Atmospheric Trace Gas Variations at Stara Zagora in the winter of 2004/2005

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Abstract

Since the end of August 1999 DOAS measurements have been provided at Stara Zagora with the automatic operating instrument GASCOD, which was developed by ISAC, Bologna, Italy. The instrument measures scattered zenith sky light for determination of the NO_2 a.m. and p.m. slant column densities at twilight in the morning and the evening. Reference spectra are registered at midday. The instrument registers in the spectral range of 410 nm to 460 nm. The winter 2004/2005 was very cold and the northern polar vortex - very strong. East and South Europe where located near the vortex edge in January/ February and at the end of March the vortex was located over East and South Europe. As a consequence, in this time period very high ozone and NO_2 variability was observed. Record low TOC was observed over Sofia and Stara Zagora ont 19/20 March in connection with an ozone minihole.

Introduction

With the beginning of the polar night over the poles, in the late autumn the polar air mass cools down adiabatically. With the density increasing, the air mass is sinking downwards. The air mass flowing to the north by the Coriolis force is directed westwards. This process causes a strong cyclone, the so-called polar vortex, over the polar region with a strong westward geostrophic wind system surrounding the vortex. Generally, this wind system (the west-wind jet or polar night jet) forms a transport barrier to the meridional air mass flux to the north. However, the air mass can be transported into the vortex over the vortex in the upper stratosphere. Planetary waves propagate from the troposphere to higher altitudes, which increase the wave amplitude, caused by the air density decrease and the energy conservation. At higher altitudes the waves break and put in their impulse and energy into the west-wind jet. The upwelling air mass decelerates the jet stream and possesses a velocity component into the vortex. In this way the planetary waves “pump” air from lower latitudes into the vortex [1]. Mass exchange is also possible by vortex erosion (e.g. filamentation), connected with low gradient of the geopotential.

Due to the distribution of land and sea in the Antarctic region, the planetary wave activities are much weaker than those of the Arctic. Subsequently, the west wind jet is much stronger and the stratospheric temperature of the Antarctic vortex is lower as at the Arctic. The dynamical disturbance of the Arctic vortex is not only much more frequent than the vortex, it is also stronger and as a consequence the polar vortex can be split. Such an event is very rare to be observed in the Antarctic [2].

The Arctic winter 2004/2005

The Artic polar vortex started developing in early October, and until November it was fully developed. The Arctic winter in December to January is usually cold and until late January no warming signs were established [1]. The stratospheric temperatures were near the record lowest ones and in December to February conditions existed for formation of polar stratospheric clouds, which allowed enhanced ozone destruction. In the northern winter in December to February there were very large parts of the Arctic region with average values of the total ozone of 30 to 45 percent lower than the

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b)
c)
d)
e)

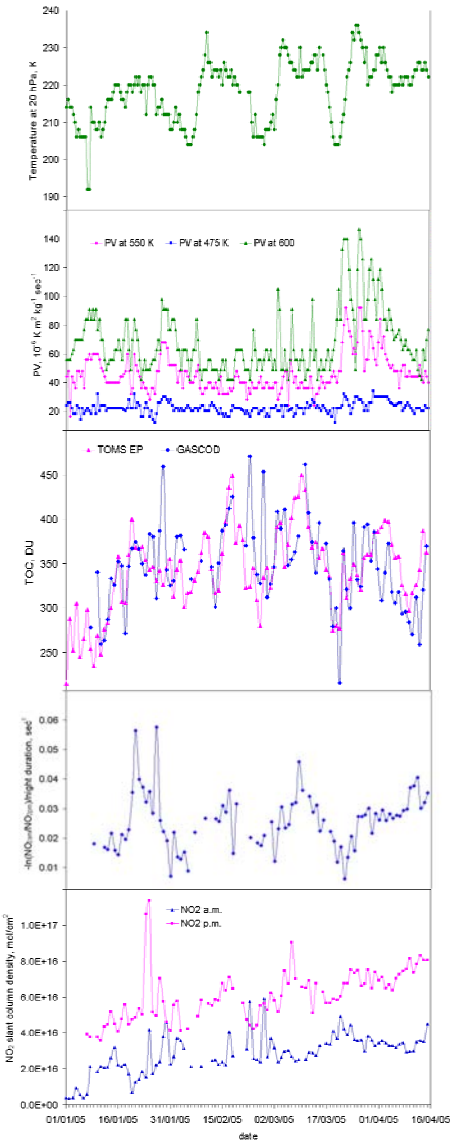


Fig. 1. a) Stratospheric temperature at 20 haP b) Polar vorticity at the level of 475K, 550 and 600K potential temperature c) total ozone amount over Stara Zagora by TOMS data and amounts measured by the GASCOD instrument, d) NO_2 a.m. and p.m. slant column amount and e) the NO_2 a.m./p.m. relation observed by GASCOD, all for the time period of 1.1 to 15.4. 2005

comparable values in the early 1980s and the size of the Arctic area with anomalously low ozone was among the largest of all years since the record started in 1979 [3]. In February the stratospheric temperatures increased dramatically. Subsequently, a significant stratospheric warming occurred and the Arctic ozone increased.

When the polar vortex is fully developed, the vorticity has very high values and the vortex extends over a great area, and the vortex displacement caused by warming can be obtained over Central Europe and in some cases over South Europe, too. The polar vortex is slightly disturbed in the beginning of January. Eroded vortex regions reach Middle and South Europe. In the beginning of February, due to planetary wave activities, the vortex is elongated and its south edge is over South Europe and the low stratospheric temperatures are observed over the Stara Zagora region since the beginning of January (see Fig. 1a and b, the temperature and the polar vorticity data are retrieved from http://www.pa.op.dlr.de/arctic/). At the same time the polar vorticities over Stara Zagora have slightly higher values. At the end of February and from the beginning to the end of March polar vortex filaments pass over the Balkan Peninsula producing peaks in the polar vorticity. After the middle of February the vortex is significantly warmed and split by wave activities on 25 February. Then the vortex recovers, yet this winter it never achieved very low temperatures. In the first decade of March the polar vortex was again disturbed and elongated, almost split in two fragments. Between 17 and 22 March the disturbances was so strong that the vortex was split into three fragments. One of them was located over North Italy and the Balkans. In this connection, low stratospheric temperatures are registered and high polar vorticities values are observed over Stara Zagora. After that the polar vortex was destroyed and the polar summer conditions returned.

GASCOD instrument measurements

In 1999 a GASCOD (*Gas Absorption Correlating Optical Differences*) UV/VIS instrument was installed at the Stara Zagora (42.42°N, 25.63°E) Department of STIL [4]. The instrument represents a spectrometer, consisting of a monochromator and a detection system and was developed by the Institute of the Atmosphere Sciences and Climate (ISAC), Bologna, Italy. To retrieve ozone and nitrogen dioxide, the instrument measures the zenith-scattered solar radiation at spectral range of 410 to 470 nm. The input optics is composed by a f/5 telescope with a focus length f of 0.5 m. The telescope focuses the light on a 100 μm entrance slit. A Jobin Yvon spherical diffraction grating with 1200 grooves/mm disperses the light and focuses it on the Hamamatsu 512 diodes array sensor. Since the DOAS (*Differential Optical Absorption Spectroscopy*) technique is applied in the morning (at sunrise) and in the evening (during sunset), the measurements are performed and the reference spectra are observed at local midday. The a.m. measurements are daily, starting 30 min before sunset and 1.5 hours before sunrise. The duration of the morning and evening measurement session is 2 hours. Reference spectra are measured for 30 min. The sunset and sunrise moments are calculated after every evening session for the following day. The instrument is computer controlled and operates automatically.

Data processing

During sunset and sunrise the light path through the atmosphere passing some 100 km along the stratosphere to the light scattering "point" over the instrument is very long. The optical path for the light transmission at midday is comparatively short. After removing the slowly varying part of all spectra, e.g. by filtration in the Fourier space or by polynomial approximation, the absorption structures of the minor gas species become evident in the ratio of long-path morning and evening spectra to the reference spectrum, measured on a clear day. Taking into account the Lambeer-Beer law and the corresponding absorption cross sections, the slant columns densities (SCD) of the minor gas species, absorbing the solar radiation in the corresponding spectral range are obtained by solution of a least square linear equation system. For this reason, the Levenberg-Marquard method was applied, optimizing the spectral alignment between the measured spectrum and the reference one. For details of DOAS, see [5]

Stratospheric NO_x Chemiestry

The nitrogen dioxide plays a major role in the ozone destruction chemistry in the stratosphere. Here NO is oxidized to NO_2 by the atmospheric ozone. By photolysis in the day NO_2 returns to NO:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$\underline{NO_2 + h\nu \rightarrow NO + O} \qquad (2)$$

$$\text{Overall:} \quad O_3 \rightarrow O + O_2$$

At lower atmospheric densities of the stratosphere and at middle and higher altitudes, where O is produced mainly by photolysis of O_2 and O_3, reactions other than O_2 become important:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

$$\underline{NO_2 + O \rightarrow NO + O_2} \qquad (4)$$

$$\text{Overall:} \quad O_3 + O \rightarrow 2\,O_2$$

In the night NO_2 can be oxidized by O_3 forming NO_3, which is a strong atmospheric oxidant and a precursor of dinitrogen pentoxide N_2O_5:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (5)$$

In the night N_2O_5 is built at the expense of NO_2 by a triple impact:

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \qquad (6)$$

Under steady-state conditions with the help of the chemical reaction kinetics the following differential equation is obtained:

$$\frac{d[NO_2]}{dt} = -2k_5[NO_2][O_3] \qquad (7)$$

with the solution:

$$[NO_2]_{am} = [NO_2]_{pm} \exp(-2k_5[O_3]\Delta\tau), \qquad (8)$$

where the square brackets contain the mixing ratios of the corresponding species, k_5 is the reaction rate (5), and $\Delta\tau$ presents the duration of the night from sunset to the following sunrise. In the polar vortex during the polar night NO_x ($NO+NO_2$) can be almost completely converted into NO_3 and N_2O_5. On the other hand, heterogeneous reactions can be important, when the temperatures in the vortex drop below the temperature limits, which determine the build up of polar stratospheric clouds. The reactions on the polar stratospheric clouds (*PSC*) leads to reduction of the NO_x abundance and to HNO_3 and converts HCl and $ClONO_2$ to species such as HOCl and $ClNO_2$ and to molecular Cl_2, which very rapidly destroy the ozone and are some of the most important species with impact on the ozone hole. The occurrence of PCS is connected with very low stratospheric temperatures. The so-called nitric acid trihydrat (*NAT*, the crystalline form of HNO_3 x $3H_2O$) PSC (type I) can be established by temperatures below -76C°. PSC (type II) consist of pure water ice and are established by temperatures below -85 C° to -90 C°. In winter 2004/2005 on the northern hemisphere conditions for establishment of PSC exist from December 2004 to the middle of March 2005.

Results

To compare the obtained ozone slant column densities by the GASCOD instrument with the total ozone column (TOC) of the TOMS Earth Probe instrument will require firstly an interpolation of gridded assimilated TOMS ozone data to determine the daily TOC over Stara Zagora. For the interpolation we use a simple bilinear algorithm. Secondly, the vertical column density (VCD) should be calculated from the SCD. Their ratio is the air mass factor, determined by calculations with models to describe the light transmission through the atmosphere. The air mass factor of 18 gives a good average accordance between the TOMS ozone data and our ozone values. The development of the ozone, expressed in Dobson units (DU, 1DU=2.7 10^{+16} mol/cm^2), in the winter from January to April 2005 for both instruments is shown in Fig.1c. The variability of the ozone values obtained by the TOMS instrument is lower than by the GASCOD instrument. A reason for this is the assimilation procedure of the TOMS data, which operate like a smoothing filter, and the different measurement geometry. At mid latitudes the ozone has a seasonal dynamically effected maximum in March/April. The ozone variations correspond to the stratospheric temperatures and show approximately a periodicity of 10 to 20 days, typically for planetary waves. In beginning of January the polar vortex is very strong and centered over the pole (see Fig 2). The temperatures (not shown) are sufficiently low to allow the PSC formation. The comparison with results obtained by the SLIMCAT model (http://www.env.leeds.ac.uk) shows that the chemical ozone loss is approximately limited to the vortex area with vorticity higher than 50 PVU at a level of 475K. The low ozone values over the entire South Europe are also with dynamic origin, probably from tropic ozone pure air mass. However, the establishment of the origin of this air with low ozone content is still in progress.

The TOMS EP instrument has been registering very low ozone columns of 275 DU in the period 19 – 21 March, just when usually the TOC are going to their seasonal maximum. Sofia is included in the list of "ozone over selected locations" of TOMS EP measurements. The record lowest ozone value of 237.1 DU was measured over Sofia in March since the start of the EP TOMS measurements on 25 July 1996. This is also the third lowest value found over SOFIA by local stations. This is in a very good agreement with the morning GASCOD measurements at Stara Zagora, which are provided in western directions (towards Sofia). A value was found below 220 DU on 21 March (compare Fig 1.c). In the middle of March the polar vortex is disturbed very strongly by Rossby waves reaching up to the lower stratosphere. Warming episodes over a geographical area, covering the Barent Sea and the Polar Sea north from Central Siberia, displace a polar vortex fragment extremely southwards (Fig. 3a). A Rosby wave ridge is located below the European polar fragment. This fact and the weakness of the vortex (no chemical ozone loss) suggest that these low TOC values are related to an ozone minihole, that is a region with low TOC (smaller than 250 DU) The TOC of the deep miniholes can be smaller than 220 DU. In contrast to the polar ozone hole, the miniholes have dynamic origin. They can generate as a result of adiabatic uplifting of the tropopause. Probably, a minihole was built up westwards of Island on 14 March and at the next days, when it was traveling to the East, the size of the minihole increasing and in its inner the TOC decreasing. It's existence from 14 until 22 March was consistent with a mini hole event. The connections between ozone miniholes and the weather systems are well established [6,7]. In the period from 13 to 19 March, the thermal tropopause over Sofia is uplifting almost by 3.1 km (Fig.4). After approximately one day the anti-cyclone system, which is connected with the observed tropopause uplifting was located over Stara Zagora.

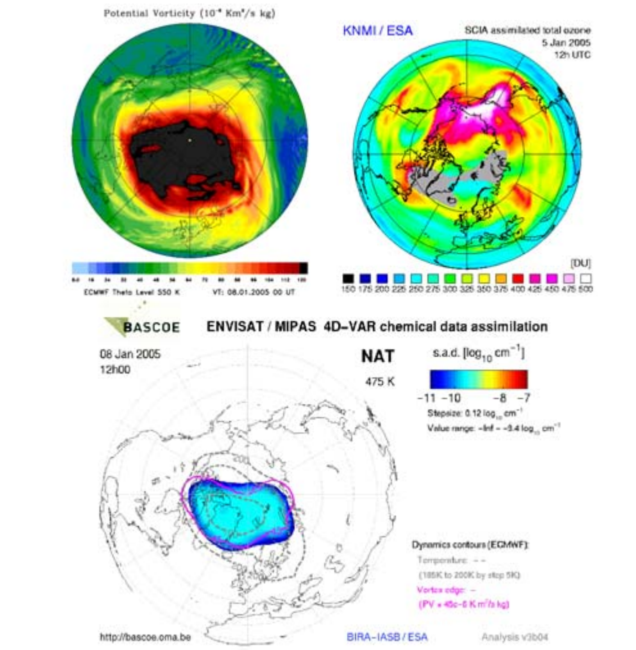
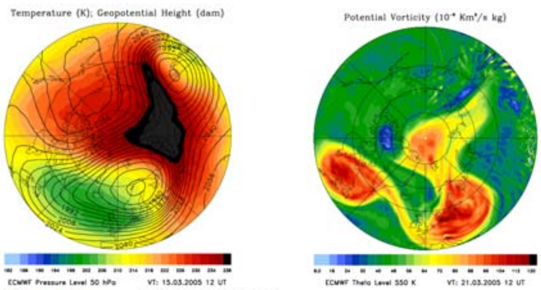


Fig. 2. a) Potential vorticity at the 550 K level of the Northern hemisphere by the ECMWF analysis b) ozone distribution by assimilated data of the SCIAMACHY ENVISAT instrument and c) Conditions for the condensation of NAT by assimilated data of MIPAS ENVISAT instrument, all for 8 January 2005.



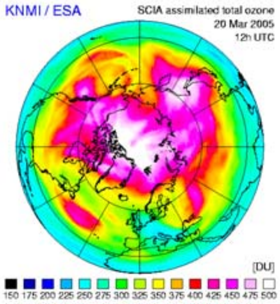


Fig.3. Development of the ozone minihole. a) Vortex displacement by stratospheric warming. b) Localization of a vortex fragment over North and East Europe c) Ozone minihole over Central and South Europe. Fig. a) and b) – by ECMWF data c) – by SCIAMACHY ENVISAT data – tropospheric uplifting see Fig. 4

By equation (8) the ozone content can be estimated. At altitudes between 10 km and 36 km the right side of the equation always has values between 0.1 and 0.5 for maximal night duration of 700 min. Thus, the Taylor series of the exponential function can be cut after its linear term. At altitudes between 14 and 27 km, where most of the ozone is concentrated, the rate coefficient $k_5 = 1.2\ 10^{-13}\exp(-2450K/T)$ $cm^3.mol^{-1}.sec^{-1}$ (see [8]) only slightly depends on the temperature and is approximately constant $1.\ 10^{-18}$ with an error of 20%. In the first order equation (8) is also valid for the total columns. The air mass factor, which means the ratio between the measured slant column amount and the vertical amount, is almost the same for the sunset and sunrise NO_2 measurements. Actually, the quantity of $-\ln(NO_{2a.m.}/NO_{2p.m.})/\Delta\tau$ (Fig. 1d) follows the course of the ozone time series (Fig. 1c), better than we have expected, taking into account the measurement errors of NO_2 amounts and the approximation gross. The similarity of the two courses explains the existence of the chemical steady-state conditions over Stara Zagora in January/March 2005 and that the variations of the abundances are in first order of dynamical origin. The comparison of the $NO_{2a.m.}$ and $NO_{2p.m.}$

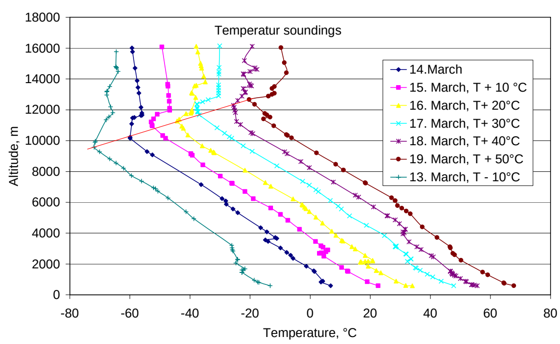


Fig. 4. Increasing of the tropopause hight from 14. to 19. of March over Sofia.

courses also show this. Is it not a period found for which NO_2 and NO_2 clearly decrease simultaneously with the ozone, what is expected in the inner vortex by denitrification and decreasing of TOC when PSC exist. As in the study of the winter-spring NO_2 variations during the cold winter of 1994/1995 by Petritoli [9, see Fig. 3.] the $NO_{2p.m.}$ values show stronger anomalies. We have also found that $NO_{2p.m.}$ decreases with the increase of PV. The $NO_{2a.m.}$ values are determined by the ozone content and the stratospheric temperatures.

Conclusion

During the cold stratospheric winter 2004/2005 the polar vortex is very strong. NO_2 SCD and TOC changes over Stara Zagora are generated by planetary wave activities around the polar vortex. By some disturbances the vortex is displaced to South toward to Europe. In this connection with an tropospheric anti-cyclon over this region over Stara Zagora at end of March a minihole and some record low TOC was observed. It was shown, that the observed NO_2 and O_3 variations over Stara Zagora in general caused by dynamic processes.

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