SEASONAL CYCLE IN ATMOSPHERIC HCL AT 45°S

W.Andrew Matthews, Nicholas B. Jones, Paul V. Johnston

National Institute of Water and Atmospheric Research,(NIWAR),
Atmospheric Division, Lauder, Central Otago, New Zealand

Curtis P. Rinsland

Atmospheric Sciences Division, NASA Langley Research Center,
Hampton, Virginia, USA

and *Aaron Goldman*

Department of Physics, University of Denver,
Denver, Colorado, USA

Abstract:
High resolution Fourier transform infrared interferometric atmospheric solar absorption measurements have been performed at the National Institute for Water and Atmospheric Research Laboratory at Lauder, New Zealand on a routine basis since October 1989. This laboratory has been selected as the Mid-latitude Charter Site of the Network for the Detection of Stratospheric Change and is at a latitude of 45°S.

Particular attention has been paid to the absorption by atmospheric hydrogen chloride at 2925.9cm^{-1} and in this paper the results of the seasonal cycle in HCl above Lauder will be presented. Because of the very clean troposphere at this site, the HCl column measured from the ground is essentially a stratospheric column measurement.

The HCl data series from Lauder is then contrasted with a series of HCl measurements from similar latitudes in the Northern Hemisphere.

Introduction:

Hydrogen chloride is an important trace gas in the stratosphere. Its presence signals the end of the catalytic cycle for active chlorine involved in ozone destruction and its variation with time gives an indication of some of the active chlorine chemistry processes that are occurring which in themselves may be difficult to measure let alone monitor directly. The main source of stratospheric hydrogen chloride is anthropogenic (WMO, 1986) through the photolysis of halocarbons, with minor sources from the reaction of the hydroxyl radical with methylchloride, which itself is released from the oceans, and sporadic injections of HCl from volcanic eruptions.

A programme to study stratospheric hydrogen chloride was started at Lauder, New Zealand, 45°S in November 1985 and some of the initial results from these measurements are reported in Matthews et al., (1989). Lauder itself is located in the southern centre of the South Island of New Zealand and is 40km away from the nearest population "centre", Alexandra (population 4000). The site is 150km from the ocean (altitude 0.35 km) and has been chosen as the Mid-latitude Southern Hemisphere Charter site for the international 5 station Network for the Detection of Stratospheric Change (NDSC). Systematic measurements of HCl on a routine basis started at Lauder in October 1990 with the permanent deployment of a high resolution FTIR interferometer system. Observations have been made on a regular basis under clear sky conditions since that time, as it is the information from this data series that is the subject of this paper.

Instrumentation:

The instrument used in this study is based around a Fourier transform interferometer (Bruker 120 HR) with a nominal apodised resolution of 0.0035cm^{-1}. This system maintains alignment over the 258cm optical movement through a servo-controlled tilt adjustment on the moving retro-mirror assembly. The system incorporates an InSb liquid nitrogen cooled detector and the solar beam is imaged into the interferometer through a PC controlled suntracking system. The spectra are of a high quality, with signal to noise ratios of greater than 300:1.

Data Analysis and Results:

Data has been recorded at Lauder on a regular basis using the Bruker interferometer since its installation at Lauder in late September, 1990. Interferograms are Fourier transformed and
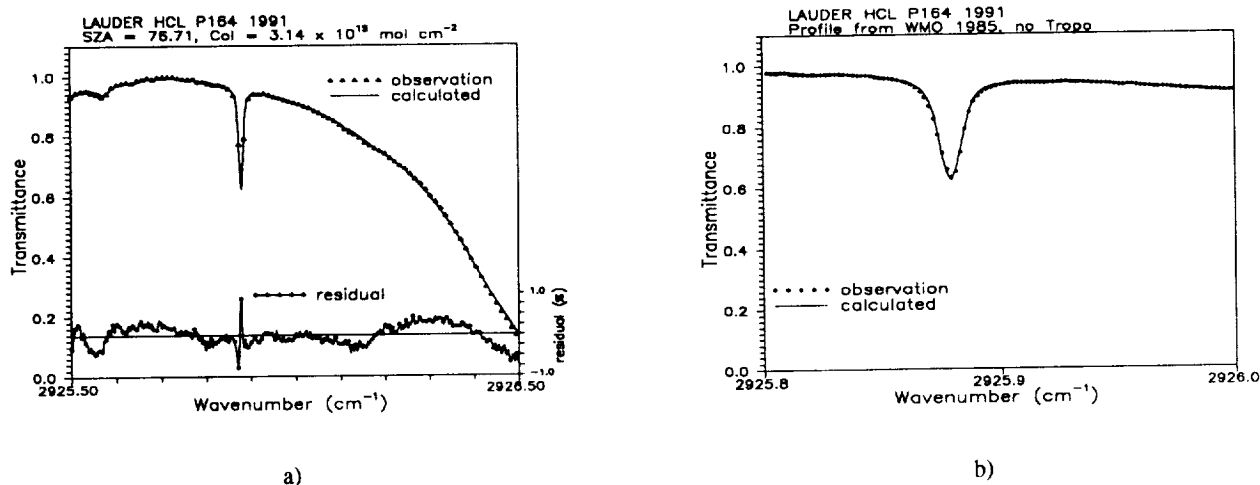
Figure 1: Sample of spectral fitting for data obtained at Lauder on June 13, 1991 at 15.15 NZST. The individual points shown in a) represent every sixth measured value while the continuous line is that of the best fit synthetic spectrum. The residual spectrum, the difference between the measured and synthetic spectrum is also shown in a) where the scale is ±1%. Graph b) is an expansion of a) to show the detail of the fit in the HCl region. In this graph each observation point has been plotted.

the resulting spectra are stored for later atmospheric abundance analysis. This analysis for the atmospheric abundance of a particular component in the Earth's atmosphere is made easier if the absorption feature that is studied is relatively free from interference from absorptions from other trace species in the same atmosphere. In the case of atmospheric hydrogen chloride, the rotational line R1 of the 1-0 band, located at 2925.897cm^{-1}, is chosen since although this line sits on the wing of a strong methane absorption feature, it is sufficiently distant from a weak water vapour absorption feature at 2925.189cm^{-1} that this water vapour feature does not effect the accuracy of the analysis. The analysis procedure uses the most up to date line parameters to create a synthetic spectrum using the known positions, ground state energies, halfwidths and line strengths of absorbing species in the region of interest. This synthetic spectrum is generated using actual atmospheric temperature profiles from concurrent ozonesonde ascents and a modelled height distribution for each gas using the real temperature regime. A multi-parameter non-linear least squares algorithm (based on Rinsland et. al., 1991) was used to minimise the difference between the synthetic spectrum and the measured spectrum. Several parameters are adjustable in this fitting procedure. In this particular case, parameters associated with the instrument level and slope of the 100% transmission curve and a frequency shift for alignment between the measured spectrum and the computed spectrum were adjusted. A mutiplicative scaling factor is used to convert an assumed mixing ratio from each defined layer into an absolute value. The analysis is similar to that used in Rinsland et al, (1982) and (1991). In this work however, a vertical distribution for HCl based on the profile from BIC-2,

figure 11-11, WMO Vol. II, (1986) has been used. Mixing ratio values were extrapolated from the tropopause value of 0.4ppbv to be zero at the ground by reducing these values by a factor of 10 every 2 km. Profile shapes consistent with that reported in figures 9-18 and 9-36, WMO Vol. II (1986), for methane and water vapour respectively have been adopted. Figure 1 shows a spectrum recorded at Lauder on June 13, 1991 at 15.15 NZST when the solar zenith angle was 76.71°. The strong R1 absorption feature is evident on the wing of the saturating methane absorption. The measured spectrum is shown as the series of stars while the synthetically generated spectrum is the continuous line. The residual spectrum, plotted on the same scale is also shown. It can be seen that the absorption features can be well matched by the synthetic spectrum and the vertical abundance calculated from this data was 3.14 ± 0.5 x 10^{15} mol. cm^{-2}. The difference plot indicates that there is still residual water vapour (2925.55 and 2925.64 cm^{-1}) and some weak channel. Similar analyses were performed for the data series at Lauder from September 1990 through May of 1992 for data collected when the solar zenith angle was 76±1°. Choosing only that subset of data with a fixed solar zenith angle means that no additional errors have been introduced through assumptions that are made in correcting slant columns measured at differing solar zenith angles to vertical column amounts. Further analysis for a range of solar zenith angles will provide some additional information on the atmospheric profile.

The sources of error and their estimated uncertainties, as they relate to the HCl column amount, have been calculated using a scheme given for similar analysis in Murcray et al., (1987). Instrumental effects (signal noise, zero level shift , line shape
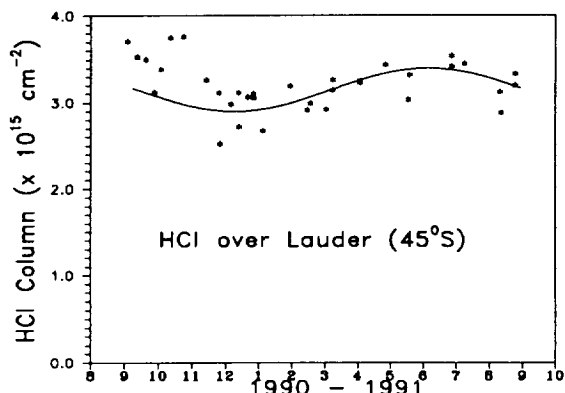
Figure 2: The seasonal variability of HCl over Lauder is shown in this figure where data from September 1990 to September 1991 have been plotted. There is evidence of shorter term variability but also an annual cycle where minimum values are seen in mid-summer. A curve with a peroid of one year has been added for clarity.

function and channel spectra) are of the order of 5%. The absolute HCl line intensities are thought to be known to ±10%. while the HCl air broadened halfwidths and temperature dependence add a further 5%. Finally the pressure / temperature profile results in a further 5% uncertainty. The total rms error in the HCl columns presented here is approximately ±15%. The choice of the HCl relative mixing ratio profile has the potential to introduce considerable uncertainty. In the analysis presented here we have used a single profile shape for all the analysis. Any seasonal change in the vertical profile shape would therefore introduce a further uncertainty into our analysis. Also noted are systematic errors that can be introduced by changes in the instrument function. Care has been taken to minimise any disturbances in the system configuration.

Figure 2 shows the HCl vertical column amounts measured over Lauder during the period September 1990 through September 1991. This data shows a peroidicity with an amplitude of approximately ±8% and a phase that has a winter maximum and a summer minimum. Such a seasonal behaviour fits the concept that the "shorter term" variation of stratospheric HCl is controlled by hydroxyl radical attack, Solomon and Garcia, (1984), and that the minimum in HCl will coincide with maximum OH concentrations in the stratosphere in mid-summer. The seasonal cycle observed over Lauder seems to differ in phase with that tentatively ascribed over the Jungfraujoch Observatory between 1983 and 1985, Zander et al, 1987 where the minimum appears in fall and the maximum in the spring. It will be interesting to see if further work substantiates this difference in phase and whether it is an hemispheric effect. The more recent data appears to be more variable and this may be a consequence of

the arrival of the Pinatubo aerosols over Lauder. A longer time series will be needed to access their impact on HCl levels over Lauder.

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