

# NO<sub>2</sub> and O<sub>3</sub> in the core of the Antarctic vortex: Observations and modelling at Belgrano station

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## 1. Introduction

A long term monitoring program for NO<sub>2</sub> and O<sub>3</sub> column by visible spectroscopy in the Antarctic region using the DOAS technique at zenith during twilight was initiated in February 1994 by an Agreement between INTA (Spain) and DNA/IAA (Argentina). At that time three unattended scanning spectrometers operating in short spectral ranges for NO<sub>2</sub> (430-450 nm) and O<sub>3</sub> (470 - 490 nm) observations were deployed [Yela *et al.*, 1998]. The stations are located between 55° and 78° South, separated by 10° in latitude providing a good information inside, at the edge, and outside the polar vortex, and very close in longitude providing meridional cross-sections across the vortex. In 1999 the observations were extended by an ozonesounding program at Belgrano station (continental Antarctica, 78°S, 35°W). The 5 years spectroscopic dataset available of this latter station are analysed and compared with the Chemical-Transport-Model SLIMCAT [Chipperfield, 1999] including heterogeneous chemistry for the same location and observational solar zenith angles.

## 2. Results

By defining the vortex at 475K level as the area with PVU values over -45 PVU, it is shown that the station remains during the winter and most of spring well inside the polar vortex as can be seen by the lower stratosphere potential vorticity record (see figure 1).

The NO<sub>2</sub> column displays a strong, photochemically driven, seasonal wave ranging from values of  $5 \times 10^{15}$  molec/cm<sup>2</sup> in summer to close to zero in winter and early spring (at the instrument sensitivity threshold) being the spring build-up delayed almost two months of what would be expected from photochemistry as result of the strong winter denitrification in the Antarctic stratosphere. In September, when the rate of ozone depletion is maximum, NO<sub>2</sub> already start to increase by photodissociation of the HNO<sub>3</sub> present in the layers above the PSCs altitudes. In spring there is almost no am-pm variability since very little N<sub>2</sub>O<sub>5</sub> is available after the polar night for diurnal conversion. The annual evolution of NO<sub>2</sub> displays small dynamical features superimposed to the seasonal wave with very little inter-annual variability.

Observations of total ozone at high latitudes during winter are sparse because of the absence of solar radiation. DOAS technique at twilight allows to extend

few weeks the direct sun record over a period in which uncertainties still exist.

Ozone above Belgrano in autumn remains in the range of 300-350 DU. In spring, the depletion starts when the light available in the stratosphere exceeds 4 hours at a rate of 4-5 DU.day<sup>-1</sup>. Data from ozonesoundings over the station show that the depletion occurs at altitudes between 335K and 630K at an almost linear rate of 0.04-0.05 ppm.day<sup>-1</sup>.

The SLIMCAT model reproduces well the observations of NO<sub>2</sub> in seasonal oscillation, in the spring recovery delay, and in the diurnal variability (am/pm ratio). The autumn decay computed by the model start, in some years, a few days earlier than the observations. The difference is maintained until the winter. During the polar night, when no data are available, NO<sub>2</sub> in the model suffer a further reduction from  $5-6 \times 10^{14}$  to almost complete disappearance.

Since 1994 a decrease in the summer maxima of -2.5% year<sup>-1</sup> is observed. Although the number of years available are too small to confirm a trend, this result is opposite of what is observed in Southern Hemisphere at mid latitudes [Liley *et al.*, 2000] suggesting a latitudinal redistribution of the NO<sub>y</sub> by changes in transport in last years.

The comparison of ozone column shows discrepancies between model and observations in early spring when it seems that the model underestimates the column. The behaviour is found to be the same for all years. The model shows a continuous decrease in the column starting at the end of the summer. By the beginning of August it is already at 225 DU in average, that is 32% lower than in January-February. Observations, on the other hand, show for August ozone amounts comparable to that in autumn. Although the accuracy spectroscopic observations in the beginning of spring are limited by the very high minimum *sza* (92° in mid August), the underestimation of the model in late winter is supported by the ozonesoundings carried out over the station. Dobson measurements at Halley Bay [Keys and Gardiner, 1991], a station close to Belgrano, agrees with our data displaying a fast depletion starting around day 240 (end of August). Unfortunately no soundings are available for the previous month and hence the Antarctic winter ozone maximum found over Faraday (67°S) [Roscoe *et al.*, 1997] cannot be verified for Belgrano. The O<sub>3</sub> autumn-winter decrease in the model is probably related to its grid size (7.5°x7.5°), too coarse for the high latitude of the station. The model

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underestimation of the O<sub>3</sub> column may be due to the inclusion of ozone poor air from lower latitudes, and underestimation of air subsidence inside the vortex, at least in winter.

From the 5 years record in the model, a negative trend is also observed in the extreme values (spring minimum and summer maximum) of 4 DU·year<sup>-1</sup> (approximately 1.6% year<sup>-1</sup> of the annual mean). The breaks in the spectroscopic data during periods with no twilight preclude an observational confirmation of this trend.

It worth to note that according to NCEP data, temperature over the station at 50hPa decreased in 3° during the studied period, and this cooling occurred mainly in summer. At higher levels there is no apparent interannual variation,

Small scale dynamical features are not seen in the model because of its coarse grid size but episodes of changes in the column due to strong temperature fluctuations occurring in spring are accurately reproduced.

**Acknowledgements.** PV data provided by NILU database (from ECMWF). Temperature data from NCEP/NCAR. This work was

supported by CICYT- ANT97-0433.

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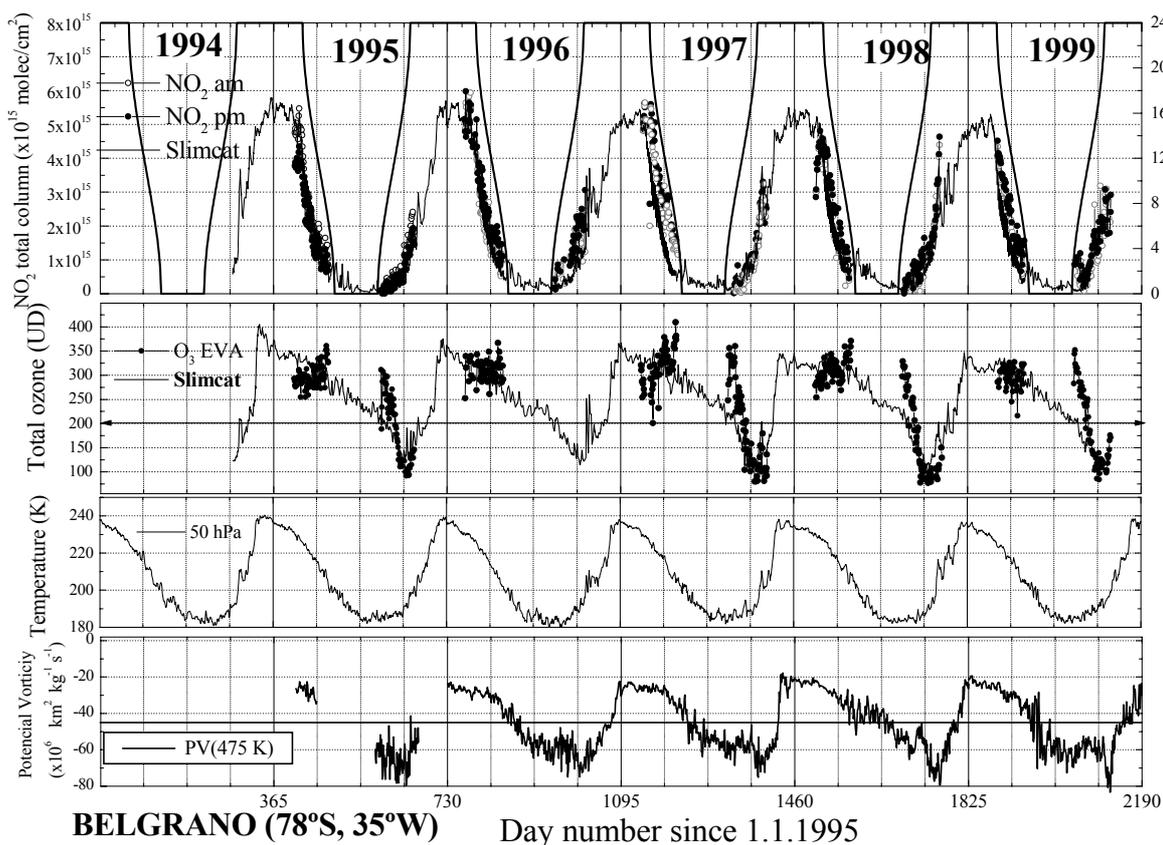


Figure 1. (panel a) Record of observed NO<sub>2</sub> (black circles PM, grey circles AM), modelled by SLIMCAT (solid thin line) and hours of sunlight at an altitude of 25 km (thick solid line). In panel b) the ozone daily mean (black circles) and model (solid line). In panel c) NCEP Temperatures at 50 hPa and in bottom panel the Potential Vorticity at 475K