Study of Atmospheric Trace Gas Amounts at the Stara Zagora Ground-Based Station

R.Werner [1], D.Valev [1], I. Kostadinov [1,3], At.Atanassov [1], G.Giovanelli [3], A.Petritoli [3], D.Bortoli [3], F.Ravegnani [3]

[1] Stara Zagora Department, Solar-Terrestrial Influences Laboratory, , BAS, Bulgaria
[2] Institute of Atmospheric Science and Climate, Bologna, CNR, Italy

Since the end of August 1999 twilight daily measurements of scattered zenith sky radiation have been carried out at Stara Zagora for determination of trace gas amounts, deploying GASCOD instrument. It was developed at the Institute of Atmospheric Science and Climate, Bologna. Reference spectra are obtained at midday. The instrument, appearing a UV-VIS spectrometer, registers the zenith sky spectra automatically and 410 nm to 460 nm spectral interval is used to retrieve NO_2 and O_3 slant column amounts (SCA) by application of the DOAS methodology. The spectral analysis uses minimum least squares fitting of the cross sections at the expected absorbers to a logarithm of the twilight spectrum and a reference spectrum.

The accumulated time series show the well-known typical seasonal variations, caused by the solar insulation. The residual time series of the removed semi-annual seasonal cycles from the measured original series show many different variations, with short periods up to inter-annual variations. Single spikes of SCA are detected and we consider them a result of over-passing weather fronts and/or lightning. Variations of SCA with time scale up to about 10 days are the consequence of weather cyclones. Some short-term variations of NO_2 and O_3 SCA are a result of intensive stratospheric-tropospheric exchange. Other residual time series periods are caused by Rossby waves, by over-passing of the polar vortex filaments. The inter-annual variations can be affected by QBO and NAO. Applying wavelet analysis of the obtained NO_2 slant column amount data series, and the total O_3 amount obtained by the GOME instrument, during the 23-rd solar cycle maximum, time intervals are found with periods of 27 days on the time scale. The applied cross-correlation analysis demonstrates a phase lag of some days of the NO_2 and O_3 response to the 27-days solar cycle.

The calculated vertical column amounts of NO_2 are used for validation of the satellite measurements, e.g. SCIAMACHY NO_2 data.

Introduction

The atmosphere is an enormous and complicated dynamic system. The changes of its components are forced by natural processes as well as by human industrial and agricultural activities. The increase of the greenhouse gases can produce a global climate change. To understand the physical and chemical processes which control the global atmosphere as an input in adequate models it is necessary to know in detail the spatial distribution and temporal behavior of several atmospheric trace gases, aerosols and clouds. To study the trends in the atmospheric amounts of the greenhouse gases, long time series are necessary. To investigate both the global distribution of the total amounts and the altitude distribution, new satellite generations were developed in the last years, with instruments aboard, allowing to measure ozone atmospheric constituents such as NO, NO_2, CH_4, BrO. ClO, OClO, SO_2. The results of the measurements obtained by new satellite measurement methods and data processing should validate the significance of the results from ground-based stations and onboard airplanes.

The aim of this paper is to present some interesting results of several scientific fields, obtained by NO_2 and O_3 measurements at Stara Zagora in the last years.

NO_2 Chemistry

The importance of the NO_2 is based on its key role in the atmospheric chemistry. As found by Crutzen in 1970 [1] and Johnston in 1971 [2], active nitric oxides (or shorter active nitrogen) $NO_x = (NO + NO_2)$ destroy the ozone catalytically. In the upper stratosphere, almost half of the ozone destruction is produced by NO_2 [3]. In contrast, in the lower stratosphere NO_2 buffers the active chlorine effect. Stratospheric nitride oxide NO is produced by the oxidation of nitrous oxide N_2O. In the troposphere NO_x is the main source of ozone. The sources of NO and N_2O in the troposphere are both natural and anthropogenic. Combustion processes, lightning and emissions from soils are the most important natural sources. NO_x produced by human activities is related to emissions of the power plants, the heavy industry, and road transport. During daytime the inter-conversion of NO and NO_2 is sufficiently rapid and the photochemical steady state equilibrium is build up very fast. At night the photolytic destruction of NO_2 is stopped. Over the night NO_2 can be oxidized to NO_3, which after an impact with NO_2 and a third molecule will convert into N_2O_5. Depending on the night duration up to … % will be converted to N_2O_5. Consequently, during the sunset the concentration of NO_2 increases very fast, and then during the night, the concentration slowly decreases. With the sun rise in the morning, NO_2 rapidly decreases by its fast photolysis. Due to the low photolysis rate of N_2O_5 with the products of NO_2 and NO_3 in comparison with the NO_2 photolysis rate, the NO_2 content slowly increases during the whole day. Therefore, the NO_2 concentration has a strong daily course. For measurements of NO2 it is necessary to note the measurement time or, as it is often practiced, the measurements are related to a determined solar zenith angle.

Details of the NO_x tropospheric and stratospheric chemistry are described in [4, 5].

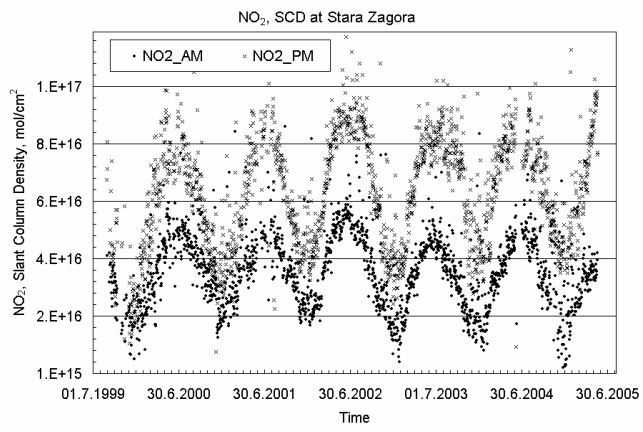


Fig.1. Original time series for the NO2 a.m. and p.m. obtained at Stara Zagora. Slant column densities started in August 1999.

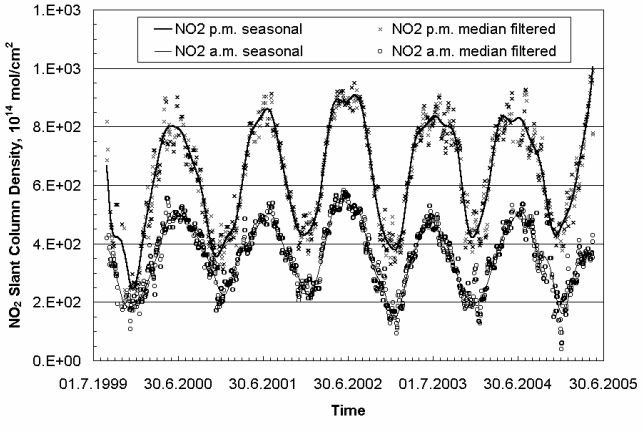


Fig.2. NO_2 a.m. and NO_2 p.m. median filtered time series and their low pass fits.

GASCOD instrument measurements

In 1999 a GASCOD (Gas Absorption Correlating Optical Differences) UV/VIS instrument was installed at the Stara Zagora Department of STIL BAS (42.42°N, 25.63°E) [6]. The instrument is 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. DOAS (Differential Optical Absorption Spectroscopy) technique is applied to retrieve the slant column densities. 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 [7].

Data set preparation

NO_2 and O_3 slant column densities were retrieved from the morning and evening measurements for a zenith angle of 90 degrees. To ensure the correct zenith angle the differences of the computer time and the real time were corrected. By harmonic analysis, based on regression, the seasonal trend can be determined. To apply methods, based on time equidistant data sets, the data gaps should be filled. The missing data for successive days up to 5 days are replaced by linearly interpolated data. The missing data for a longer time interval are replaced by harmonic analyses, taking into account higher frequencies.

Results

The original time series of the obtained NO_2 slant column amounts is shown in Fig. 1. The registered time series allow to study shorter cycles and seasonal cycles. The obtained cycles at the 27–day timescale and their connection with the solar rotational period were reported in [8]. To determine the seasonal cycle the series are linearly detrended and the peaks (originating as a result of strong pollution events or bad weather conditions) are filtered out by a median filter with time length of 7 days. Fig 2 shows the median filtered time series and the series fitted by harmonical analysis, taking into account periods from 5 years to 3 months. The one-year terms of this analysis present the seasonal cycle. The relation of the seasonal a.m. and p.m. amplitudes is 0.65 and the maximal values are observed at the summer solstice. The seasonal cycle is generated mainly photolytically by day-to-night N_2O_5 inter-conversion, as described in the section of NO_2 chemistry. The relation depends also on the latitude caused by the change of the day duration [9].

Besides, the time series of the trace gas SCD allow to study the influence of the QBO, the solar cycles as well as terms, describing the tele-connection patterns, related to dynamical processes [10]. In addition, relations to climate connections are being searched. In this context it is important to establish long-time trends of the trace and greenhouse gases. Observations by ground-based stations have shown a significant upward trend of the NO_2 amount of about 5% - 7% per decade [11, 12]. The increasing NO_2 content can

decelerate the ozone recovery. The long-time ozone trend is regionally different. In general, the negative ozone trend increases along with the latitude. At the time scale of days, the time series can be used to study pollution events such as contamination from power plants, arriving by transport processes to the probed region, or lightning-generated events. Using additional information for the weather condition, the distribution of the geopotential, the potential vorticity etc., the time series can be used to examine dynamical processes, too. Results are presented below, demonstrating how the lightning and transport events can be studied, and the third point shows an example of the result of the satellite data validation.

Study of lightning events

As mentioned above, the lightening is a natural source of NO_2. In the flash channel the high temperature dissociates O_2 to atomic oxygen, which can be oxidized molecular nitrogen or nitrogenoxide NO. NO_2 is then produced by the fast oxidation of NO by molecules with peroxide groups such as O_3, HO_2 and RO_2. Approximately 10% of the atmospheric NO_2 is lightning generated. However, the exact lightning contribution to NO_2 is not known yet. It was pointed out above that strong pollution events are smoothed by the median filtration. Thus, the pollution events can be obtained by the difference of the original data (Fig.1) and the low pass fits of the median filtered time series (the lines in Fig.2). The result is shown in Fig.3. Episodic jumps of NO_2 SCD are clearly observed. These jumps are a result of different reasons

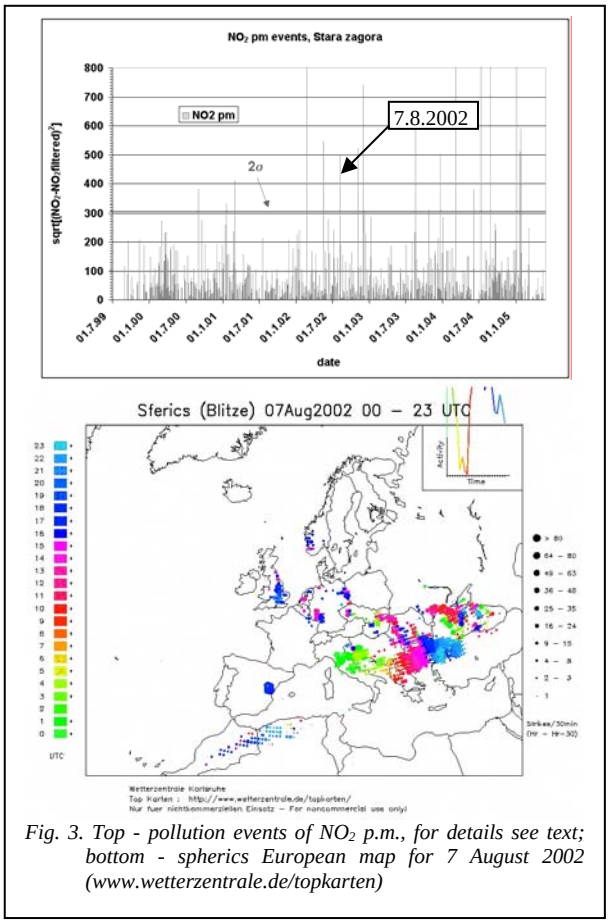


Fig. 3. Top - pollution events of NO_2 p.m., for details see text; bottom - spherics European map for 7 August 2002 (www.wetterzentrale.de/topkarten)

- the transport of polluted air masses to the probed region from the planetary boundary layer, NO_2 and ozone generation as a result of thunderstorms (lightning), Sahara dust storm etc. [13]. It is known that NO_2 SCD increase is observed in the thunderstorm clouds, exceeding 300% [14]. A case of extremely high NO_2 jump in Stara Zagora is observed on 7-8.8.2004, which was a result of intensive thunderstorm activity.

An atmospheric front passes over Bulgaria on 7-8.08.2002, accompanied by heavy rainfall and intensive thunderstorm activity (see Fig. 3 bottom). The center of a quickly moving cyclone, formed over the Adriatic Sea moves eastwards, as the thunderstorm moves in the same direction. During the measurements of NO_2 p.m. on 07.08.2002 (16:00UT – 18:00UT) the slant column where NO_2 is determined, has been located westwards from Stara Zagora. The thunderstorm activity was very strong over Stara Zagora and westwards from Stara Zagora in the interval 14:00UT – 17:00UT on the same day. It is presumed that in this interval under the influence of the intensive thunderstorm activity westwards from Stara Zagora, a considerable NO_2 quantity has been generated and accumulated.

This NO_2 increase was registered during the evening measurements, which show concentration increase of several times as compared to the control (undisturbed by lightning) day. On 08.08.2002 the NO_2 measurements are from 3:00UT until 5:00UT, directed to the Black Sea. In this interval and in the previous few hours the thunderstorm was over the West Black Sea area but its intensity had decreased. Consequentially, the morning measurements show a weaker NO_2 jump as compared to the previous day (not shown here).

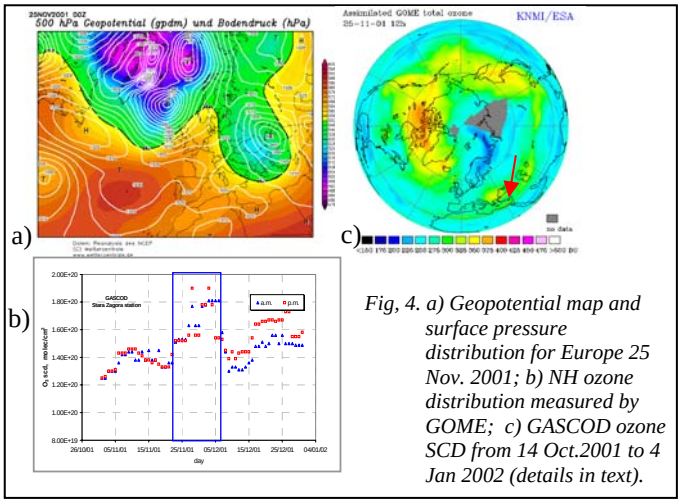
It is found out that almost 30% of the cases of quick NO_2 SCD changes (jumps) in Bulgaria present some thunderstorm activity in the measurement day or in the previous one.

Study of a STE event

The lifetime of the active nitrogen is of the order of one day in the lower troposphere and perhaps of 4 – 7 days in the upper troposphere. NO_2 can be transported over a range up to 2000 km in the form of peroxyacetyl nitrogen (PAN), which has a very long lifetime, NO_2 can be transported by very large ranges. These dynamical processes are also important for the analysis of the NO_2 distribution and the time series. One of the effective transport mechanisms of the stratospheric air masses to the troposphere is the exchange via tropopause folds [Holt].

On 25 November 2005 an anti cyclone ridge is located over South- East Europe. Neighboring cyclone pressure systems are situated over Greenland and over the whole East Europe (see Fig.4a). The geopotential height map for 50 hPa pressure level and the vector winds maps shows, that the eastward stratospheric wind was prevailing over the middle Atlantic and an intrusion of a low latitude poor ozone air mass to West Europe could be observed (see Fig.4b). The intrusion is obviously on the map of the geopotential height for 500 hPa pressure level on 25 November. The intrusion covered the Atlantic westwards from Europe up to the South of the Scandinavian Peninsula and its dimension was over two thousand kilometers. During the stay of the low pressure system over Bulgaria the higher ozone slant column densities are measured by the Stara Zagora GASCOD instrument (Fig.4b, data inner the marked black frame). A tropopause jump, characterizing fold situations, is registered at the

meteorological station Undine, North Italy. The tropopause height from the evening to the morning soundings decreases more than 1 km. In the evening of 25 November over Undine



Fig, 4. a) Geopotential map and surface pressure distribution for Europe 25 Nov. 2001; b) NH ozone distribution measured by GOME; c) GASCOD ozone SCD from 14 Oct.2001 to 4 Jan 2002 (details in text).

dry air mass is transported in the upper troposphere. The observed airmass transport is in agreement with the trajectory calculations [15]. The situation observed here is very similar to the one, described by Holton [16].

Satellite data validation

The geometry of satellite spectrometric measurements to retrieve trace gases is basically different from the ground-provided one. Therefore, the radiation transfer to the instrument on board a satellite, airplane platform, or to the ground is different. The influence of clouds and the surface albedo on the measurement results depends on the applied method. That is why it is necessary the results obtained by new methods to be compared with methods, which have produced significant results. The differences in the results should be analyzed.

The contribution of the ground-based stations for the satellite data validation is very important. GASCOD NO_2 data was used by the Energy Transport & Minor Gases in Atmosphere group of ISAC, Bologna, Italy in the validation procedure analyses of the SCIAMACHY data [17, 18]. A

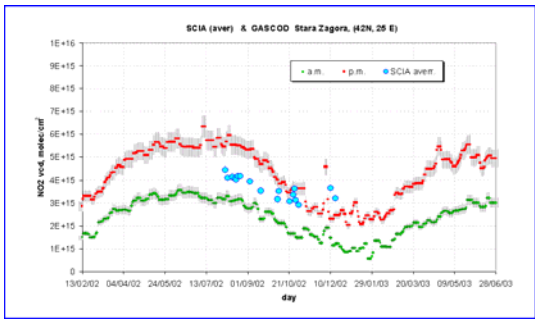


Fig. 5. Comparison of NO_2 data from SCIAMACHY and the GASCOD Stara Zagora instrument

comparison of the ground-based and satellite data is shown in Fig.5; for detailed analysis of the results, see the reference [18].

Conclusions

This work presents several studies based on the NO_2 time series, obtained at the Stara Zagora station. They demonstrate that the results can be used in very different fields of the atmospheric research.

Acknowledgment

We want to acknowledge the GOME at the Heidelberg University and KNMI and the Department of Atmospheric Sciences at the Wyoming University for the data collection of soundings and their publication. We are thankful to K. Takucheva and T. Miteva for the technical support.

References

[1] P.J. Crutzen, "The influence of nitrogen oxide on the atmospheric ozone content", *Quart. J. Roy. Met. Soc*, Vol. 96, 1970, p. 320.

[2] H.S.Johnston, "Reduction of stratospheric ozone by nitrogen ozone catalysts from supersonic transport exhaust", *Science*, Vol. 173, 1971, p. 517.

[3] R.R. Garcia, S.Solomon, "A new numerical model of the middle atmosphere, 2, Ozone and related species", *J. Geophys. Res*., Vol. 99, 1994, pp. 12,937-12,951.

[4] G.P. Brasseur, J.J. Orlando, G.S.Tyndall, "*Atmospheric Chemistry and Global Change*", New York, Oxford, Oxford University Press, 1999.

[5] S. Solomon, "Stratospheric Ozone Depletion: A Review of Concepts and History, *Rev. of Geophysics*, Vol. 37, No 3, 1999, pp. 275-316.

[6] R.Werner, et al., "Spectrometric Measurements of NO_2 Slant Column Amount at Stara Zagora Station (42°N,25°E)", *Adv. Space Res*., Vol. 31, No.5, 2003, pp. 1473-1478.

[7] U. Platt, "Differential optical absorption spectroscopy (DOAS)", in: *Air Monitoring by Spectroscopic Techniques*, W.Sigris (ed.), *Chemical Series*, 1994, Vol. 127.

[8] R.Werner, et al., "NO_2 Column Amount and Total Ozone at Stara Zagora (42°N, 25°E) and their Response to the 27-day Solar Activity" Cycle, *Proc. of the Quadrennial Ozone Symposium*, Kos, Greece, 1 - 8 June, 2004, Christos S. Zerefos (ed.), University of Athens, 2004, pp. 1049-1050.

[9] D.Bortoli, et al. "Stratospheric NO_2, observation at mid and high latitudes performed with ground-based spectrometers", *Proc. SPIE*, Vol. 4168, 2001, pp. 297-308.

[10] G.Hansen, T,Svenø, "Multilinear regression analysis of the 65-year Tromsø total ozone series", *J. Geophys. Res.*, Vol. 110 No D10, 2005, D10103.

[11] J.B. Liley, et.al., "Stratospheric NO_2 variations from long time series at Lauder", New Zealand, *J. Geophys. Res*., Vol. 105, No D09, 2000, pp. 11, 633-11, 640.

[12] Petritoli, A. et al., "Stratospheric NO_2 climatology trend at northern midlatitudes from 8 years of ground based observations at Mt. Cimone station", *IEEE*, 2002, pp. 2331-2333.

[13] H. Huntrieser et al., "Transport and production of NO_x in electrified thunderstorms: Survey of previous studies and new observations at midlatitudes", *J. Geophys. Res*., Vol. 103, No D21, 1998, pp. 28247-28264.

[14] T.Winterrath, "Enhanced O_3 and NO_2 in Thunderstorm Clouds: Convection or Production?", *Geophys. Res. Lett*., Vol. 26, 1999, pp.1291-1294.

[15] I.Kostadinov, et al., "Ground-Based Monitoring of Stratospheric O_3 and NO_2 and their response to STE events", *Proceedings of the Quadrennial Ozone Symposium*, Kos, Greece, 1-8 June, 2004, Christos S. Zerefos (ed.), University of Athens, 2004, pp. 984-985.

[16] J.R.Holton et al., "Stratosphere-troposphere exchange, Rev. Geophys.", Vol. 33, 1995, pp. 403-439.

[17] A.Petritoli, et al., "SCIAMACHY validation of NO_2 total column by means of ground-based DOAS measurements at Mt. Cimone (44N, 11E) and Stara Zagora (42N, 25E) stations", *Proc. ENVISAT Validation Workshop*, Frascati, Italy, ESA SP-531, 2003.

[18] I. Kostadinov, "Validation of SCIAMACHY NO_2 Vertical Column Densities with Mt.Cimone and Stara Zagora ground-based zenith sky DOAS observations", *Proc. of the Second Workshop on the Atmospheric Chemistry, Validation of Envisat* (ACVE-2), 3-7 May 2004, ESA-ESRIN, Frascati,Italy, 2004.