ANNALS OF GEOPHYSICS, VOL. 50, N. 3, June 2007

Millimeter wave spectroscopic measurements of stratospheric and mesospheric constituents over the Italian Alps: stratospheric ozone

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Abstract

Measurements of rotational lines emitted by middle atmospheric trace gases have been carried out from the Alpine station of Testa Grigia (45.9°N, 7.7°E, elev. 3500 m) by means of a Ground-Based Millimeter-wave Spectrometer (GBMS). Observations of species such as O_3, HNO_3, CO, N_2O, HCN, and HDO took place during 4 winter periods, from February 2004 to March 2007, for a total of 116 days of measurements grouped in about 18 field campaigns. By studying the pressure-broadened shape of emission lines the vertical distribution of the observed constituents is retrieved within an altitude range of ~17-75 km, constrained by the 600 MHz pass band and the 65 kHz spectral resolution of the back-end spectrometer. This work discusses the behavior of stratospheric O_3 during the entire period of operation at Testa Grigia. Mid-latitude O_3 columnar content as estimated using GBMS measurements can vary by large amounts over a period of very few days, with the largest variations observed in December 2005, February 2006, and March 2006, confirming that the northern winter of 2005-2006 was characterized by a particularly intense planetary wave activity. The largest rapid variation from maximum to minimum O_3 column values over Testa Grigia took place in December 2006 and reached a relative value of 72% with respect to the average column content for that period. During most GBMS observation times much of the variability is concentrated in the column below 20 km, with tropospheric weather systems and advection of tropical tropospheric air into the lower stratosphere over Testa Grigia having a large impact on the observed variations in column contents. Nonetheless, a wide variability is also found in middle stratospheric GBMS O_3 measurements, as expected for mid-latitude ozone. We find that O_3 mixing ratios at ~32 km are very well correlated with the solar illumination experienced by air masses over the previous ~15 days, showing that already at 32 km altitude ozone photochemistry dominates over transport processes. The correlation of lower stratospheric ozone concentrations with potential vorticity as an indicator of transport is instead not as clear-cut, due to very complex mixing processes that characterize stratospheric air at mid-latitudes. Correlations of O_3 over Testa Grigia with stratospheric tracers such as N_2O and HCN, also observed by means of the GBMS, are planned for the future, in order to better characterize lower stratospheric dynamics and therefore lower stratospheric ozone concentrations at mid-latitudes.

Key words *millimeter-wave spectroscopy – stratospheric ozone – isentropic transport*

1. Introduction

From February 2004 to March 2007 a collaboration among the University of Rome «La Sapienza», the State University of New York at Stony Brook (SUNYSB), and the Istituto Nazio-

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nale di Geofisica e Vulcanologia, with the logistic support of the Istituto di Fisica dello Spazio Interplanetario (INAF/IFSI), operated a ground-based millimeter-wave spectrometer (GBMS) measuring middle atmospheric trace gases from the Alpine site of Testa Grigia (or Plateau Rosa, 45.9°N, 7.7°E, elev. 3500 m above mean sea level), at the border between Italy and Switzerland. The high elevation makes Testa Grigia (hereafter referred to as TG) an excellent site for carrying out atmospheric or astronomic measurements at mid-latitudes with instruments, such as the GBMS, which operate at frequencies where atmospheric transparency depends heavily on water vapor and therefore a low water vapor columnar content is necessary. Daily spectroscopic measurements were carried out during several field campaigns mostly during fall and winter, when water vapor columnar content (or precipitable water vapor, PWV) is the lowest. The GBMS observed rotational emission lines of O_3 at 276.923 GHz, HNO_3 at 269.211 GHz, CO at 230.538 GHz, N_2O at 276.328 GHz, HCN at 265.886 GHz, and HDO at 255.050 GHz. The pressure-broadened spectral line shapes allow retrieval of the vertical distribution of the emitting trace gases between approximately 17 and 75 km (see Section 2 for details).

This work discusses the behavior of stratospheric O_3 observed during a total of 116 days over 4 winters, grouped in about 18 field campaigns. At mid-latitudes total ozone is controlled by both transport and chemistry. Ozone forms mainly in the tropical stratosphere and is advected poleward leading to an increasing total ozone column at higher latitudes during winter and spring. At mid-latitudes stratospheric ozone is characterized by a considerable seasonal variability with lowest values in autumn and a strong variability on time scales from days to months which leads to variations in total ozone that can exceed 50% of average values. Events with very low and very high total ozone values are often called miniholes and minihighs, respectively (*e.g.*, Koch *et al.*, 2005; Stick *et al.*, 2006), and are identified as synoptic-scale regions characterized by total column ozone values significantly below/above a certain threshold.

Ozone miniholes are primarily the result of dynamic-atmospheric processes, given that they evolve too rapidly to be the result of an ozone chemical destruction mechanism (Koch *et al.*, 2005). The dynamic origin of such extreme ozone events was already noted by Dobson *et al.* (1929), who described an interrelation between fluctuations in total ozone and the passing of weather systems. Currently, the exact dynamical mechanisms of their formation are under dispute, with two main hypotheses: i) the buildup of an intense tropospheric high-pressure system with an elevated tropopause and the subsequent generation of a reduced ozone layer thickness (Teitelbaum *et al.*, 2003); ii) the generation of an air column with low ozone mixing ratios caused by meridional isentropic transport of air from the subtropics between 340 and 440 K (190-70 hPa) and, independently, from polar regions between 530 and 700 K (30-15 hPa), both carrying air with climatologically low ozone mixing ratios (Koch *et al.*, 2002). Koch *et al.* (2005) studied the relative importance of the two mechanisms, quantified statistically for all miniholes and minihighs observed over Payerne, Switzerland, in the time period 1980-1989 and concluded that fast isentropic transport is by far the most important process for minihole genesis.

From a study by Hood *et al.* (2001) on 71 miniholes between 1980 and 1993, ozone loss at polar latitudes caused by heterogeneous chemistry due to the presence of Polar Stratospheric Clouds (PSCs) was estimated to contribute less than 1% to the observed low column ozone at mid-latitudes, although more recently a PSC and a conspicuous related chemical ozone depletion was observed over Southern Europe in January 2006 (Keckhut *et al.*, 2007; Keil *et al.*, 2007).

2. Observing technique and profile retrieval

The GBMS is currently a state-of-the-art system that employs a Superconductor-Insulator-Superconductor (SIS) tunnel junction mixer to convert millimeter wave signals arising from molecular rotational transitions to lower «Intemediate» Frequencies (IF) by heterodyning them with a local oscillator. The IF output is fed to a «wide band» Acousto-Optical Spectrometer (AOS) characterized by a band pass of 600 MHz and a spectral resolution of 1.2 MHz, and to a «narrow band» AOS with a 50 MHz band pass and 65 kHz of resolution. The 50 MHz window of the narrow band AOS is adjusted within the 600 MHz band pass of the wide band AOS in order to gain a higher resolution of spectral line centers associated with high altitude emission.

Our GBMS system is employed to measure molecular rotational lines of several trace gases that emit in the frequency range between 230 and 280 GHz. Since spectral line shapes are determined by a convolution of the vertical concentration profile (typically unknown) and the atmospheric pressure profile (typically known), the latter can be used, along with the observed line shape, in a mathematical deconvolution process to find the emitting molecule's concentration as a function of altitude. The overall spectral band pass and resolution of the GBMS are therefore key elements to determine the altitude range where trace gases concentration can be measured. Assuming a generic line pressure broadening of ~3 MHz/mbar, with the aid of pressure and temperature vertical profiles the GBMS allows the retrieval of vertical distributions of trace gases concentration between ~17 and ~70-75 km altitude. Above 70-75 km, pressure broadening is overcome by Doppler broadening, and only the overlying column density can be determined with confidence. GBMS measurements are integrated over time intervals between 10 min and several hours, depending on the intensity and therefore the signal to noise ratio of the spectral line being observed.

In this work we discuss measurements of the pure rotational transition line of O_3 at 276.923 GHz. This line is strong enough to give signal-to-noise ratios at line center larger than 100:1 in a 10 to 20 min integration, though still weak enough to show relatively little self-absorption by lower levels for radiation originating in upper layers of the stratosphere. Spectra have been processed with the Chahine-Twomey deconvolution technique (Twomey *et al.*, 1977) to retrieve vertical profiles from the measured line shapes. The wing of a second, strong ozone line centered at 274.478 GHz, outside the spectral window, contributes background curvature and is subtracted from the measured spectra in the data pre-processing phase.

The inversion procedure starts by synthesizing the O_3 line that would be generated by an initial O_3 volume mixing ratio (vmr) vertical profile, knowing the physical characteristics of the rotational transition observed. The modeled spectrum is then compared to the measured one and the initial vmr profile is modified iteratively until the differences between computed and measured spectral line shapes are minimized. Changes to the initial O_3 vertical profile are generated that are based on weighting functions (or averaging kernels) which relate the shape of the O_3 rotational line over a given frequency range (measured from the line center) to the concentration of O_3 over a specific altitude range. The O_3 vmr vertical profile cannot be retrieved below altitudes where the pressure broadening is much greater than the total spectral bandwidth. The GBMS's 600 MHz spectral window thus limits the bottom altitude level of our retrievals to ~15-17 km altitude. In practice, GBMS O_3 retrievals are computed down to ground level, but they rely almost entirely on initial profiles below ~15 km altitude (see next paragraph).

Deconvolutions were performed using several choices of starting O_3 vmr vertical profiles and weighting functions to minimize any biasing from a particular set of inputs, and the recovered vertical profiles were averaged. Initial profiles below 20 km altitude were computed using ozone sonde measurements carried out by MeteoSwiss from Payerne (*e.g.*, Jeannet *et al.*, 2007), Switzerland, about 100 km away from TG. Atmospheric pressure and temperature profiles used in the analysis were obtained from the National Center for Environmental Prediction (NCEP) for appropriate dates and location. Ozone mixing ratios are retrieved every km, although due to the finite width of the millimeter-wave averaging kernels (*i.e.*, the radiation measured at a frequency separated $\Delta\nu$ from the line center depends on O_3 molecules emitting from a wide range of altitudes, not a very thin layer), uncorrelated information is obtained at layers separated by ~6 km in the lower to mid-stratosphere, increasing to more than 10 km in the upper stratosphere, determined by the Full Width at Half-Maximum (FWHM) of the averaging kernels used in the inversion algorithm. Figure 1 gives an illustration of the spectral line shape quality, after removal of minor background

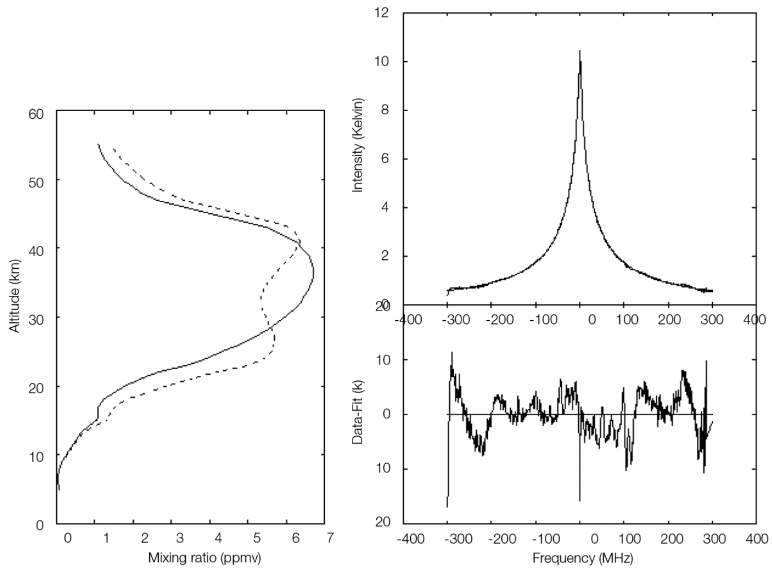

Fig. 1. (*Top, right*) Measured spectral line data after subtraction of computed background from other nearby ozone transitions. A line shape synthesized from the retrieved vertical profile (solid line, left panel) is superimposed on the observed spectrum, but can be barely distinguished. The difference spectrum between these is shown on an enlarged scale (*bottom, right*). Spectral intensity is given in kelvins for the equivalent emission temperature in the Rayleigh-Jeans approximation. The dashed line in the left hand panel is one of three starting profiles used for deconvolution of each day's data. The solid line is the profile retrieved from the data in the upper right panel.

contributions from other ozone emission, along with a typical starting profile, the retrieved vmr profile, and the residual between the observed line shape and a line shape synthesized from the retrieved profile.

Uncertainties on GBMS O_3 vmr vertical profiles have several sources. The most important contributions are: background removal process; choice of starting profiles and averaging kernels; input parameters such as transition line intensity, molecular partition function, pressure-broadening coefficient; random noise in spectral data; calibration, *i.e.* the radiometric conversion from voltages to radiances; and evaluation of the tropospheric attenuation of stratospheric signals. Assuming that the most important contributions to the overall uncertainty are independent from one another, we added them in quadrature and obtained an overall ±13% uncertainty on GBMS O_3 vmr values.

The millimeter-wave emission spectroscopy employed by the GBMS has several advantages over other techniques for measuring atmospheric constituents. With respect to balloonsonde data, GBMS vertical profiles of chemical compounds reach much higher altitudes (a maximum altitude of 70-75 km instead of ≤35 km), although they have much lower vertical resolution. Once the millimeter-wave receiver is set up, measurements can be carried out daily over several months, and at relatively low cost, by a single operator. Furthermore, balloon sondes typically carry out measurements of one single chemical species on each flight, (unless the sonde carries expensive instrumentation that will need to be recovered after the flight, with the risk of being lost), while the GBMS can be rapidly tuned to different frequencies and measure the emission from several species within 24 h.

With respect to remote sensing techniques at infrared (IR) or visible wavelengths, millimeter-wave spectroscopy is able to exploit the pressure broadening characteristics of spectral lines, because this is much larger than Doppler broadening at the long wavelengths and correspondingly lower frequencies employed. The measure of pressure broadening allows the retrieval of vertical profiles, which with rare exceptions cannot be obtained by ground-based IR and visible techniques, so that the latter are primarily capable of measuring only columnar content. IR and visible spectroscopy are able to produce reliable vertical profiles when instruments are used in a limb-sounding mode onboard satellites or very high altitude airplanes, but such experiments are orders of magnitude more expensive than ground-based techniques, and typically have a much shorter operational duty cycle. Optical spectroscopy from any platform is also limited to daylight hours and thus unsuitable for species which may only form during the night.

The GBMS was deployed mostly to polar regions: to the Antarctic Amundsen-Scott base (90°S) during 1993, 1995, and 1999 (*e.g.*, Cheng *et al.*, 1996; de Zafra *et al.*, 1997), and to Thule (76.5°N, 68.7°W), Greenland, during the winters of 2001-2002 and 2002-2003 (de Zafra and Muscari, 2004; Muscari *et al.*, 2007). The overall design and details of the observing technique have been discussed at length by de Zafra (1995) and Parrish *et al.* (1988), while a summary on the accuracy of the inversion procedures used to deconvolve the different spectral lines can be found in Muscari *et al.* (2007) and in references therein.

3. Results and discussion

Figure 2 shows O_3 column contents derived from GBMS vertical profiles from the ground to 50 km (contribution from higher altitudes is negligible), with larger solid symbols representing the average value for each group of data (*i.e.*, field campaign, with its first and last day of measurements indicated at the top of the corresponding panel in fig. 5, discussed later). Below 15 km GBMS vertical profiles, and therefore column contents, rely significantly on ozone sonde measurements from Payerne, as discussed in Section 2. A weighted average of the uncertainty contributions from ozone sonde and GBMS to the final O_3 column contents provides an estimate for the total uncertainty of ±12% (Cheng *et al.*, 1996).

In figure 2 we notice that O_3 columnar contents measured within a few days can be scattered over a wide range of values, with the largest vari-

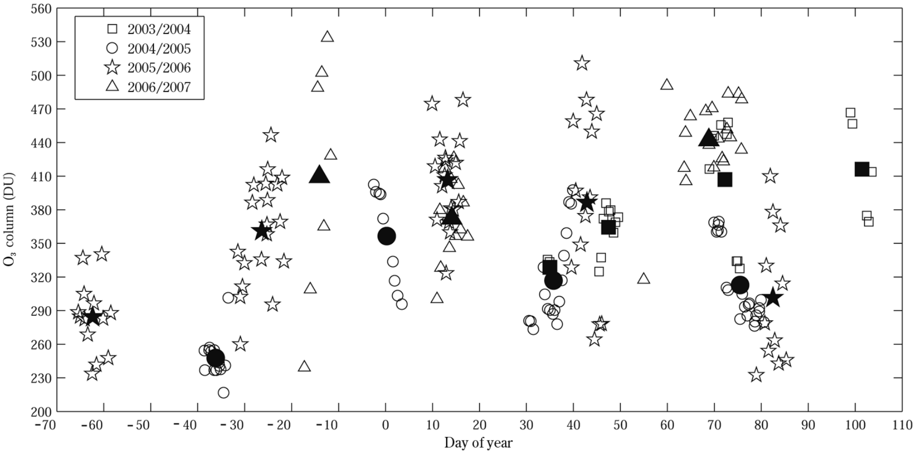

Fig. 2. GBMS O3 total column density (in Dobson Units) *versus* day of the year for all 4 winter periods, with 31 December at 12 GMT as day −0.5 and 1 January as day 1. The legend shows which symbol represents each winter. Solid symbols are average values for each field campaign with first and last day of each campaign indicated in fig. 5.

ations observed in December 2005 (52% of the campaign average value indicated with a solid star), February 2006 (64% of the campaign average value indicated with a solid star), March 2006 (59% of the campaign average value indicated with a solid star) and December 2006 (72% of the campaign average value indicated with a solid triangle). Interestingly, in most periods a large variability is concentrated in the column below 20 km (not shown), suggesting that tropospheric weather systems and advection of tropical tropospheric air into the lower stratosphere over TG has a large impact on the observed variations in column contents. Furthermore, out of the 4 mentioned periods of particularly large O_3 column variability, 3 took place during winter 2005-2006, which proved to be a period of large planetary wave activity, starting with a Canadian Warming and the intensification of the Aleutian high pressure system at the end of November (Braathen, 2006), just before the December 2005 GBMS field campaign. Afterwards, several more perturbations took place until on 21 January a major midwinter warming [which is considered to happen when at 10 hPa and above the temperature difference between the pole and 60°N is reversed

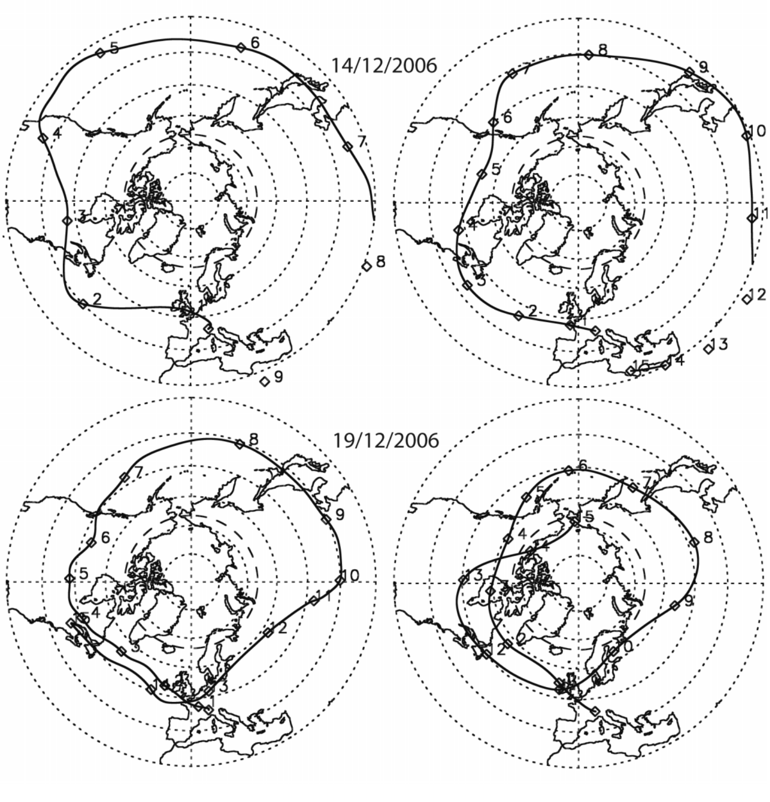

Fig. 3. 15-day back trajectories at 350 K (~13 km altitude; *top* and *bottom left*) and 430 K (~18 km altitude; *top* and *bottom right*) ending over Testa Grigia on 14 December (*top*) and 19 December (*bottom*), 2006. For each of the four plots, five trajectories were calculated and only the resulting average trajectory is shown (see text for details). Numbers along each trajectory indicate the distance in days before the arrival of the air parcel at Testa Grigia. Trajectories are not drawn when they pass below 30°N. Back trajectory calculations are from the NASA/Goddard Space Flight Center (NASA/GSFC) «automailer» system initiated with NCEP reanalysis meteorological data (Schoeberl and Sparling, 1994).

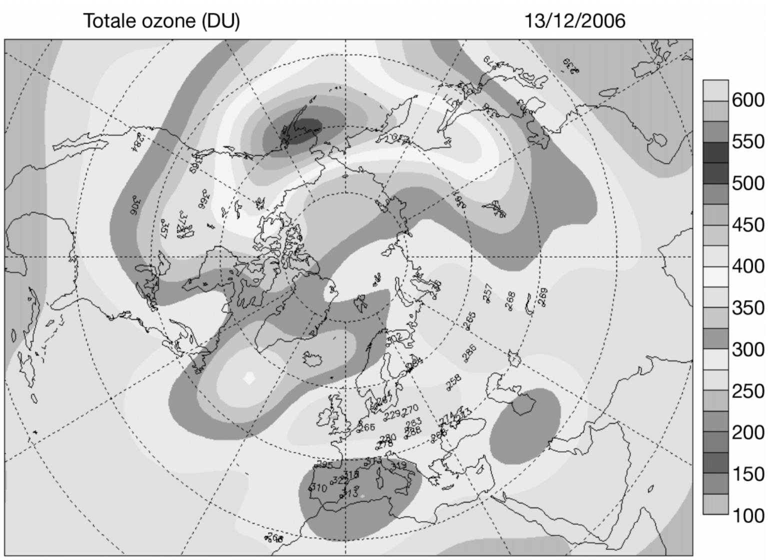

Fig. 4. Ozone total column contour map in Dobson Units from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) in Toronto (<http://es-ee.tor.ec.gc.ca>) for 13 December, 2006.

(positive) and the mean zonal wind at 60°N reaches negative values (easterlies)] occurred in the Arctic stratosphere. This is considered one of the strongest and most prolonged sudden warmings on record, lasting for about 4 weeks (Manney *et al.*, 2007) and altered O_3 concentrations at mid-latitudes.

As for December 2006 (empty triangles in fig. 2), we examined in more details stratospheric dynamics between days 14 to 19 of December, when the GBMS observed the minimum and maximum column contents, respectively. The low ozone contents measured by the GBMS on 14 December seems to be caused by air masses that reached the lower stratosphere above TG originating from the ozone deprived upper tropical troposphere, as suggested by isentropic air parcel trajectories advected back 15 days at 350 and 430 K of potential temperature (~13 and 18 km, respectively) and shown in fig. 3. For each of the four plots shown in the figure, five trajectories were calculated and only the resulting average trajectory is shown. One of the five trajectories ends exactly at Testa Grigia while the other four end at locations surrounding Testa Grigia at four cardinal points separated by 90°. This effort aimed at gaining more confidence in the history of air masses passing over TG by observing the behavior of a larger volume of air with respect to the volume corresponding to one location only. Back trajectory calculations are from the NASA/Goddard Space Flight Center (NASA/GSFC) «automailer» system initiated with NCEP reanalysis meteorological data (Schoeberl and Sparling, 1995). Large O_3 values observed on 18 and 19 December can instead be explained by the advection over TG of stratospheric air rich in O_3 from the Aleutian region, as suggested by the dynamics of air parcels that 7 days before their passage over TG were found over the high ozone region. This conclusion is illustrated by the combination of air trajectories in fig. 3 and the O_3 map provided by the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) in Toronto (<http://es-ee.tor.ec.gc.ca>) for 13 December, shown in fig. 4.

Throughout the field campaigns that show large O_3 column variability, O_3 total column values provided by the WOUDC and by the Ozone Monitoring Instrument (OMI) onboard the EOS AURA satellite (<http://acdisc.sci.gsfc.nasa.gov>)

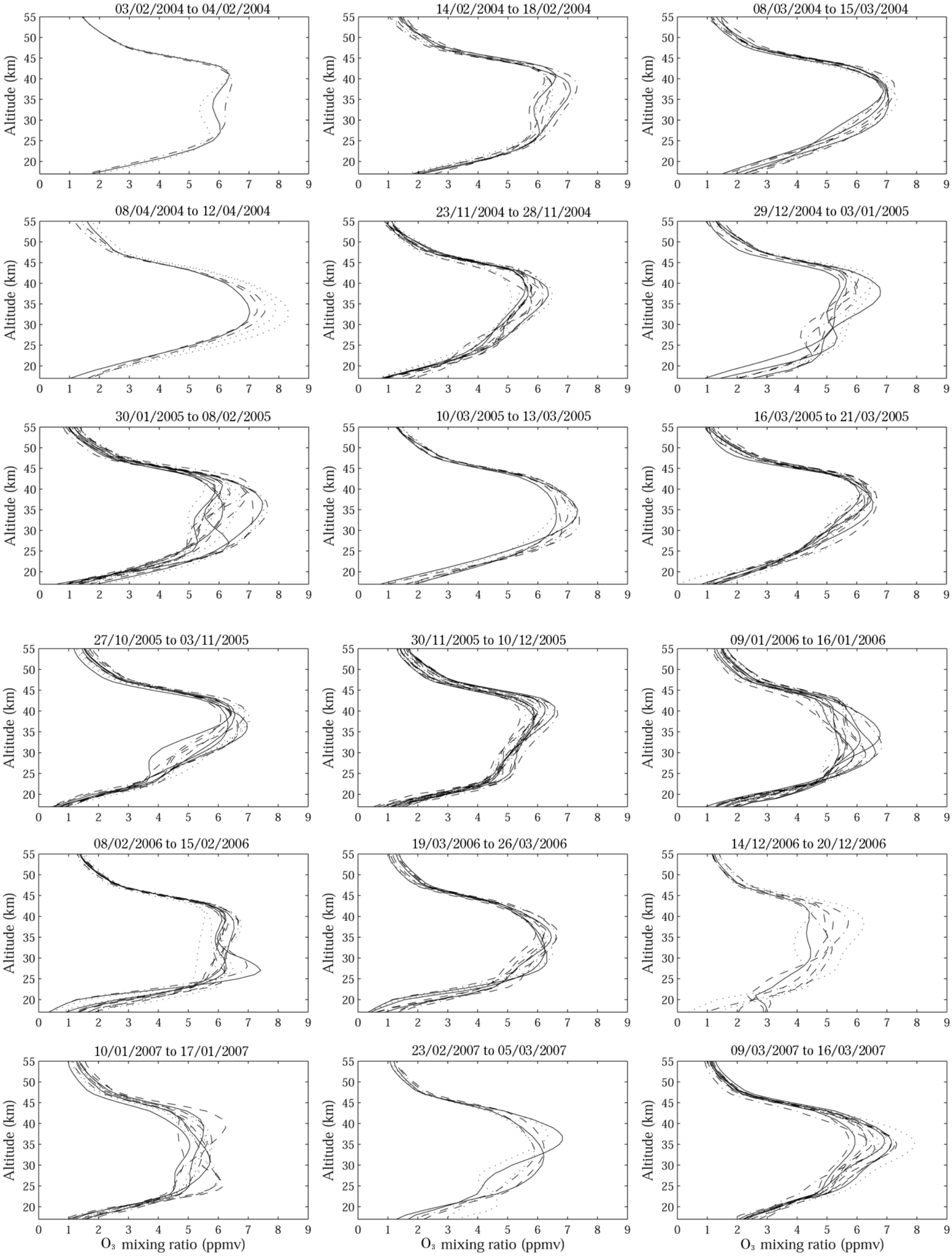

Fig. 5. GBMS O_3 mixing ratio vertical profiles from 17 to 55 km altitude from Testa Grigia. Each panel depicts measurements from one field campaign, with first and last day of measurements indicated at the top of each panel.

confirmed qualitatively the large variations observed by the GBMS over TG. In particular, for all the extreme events (very large or very little O_3 content) observed by the GBMS we found a good correspondence in timing (*i.e.*, days of occurrence) with maxima and minima O_3 total column values over TG found in WOUDC and OMI/AURA databases, although the latter dataset has a coarser horizontal resolution and therefore shows smaller variations with respect to those observed by the GBMS.

Column contents are most sensitive to changes in O_3 concentrations in the lower stratosphere. In order to discuss observations of middle stratospheric O_3 all the vertical profiles obtained from GBMS field campaigns at TG are displayed in fig. 5. Figure panels depict measurements obtained during each campaign, with their first and last day of measurements indicated at the top of each panel. The same data set is shown in fig. 6 by means of contour maps in order to better illustrate the time periods covered by GBMS measurements.

Ozone vmr vertical profiles confirm the large degree of variability over short time spans observed for column contents and characteristic of mid-latitude ozone concentrations. Interesting features are the double peaked structure observed in several profiles and usually addressed with the term «low ozone pocket» identified by the decrease in ozone mixing ratio between 30 and 35 km altitude and usually characteristic of air from polar regions during winter, when air can remain isolated in the dark for several days and reaches a different photochemical equilibrium (towards lower ozone values) with respect to mid-latitude and tropical air (*e.g.*, Cheng *et al.*, 1996; Muscari *et al.*, 2007, and references therein). Since ozone sonde measurements barely reach 30 km altitude, the large set of ozone sondes launched at mid-latitudes completely miss this feature in O_3 mixing ratio profiles. Low ozone pockets are not as deep at mid-latitudes as they are over the Antarctic continent during winter (Cheng *et al.*, 1996). However, just as it can be shown from observations at polar latitudes (Muscari *et al.*, 2007), also at mid-latitudes there is a strong correlation between ozone mixing ratio at ~32 km and the illumination fraction (defined as the ratio between the time interval during which the air parcel received solar illumination and the total duration of the trajectory) experienced by air parcels in the preceding 10 days. Figure 7 displays such a correlation at a potential temperature of 850 K (~32 km). The entire GBMS O_3 data set from TG is shown with solid circles, the GBMS data set from the 2002 field campaign at Thule (76.5°N, 68.7°W), Greenland, is shown with open squares (see also Muscari *et al.*, 2007), and stars superimposed to open squares are measurements at TG during 18-21 March, 2005.

The correlation of the two datasets with illumination fraction is strong, with correlation coefficients of 0.66 and 0.82 for TG and Thule data, respectively, demonstrating that already at 32 km altitude the ozone photochemical lifetime is comparable to transport time scales, *i.e.*, ozone concentrations are driven as much by photochemistry as by transport. The offset that separates the two correlations, indicated by the two different linear fits (dotted and solid lines for TG and Thule, respectively) in fig. 7 is possibly due to the different history (preceding the 10-day period examined with the use of air trajectories) of the air masses sampled in the two regions. This includes the exposure of the two sets of air masses to atmospheric physical properties, *e.g.*, diabatic descent or average temperature, that can be very different at polar *versus* mid-latitudes. Air masses sampled in the period 18-21 March, 2005 (stars overlaid on empty squares in fig. 7), belong to the inner polar vortex and arrived from the polar vortex to TG very rapidly, as shown by air parcel trajectories depicted in fig. 8. In fact, during this period, at potential temperatures between 550 K and at least 1000 K (~24-34 km altitude) Potential Vorticity (PV) maps (not shown) prove that the polar vortex shifted over Central Europe and lay directly over TG. The corresponding data points in fig. 7 fit very well with the linear trend for Thule 2002 data. Only about 50% of the remaining outliers in the TG O_3/illumination fraction correlation (that agree well with the correlation from Thule) can be clearly explained as characteristic of air rapidly advected from the Arctic region to mid-latitudes. During this same period, fig. 2 shows consistently low O_3 column contents (empty circles) with respect to season

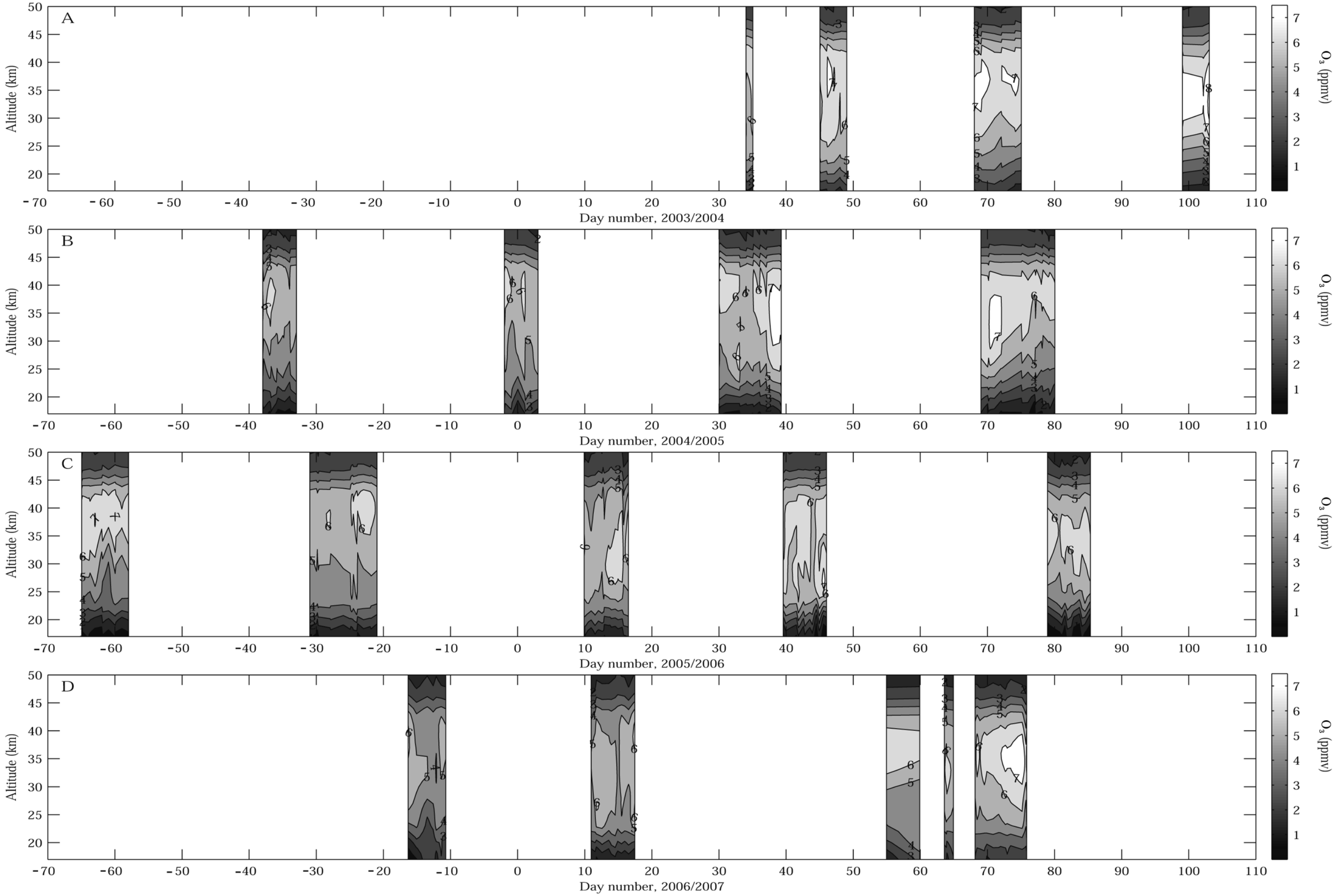

Fig. 6. Contour maps of GBMS O3 mixing ratio vertical profiles from 17 to 50 km carried out at Testa Grigia during 4 winter periods. Each panel depicts one winter period, from winter 2003-04 (panel A, *top*) to winter 2006-2007 (panel D, *bottom*), with 31 December at 12 GMT as day −0.5 and 1 January as day 1. The relative gray scale is to the right of each panel.

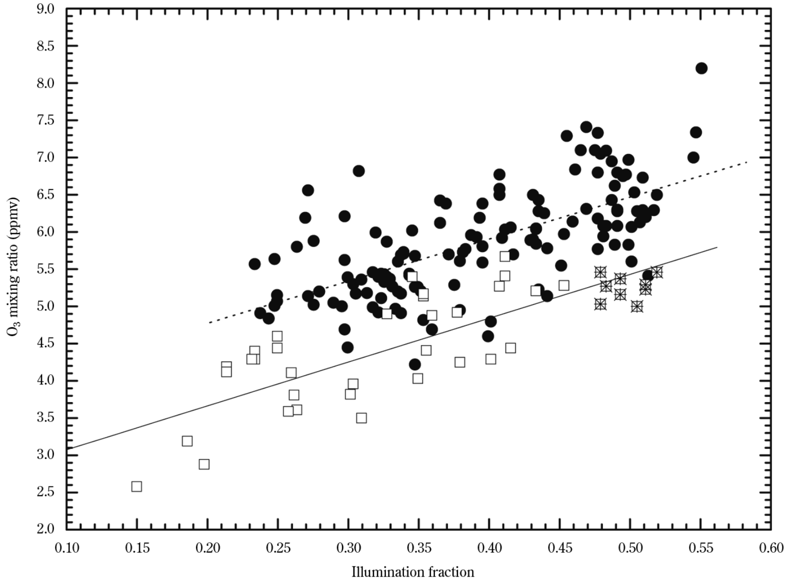

Fig. 7. Correlation scatterplot between all the Testa Grigia GBMS ozone mixing ratio values at 850 K and illumination fraction values along 15-day back trajectories at 850 K (solid circles), and between the same quantities but from the winter 2001-2002 Thule field campaign (open squares; see also Muscari *et al.*, 2007). Stars superimposed to open squares are measurements from 18-21 March, 2005 (see text for details). Dotted and solid lines are linear fits to Testa Grigia and Thule data, respectively. The illumination fraction is defined as the ratio between the time interval during which the air parcel received solar illumination and the total duration of the trajectory. The correlation coefficients are 0.66 and 0.82 for Testa Grigia and Thule data, respectively.

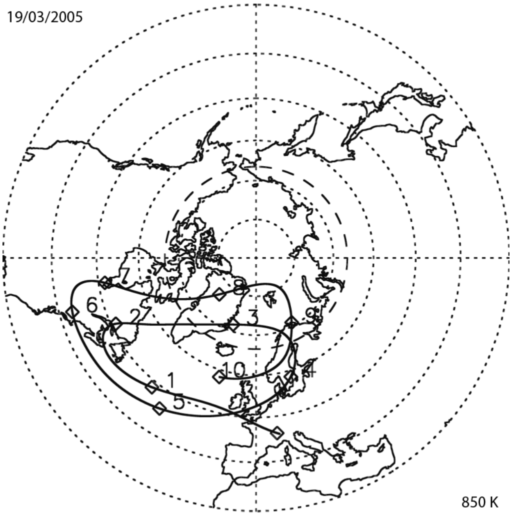

Fig. 8. 10-day NASA/GSFC back trajectory at 850 K arriving over Testa Grigia on 19 March, 2005. Five trajectories were calculated and only the resulting average trajectory is shown (see text for details). Numbers along the trajectory indicate the distance in days before the arrival of the air parcel at Testa Grigia. Back trajectory calculations are from the NASA/Goddard Space Flight Center (NASA/GSFC) «automailer» system initiated with NCEP reanalysis meteorological data (Schoeberl and Sparling, 1994).

averages, in agreement with OMI/AURA and WOUDC datasets. This is due to the advection over TG of polar vortex air also at altitudes lower than the 850 K isentropic surface.

Figure 9 displays the correlation between GBMS column values of O_3 from 24 to 29 km

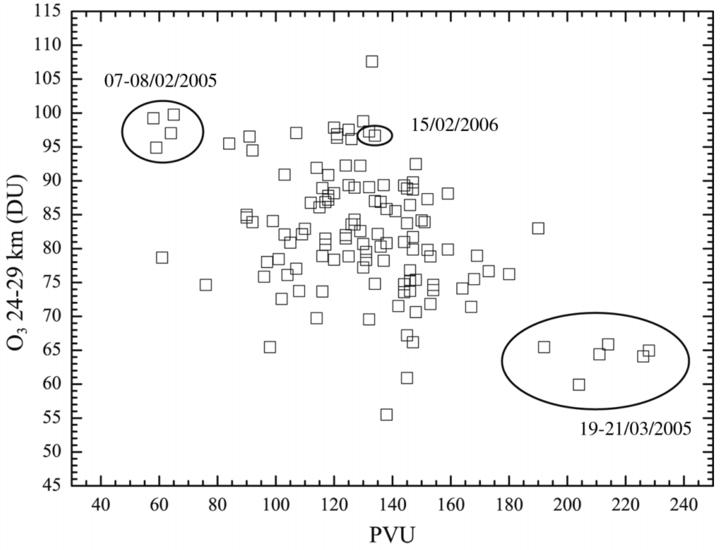

Fig. 9. Correlation scatterplot between Testa Grigia GBMS column density values between 24 and 29 km altitude (in Dobson Units) and averages of Potential Vorticity values along 15-day back trajectories at 650 K (~27 km altitude). Specific dates are circled and indicated in the figure (see text for details). PVU stands for Potential Vorticity Unit with 1 PVU = 10^{-6} $\mathrm{K\,m^2kg^{-1}s^{-1}}$.

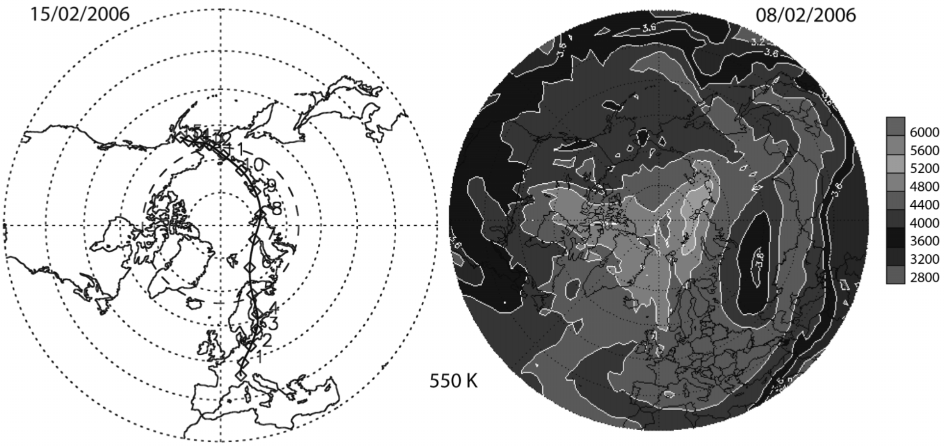

Fig. 10. NASA/GSFC 15-day back trajectory at 550 K (~25 km altitude) arriving over Testa Grigia on 15 February, 2006 (*left*) and an ozone mixing ratio contour map at 550 K for 8 February, 2006 (*right*) produced by the REPROBUS model calculations downloaded from <http://ether.ipsl.jussieu.fr/etherTypo>.

and the PV at a potential temperature of 650 K (~27 km). This analysis was aimed at studying the variations of O_3 in the middle stratosphere in connection with a parameter related to stratospheric dynamics that could discriminate air masses belonging to the polar vortex (high PV) against air masses advected over TG from the tropical region (low PV). Although the overall correlation is poor, we circled two sets of datapoints which show characteristic values of the tropical lower stratosphere (7-8/02/2005) and of polar vortex air (19-21/03/2005). Their different origin was confirmed by air parcel trajectories at 650 K. As for all the data points in between the two extreme conditions, the lack of correlation is due to the very complex mixing processes that characterize stratospheric air at mid-latitudes. Even if a certain air mass observed at mid-latitudes is clearly advected from the Arctic region, this parcel can have very different characteristics depending on whether it carries air from the Aleutian high or from the polar vortex. This is the case, for example, for February 2006 (February 15 is also circled in fig. 9, February 14 is the nearby point with the largest O_3 content, ~108 DU) when air masses reaching TG appear to have been advected from a region where a large gradient in O_3 vmr exists, as shown in fig. 10. Sorting datapoints within the correlation shown in fig. 9 in order to quantitatively pin down the origin of the air masses sampled is therefore very difficult. The use of atmospheric tracers such as N_2O, also measured by the GBMS, will be implemented in a future work in order to better characterize lower stratospheric dynamics.

Acknowledgements

This research was carried out with a grant from Italy's National Program for Antarctic Research (PNRA) and with support from MIUR PRIN 2005, project #2005025202/Area 02. We made considerable use of the NASA-Goddard «Automailer» system in tracking the dynamics of stratospheric air over Testa Grigia, and we thank Leslie Lait, Paul Newman, and Mark Schoeberl for providing this service for external users. We thank Meteoswiss for making available their ozone sonde measurements from Payerne through the Network for the Detection of Atmospheric Composition Change (NDACC) website. We are indebted to Michael Pezzopane and Giorgio di Sarra for helpful comments on the original manuscript and to the Istituto di Fisica dello Spazio Interplanetario (INAF/IFSI) and the Centro Nazionale di Meteorologia e Climatologia Aeronautica (CNMA) for logistic support at Testa Grigia.

REFERENCES

BRAATHEN, G. (2006): Joint WMO/EU Arctic Ozone Bulletin, Winter/Spring Summary (World Meteorological Organization/European Ozone Research Coordinating Unit), *Tech. Rep. 2006-1* (available on line at: <http://www.wmo.int/pages/prog/arep/gaw/ozone/index.html>).

CHENG, D., R.L. DE ZAFRA and C. TRIMBLE (1996): Millimeter wave spectroscopic measurements over the South Pole, 2. An 11-month cycle of stratospheric ozone observations during 1993-1994, *J. Geophys. Res.*, **101**, 6781-6793.

DE ZAFRA, R.L. (1995): The ground-based measurements of stratospheric trace gases using quantitative millimeter wave emission spectroscopy, in *'Diagnostic Tools in Atmospheric Physics', Proceedings of the International School of Physics «Enrico Fermi»*, edited by G. FIOCCO and G. VISCONTI (Elsevier, New York), **124**, 23-54.

DE ZAFRA, R.L. and G. MUSCARI (2004): CO as an important high-altitude tracer of dynamics in the polar stratosphere and mesosphere, *J. Geophys. Res.*, **109** (D06105), doi: 10.1029/2003JD004099.

DE ZAFRA, R. L., V. CHAN, S. CREWELL, C. TRIMBLE and J.M. REEVES (1997): Millimeter wave spectroscopic measurements over the South Pole, 3. The behavior of stratospheric nitric acid through polar fall, winter, and spring, *J. Geophys. Res.*, **102**, 1399-1410.

DOBSON, G.M.B., D.N. HARRISON and J. LAWRENCE (1929): Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, *Proc. R. Soc. London A*, **122**, 456-486.

HOOD, L.L., B.E. SOUKHAREV, M. FROMM and J.P. MCCORMACK (2001): Origin of extreme ozone minima at middle to high northern latitudes, *J. Geophys. Res.*, **106** (D18), 20,925-20,940.

JEANNET, P., R. STÜBI, G. LEVRAT, P. VIATTE and J. STAEHELIN (2007): Ozone balloon soundings at Payerne (Switzerland): reevaluation of the time series 1967-2002 and trend analysis, *J. Geophys. Res.*, **112** (D11302), doi: 10.1029/2005JD006862.

KECKHUT, P., C. DAVID, M. MARCHAND, S. BEKKI, J. JUMELET and A. HAUCHECORNE (2007): Observation of Polar Stratospheric Clouds down to the Mediterranean coast, *Atmos. Chem. Phys. Discuss.*, **7**, 6557-6572.

KEIL, M., D.R. JACKSON and M. C. HORT (2007): The January 2006 low ozone event over the U.K., *Atmos. Chem. Phys.*, **7**, 961-972.

KOCH, G., H. WERNLI, J. STAEHELIN and T. PETER (2002): A lagrangian analysis of stratospheric ozone variability and long-term trends above Payerne (Switzerland) during 1970-2001, *J. Geophys. Res.*, **107** (D19), 4373, doi: 10.1029/2001jd001550.

KOCH, G., H. WERNLI, C. SCHWIERZ, J. STAEHELIN and T. PETER (2005): A composite study on the structure and formation of ozone miniholes and minihighs over Central Europe, *Geophys. Res. Lett.*, **32** (L12810), doi: 10.1029/2004GL022062.

MANNEY, G.L., W.H. DAFFER, K.B. STRAWBRIDGE, K.A. WALKER, C.D. BOONE, P.F. BERNATH, T. KERZENMACHER, M.J. SCHWARTZ, K. STRONG, R.J. SICA, K. KRÜGER, H.C. PUMPHREY, L. FROIDEVAUX, A. LAMBERT, M.L. SANTEE, N.J. LIVESEY, E.E. REMSBERG, M.G. MLYNCZAK and J.R. RUSSELL III (2007): The high Arctic in extreme winters: vortex, temperature, and MLS and ACE-FTS trace gas evolution, *Atmos. Chem. Phys. Discuss.*, **7**, 10235-10285.

MUSCARI, G., A. G. DI SARRA, R. L. DE ZAFRA, F. LUCCI, F. BAORDO, F. ANGELINI and G. FIOCCO (2007): Middle atmospheric O_3, CO, N_2O, HNO_3, and temperature profiles during the warm Arctic winter 2001-2002, *J. Geophys. Res.*, **112** (D14304), doi: 10.1029/2006JD007849.

PARRISH, A., R.L. DE ZAFRA, P.M. SOLOMON and J.W. BARRETT (1988): A ground-based technique for millimeter wave spectroscopic observations of stratospheric trace constituents, *Radio Sci.*, **23**, 106-118.

SCHOEBERL, M.R. and L.C. SPARLING (1995): Trajectory modelling, in *'Diagnostic Tools in Atmospheric Physics', Proceedings of the International School of Physics «Enrico Fermi»*, edited by G. FIOCCO and G. VISCONTI (Elsevier, New York), **124**, 289-305.

STICK, C., K. KRÜGER, N.H. SCHADE, H. SANDMANN and A. MACKE (2006): Episode of unusual high solar ultraviolet radiation over Central Europe due to dynamical reduced total ozone in May 2005, *Atmos. Chem. Phys.*, **6**, 1771-1776.

TEITELBAUM, H., C. BASDEVANT, A. HERTZOG and N. SEMANE (2003): Comment on «A Lagrangian analysis of stratospheric ozone variability and long-term trends above Payerne (Switzerland) during 1970-2001» by G. KOCH, H. WERNLI, J. STAELIN and T. PETER, *J. Geophys. Res.*, **108** (D21), 4674, doi: 10.1029/2003JD003687.

TWOMEY, S., B. HERMAN and R. RABINOFF (1977): An extension of the Chahine method of inverting the radiative transfer equation, *J. Atmos. Sci.*, **34** (7), 1085-1090.

(received September 14, 2007;
accepted October 29, 2007)