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The September 2002 Antarctic vortex major warming as observed by visible spectroscopy and ozone soundings

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The record of O_3 total column and NO_2 obtained by visible spectroscopy at Ushuaia (55° S), Marambio (64° S) and Belgrano (78° S) and vertical ozone profiles from the latter station provide insight into the unprecedented major warming observed above Antarctica in the last week of September 2002. From 18 September to 25 September the temperature increased 54°C at the isentropic level of 700 K. The temperature anomaly was observed down to the level of 300 K in which a well-defined tropopause was established. From comparison of the ozone profiles before and during the event, it can be seen that a fast increase in O_3 took place basically above 500 K, but the layer where the ozone hole occurs was barely affected. Low potential vorticity values above Belgrano occurred only at levels above 500 K, confirming that the vortex split was confined to heights above the layer of the Antarctic spring depletion. The signature of poleward-transported air is clearly visible from the NO_2 column departure from the envelope of the previous years in all three stations. NO_2 columns larger than typical for ozone hole conditions by 400% were observed at Belgrano. Diurnal variations provide evidence of non-denitrified extra-vortex air.

1. Introduction

The dynamics of the Antarctic stratosphere in winter and spring are characterized by a strong, large-scale low pressure system centred around the pole. The structure is called the Antarctic vortex and it extends from the tropopause to the middle stratosphere. The maximum gradient of the strong winds defining the edge of the vortex preclude air mass exchanges between the pole and mid-latitudes (Li *et al.* 2002) Under these conditions, ozone depletion occurring through reactions involving halogens activated by Polar Stratosphere Clouds (PSCs) in a very cold and dark stratosphere remains until late spring, when the vortex collapses. The persistence of the isolated vortex plays a determinant role in the evolution of the ozone depletion until its complete removal in the lower stratosphere.

During the Southern Hemisphere winter and spring of 2002 the Antarctic vortex showed an unusual behaviour when compared with the record from previous years (Varotsos 2002). A warm and weak vortex led to the first major warming ever observed in the Austral Hemisphere (Naujokat and Roscoe 2005). Although

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anomalies in temperature were observed throughout the winter (Newman and Nash 2005), the strongest phenomenon occurred in late September when the vortex drifted from the Pole towards the Weddell Sea and elongated from the Pacific Ocean to South Africa. The upper part of it completely split into two separate lobes over successive days. The western vortex moved to the Pacific and was dissolved after two weeks, while the eastern one strengthened and recovered the circumpolar position in October. By the first days of November this weak and elongated vortex was displaced off the pole, towards the southern tip of South America before the final vortex breakdown.

As a result of the anomaly, the ozone column in the central area of the Antarctic continent recovered the values typical of mid-latitudes. The minimum O_3 value during the phenomenon between 40° S and 90° S was above 80 Dobson units (DU) of the late September mean for eight years (between 1990 and 2001) where Total Ozone Mapping Spectrometer (TOMS) data are available (Stolarski *et al.* 2005). These values represent between 30% and 50% higher columns than the previous largest minimum for the date.

The evolution of this unprecedented event is examined by means of the records of NO_2 and O_3 total column obtained by visible spectroscopy at Belgrano (78° S, 35° W), Marambio (64° S, 55° W) and Ushuaia (55° S, 68° W) and by vertical ozone profiles from electrochemical sondes for the first station. The stations are close in longitude, separated by 10° in latitude, providing good information inside, at the edge and outside of the polar vortex. Observations are performed in Argentinean stations in the frame of a long-term monitoring programme established in 1994 between Instituto Nacional de Técnica Aeroespacial (INTA) and Dirección Nacional del Antártico (DNA), for ground-based spectroscopy, and extended to the year 1999 with the installation of the ozone sounder.

The results of measurements in the vertical ozone distribution are used to describe the different behaviour of ozone with altitude and are compared with values from previous years, providing new data for insight into the strength of the anomaly. The NO_2 data are compared with typical values for the season based on the available record of ten years, providing further evidence on the exceptional situation in poleward transport, subsidence and photochemistry in September 2002.

Nitrogen oxides play a significant role in atmospheric chemistry by destroying ozone at altitudes between 25 km and 40 km via gas-phase catalytic reactions. NO_2 in the stratosphere presents a seasonal evolution dominated mainly by photochemistry with maxima around the solstices and minima at the equinoxes. Transport modulates the seasonal wave on a shorter scale of a few days to weeks. NO_2 displays a diurnal wave controlled by the hours of light. During the night NO_2 is converted to N_2O_5. In the winter polar regions most of the NO_2 is in the form of the N_2O_5 reservoir. If PSCs are present, HNO_3 is formed by N_2O_5 hydrolysis on the surface of the particles, thus removing all nitrogen oxides ($NOx = NO + NO_2$) in the gas phase (denoxification). Sedimentation of PSC can irreversibly remove inorganic nitrogen from the stratosphere (denitrification). These processes occur regularly during the Antarctic winter and are necessary conditions for maintaining active halogen oxides and hence allowing ozone depletion to progress until its complete removal.

During the major warming event, Belgrano station was located with respect to the vortex at the splitting point. Marambio and Ushuaia remained under the influence of a secondary high-pressure system developed in the South Atlantic sector during the main phase of the event (figure 1). A detailed analysis of the meteorological

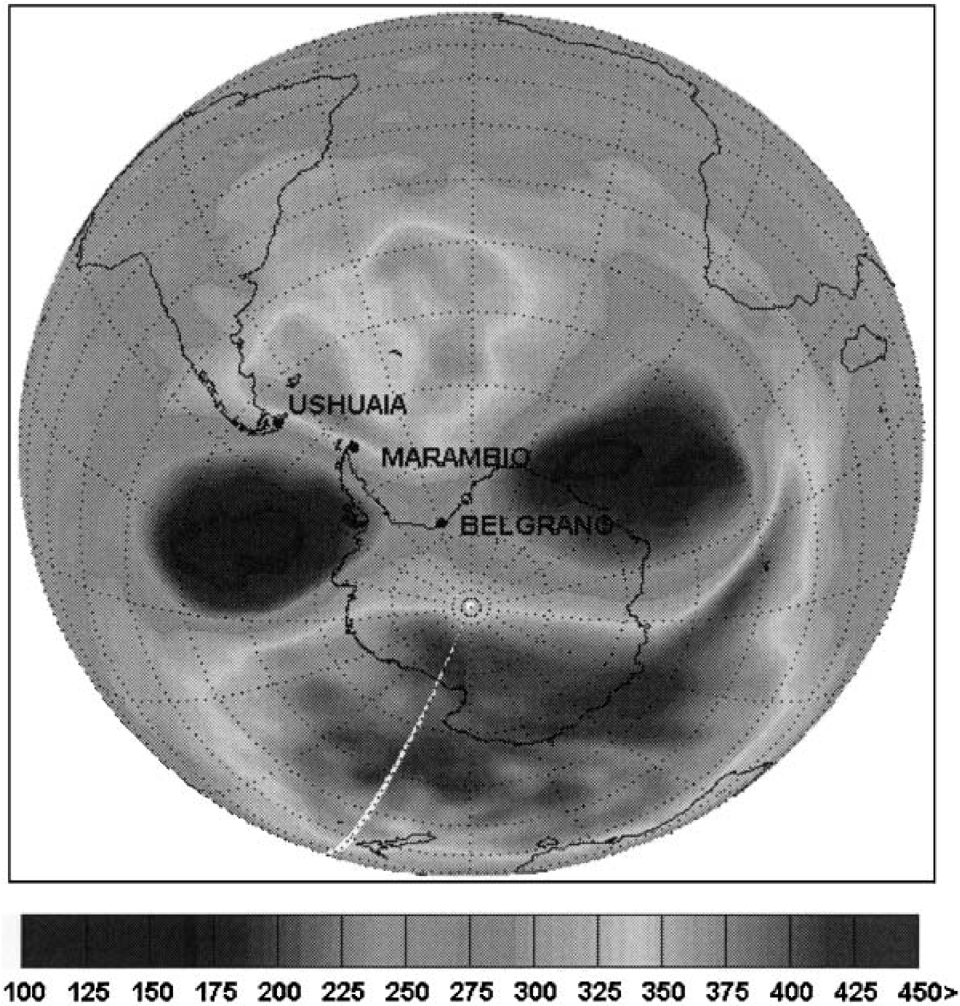


Figure 1. Location of the three observing stations in the Antarctic area superimposed on the map of the GOME (Global Ozone Monitoring Experiment) total ozone assimilated by the Royal Netherlands Meteorological Institute (KNMI) for 25 September 2002.

situation of the Southern Hemisphere during the developing and main phase of the vortex splitting can be found in Simmons *et al*. (2005).

The interpretation was carried out with the help of the European Centre for Medium-Range Weather Forecasts (ECMWF), potential vorticity (PV) fields on isentropic levels in the lower stratosphere and from isentropic back-trajectories.

2. Instruments and data

Vertical NO_2 and O_3 columns were retrieved from visible spectrometers based on the Differential Optical Absorption Spectroscopy (DOAS) technique. The instruments collect scattered sunlight at zenith during the twilight period and record the spectra by a thermally regulated photomultiplier after passing a dispersive ruled grating. All year-round data are available for separated twilights in Ushuaia and Marambio. At

Belgrano, only two periods of measurements between mid-February–end April and from the beginning of August–end of October are possible due to the requirement of a solar zenithal angle (sza) lower than 92°. The spectrometers operate in the range of 430–450 nm for NO_2 and 470–490 nm for O_3 (Gil and Cacho 1992, Yela *et al.* 1998). A fully automatic version, PC-controlled through a serial line and regulated for temperature was developed for this application. Sets of 30 spectra, 200 samples each, were accumulated for each measurement in order to reduce the instrumental photomultiplier noise. Averages of ozone and NO_2 morning and evening vertical columns were derived from measurements taken between 88° and 92° sza. The spectrometers were compared with each other after one year of measurements with the help of a NO_2 cell containing a known amount of gas at a given temperature. The discrepancy among the three instruments was found to be below 4%. Instrumental errors in individual spectrometers are estimated to be 1×10^{14}–2×10^{14} molec. cm^{-2} in the vertical column for NO_2 and 10–15 DU for O_3. Intercomparison of the ozone column between an identical spectrometer to those used here and the Brewer 157 — presently the European reference (Vanicek and Cuevas 2002) — at the GAW (Global Atmosphere Watch) and Network for the Detection of Stratospheric Change (NDSC) Subtropical Izaña Observatory during the year 2001, showed an offset of 3.4% and a standard deviation of 2.4%. While slightly sensitive to the vertical distribution of aerosols and to the shape of the ozone profile, the DOAS at zenith has provided to be a very valuable technique in polar regions when only very high solar zenith angles are reached.

An instrumental failure took place in the Marambio instrument between May and July 2002 and no data are available for that period.

The spectroscopic technique at zenith requires knowledge of the path of the radiation through the atmosphere for a proper conversion of the measured slant column to a vertical column. The ratio between those two magnitudes is called Air Mass Factors (AMF) and these are dependent, to some extent, on the air temperature profile and on the vertical distribution of the molecule to be measured. However, in studies concerning seasonal or longer periods, AMF are generally taken as constant.

Studies on AMF sensitivity to changes in temperature and the vertical distribution of species (Sarkissian *et al.* 1995, Frieß 2001) show that AMF for NO_2 may vary by 3% from winter to summer. AMF for O_3 considering 'normal' and 'ozone hole' conditions vary by $\pm 5\%$. These changes were calculated for Belgrano by using ozone profiles and air density measured above the station in three cases, including 'normal', 'ozone hole' and 'pre-ozone hole' conditions. Results show that the differences at 90° are surprisingly small, even for severe 'ozone hole' conditions. The correction factor encountered for the measurement period (88° to 92° every 1°) is below 6% in all three cases.

Regular ozone soundings have been performed in Belgrano since 1999 using a Väisala DigiCora ground unit and Science Pump Corporation model ECC-6A sensors mounted on modified RS80 radiosondes. A TOTEX Balloon TX1200 designed for low temperature conditions is used. Oil bath dipping treatment was applied in winter when temperatures dropped below −90°C. Using this procedure, burst cases below the ozone maximum are minimized. Mean burst height is 28 km. During normal flight operation, ozonesondes were coupled via special interfacing electronics with radiosondes for data transmission. In addition, regular Pressure Temperature Humidity (PTU) parameters were measured by the radiosonde. Data were telemetered to the ground station for further data processing. The standard procedures used in the ozonesonde operation are those agreed upon at the NDSC ozonesonde PI meeting in Potsdam in June 1998 (NDSC 1998).

Back-trajectories were computed by the scheme developed at the Free University of Berlin. They were based on ECMWF analyses and forecasts (up to three days) at $2.5^\circ \times 2.5^\circ \times 6$ hours resolution. The isentropic motion of each trajectory was calculated using an integration time step of 10 minutes. For each integration step diabatic motions were applied which were assumed to result only from radiative processes. For the real-time calculation of the trajectories these heating/ cooling rates were estimated by the scheme from Lacis and Hansen (1974) for the short-wave heating and by a Newtonian cooling approach for the infrared cooling (Dickinson 1973). The scheme ensures that energy is conserved in the individual air parcel (Rex *et al.* 1999).

3. Results

3.1 *Ozone total column*

The daily evolution of total ozone (TOZ) in 2002 retrieved from visible spectrometers at the three stations are shown in figure 2. For Belgrano, the ozone column obtained from integration of the ozone soundings are also plotted. In order to illustrate the anomalous behaviour of the ozone during the major warming, the TOMS-V8 seasonal mean for the period 1996–2001 is shown as a reference. The gaps over Belgrano and Marambio are due to an absence of measurements in periods when the minimum solar zenith angle is larger than 84°.

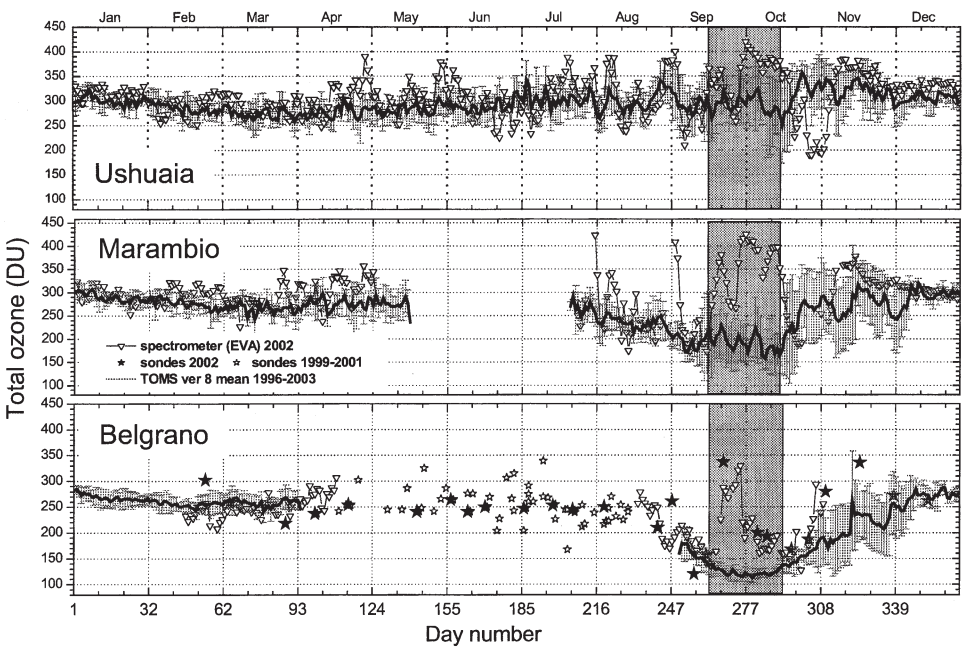


Figure 2. O_3 total column for year 2002 as measured by the zenith spectrometer (open triangles) superposed on to the TOMS V8 1996–2001 daily mean (solid line). Error bars denote one standard deviation. Open stars represent integrated ozonesonde profiles after extrapolation to zero atmosphere, assuming a constant mixing ratio from the burst altitude. Solid stars, the same for year 2002. The major warming period is shaded.

At Belgrano the typical seasonal evolution of ozone is characterized by a slow decrease from summer to autumn. During the winter polar night only data from ozonesondes are available. From the integration of the five-year profiles it can be deduced that the column during winter remains at an almost constant level (mean=252 DU) with a moderate scattering (1σ=27 DU) and no clear seasonal decreasing trend until the beginning of September when the chemical depletion starts.

During the period of the ozone hole, the interannual variability is very small, indicating the location of the station inside the vortex. In November, ozone increases again when the vortex weakens and the rich-ozone air of mid-latitudes reaches the station. At Marambio ozone depletion starts one month earlier due to its lower latitude and exhibits a larger year-to-year variability as result of its position at the edge of the vortex. Ushuaia displays an ozone seasonal wave typical of mid-latitudes, with short periods of low ozone at the end of the spring when the vortex tends to shift towards the Antarctic Peninsula.

During the first months of 2002 the total ozone at the three stations was generally close to their mean values. In winter, three minor warming events led to high ozone at Marambio and Ushuaia. At Belgrano only one of the warmings was observed during the polar night. Ozone column integrated from ozone soundings does not show any evidence of the anomaly. Columns around 250 DU were measured from April to the end of August. In early spring, as a consequence of the major warming event, anomalously high ozone was observed at the three stations, reaching a total column value twice as much as its mean values. The peak values recorded were 330 DU at Belgrano, 425 DU at Marambio and 420 DU at Ushuaia. Ozone depletion stopped earlier than in previous years and the minimum total column values were relatively high. By the end of October very low ozone values, typical of the polar vortex, were observed over Marambio and Ushuaia due to the displacement of the polar vortex.

3.2 *Vertical ozone distribution*

The vertical distribution and temporal evolution of O_3 in the core of the Antarctic polar vortex has been well characterized during the past few years, with the help of ozone sounding programmes (Hofmann *et al*. 1997, Karhu *et al*. 2003) and with the POAM-II (Bevilacqua *et al*. 1997) and POAM-III (Hoppel *et al*. 2003) orbital instruments. The weak planetary wave activity in the Southern Hemisphere resulted in a strong, quite stable and almost circumpolar vortex that remained undisturbed until the end of spring, prior to the final warming. Under these conditions, the ozone vertical distribution in spring was controlled by chemical halogen heterogeneous reactions, the dynamics being of secondary importance. As temperatures during the winter were well below the threshold of PSC formation and their interannual variability in the lower stratosphere is small, the process of ozone depletion is, with a number of exceptions, repetitive from year to year (Hofmann *et al*. 1997). Integrated ozone profiles between 350 K and 500 K isentropic levels computed from Belgrano ozone soundings between the available years in 1999 and 2003, display a steady reduction of 3–4 DU per day starting on 8 August (day number 220). By 2 October (day 275), almost all the ozone is removed (figure 3(*b*)). The 2002 record follows the typical evolution until day 260. From that date no further reduction occurs and the layer remains at 30–50 DU until the vortex dilution. Data indicate that, following the major warming, the ozone depletion was abruptly stopped even inside the vortex

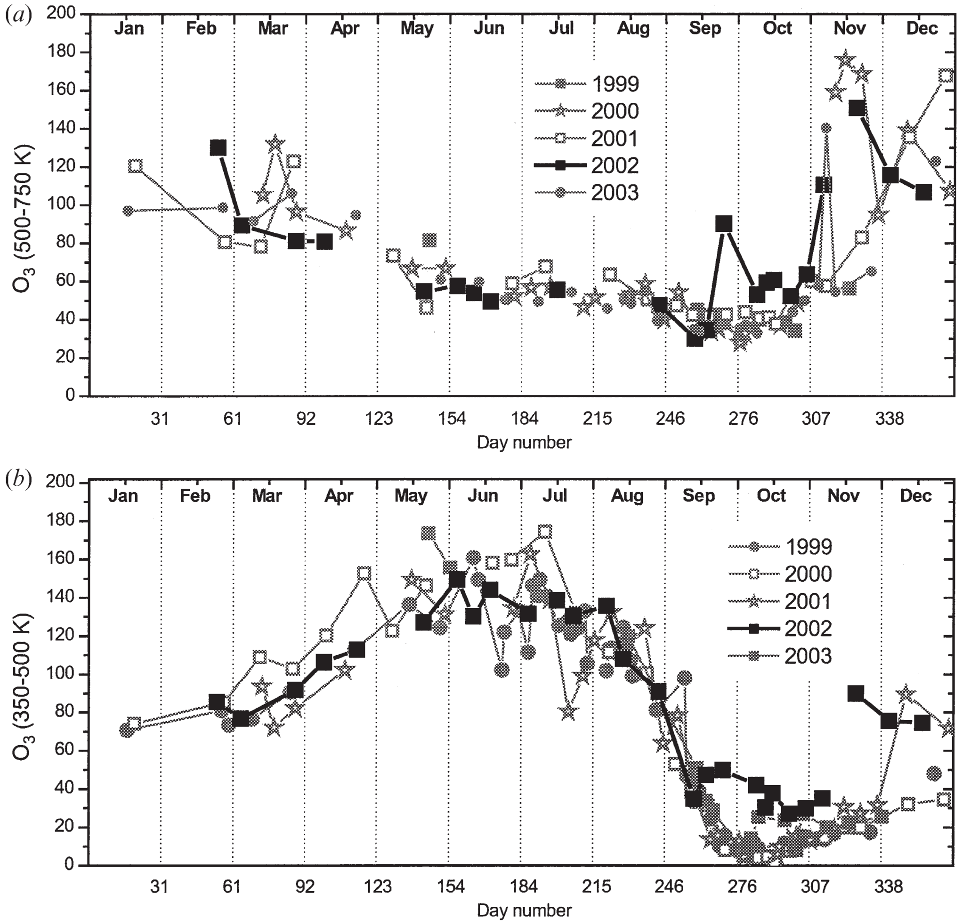


Figure 3. Ozone column for (*a*) the 500–700 K and (*b*) 350–500 K isentropic levels integrated from ozonesonde balloon flights at Belgrano.

above the station. At upper layers a sharp increase was observed. The integrated column between 500 K and 750 K reached 90 DU (figure 3(*a*)). This large ozone amount is typical of November after the vortex dilution but has never been observed as early as September. By the end of October the eastern vortex recovered the circumpolar position and Belgrano was again inside it, but the complete ozone removal observed in other years never took place.

During 2002, ozonesondes were launched on 18 September (S18 from here onwards), prior to the vortex major distortion, and on S25 when the vortex broke up into two parts (figure 4). Temperatures between the two soundings increased to 54° at the isentropic level of 700 K. The anomaly extended downwards to the 300 K level (8 km), where a well-defined thermal tropopause was established. The ozone profile on S25 displays an increase above 500 K, peaking at 720 K with 20 mPa (7.5 ppm), a factor of seven larger than the previous sounding.

The ozone distribution inside the vortex on S25 exhibits large laminae structures when compared to S18. This small-scale layering is a common feature in the Arctic lower stratosphere (Bird *et al.* 1997). The laminae have been reported from observations (Reid *et al.* 1993) and reproduced by model (Orsolini *et al.* 1995,

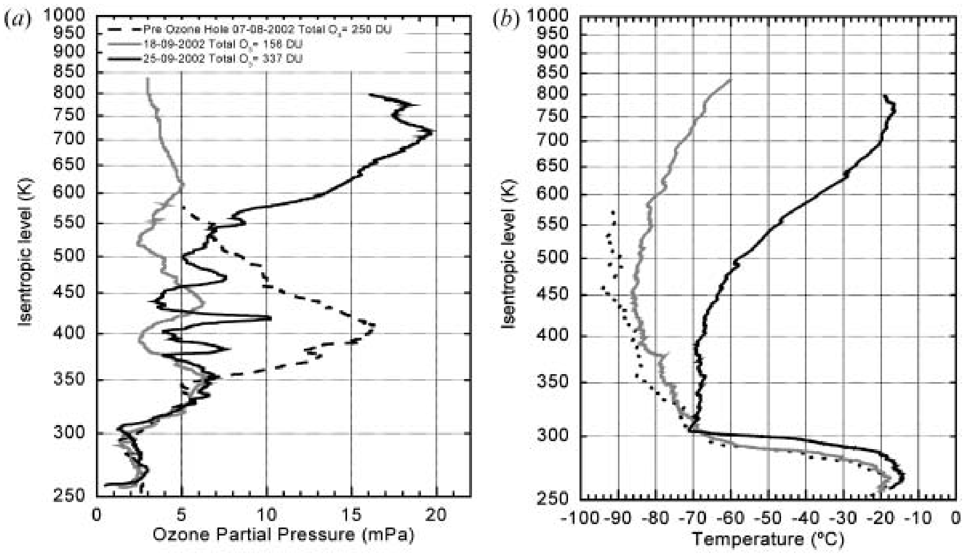


Figure 4. (*a*) Vertical ozone profiles before (grey line) and during (black line) the major warming. A winter profile representative of the pre-depletion date is shown as a reference

Manney *et al.* 1998). It is not uncommon to observe layering inside the vortex during the process of chemical ozone depletion due to inhomogeneities in the vertical distribution of PSCs and, hence, in Cl_2 amounts. In the absence of chemical losses, laminae provide an indication of air trajectories passing close to the vortex edge, particularly in a situation in which the vortex is drifting (Bird *et al.* 1997, Reid *et al.* 1998). Following the major warming, ozone depletion was stopped abruptly and streamers of low PV inside the vortex were observed in the output of the ECMWF analysis (Simmons *et al.* 2005) and in the ClaMS model (Grooß *et al.* 2005). This indicates that the observed layering can be attributed to streamers of air containing higher ozone eroded from the vortex edge under the unusually disturbed, elongated and drifting vortex.

Backward trajectory analysis at the barely affected level of 475 K shows that the air mass of day S25 passed by close to the station on S17 and remained inside the vortex during the period. The 675 K level air mass, on the other hand, suffered a significant adiabatic heating, raising the temperature by 23°C due to downward transport from 25 400 m to 22 900 m from ten to four days before reaching Belgrano, contributing to the increase in ozone observed at this level.

PV fields on S25 present an unusual structure departing from barotropy. In the lower level of 350 K, a single elongated vortex remains while in the upper levels the vortex has split into two well-separated parts acquiring a binocular shape (figure 5). Belgrano stayed inside the vortex up to around 550 K but remained in between the two vortexes at the levels where the abrupt increase of ozone takes place (figure 6). This vertical vortex structure above Belgrano can be observed clearly by plotting the modified PV (MPV) evolution with time at representative levels from the vortex base (figure 7). The modified PV (Lait 1994) is used as a normalization factor to reduce the rapid increase of PV with height. For each level MPV is computed as $PV(\theta/\theta_0)^{-9/2}$, where PV is the potential vorticity, and θ, θ_0, the potential temperatures at a given level and the reference of 475 K, respectively. The central

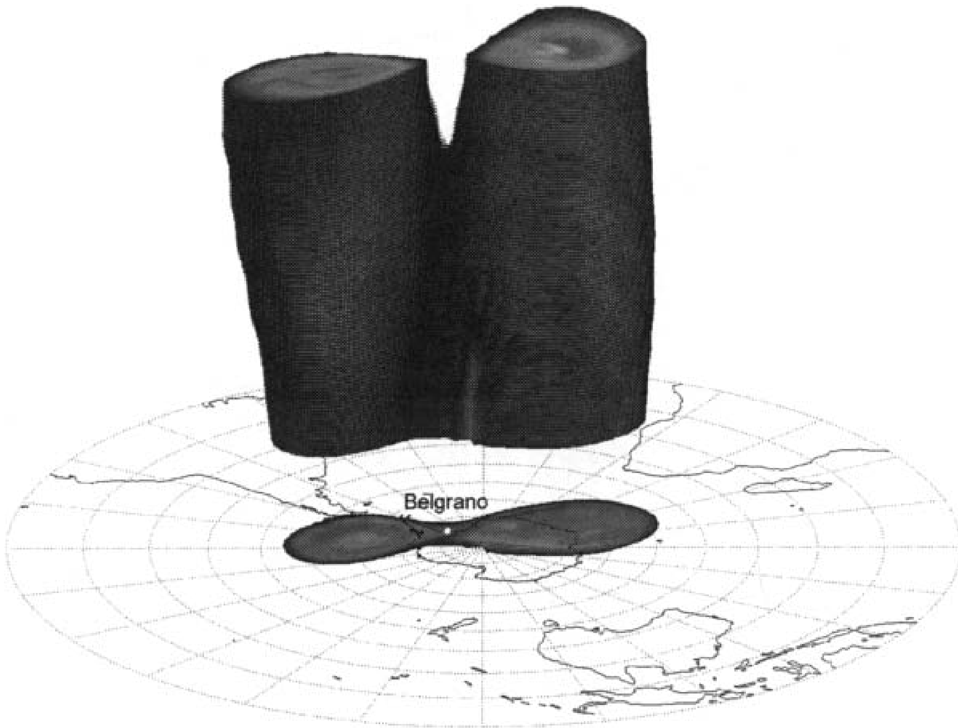
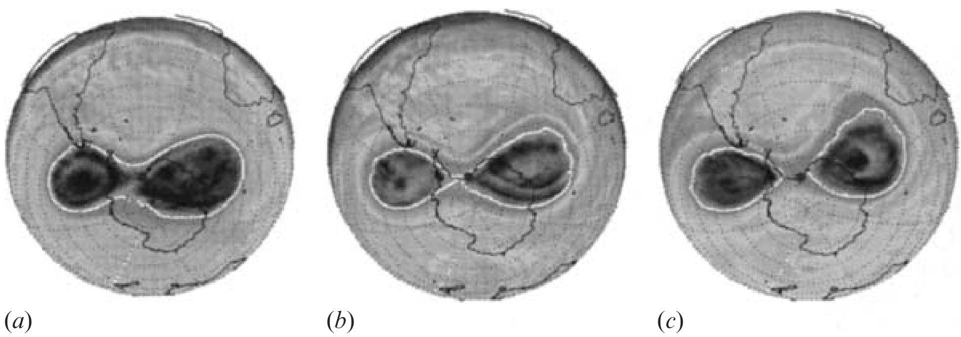


Figure 5. Vortex structure on 25 September computed from the ECMWF potential vorticity fields in a stereographic projection. The boundary has been selected as 40 MPV units (see text). The base in the figure is 350 K (12.5 km) and the top 700 K (23 km). At approx. 550 K (20 km) the vortex splits. The lowest level has been projected on to a polar map for clarification purposes.

upper part of the vortex above 550 K collapsed two days prior to the 25 September sounding. This vortex structure explains why layers above the critical level (the top of the central part of the vortex) undergo a dramatic increase in ozone from extra-vortex ozone-rich subsiding air, while the lower stratosphere was barely affected. This finding has been reported recently by Hoppel *et al.* (2003) and Allen *et al.* (2003), as observed by POAM III profiles.



(*a*) (*b*) (*c*)

Figure 6. Potential vorticity maps on 25 September 2002 for the levels of (*a*) 475 K, (*b*) 550 K and (*c*) 675 K. The red dot denotes the position of the Belgrano station. The approximate vortex edge, based on maximum PV gradients, is plotted as a white line.

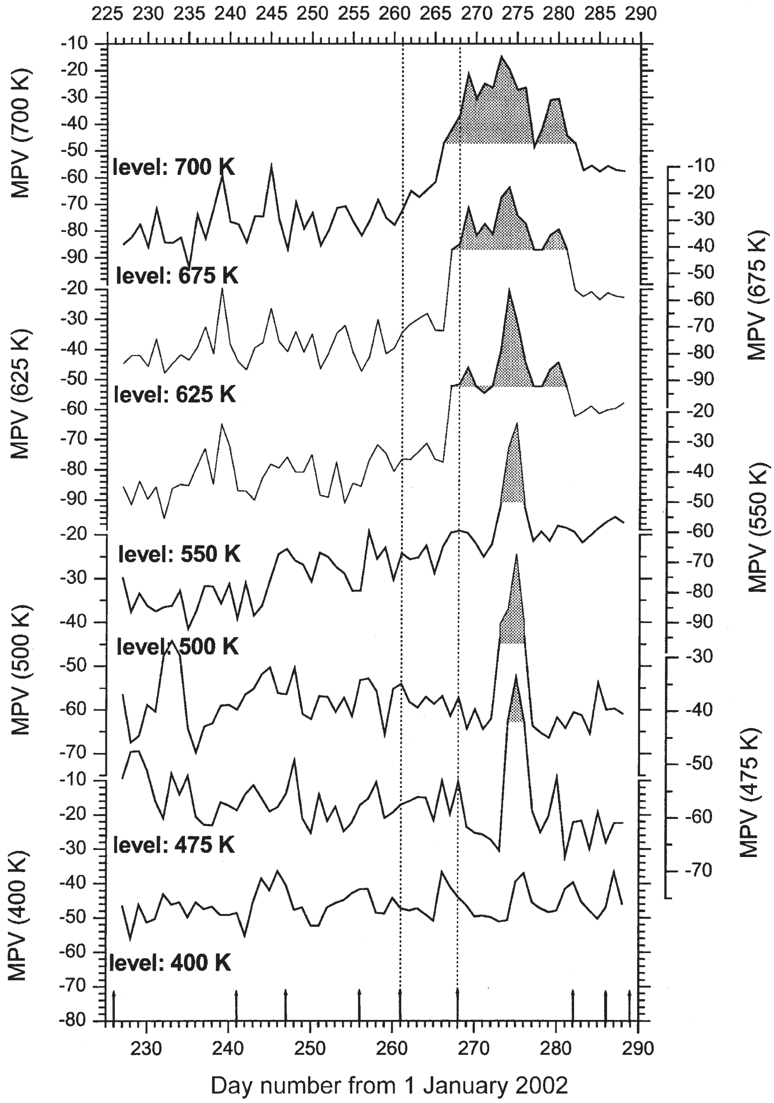


Figure 7. Evolution of the modified potential vorticity (MPV) above Belgrano for the period before and after the vortex break up ($MPV = PV(\theta/\theta_0)^{-9/2}$). The arrows denote the days when ozonesondes were launched.

It is worth noting that under these peculiar conditions the satellites measuring integrated columns provided an unreliable interpretation of the situation. The large ozone columns at Belgrano station observed in satellite colour maps can be interpreted incorrectly as either a complete split of the vortex at all heights or as a vortex filling in. However, the ozone layer below 550 K remained depleted. The enormous ozone increase took place at altitudes above the layer where the depletion occurs.

3.3 *NO_2 column*

A picture of the meridional distribution of the NO_2 vertical column in the high latitudes austral hemisphere for different seasons can be obtained through the ten-year daily mean (1994–2003) measured in the three stations (figure 8). Two records per each station are representatives of dawn (a.m.) and dusk (p.m.). Data are referred to a sza of 90°. Dusk columns are larger since NO_2 increases along the day due to the photodissociation of the night reservoir of N_2O_5.

Ushuaia displays a behaviour typical of a mid-latitude station. The seasonal wave is in phase with the number of hours of light at the height of 25–27 km, where the maximum of NO_2 is located (i.e. Taha *et al*. 2003). The p.m. data are larger than the a.m. all the year round. Marambio presents very low values in winter and little a.m. to p.m. differences in spring, indicating an effective denoxification by conversion of NO_2 to N_2O_5 and a latter heterogeneous conversion to HNO_3 on PSC particles during the winter. In mid-winter and mid-summer there is only one twilight and a.m. and p.m. measurements are very close in time, resulting in almost identical columns. NO_2 build up in spring is delayed with respect to the number of hours of light. The asymmetry between the amounts in autumn and spring is observed clearly in Marambio and is still even more apparent in Belgrano, providing a signature of the denitrification that takes place inside the Antarctic vortex in winter when nitrogen compounds are almost completely removed from the stratosphere. The a.m. to p.m. difference is larger at Marambio and Ushuaia than at Belgrano due to the fewer hours of light in the latter.

Data from the year 2002 are superposed on to the previous years (figure 8, open circles). During autumn, the NO_2 observations at all three stations follow the expected decrease due to a shift towards N_2O_5 as the number of darkness hours increases. Before the major warming, NO_2 data show much lower values are inside the polar vortex (Belgrano, 5×10^{14} molec. cm^{-2}) than outside (Ushuaia, 3.5×10^{15} molec. cm^{-2}).

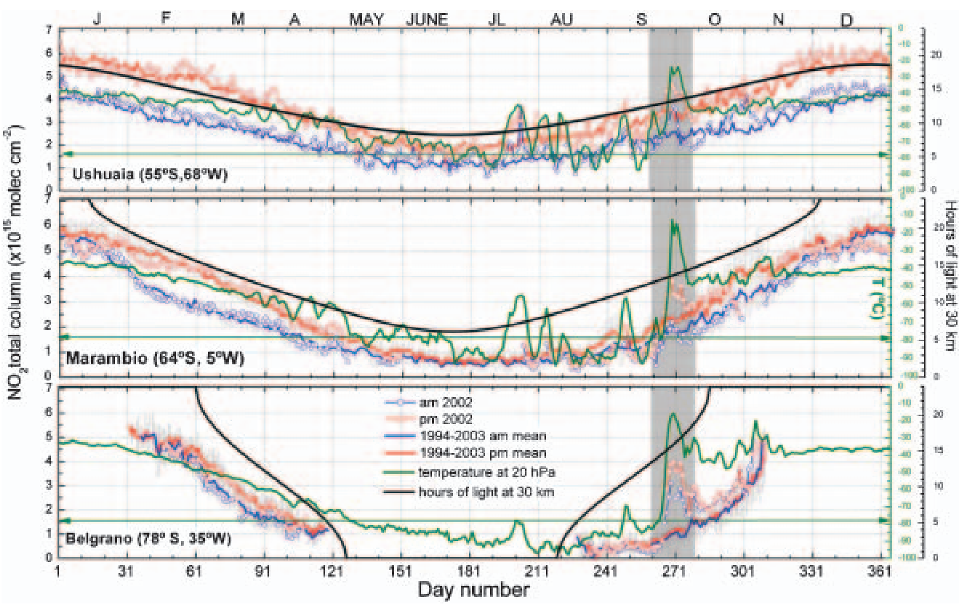


Figure 8. Mean seasonal evolution of the NO_2 column in Ushuaia, Marambio and Belgrano obtained from the 1994–2003 period (blue, a.m.; red, p.m.). Small vertical lines denote one standard deviation. 2002 data are superimposed in open circles. Temperature at 20 hPa is shown in green and hours of light at 30 km in black. Horizontal green lines denote the PSC type-I threshold temperature (−78°C). The shaded area delimits the major warming period.

This meridional negative gradient characteristic of the season vanished during the late September event. All three stations show increases in NO_2 and the O_3 column. The p.m. columns at Marambio and Belgrano peaked to 4×10^{15} molec. cm^{-2}, being relatively more important at higher latitudes. On days around 270 (S27) the increase represents 400% at Belgrano and 150% at Marambio of the mean values for the season. The increase in Ushuaia is 50–60%. A 3D-CTM Slimcat model calculation displays the anomalous spatial structure of the column (Chipperfield, pers. comm.) with very large values around the pole extending toward the Antarctic Peninsula, in good agreement with our observations. This unprecedented large patch of NO_2 for the season at the polar region was recorded by the GOME orbiting instrument as well. Values as high as 5×10^{15} molec. cm^{-2} were recorded near the pole on day S27 (Richter *et al.* 2005).

Stratospheric NO_2 concentrations are very well correlated with the temperature at the 20 hPa level (figure 8, green line). As mentioned previously, during the year 2002 positive anomalies had already been observed in mid-winter related to a number of recurring warming–cooling episodes that took place mainly at the edge of the vortex during July and August. During those oscillating events, associated with the rotation of an elongated vortex, the temperature at 20 hPa increased by 20°C and decreased below 12°C of the seasonal mean. These numbers are on the order or above of two sigma of the ECMWF temperature mean for 1992–2001. NO_2 columns displayed large oscillations in phase with the temperature of the stratosphere. Just before the major warming event, NO_2 columns in the three stations remained at levels even below the mean of the season.

From 18–25 September (days 261–268) the temperature increased at Belgrano and Marambio from below Nitric Acid Trihydrate (NAT) (−78°C) to −15°C at the isobaric level of 20 hPa. This dramatic rise in temperature stopped the formation of PSCs and then the conversion of N_2O_5 to HNO_3. On 27 September and 2 October no PSCs were observed by SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) (von Savigny *et al.* 2005), confirming the strong decline in NAT PSCs and complete absence of ice PSCs after the major warming event as observed by POAM III (Nedoluha *et al.* 2003). In addition, the increase in temperature at the levels where NO_2 reached its maximum concentration contributed to the large recorded columns. The ECMWF T-fields for S25 and following show that the high temperature over the stations extended at the level of 20 hPa over a large area that completely covered the Antarctic continent and extended towards Patagonia in Argentina.

Information on the air masses can be obtained from the ratio (R) of the columns measured at dawn and dusk. Outside of the vortex NO_2 increases during the day due to the N_2O_5 photodissociation. Inside the vortex, on the contrary, very little N_2O_5 is available in spring and R is close to unity. This behaviour can be seen in figure 9. Mean values for R by the end of September are 0.7 in Ushuaia, 0.8 in Marambio and 0.9 in Belgrano. During the 2002 warming each station behaves in a different manner even though a decrease in R in all three sites can be observed.

Assuming that heterogeneous chemistry was stopped abruptly during the warming, a simple model can be used for calculating R by considering only N_2O_5 chemistry. It is based on

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad k = 1.2 \times 10^{-13} e^{-2450/T} \quad \text{(JPL 2003)} \tag{1}$$

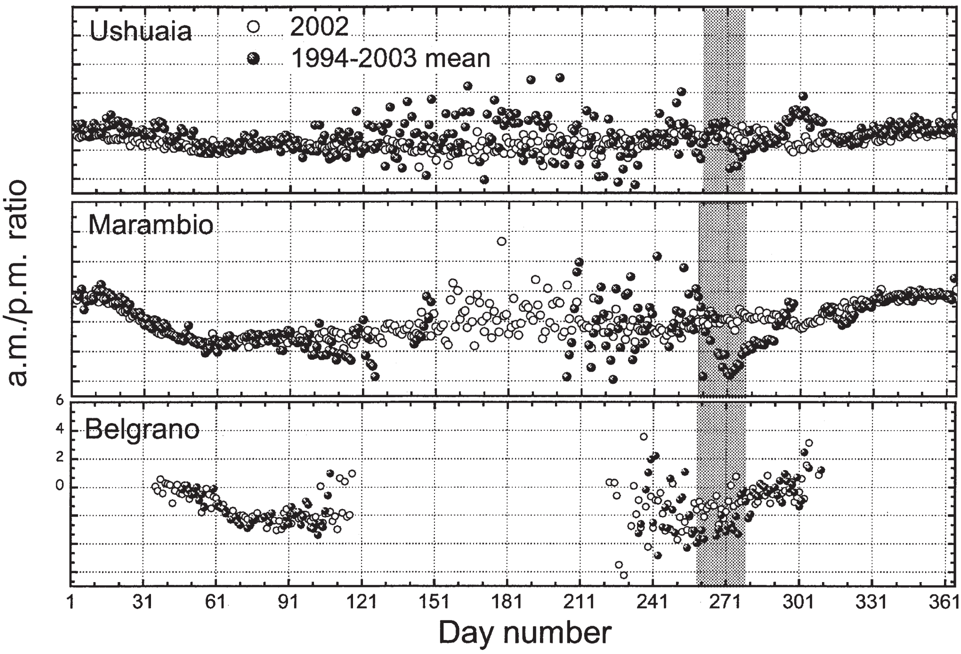


Figure 9. Mean seasonal evolution of the NO_2 column diurnal variation presented as a.m./p.m. ratio (solid spheres). The 2002 data are superimposed as open circles.

where k is the constant of the reaction (Solomon and Garcia 1983, Keys and Gardiner 1991).

Then, R for a given altitude approximates to

$$R = \exp(-2k[O_3]\Delta t) \qquad (2)$$

where $[O_3]$ is the ozone concentration and Δt is the duration of darkness. R decreases with the ozone concentration and with the temperature through the reaction k. Simple calculations using the measured temperature and ozone concentration for the level where climatological NO_2 is maximum yield lower R values than observed, providing evidence that this estimate does not work well in a situation where large vertical and horizontal transport occurs. Advection of mid-latitude non-denoxified air masses to the polar regions may also contribute to the appearance of NO_2 diurnal variation in the Antarctic spring, as has been pointed out by Frieß *et al.* (2005) from observations in Neumayer and Arrival Heights. The trajectory analysis from Belgrano at isentropic levels above 550 K also supports this hypothesis. The different behaviour of the diurnal variation at the three stations is probably the result of a weighted combination of both effects.

4. Conclusions

The effects of the unprecedented major warming in the 2002 spring Antarctic stratosphere in O_3 and NO_2 was observed by ground-based instrumentation in separate locations of the Antarctic and sub-Antarctic regions. An ozonesonde launched at the vortex splitting point on 25 September provided insights into the vertical structure of O_3 and temperature. From comparison with the 18 September profile, it can be seen that the perturbation in temperature extended downwards to the 300 K (8 km) level. A well-defined tropopause never seen before at that time of the season was established. The anomalies increased with altitude, peaking at the 700 K level with a 54°C rise over the previous sounding. Ozone at the 350–500 K layer where the depletion takes place displayed vertical layering but no increase was observed during the episode. The rise in temperature precluded further ozone depletion from that date, and, for the first time in the record no complete removal occurred. At upper levels very large concentrations were found, contributing to columns about twice as large as typical values for the end of September.

The NO_2 column measured at Ushuaia, Marambio and Belgrano stations presented anomalies throughout 2002 in phase with recurrent warming–cooling episodes in the lower stratosphere. The meridional negative gradient characteristic of the season vanished during the late September major warming event. The p.m. columns at Belgrano and Marambio peaked to 4×10^{15} molec. cm^{-2}, representing an increase of 400% and 150%, respectively, above the mean values. Normal values for the season were recovered after the episode. Large decreases in the a.m./p.m. ratio were observed, indicating the presence of N_2O_5 during these days probably as a combination of the poleward transported non-denoxified air and the strong increase in temperature and O_3.

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