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NO_2 COLUMN CHANGES INDUCED BY VOLCANIC ERUPTIONS

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ABSTRACT

Nitrogen dioxide slant column amounts measured by ground-based remote sensing from Lauder, New Zealand (45°S) and Campbell Island (53°S) during the second half of 1991 and early 1992 show anomalously low values that are attributed to the effects of volcanic eruptions. It is believed that the eruptions of Mount Pinatubo in the Philippines in June 1991 and possibly Mount Hudson in Chile in August 1991 are responsible for the stratospheric changes, which first became apparent in July 1991.

The effects in the spring of 1991 are manifested as a reduction in the retrieved NO_2 column amounts from normal levels by 35 to 45 percent, and an accompanying increase in the overnight decay of NO_2. The existence of an accurate long-term record of column NO_2 from the Lauder site enables us to quantify departures from the normal seasonal behaviour with some confidence. Simultaneous retrievals of column ozone agree well with Dobson measurements [*Johnston et al.*, 1992], confirming that only part of the NO_2 changes can be attributed to a modification of the scattering geometry by volcanic aerosols. Other reasons for the observed behaviour are explored, including the effects of stratospheric temperature increases resulting from the aerosol loading, and the possible involvement of heterogeneous chemical processes.

1. INTRODUCTION

Mount Pinatubo (15°N, 121°E) erupted strongly in June 1991, injecting large quantities of SO_2 and other gases into the stratosphere to altitudes > 25 km. The magnitude of the eruption was reported to be significantly larger than the El Chichon eruption of 1982, and the aerosols which were subsequently formed were transported more rapidly to the Southern Hemisphere. Consequently, the effects of the eruption on NO_2 levels measured in New Zealand were much greater than those seen following the El Chichon eruption of 1982, and resulted in a depletion of 35-45% in the NO_2 column by late 1991 [*Johnston et al.*, 1992].

The measurements use the small absorptions by atmospheric NO_2 seen in solar radiation at wavelengths near 450 nm, which has been scattered from the zenith sky at twilight. Although changes to NO_2 slant columns may be expected due to changes in scattering geometry, sensitivity tests have shown that expected changes would be relatively small [*Perliski and Solomon*, 1992]. Similarly, any changes in column NO_2 due to perturbed photolysis rates and stratospheric temperatures are likely to be small [*Michelangeli et al.*, 1989]. These considerations led us to speculate that heterogeneous processes may be causing the NO_2 reduction, as predicted earlier from theoretical considerations [*Austin et al.*, 1986, *Rodriguez et al.*, 1991].

Here we present more recent NO_2 column measurements from Lauder New Zealand (45°S), and new data from Campbell Island (53°S). These data show that the NO_2 was depleted over a wide range of latitudes. The greatest effects were seen in late 1991. Measurements of HNO_3 and profiles of atmospheric aerosol provide further evidence that heterogeneous processes are involved in the NO_2 reduction (work in preparation).

2. MEASUREMENTS

Daily observations of atmospheric NO_2 column amounts have been made at sunrise and sunset at Lauder since December 1980, so that the seasonal and diurnal variability of NO_2 is now well characterized at this site. Examination of the full 11 year data set shows longer term features that are believed to be linked to the El Chichon eruption in 1982, and the phase of the solar cycle [*Johnston and McKenzie*, 1989].

In order to investigate the impact of Pinatubo, we first compare the data after the eruption with data from 1990. There was a reduction in solar activity over this period, but it would lead to only a small reduction under normal conditions [*NOAA*, 1991]. In the latter part of 1991 and the first months of 1992, the NO_2 behaviour was very different from 1990 and early 1991. Time series of morning and evening slant column NO_2 amounts measured at Lauder are shown in Figure 1. In this Figure (and in Figure 2), the slant column amounts may be converted to approximate vertical column amounts by dividing by 15 [*McKenzie et al.*, 1991]. However, this conversion factor depends on the vertical distribution of NO_2 which may be influenced by the presence of aerosols.

Data from 1990, which are overlaid in Figure 1, exhibit the normal photochemically-driven diurnal and seasonal variability. The shorter term variations in both years are due to dynamical effects, and there are occasional transients which we attribute to rare events of local pollution. The large day to day variation in the slant column amounts (with standard deviation typically 0.3 x 10^{16} molecule cm^{-2}) results from dynamical variations rather than measurement noise, which is < 0.1 x 10^{16} molecule cm^{-2}. The figure illustrates that despite the large day to day differences in NO_2, the column amounts since August 1991 have been depressed significantly. The depletions are the largest anomaly we have seen in the 11 year continuous record of NO_2 measurements from this site, and exceed the effects of El Chichon by more than a factor of 2 [*Johnston et al.*, 1992].

The anomalies first appeared around day 220 to 230, about the same time as the first visual sightings of aerosol effects. Instead of the NO_2 increasing as normal in the spring, it remained close to normal winter levels. The morning observations were depressed most, so that the normal July "winter" minimum was delayed until September. In late October (around day 290), the mean NO_2 measured at sunrise was depressed by 35-45% compared with 1990. The effect was smaller at sunset, and the corresponding depletions were 30-40%. The period of maximum depletion appears to be near the end of 1991, and by the end of the data record the NO_2 levels appear to close to normal. It is too early to estimate the time scale of recovery from this data, but after the El Chichon eruption, effects were still probably influencing our NO_2 measurements 2 to 3 years later, and we would expect a similar long term effect from Pinatubo. Aerosol profiles measured at Lauder show little change in the aerosol loading between Feb 1992 and May 1992 (data from Dr. J. Rosen, University of Wyoming), but a settling to lower altitudes, so that the peak altitude of 22 km in Feb had reduced to 19 km in May. There has therefore been progressive reduction in altitude of the volcanic aerosol. This reduction in altitude may be an important factor in the recovery of NO_2, which is distributed at higher levels.

Systematic differences in the am/pm ratio have also been observed. This am/pm difference arises because during the night NO_2 is converted to N_2O_5. During the day this N_2O_5 is photolysed to regenerate NO_2, giving larger amounts in the afternoons. Typically, the am/pm ratio is 0.65, although in spring the ratio tends to be lower [*Johnston and McKenzie*, 1989], because ozone levels and temperatures are higher, and as a consequence, night time N_2O_5 formation is accelerated. In all previous years, the mean am/pm ratio in spring has been greater than 0.5. It was less than 0.5 in September 1991 however, giving further evidence that chemical changes, as well as geometric changes, have occurred.

NO_2 data obtained from Campbell Island (52.5°S, 169°E) is shown in Figure 2. Although some data is available from earlier periods, there is no climatology of NO available from this site. However the available data show departures apparently due to the volcanic aerosol that are similar in magnitude and timing to those seen at Lauder. Thus the extent of the perturbation to NO_2 is clearly widespread in the Southern Hemisphere. We have also seen depletions in the Northern Hemisphere NO_2 at similar periods from our instruments located in Sweden and Japan (work in progress).

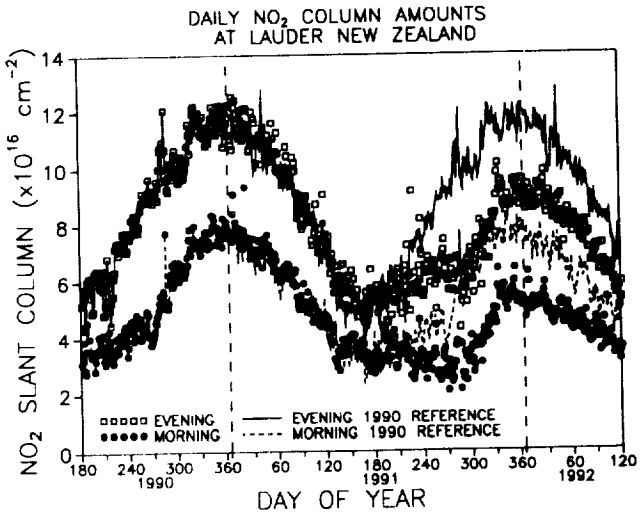

Fig. 1. Time series showing the variability of daily sunrise and sunset NO_2 measurements at Lauder since mid 1990. The variations in 1990 are repeated in later years as a reference to show the extent of the perturbation due to volcanic aerosol.

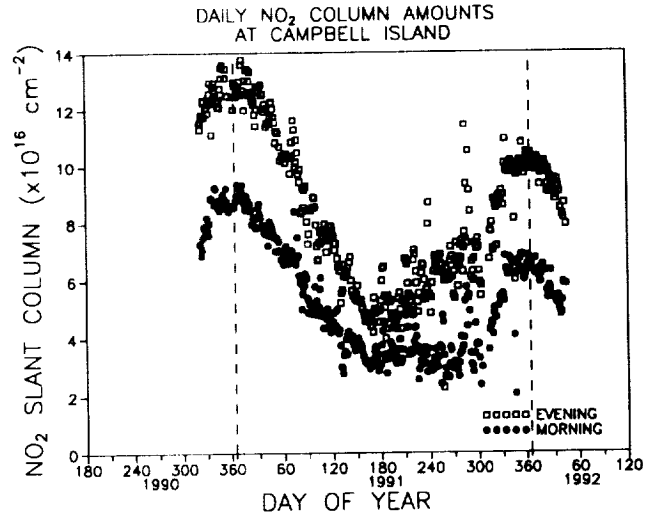

Fig. 2. Time series showing the variability of daily sunrise and sunset NO_2 measurements at Campbell Island since measurements commenced in 1991.

3. DISCUSSION

Some of the observed differences in NO_2 are due to changes in scattering geometry caused by the aerosols, as discussed in *Johnston and McKenzie* [1989] in reference to the effects of El Chichon. However, sensitivity tests comparing ozone measurements, and preliminary model calculations of the sensitivities of enhancement factors to aerosol loadings suggest that only a small fraction of the observed decrease can be attributed to changes in scattering geometry [*Perliski and Solomon*, 1992].

In Figure 3 we attempt to put the observed changes in NO_2 at Lauder into perspective compared with previous changes. This figure also gives an indication of the development and recovery of the NO_2 perturbation at Lauder. Monthly averaged data is used, to reduce noise due to natural dynamical variations. The data shown are the monthly NO_2 columns expressed as fractions of the means for each month calculated for years (1981, 1989, 1990) which had similar solar activity, and which were not influenced by volcanic aerosols. Prior to the eruption, the anomalies are positive because the period of interest is close to solar maximum, when NO_2 levels also have a maximum. The maximum perturbation (40% apparent reduction) occurs in October 1991. Recovery begins in November 1990 and continues until the end of the data record currently available. The reductions are more pronounced in the sunrise data than in the sunset data.

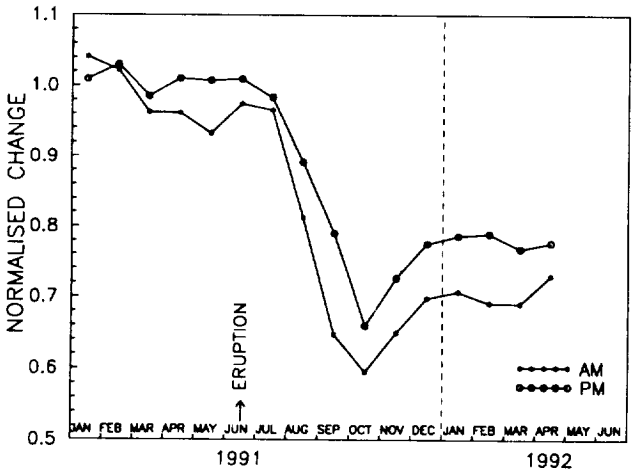

Fig. 3. Monthly mean NO_2 columns in 1991 and 1992 at Lauder, expressed as fractions of the means for the corresponding months during unperturbed years with similar solar activity (ie 1981, 1989, and 1990).

A detailed investigation of the reasons for these changes is not considered here. NO_2 columns at twilight, and the am/pm ratios are dependent on many factors including stratospheric temperature, ozone amount, surface albedo; all of which may be influenced by the presence of volcanic aerosol. Model calculations by *Michelangeli et al* [1989] suggest that for the aerosol loadings observed at Lauder, homogeneous chemistry effects on NO_2 are small.

However, the possibility of heterogeneous reactions on aerosol surfaces removing active nitrogen is of considerable interest, because with current atmospheric chlorine levels, they have the potential to reduce global ozone levels. We previously suggested [*Johnston et al.*, 1992] that the NO_2 perturbation could provide evidence for the heterogeneous reaction [*Hofmann and Solomon*, 1989; *Rodriguez et al.*, 1991]:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \text{ (on sulphate aerosol)}$$

which has been observed to occur in the laboratory. It is expected that the conversion rate would be increased as the concentrations of sulphate aerosols increase, leading to a decrease in NO_2 and ozone, and an increase in HNO_3 [*Rodriguez et al.*, 1991]. During the NZ summer of 1991/1992, when the volcanic perturbation was a maximum, ozone levels were normal. Preliminary analysis of FTIR data from Lauder suggests that HNO_3 has increased.

4. CONCLUSIONS

Following the arrival of volcanic aerosol from Pinatubo, depletions of NO_2 have been observed over wide range of latitudes in the Southern Hemisphere.

The depletions were largest in the sunrise data from the spring of 1991, when depletions of 35-45% were observed. Depletions of 30-40% were also seen in the sunset measurements. Only a small fraction of these changes can be attributed to changes in aerosol scattering.

We therefore conclude that a real chemical reduction in NO_2 of > 20% occurred as a result of the presence of the volcanic aerosol. The largest effects were seen in late 1991, a time when the volcanic aerosol was within the region of highest concentrations of NO_2 (above 22 km).

There is a strong possibility that heterogeneous chemical reactions are involved in the NO_2 losses. This is supported by the observations that (1) HNO_3 levels appear to have increased, and (2) the perturbation had decreased as the aerosol descended below the NO_2.

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