MEASUREMENTS OF STRATOSPHERIC ODD NITROGEN AT
ARRIVAL HEIGHTS, ANTARCTICA, IN 1991

J.G. Keys and P.V. Johnston
National Institute of Water and Atmospheric Research (NIWAR)
Atmospheric Division, Lauder, Central Otago, New Zealand

R.D. Blatherwick and F.J. Murcray
Physics Dept., University of Denver, Boulder, Co.

ABSTRACT

An FTIR spectrometer was installed at Arrival Heights, Antarctica (78°S, 167°E) in February 1991 to measure the evolution of stratospheric HNO$_3$ during the year. In particular, it was the intention to make the first observations of HNO$_3$ trends during autumn, concurrently with ongoing measurements of column NO$_2$ made with a grating spectrometer.

The time-series of NO$_2$ in the Antarctic shows a rapid decline in the column amount during autumn, and a slow recovery in spring, as the photochemical conditions move the species to and from higher storage reservoirs. The new nitric acid data show for the first time that during autumn the vertical column increases from approximately 1.9 x 10$^{16}$ molecule cm$^{-2}$ at day 30 to approximately 3.1 x 10$^{16}$ molecule cm$^{-2}$ by day 100. When the sun returns in spring, it is found that the column amount has fallen to about half the value at the end of autumn. Spring amounts are variable, but as found in the data from previous years remain low inside the vortex. The autumn increase is attributed to the heterogeneous conversion of N$_2$O$_5(2)$:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (1)
\]

\[
\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \quad (2)
\]

As spring progresses, the NO$_2$ recovers through repartitioning of NOy and also through mixing with lower latitude air. The spring column shows large cyclic increases which are caused by the NO$_2$ depleted polar vortex moving away from the observing site. When the NO$_2$ trends are compared with model calculations, it is found that agreement is best when a parameterisation of heterogeneous chemistry is included. The implication is that in both autumn and spring the conversion of N$_2$O$_5$ to HNO$_3$ on aerosols is important via the reaction:

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (3)
\]

DISCUSSION

The role of heterogeneous chemistry in the stratosphere is one of the most important issues in current atmospheric studies. Of particular interest are those reactions that influence ozone depletion in polar regions, given the ability for heterogeneous chemistry to take place on aerosols in the polar night. Nitrogen compounds have a special significance because of the role they can play in moving chlorine between reactive and less reactive forms. Measurements at the New Zealand Antarctic site of Scott Base (laboratory at Arrival Heights, 78°S, 167°E) have concentrated on remote sensing of NO$_2$, O$_3$, and more recently HNO$_3$. A long term NO$_2$ and O$_3$ record has been built up since measurements started in 1982, using differential absorption spectroscopy techniques. A scanning spectrometer records the spectral signature from 430nm to 470nm of scattered sunlight in the zenith sky. Retrievals of NO$_2$ and O$_3$ are carried out by least squares fitting the experimental data with laboratory derived absorption cross sections (1). Fig. 1 shows how NO$_2$ is removed from the atmosphere in autumn, and restored during spring. In autumn the NO$_2$ is believed to move into the temporary storage reservoir of N$_2$O$_5(2)$:

![Fig. 1. Nitrogen dioxide vertical column 3-day running averages for 1991, for morning (circles) and evening (squares) when the sun is at a solar zenith angle of 90°.](https://ntrs.nasa.gov/search.jsp?R=19950004635)
In autumn the reaction is assumed to take place on background sulphate aerosols, and in spring on the surface of polar stratospheric clouds (PSC's). Actual measurements of HNO₃ at Arrival Heights over the course of a year were seen as an important test of this hypothesis, and new equipment was installed in the laboratory there in January, 1991.

Nitric acid measurements are made at the Arrival Heights laboratory using direct sunlight and a Fourier transform spectrometer (FTIR) which has a nominal resolution of 0.06 cm⁻¹. The resulting interferograms are transformed to give an absorption spectrum such as the one given in Fig. 2, which shows strong ν₅ absorption bands of HNO₃ near 870 cm⁻¹ in the infrared region of the spectrum.

The Antarctic spectra are of very good quality, and compared with data from lower latitudes are relatively unaffected in this region of the spectrum by other absorbers such as NH₃ and H₂O. Column amounts of the absorber(s) are generated in a conventional manner by fitting the experimental spectrum to a synthetic spectrum derived from theoretical absorber line strengths, and considering a multi-layered atmosphere. For our autumn retrievals we have assumed the HNO₃ vertical profile for May at 65°S obtained from the LIMS satellite(5), and stratospheric temperatures from the 80°S zonal mean climatology of Barnett and Corney(6). Temperatures for spring were taken from the sondé flights of Johnson et. al(7).

In order to test the significance of this on the retrievals a profile has been assumed where all the nitric acid is removed between 15 and 20 km. This results in an underestimate of the column amount by about 17 percent, so that discrepancies of this order may result when extreme changes to a normal profile take place and are not accounted for. Trends such as that observed in autumn will not be substantially affected.

The resulting nitric acid vertical column amounts at Arrival Heights are shown in Fig.3. There is a steady increase in the column amounts during autumn that is attributed to the heterogeneous conversion of N₂O₅ to HNO₃ on background aerosols. Gas phase models, by contrast, predict no substantial increase over this autumn period (Susan Solomon, private communication). When measurements resume with the return of the sun in spring it can be seen that the HNO₃ column amount has fallen to about half the late autumn value. The decrease is believed to be due to the conversion of gas phase HNO₃ to the solid phase on the surface of polar stratospheric clouds as temperatures fall below the threshold temperature of approximately 196K to form the nitric acid trihydrate:

\[ \text{HNO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{HNO}_3\text{.3H}_2\text{O(s)} \]  \hspace{1cm} (4)

This is the second step, then, in the "denoxification" of the atmosphere that is a necessary condition for ozone depletion.
ACKNOWLEDGEMENTS

We are indebted to Alan Thomas and Grant Avery for operating equipment in Antarctica, to Dr. Shelle David for assistance with data analysis, and to DSIR Antarctic for logistic support.

REFERENCES