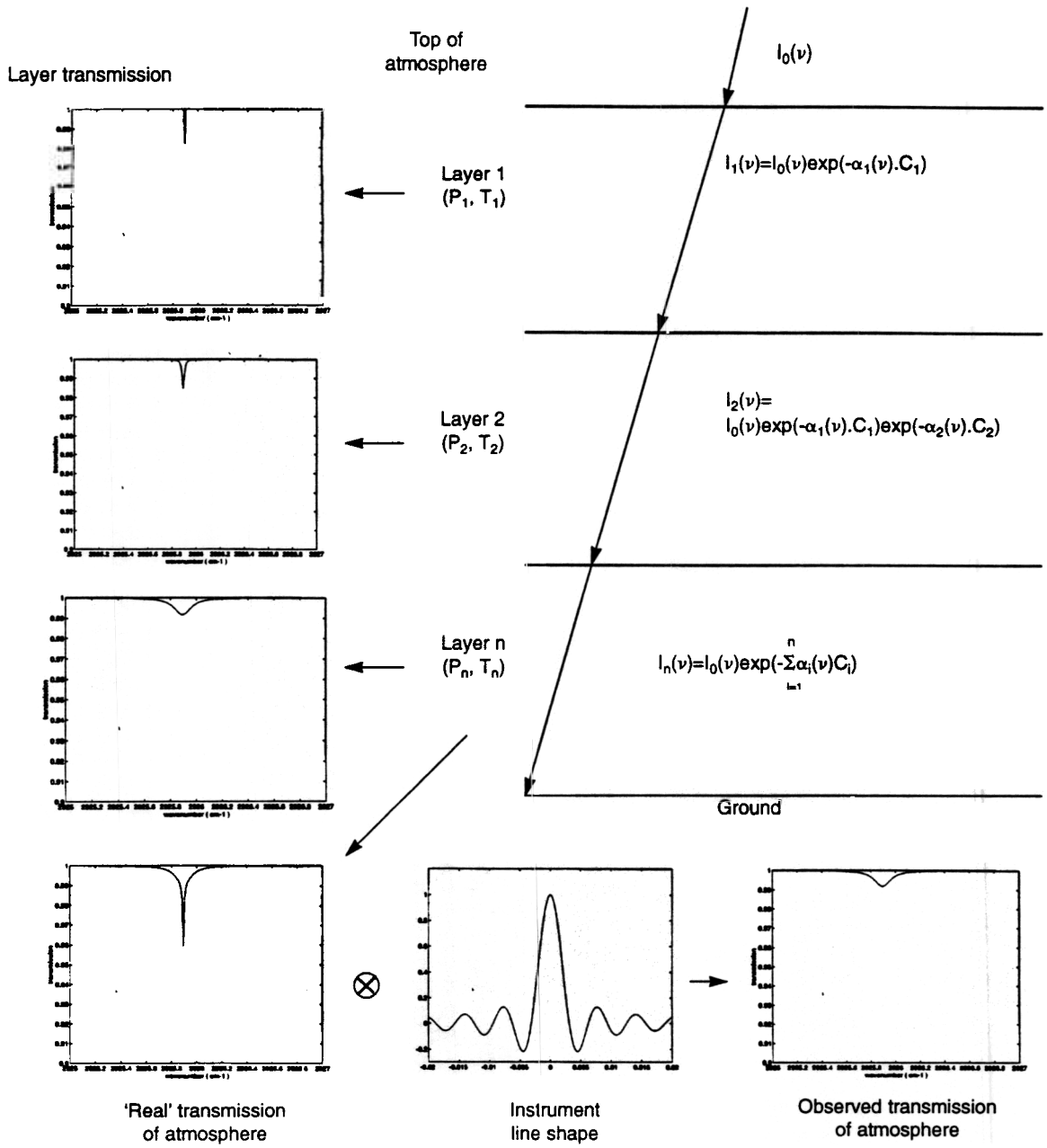


Figure 1: Transmission of the atmosphere, from the ground in the infrared region from 500-4000 m^{-1}.



Definitions

$I_0(\nu)$: light intensity at top of atmosphere, as a function of wavenumber

$I_i(\nu)$: light intensity at bottom of layer i, as a function of wavenumber

P_i: mean pressure in atmosphere layer i

T_i: mean temperature in atmosphere layer i

$\alpha_i(\nu)$: absorption coefficient as a function of wavenumber, in layer i derived from P_i, T_i and spectral line parameters

C_i: column of absorber in layer i

$\otimes$ convolution operator

02269

Figure 2: Schematic diagram showing the principles of groundbased solar aborption spectroscopy.

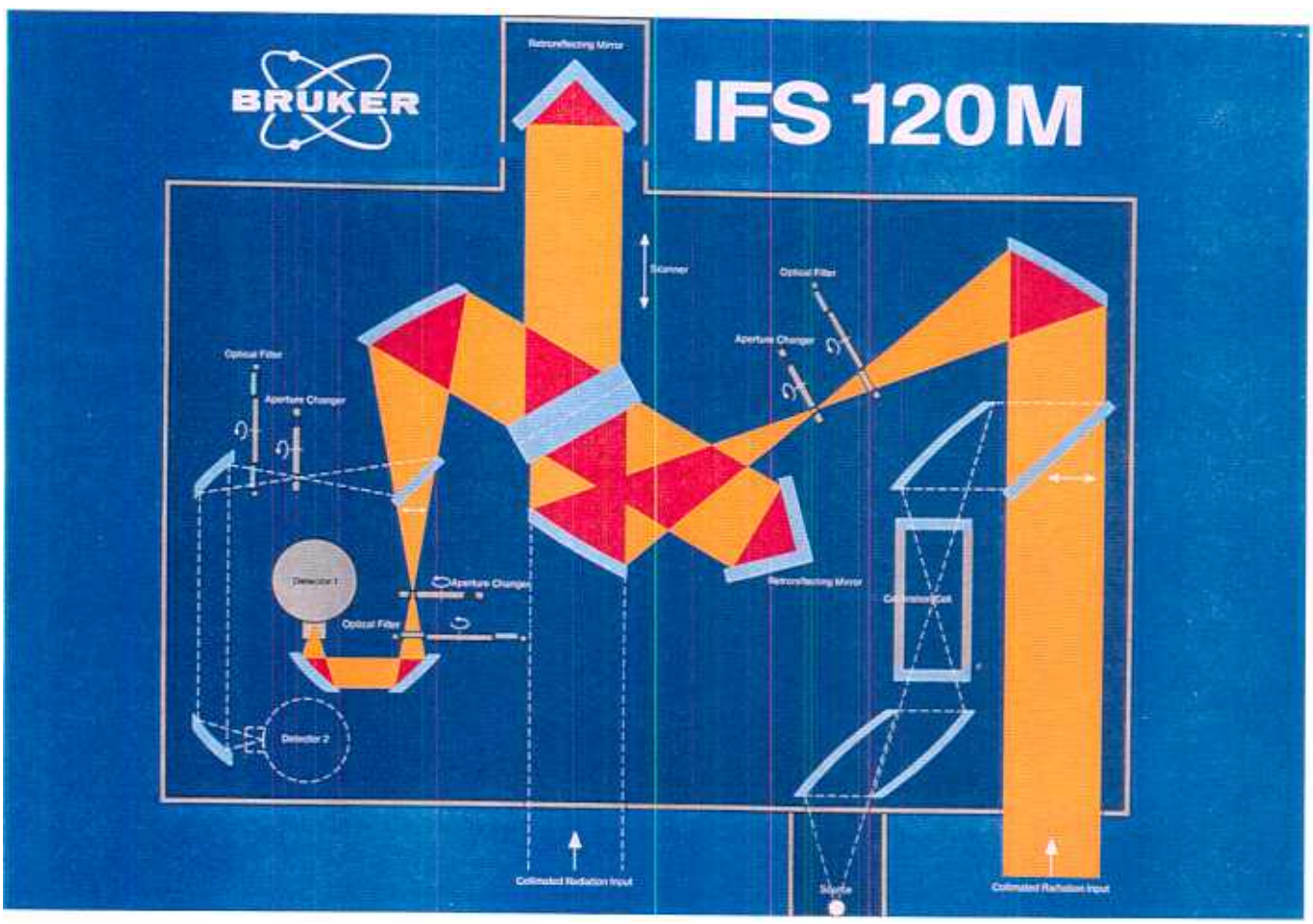


Figure 3: **Schematic diagram of NPL Fourier Transform-Infrared spectrometer.**

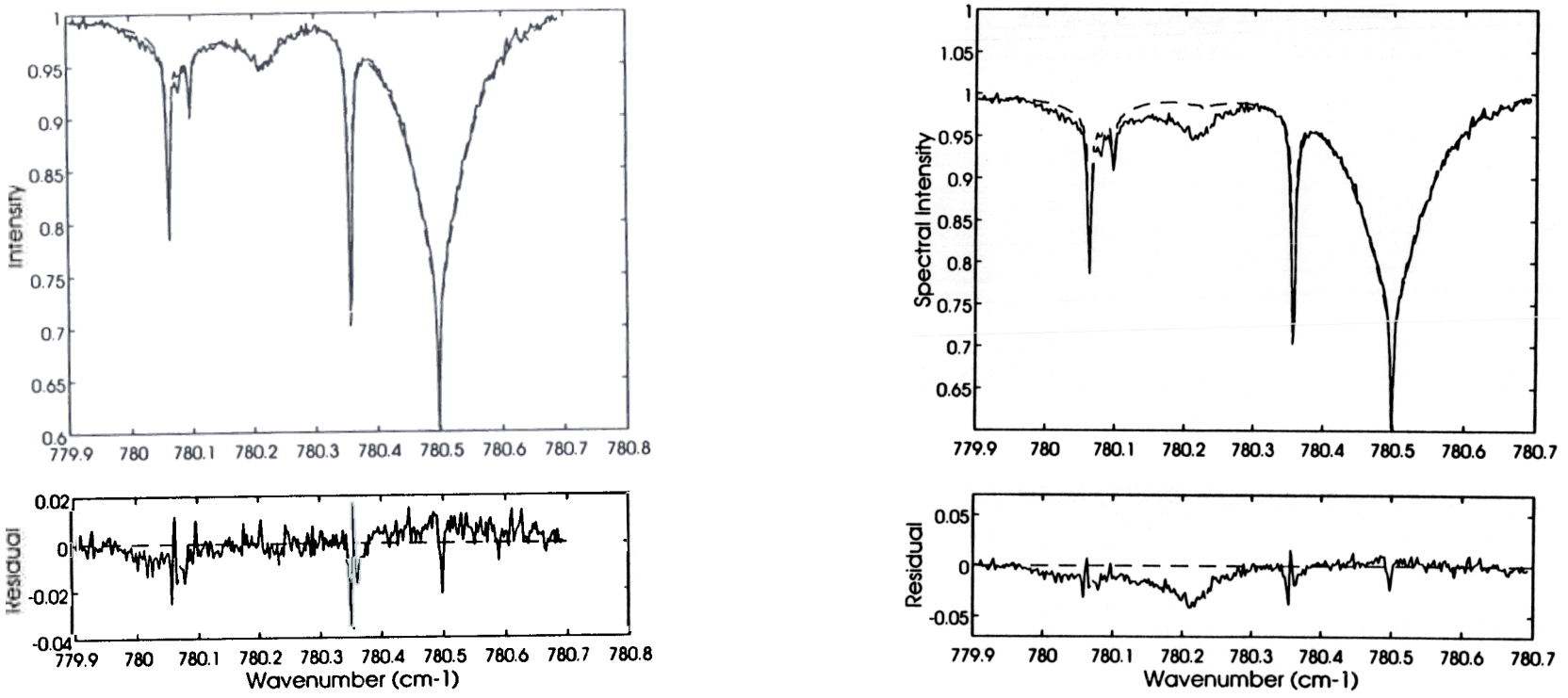


Figure 4: **Atmospheric spectrum in the region of the chlorine nitrate ($ClONO_2$) ν_4 Q-branch absorption, obtained using NPL FTIR. The left hand figure shows a synthetic spectrum (dotted line) together with data (solid line) and residuals (observed - calculated, lower plots) assuming a $ClONO_2$ vertical column of 6.6×10^{15} mol.cm^{-2}. The right hand fit assumes no chlorine nitrate. The spectrum was obtained at a solar zenith cycle of 58.5°.**

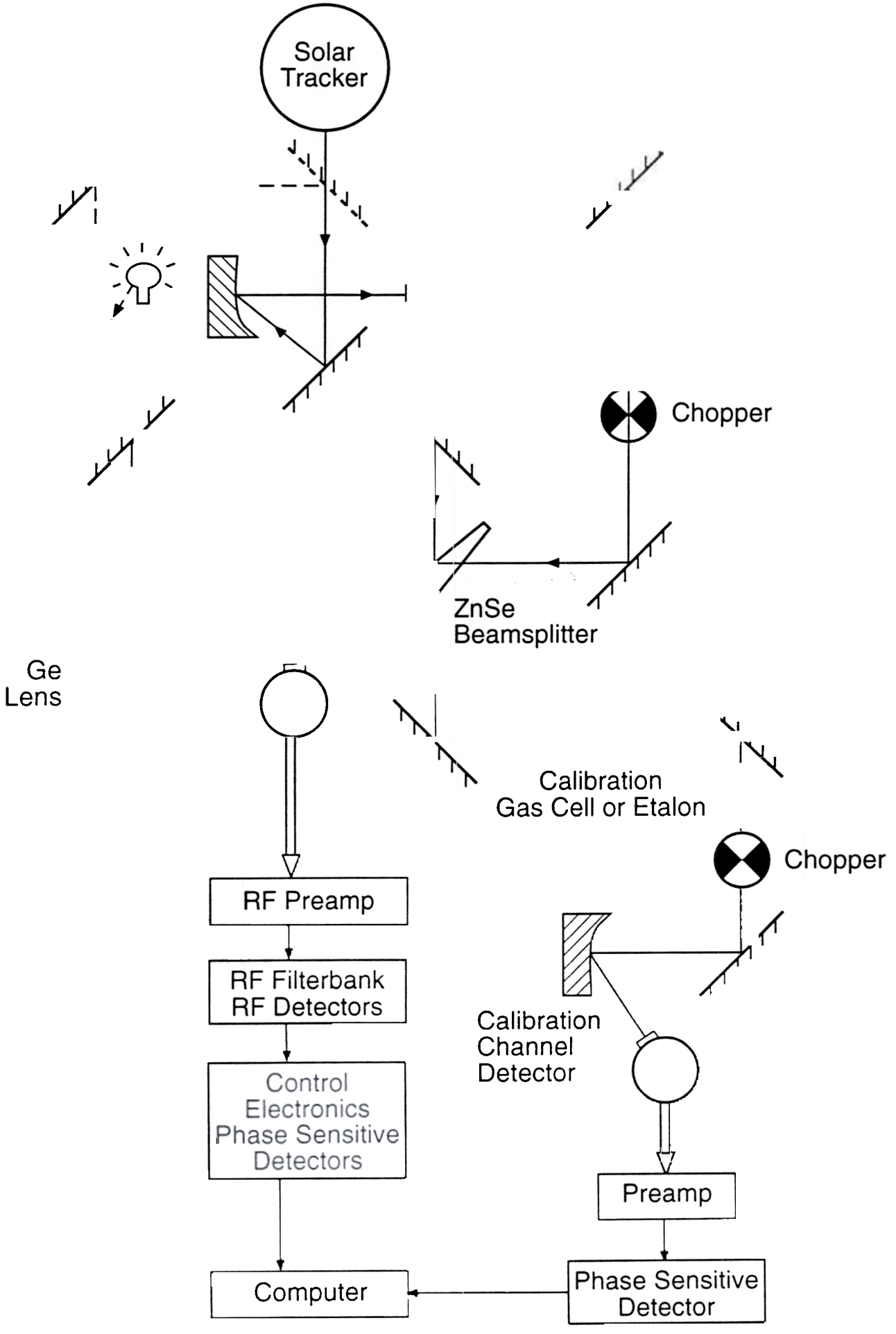

Solar
Tracker
Chopper
ZnSe
Beamsplitter
Ge
Lens
Calibration
Gas Cell or Etalon
Chopper
RF Preamp
RF Filterbank
RF Detectors
Control
Electronics
Phase Sensitive
Detectors
Calibration
Channel
Detector
Preamp
Computer
Phase Sensitive
Detector

Figure 5:

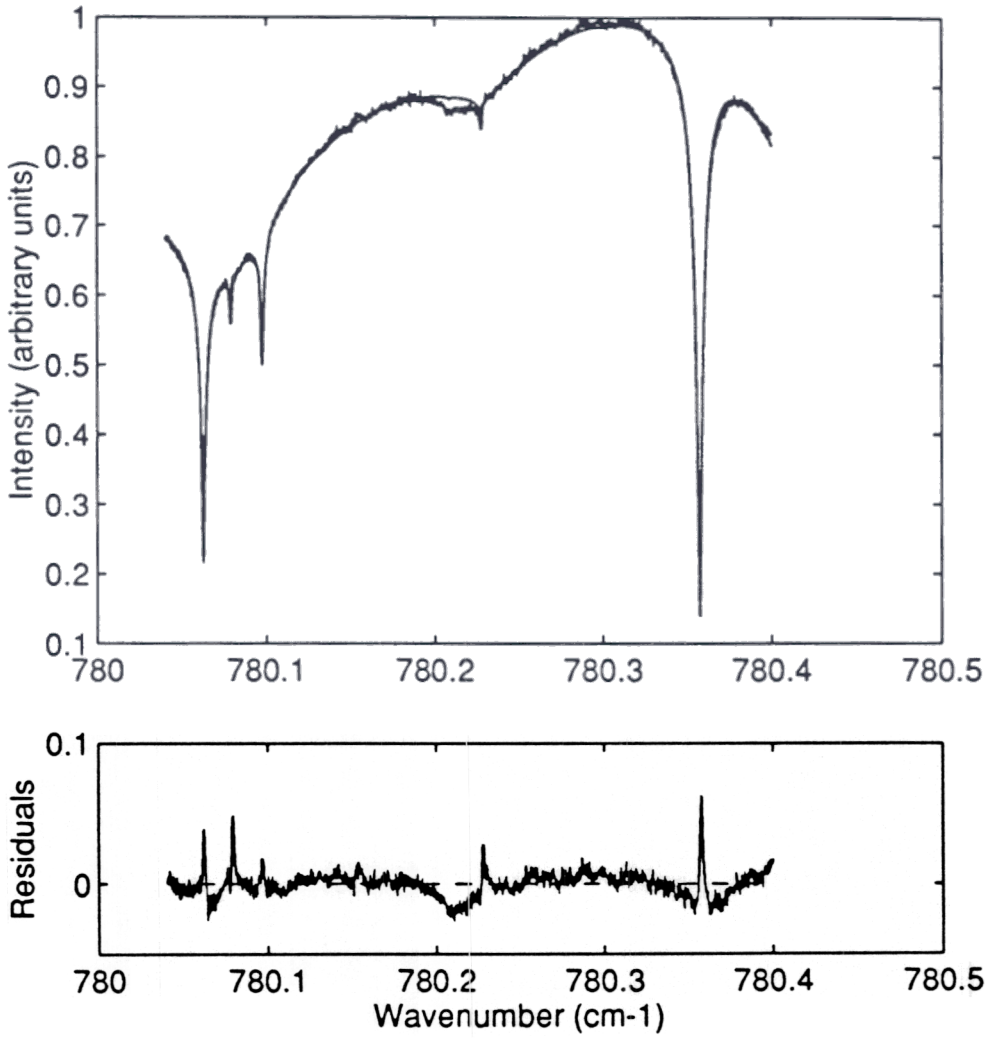


Figure 6: TDLHS atmospheric spectrum, in the region of the $ClONO_2$ ν_4 Q-branch absorption

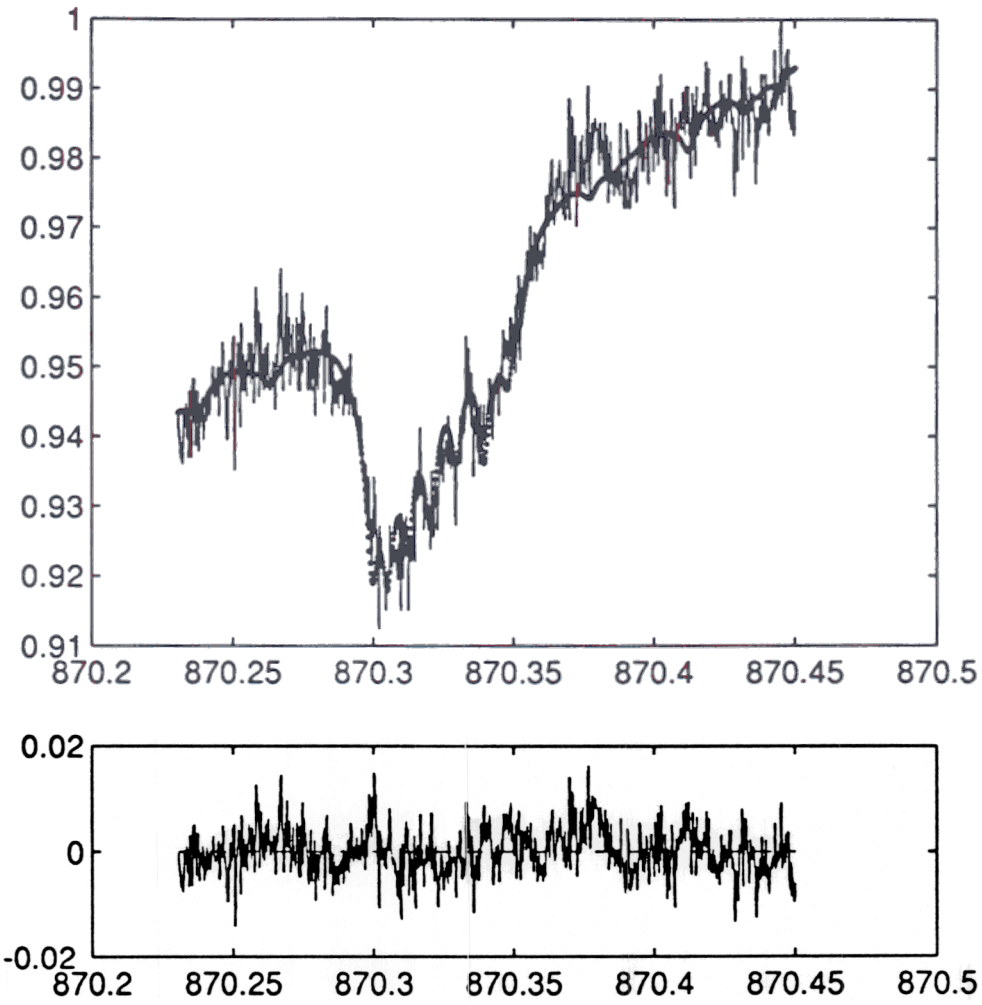


Figure 7: TDLHS atmospheric spectrum, showing HNO_3 absorpton feature

Figure 8: CO_2/TDL heterodyne linewidth measurement with and without external feedback

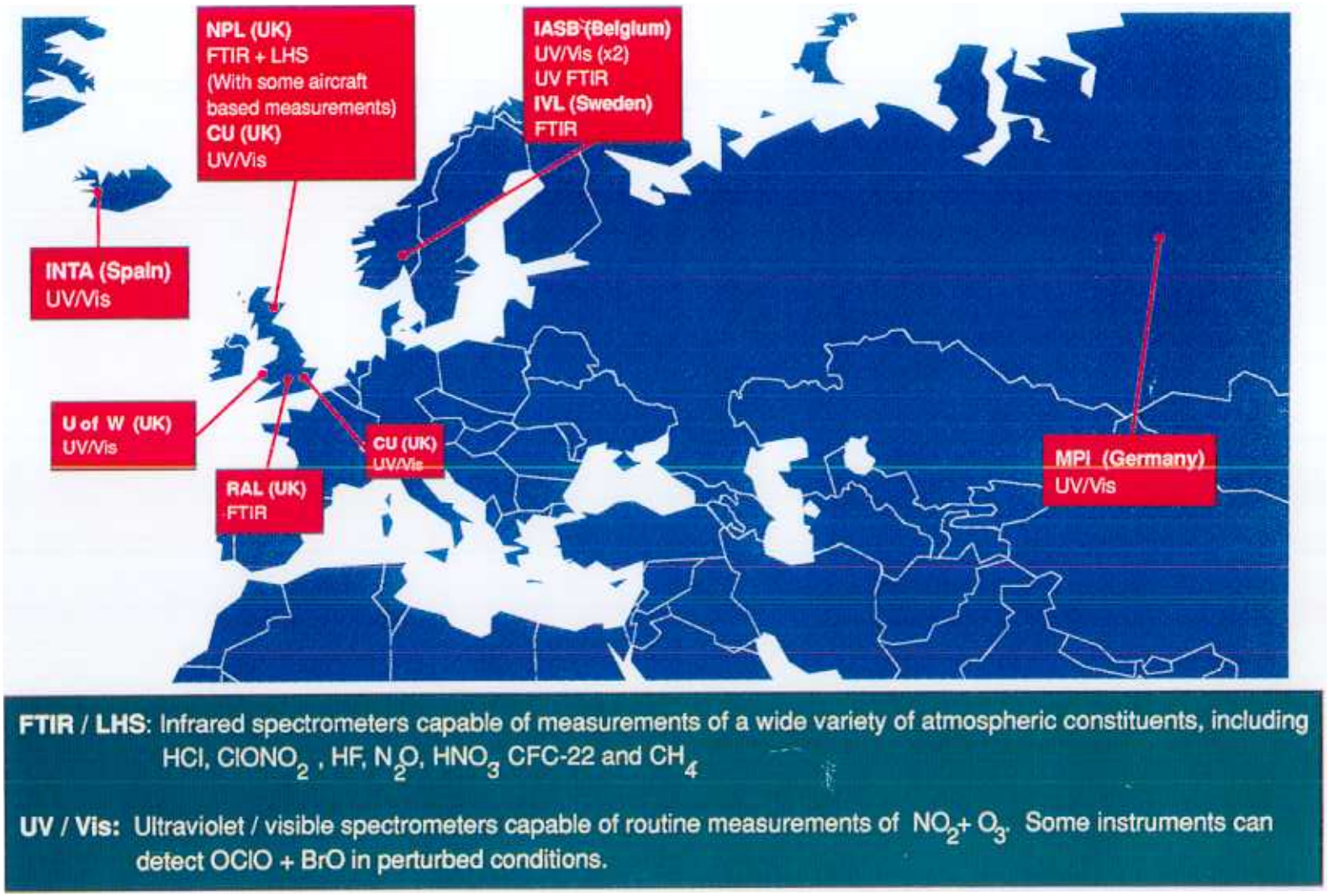


Figure 9: 'Groundbased measurements at 60°N' project measurement sites.

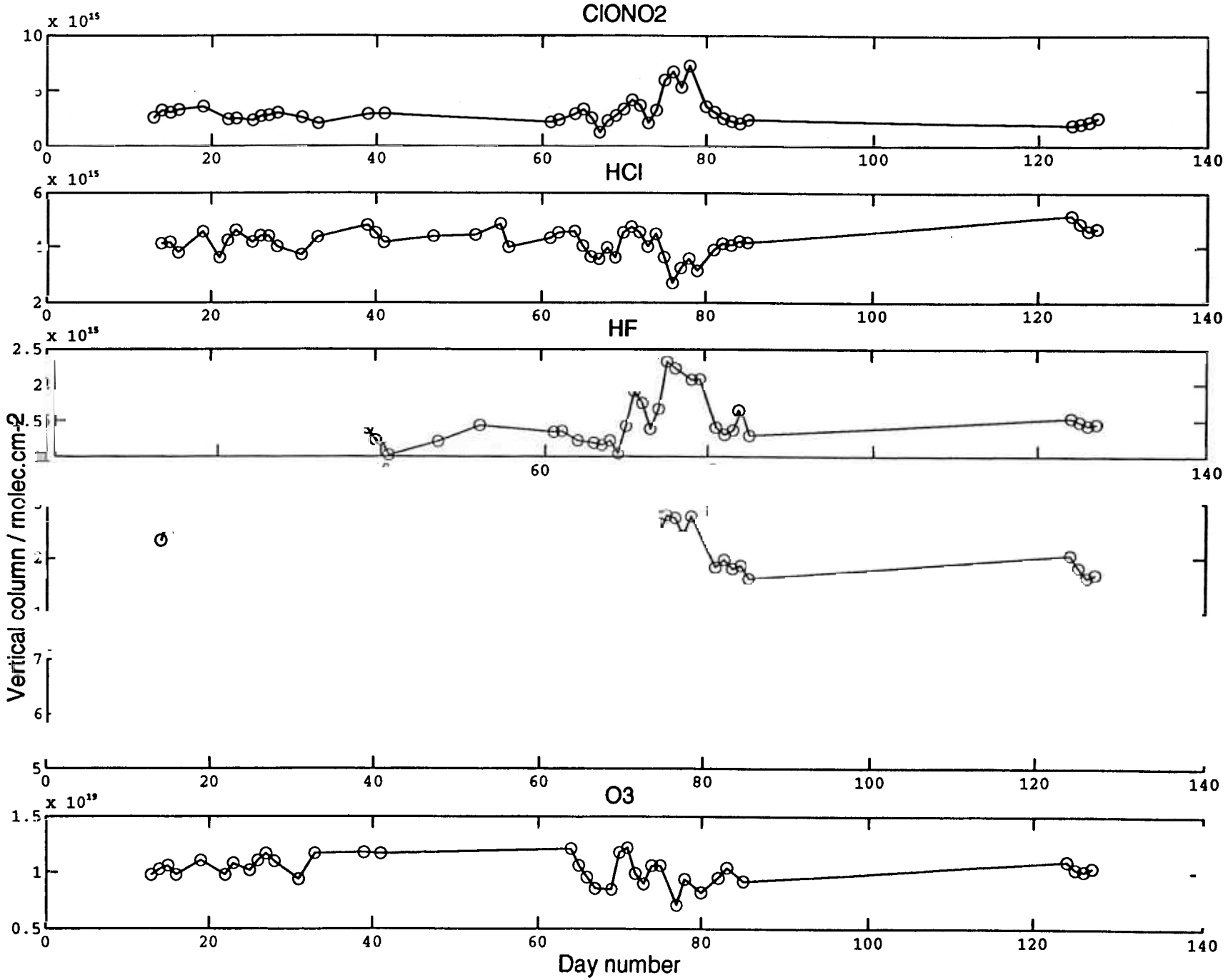


Figure 10: Time series of vertical column amounts of HCl, $ClONO_2$, HF, N_2O, HNO_3 and O_3 measured over Aberdeen during winter/spring of 1994.

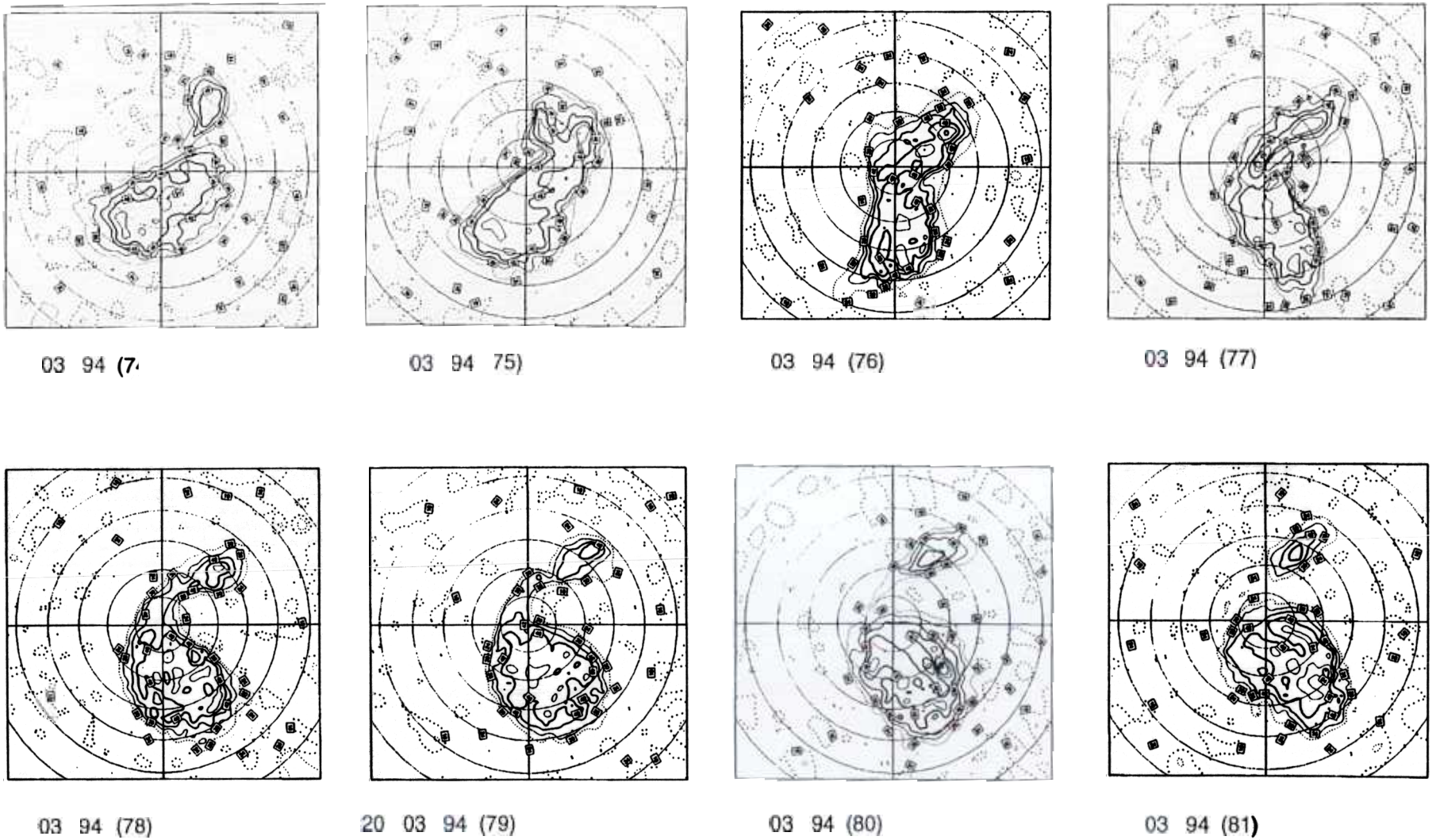


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Figure 11: Potential orticity at 475K in the period day 74 to 81, 1994.

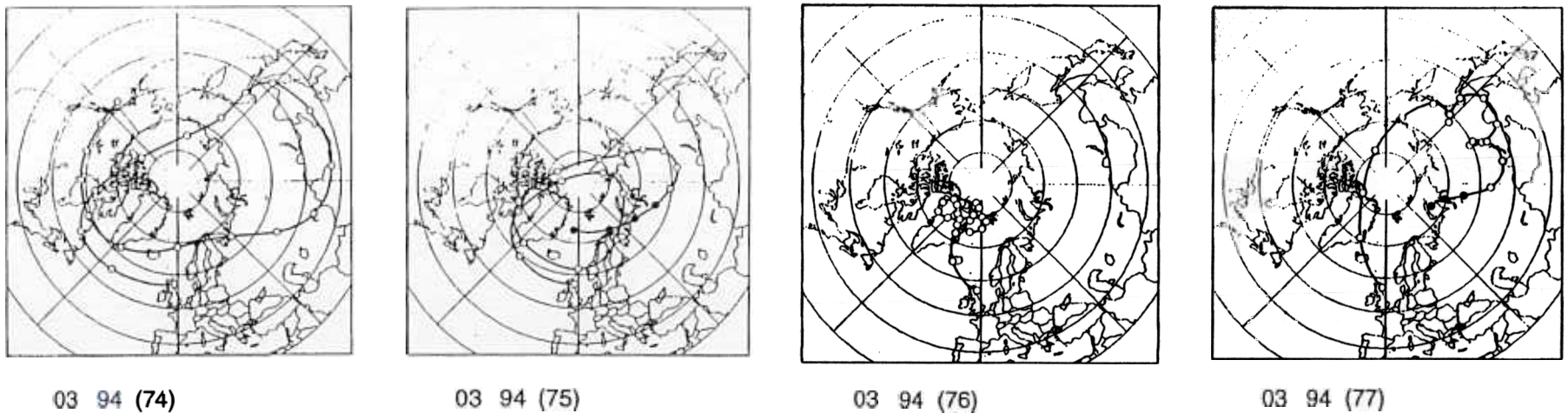

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Figure 12: Back trajectories ending Aberdeen in the period day 74 to day 81, 1994.

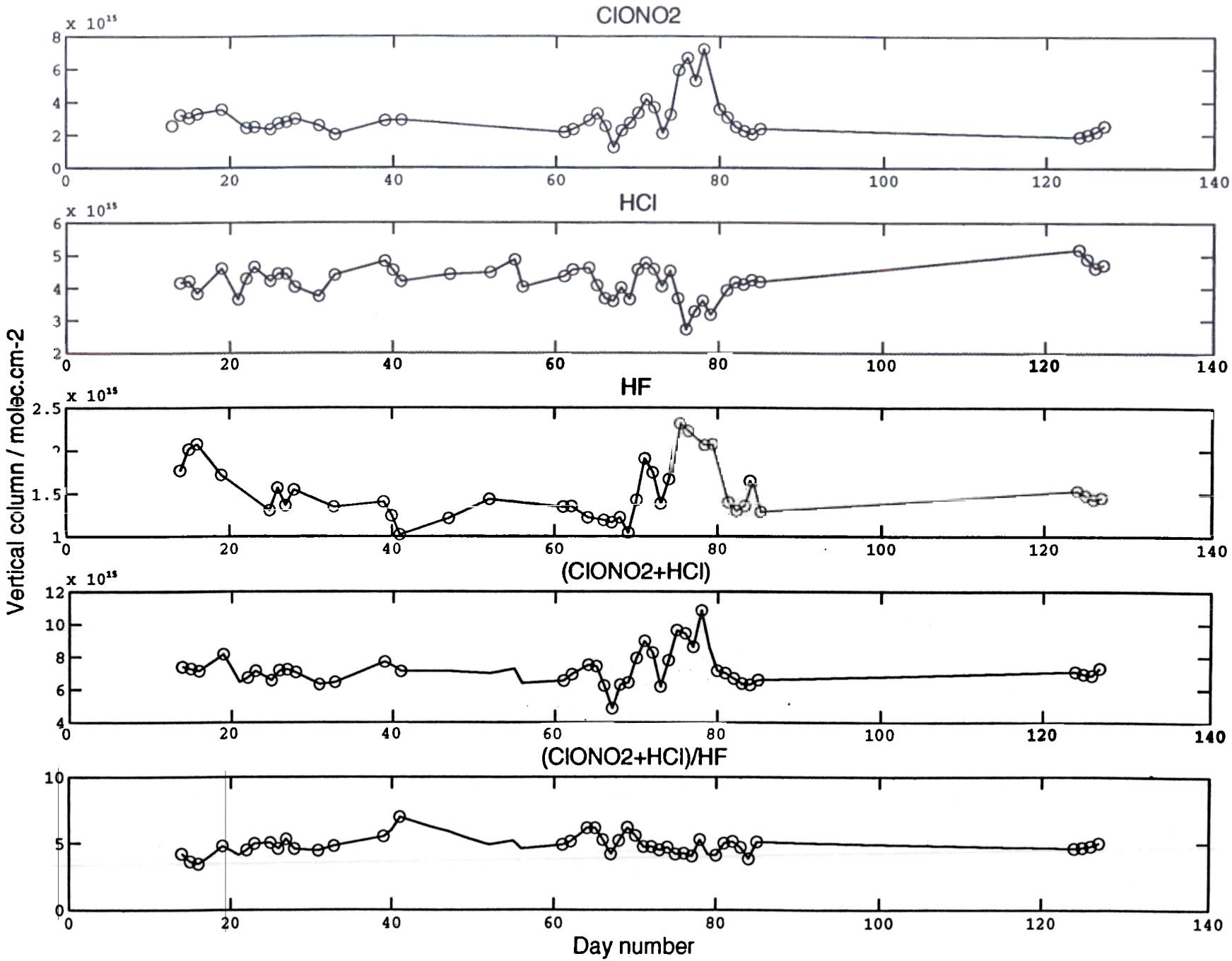

Figure 13: Time series of HCl, $ClONO_2$ and (HCl + $ClONO_2$)/HF over Aberdeen during winter/spring of 1994.

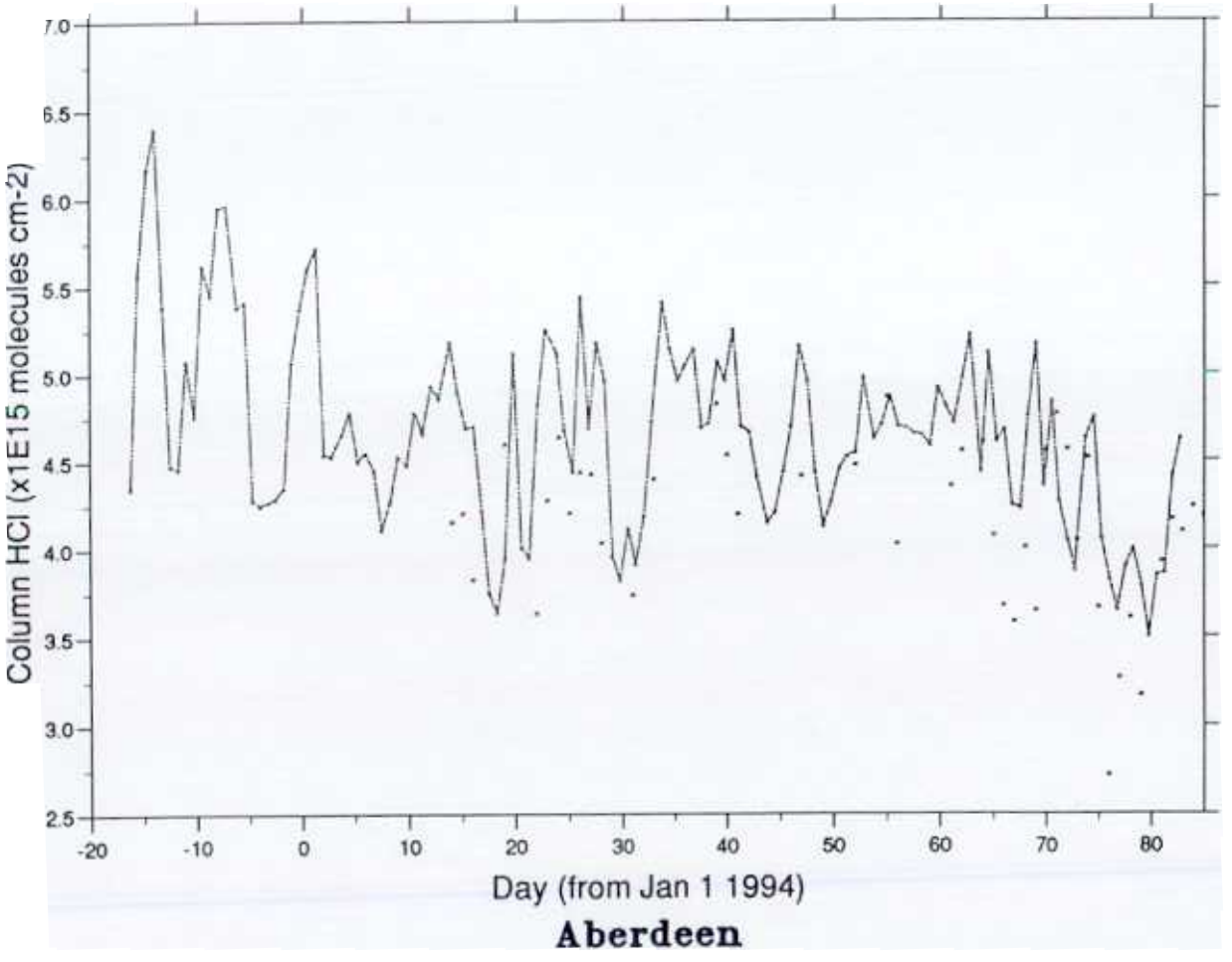

Figure 14 (a): Modelled (TOMCAT 3D) versus measured HCl vertical columns over Aberdeen during winter-spring of 1994. Crosses (x) indicate measured values, dotted line indicates modelled values.

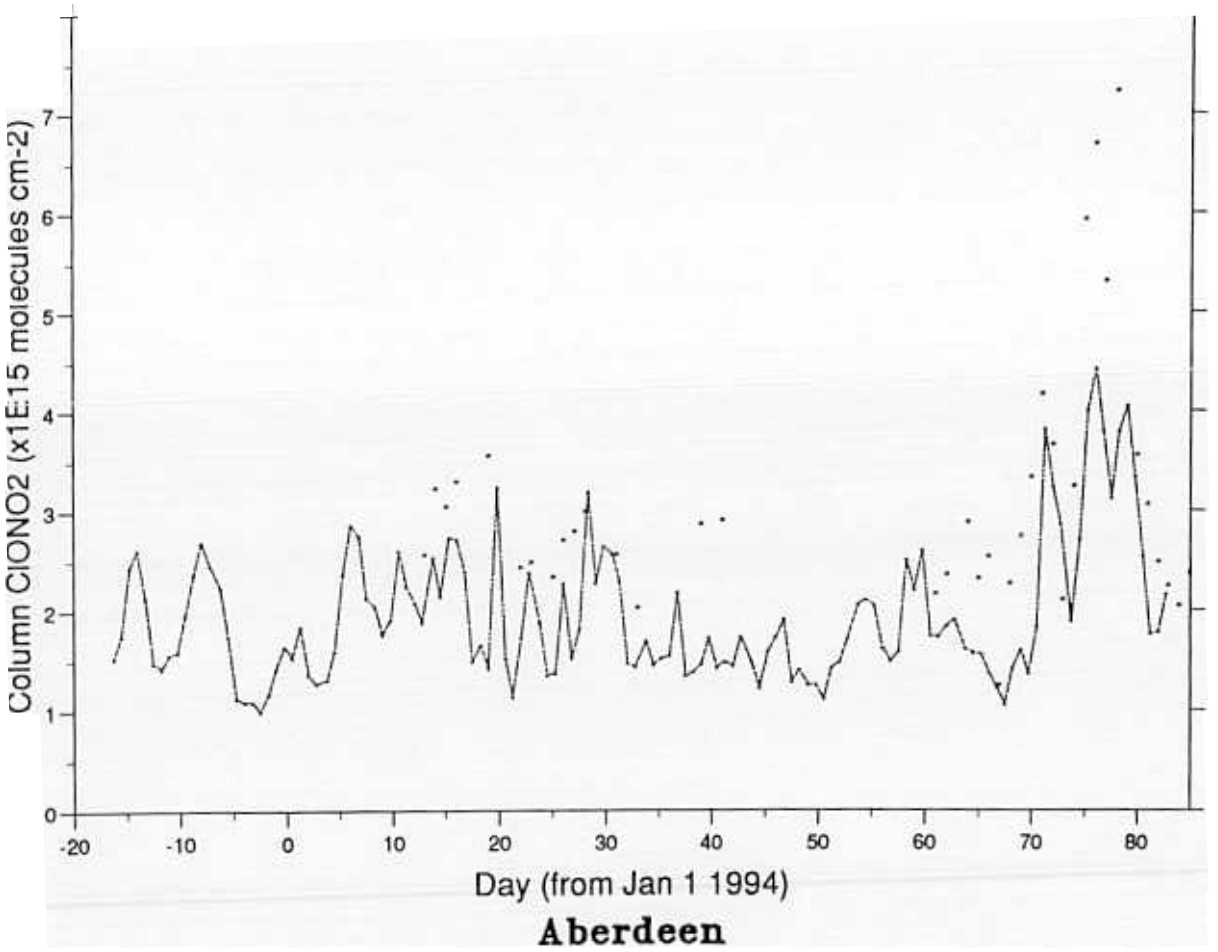

Figure 14 (b): Modelled (TOMCAT 3D) versus measured $ClONO_2$ vertical columns over Aberdeen during winter-spring of 1994. Crosses (x) indicate measured values, dotted line indicates modelled vlaues.

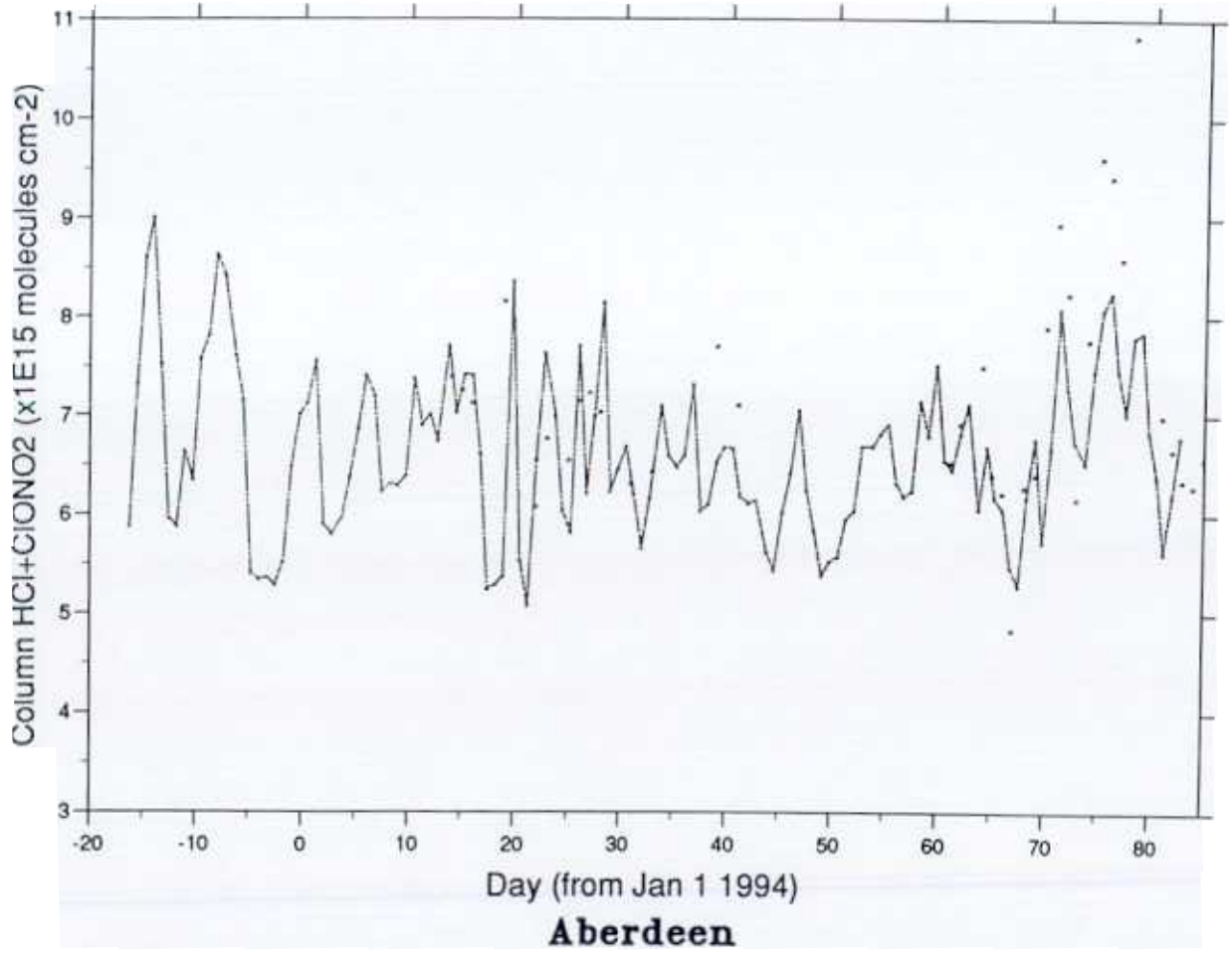

Figure 14 (c): Modelled (TOMCAT 3D) versus measured HCl + $ClONO_2$ vertical columns over Aberdeen during winter-spring of 1994. Crosses (x) indicate measured values, dotted line indicates modelled vlaues.