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Ground-based measurements of stratospheric NO_2 at Macquarie Island

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Slant column amounts of nitrogen dioxide (NO_2) have been measured at twilight at Macquarie Island using differential absorption spectroscopy. The data show a large seasonal cycle and diurnal variations. These changes are dominated by photochemistry. There are also smaller day-to-day variations that are probably caused by dynamical effects.

Introduction

Large reductions in ozone have been observed during the winter months in the southern Australasian high mid-latitude region (Stolarski et al. 1991; Lehmann et al. 1992a). A study of total ozone measurements from Macquarie Island (54.5° S, 159.0°E) has suggested that this ozone loss could be caused by the photochemical destruction of ozone (Lehmann et al. 1992b).

This paper presents measurements of stratospheric nitrogen dioxide (NO_2) from Macquarie Island. NO_2 and nitrogen oxide (NO) are the active species of the nitrogen cycle which participate directly in the catalytic reactions that destroy odd oxygen. In this way, the nitrogen cycle plays an active role in the oxygen cycle. The nitrogen cycle undergoes relatively rapid gas-phase chemical conversion processes in darkness. The primary night-time reaction mechanism involves converting NO to NO_2, then NO_2 to NO_3, and finally forming the reservoir species N_2O_5, in a three-body reaction between NO_2 and NO_3. During the daytime N_2O_5 is slowly photolysed back to NO_2. The partitioning between the active and inactive nitrogen species plays an important role in the processes that control ozone depletion.

Instrumentation

NO_2 observations have been made each day at sunrise and sunset from Macquarie Island since January 1996. The instrument in use at Macquarie Island is a Jobin-Yvon (JY) diffraction grating spectrometer, which scans over the wavelength range 430-490 nm. Similar instrumentation is used at Lauder, New Zealand (45°S) (McKenzie and Johnston 1982; Johnston and McKenzie 1989; Johnston et al. 1992), and in the Antarctic at Arrival Heights (78°S) and Halley Bay (76°S) (McKenzie and Johnston 1984; Keys and Johnston 1986; Solomon and Keys 1992).

The measurement technique, which is called differential absorption spectroscopy, uses the highly structured NO_2 absorptions which are present in sunlight scattered from the zenith sky in the region of 450 nm. At twilight the observed scattered sunlight passes through a long stratospheric slant path, which enhances the weak NO_2 absorptions. The spectra obtained at twilight are ratioed with a selected spectrum that was obtained at midday, so as to remove the Fraunhofer structure. Slant column amounts of NO_2 are then deduced from the resulting ratio spectra using the method described in detail by Johnston and McKenzie (1989).

The NO_2 data have been processed using the scanned data from the wavelength range 432-457 nm. The NO_2 cross-sections that are used in the data processing were determined at room temperature (H.S. Johnston, private communication). Recent work has shown that using room temperature cross-sections can lead to a temperature-dependent overestimate of the NO_2 column of 18 per cent at typical stratospheric temperatures (Harder et al. 1997). At Macquarie Island the seasonal cycle in temperature, at an altitude

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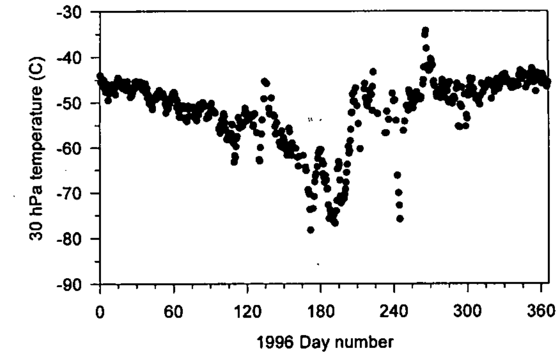
Fig. 1 **Daily stratospheric temperatures for the 30 hPa level for 1996, which corresponds to an altitude of about 24 km, obtained from radiosondes.**



close to the peak NO_2 concentration, has a range of 35°C (Fig. 1); so neglecting the temperature dependence of the NO_2 absorption cross-sections will lead to an underestimate of the summer slant NO_2 columns of about five per cent relative to the winter slant columns (Solomon and Keys 1992).

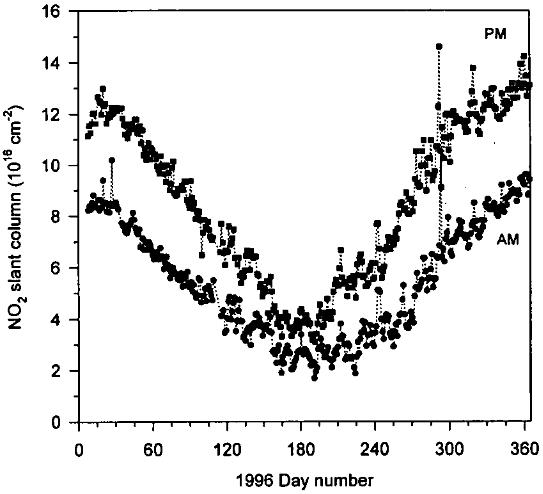
Results

Seasonal and diurnal variation

Figure 2 shows the NO_2 slant column amounts measured at a solar zenith angle of 90°. The data show a striking seasonal pattern, with maximum values occurring in summer and minimum values in winter. The summer values are between three and four times larger than the winter values. There is also a diurnal pattern with the sunrise values being lower than the sunset values. Similar seasonal and diurnal patterns have been reported for other sites (e.g. Noxon et al. 1979; Syed and Harrison 1981; Johnston and McKenzie 1989; Solomon and Keys 1992; Kondo et al. 1994). The mid-summer NO_2 values at Macquarie Island are about five per cent higher than the values from Lauder, New Zealand (45°S), and the mid-winter values are marginally lower than at Lauder.

The seasonal and diurnal patterns are caused by the changing partitioning between NO_2 and N_2O_5. During the night NO_2 is oxidised into N_2O_5, and during the day N_2O_5 is photolysed to regenerate NO_2. This results in larger NO_2 values at sunset than at sunrise. The seasonal pattern is therefore largely influenced by the changing length of the night with season. The lowest NO_2 values are observed during the winter which is when the nights are longest. However there are other sources of variability since, as shown in Fig. 2, the curves are not symmetric about the winter solstice, with the decline in NO_2 in autumn occurring more rapidly than the springtime recovery.

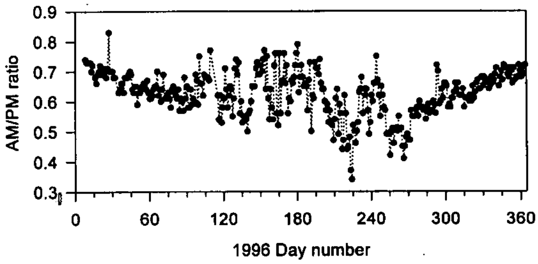
Fig. 2 **Sunrise (AM) and sunset (PM) NO_2 slant columns from Macquarie Island for 1996.**



The ratio of the sunrise NO_2 slant column to the sunset NO_2 slant column indicates the proportion of evening NO_2 remaining after the night-time conversion to N_2O_5, and so illustrates the diurnal variability in NO_2. The value of the sunrise/sunset NO_2 ratio will clearly be influenced by the duration of the night. Figure 3 shows that at Macquarie Island the sunrise/sunset ratio varies from 0.3 to 0.8, and has an average value of 0.6. There is an interesting seasonal change in the sunrise/sunset ratio with a steady decline during the first three months of the year, a steady increase during the last three months of the year, and a large degree of variation from April through to the end of September.

The night-time oxidation of NO_2 into N_2O_5 proceeds at a rate that depends on the ozone density and the stratospheric temperature. Figures 1 and 4 show

Fig. 3 **Sunrise/sunset NO_2 ratios for each day for 1996.**



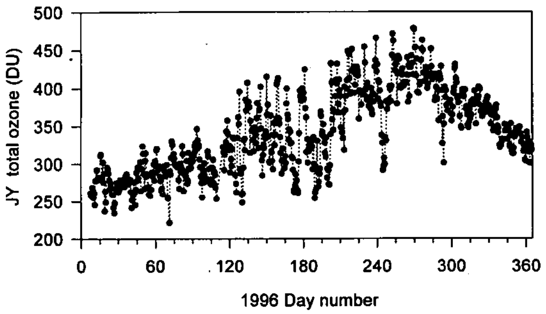
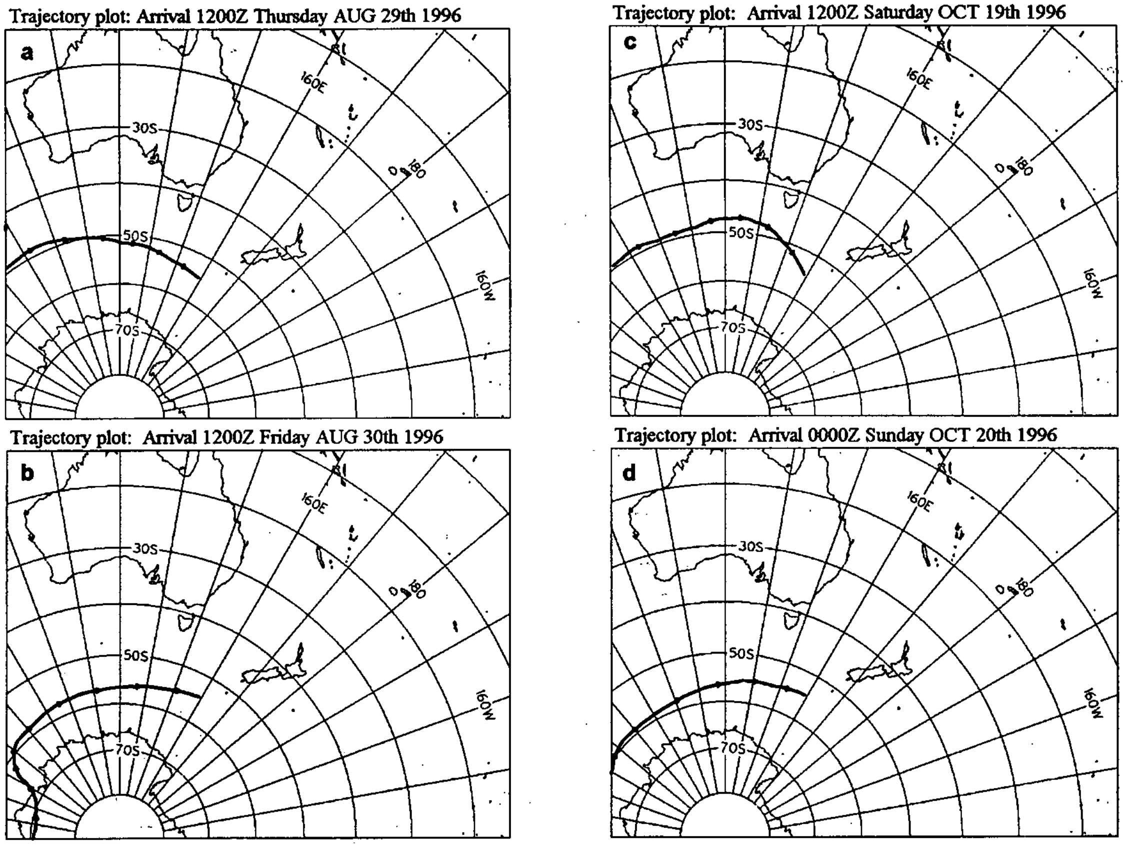


Fig. 4 Daily total ozone values for 1996, obtained simultaneously with the NO_2 values, from the JY spectrometer.

that the variability in the sunrise/sunset ratios is a reflection of that seen in the total ozone values and stratospheric temperatures. The lowest ratios are observed during the late winter and early springtime (day 210 to day 270), which is when ozone levels and stratospheric temperatures tend to be higher, and as a consequence the night-time N_2O_5 formation is accelerated (Johnston et al. 1992). This results in the springtime recovery in NO_2 occurring more slowly than the autumn decline.

The ozone measurements in Fig. 4 are from the JY spectrometer (McKenzie and Johnston 1983); they are obtained from processing the scan data over the wavelength range 445-488 nm. Although these measurements are less accurate (~±15 per cent) than total ozone values from a Dobson spectrophotometer (Nichol et al.

Fig. 5 Air parcel back-trajectories for arrival at 100 hPa at Macquarie Island relating to the high NO_2 events. The time interval corresponding to the distance between the adjacent arrowheads on the trajectory is six hours. Trajectories (a) and (c) are for midnight 29 August 1996 and midnight 19 October 1996 respectively, which are occasions with high NO_2 values. Trajectories (b) and (d) are for midnight 30 August 1996 and midday 20 October 1996 respectively; these occasions mark the onset of low stratospheric temperatures, and the trajectories indicate airflow from high latitudes.


Trajectory plot: Arrival 1200Z Thursday AUG 29th 1996

Trajectory plot: Arrival 1200Z Saturday OCT 19th 1996

Trajectory plot: Arrival 1200Z Friday AUG 30th 1996

Trajectory plot: Arrival 0000Z Sunday OCT 20th 1996

1996), they are useful since they are obtained simultaneously from the same sampled volume as the NO_2 amounts.

Day-to-day variability

Figure 2 shows that besides the seasonal and diurnal changes in NO_2, there are also changes from day to day (i.e. comparing sunrise values with sunrise values, and sunset values with sunset values) that are often of the order of 10-20 per cent, but can be as high as 40 per cent. These changes, which tend to occur from autumn through to spring, may be related to variations in the stratospheric circulation and planetary wave activity.

There are two interesting events which illustrate this day-to-day variability. These events occur between 29 August and 1 September (day 242 to day 245), and 19-20 October (day 293 and day 294). During these events there is unusually high NO_2, so that the day-to-day variability is as great as 30-40 per cent, as shown in Fig. 2. The NO_2 slant column measured at sunset on 19 October was the highest NO_2 measured throughout the whole year; the NO_2 slant column at sunrise on 20 October was also very high, and in fact had a similar value to the typical evening NO_2 values from that time of year.

These events are also linked with unusually low total ozone (Fig. 4) and low stratospheric temperatures, particularly in the case of the 29 August-1 September event (Fig. 1). The high NO_2 events lead the onset of low total ozone/low stratospheric temperatures by one or two days. Analysis of back-trajectories shows that for both events the onset of the low temperatures coincides with the arrival of stratospheric air at Macquarie Island that has recently been confined to high latitudes. This is particularly so with the 29 August-1 September event (Fig. 5).

Summary

The twilight measurements of slant column NO_2 from Macquarie Island show a large seasonal and diurnal cycle. The maximum values occur in summer and minimum values in winter; in addition, the sunset values are higher than the sunrise values. These cycles are dominated by photochemistry, and reflect the changing partitioning between NO_2 and N_2O_5. The springtime recovery in NO_2 occurs more slowly than the autumn decline, indicating that the ozone density and stratospheric temperatures also play a role in the partitioning between NO_2 and N_2O_5.

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