DETERMINATION OF THE STRATOSPHERIC NO_2 SLANT COLUMN BY MEANS OF GASCOD TYPE INSTRUMENT AT STARA ZAGORA STATION

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Abstract

NO_2 is a member of the nitrogen oxides family, which takes part in a large number of homogeneous chemical and photochemical reactions. They are very important for the distribution of the stratospheric ozone and the ozone decline and hence contribute to the global climate changes. So, it is clear that (understanding of the temporal and space NO_2 variations could contribute to improvement of the knowledge in this field) plays a significant role in understanding the climate change processes.

The study of the photochemistry and transport phenomena of NO_2 requires long-time measurements.

Since 1993 a ground-base UV-VIS spectrometer, named GASCOD and developed at the Institute for Atmospheric and Oceanic Sciences (ISAO), is operating at Mt.Cimone station (42°N, 11°E, 2165m a.s.l.) near Bologna, Italy, and is employed for detection of atmospheric trace gases – ozone, NO_2 etc.

Since August 1999 a similar instrument has been installed at the observatory in Stara Zagora (44°N, 25°E, 269m a.s.l.), Bulgaria, at the Department of the Solar-Terrestrial Influences Laboratory for diurnal and long-time studies, simultaneous at Mt.Cimone and Stara Zagora.

The Stara Zagora GASCOD type instrument is placed on the roof of one of the observatory buildings and the diffused zenith skylight is directed to the spectrometer by means of a 45° mirror and via a f/5 telescope it is focused on the entrance slit. The incoming radiation is spectrally split by a holographic grating of 1200 groves/mm. The spectra are registered by a multichannel detector of 512 diode array of a Hamamatsu type. The spectral dispersion is 2.4 nm/mm and the resolution is about 0.5 nm. The integration time is automatically selected for each measurement and ranges from few seconds at noon to several minutes at twilight. The instrument records the spectra in the range of 410 nm to 460 nm. DOAS methodology is applied for retrieving the NO_2 slant column. The spectral analysis uses minimum least squares fitting of the cross sections at the expected absorbers to logarithm of the twilight spectrum and a reference spectrum. The twilight spectra are measured daily in the morning and in the evening. The reference spectra are registered at noon. The preliminary results are shown and a comparison is made between the measurements carried out at Mt.Cimone station and Stara Zagora station.

1. INTRODUCTION

The atmosphere is an enormous and complicated dynamic system. The changes of its components are forced by human industrial and agricultural activities. The increase of the greenhouse gases produce 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 behaviour of several atmospheric trace gases, aerosoles and clouds.

Important scientific results have been obtained by ground-based networks (such as ALE/GAGE – Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment and CMDL – Climate Monitoring and Diagnostics Laboratory), Network for Detection of Stratospheric Changes (NDSC); satellite projects (as UARS- Upper Atmospheric Research Satellite) and airborne projects (by help of aircrafts of types such as ER-2 and M-55), provided in the last decades of the century.

For the investigation of tropospheric and stratospheric trace gases in the last years the Institute of Atmospheric and Oceanic Sciences (ISAO) of the Italian Academy of Sciences, Bologna, has developed a number of spectrometric systems, applying differential optical absorption spectrometry (DOAS) as a retrieving method. One of the designed instruments has been operating since 1995 at the Italian Antarctic station at Terra Nova Bay. In the period 1998 – 1999 a new version of the spectrometric system has been developed. It flew on board the stratospheric aircraft M55-Geophysica and investigated successfully the physical and chemical processes responsible for the depletion of Antarctic stratospheric ozone within the terms of the International Program Airborne Polar Experiment Geophysica Aircraft in Antarctica [1].

At the end of August 1999, within in the frame of the collaboration between ISAO – Bologna and the Department of the Solar-Terrestrial Influences Laboratory in Stara Zagora, the Italian party supplied to STIL one of the GASCOD instruments for gas traces investigation. A similar instrument has been installed in 1993 at the Observatory in Mt. Cimone, located in the Italian Apennines at an altitude of 2165 m, about 50 km southwest from Bologna [2]. Joint research is envisaged of photochemical processes and transport mechanisms, connected with the nitrogen atmospheric components, more precisely with the nitrogen dioxide.

The research conducted in Stara Zagora and Mt. Cimone is included in the SENSES project (South European Network for Stratospheric Exchange Study. The

obejctive of SENSES is to integrate in a network the existing UV/VIS DOAS instruments, used for retrieving of the stratospheric trace gases content in the Mediterranean area as a part of the Global Observing System and to give contribution to understanding of the Stratospheric Tropospheric Exange [3].

Stara Zagora, Bologna and Mt. Cimone are located at about 43 degrees northern latitude. This allows the investigation of transport mechanisms in the zone near this geographic latitude from 10 to 25 degrees east latitude. Besides, efforts are made to involve research teams with similar scientific program's at stations, located in France, Greece, Portugal and Spain and in this way to cover the Mediterranean zone.

2. PHOTOCHEMISTRY OF THE NITROGEN DIOXIDE

The nitrogen dioxide NO_2 is a part of the nitrogen family NO_x. As it is known, it participates in the catalytic cycles of the ozone destruction [4,5]. Some of these cycles are reactions in which NO_2 is formed:

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

on the other side, NO is formed by NO_2 destruction:

$$NO_2 + O \rightarrow NO + O_2 \qquad (b)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 . \qquad (c)$$

and during the day

$$NO_3 + h\nu\ (\lambda<670nm) \rightarrow NO + O_2 . \qquad (d)$$

The last equation underlines the fact that the photochemical diurnal balance is different from nighttime one. During the day, the ozone is distracted additionally by reactions (a) and (c), followed by the photodissociation (d). By NO_2 the reservoir gases are formed by triple impacts:

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

$$NO_2 + HO_2 + M \rightarrow HO_2NO_2 + M$$

$$NO_2 + ClO + M \rightarrow ClONO_2 + M$$

and

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

These reactions, on the one hand, remove the active NO_x and curtail the O_3 destruction and, on the other hand, they transform the radicals HO_x and ClO_x, which destruct catalytically the ozone, into reservoir species. The reservoir gases are characterized by their relative inertness, i.e. they have a long
lifetime. In the day the reservoir gases are destructed photodissociatively:

$$N_2O_5 + h\nu\ (\lambda<380nm) \rightarrow NO_3 + NO_2,$$
$$HNO_3 + h\nu\ (\lambda<320nm) \rightarrow NO_2 + OH,$$
$$ClONO_2 + h\nu\ (\lambda<400nm) \rightarrow ClO + NO_2$$
$$\rightarrow Cl + NO_3\,.$$

NO_2 is destructed photodissociatively, too:

$$NO_2 + h\nu\ (\lambda<420nm) \rightarrow NO + O\,.$$

During these reactions In the sun-illuminated part of the atmosphere above mentioned photochemical reactions dominate, leading to formation of radicals on account of the reservoir gases, while during the night the reverse process take place.
Furthermore heterogeneous chemical reactions on the surface of Polar Stratospheric Clouds (PSC) are very important for the atmospheric chemistry, more precisely for the formation of the “Ozone Hole” in the polar region. The reactions on sulfate aerosol surfaces are important at all latitudes. A reduction of the column abundance of NO_2 was observed after volcanic eruptions, such as those after the Pinatubo eruption.
The above reactions, connected with NO_2 are far not complete. In order to understand the atmosphere photochemistry and its dynamics, two- and three-dimensional models have been developed, including a multitude of reactions and transport mechanisms.

3. PRINCIPLE SCHEME OF THE GASCODINSTRUMENT

By the help of an input objective, Cassegrain type, with focal length 1 m and aperture f/5 the incoming light flux is focused on an input slit with 0.1 mm width and

2 mm height. Two discs are mounted along the optical axis in front of the input slit. The first is provided for cells assembly, containing gas with certain concentration and on the second one filters are mounted for scattering curtail. The two discs are driven by step motors. The light flux is analyzed by a holographic spherical diffraction grating of the Jobin Yvon company with 1200 groves/mm, with linear dispersion of 2.4 nm/mm at 300 nm, with focal distance 0.3 m. The grating moves by the help of a step motor. In this way the instrument covers a spectral range of 250 nm to 700 nm with steps of about 50 nm. A detector is located in the focal plane of the diffraction grating. It is of the Hamamatsu type (Multichannel detector C4350) and it consists of a diode line with 512 elements (pixels) each of 0.05 mm x 2.5 mm sizes, i.e. the optical dispersion is about 0.12 nm for a single diode. The spectral resolution is about 0.5 nm. For the expected spectrometric analysis of the zenith light flux the necessary exposure time is in the interval (1 – 20) sec. This allows the detector to operate at almost 5^0 C. A mercury lamp is mounted at the objective input for the spectral calibration. The disposition of strong Hg-lines on preliminary selected pixels is controlled automatically. The reproduction precision of the wavelength by pixels is 1 to 2 pixels. The instrument is controlled by a microprocessor system. This enables the automatic selection of exposure time according to the incoming light intensity as well as to switch on and off the instrument automatically according to a determined programmable scheme, to clear the dark signal from the measured one. The above mentioned spectral calibration includes disc positioning of the cells and filters, conversion of the signals from analogue to digital and transmission of the signals by RS 232 to a personal computer. The computer disc stores every day files with spectra of the calibration source, the measured spectra with cleared dark signal and the calibration spectra for selection of the exposure time. The instrument is described in detail in [2].

4. PERFORMANCE OF THE GASCOD INSTRUMENT IN STARA ZAGORA

NO_2 as well as the other radicals show strong diurnal variations. In the night the NO_2 concentration slightly decreases. With the sunrise the concentration initially strongly decreases as a result of the photodissociative destruction until a balance is reached, after which it slowly increases. At sunset the concentration quickly increases. As a result of the specific character of NO_2 dynamics, it is appropriate to determine NO_2 in the morning about and after sun rise as well as before and during sunset.

Besides, at large zenith angles, the optical path is long and the NO_2 absorption by the DOAS technique is measurable [6]. For this reason, the instrument starts 30 min. before sunrise and continues to work 90 min. after that. In the evening it is the opposite – the instrument starts 90 min. before sunset and continues to work 30 min. after that. Each measurement cycle begins with a spectral calibration. Subsequently, it determines in automatic mode the exposure time, followed by five consequent measurements. This cycle is repeated until exhaustion of the operating time of 120 min. or the purpose of the DOAS method, applied for NO2 retrieving, a reference solar spectrum is detected also during noon period in order to minimize the effects of other atmospheric absorbers.

The instrument operates in a spectral range of 410 nm to 460 nm. In this range the NO_2 absorption is very strong and structured. Errors could arise in the retrieved NO2 slant column, if O_4 and H_2O absorption [7] is not correctly eliminated in the retrieved procedure. After the evening seance the start and the end of operating periods for the next day are computed by a programme in the control computer.

The GASCOD instrument has been operating at the Department of STIL in Stara Zagora since 27.08.1999 with very short temporal interruptions, due to technical reasons. Data processing is carried out by algorithm described in [8].

5. RESULTS

A complete picture of NO_2 SCD for the zenith angle of 90 degrees is presented in Fig. 1. The seasonal variation is seen as a negative trend from the autumn to the spring months in the a.m. as well as in the p.m. values. Typical the a.m. slant column densities are higher than the values, registered during sunset.

A comparison of p.m. data from Mt. Cimone and Stara Zagora show, that the seasonal trend at the Mt. Cimone station is stronger than the one at the Stara Zagora station for the specified period of time [9].

About the period of February/March, the a.m./p.m. relation shows oscillations, while a.m. values remain quite invariable. This behavior now is still discussed.

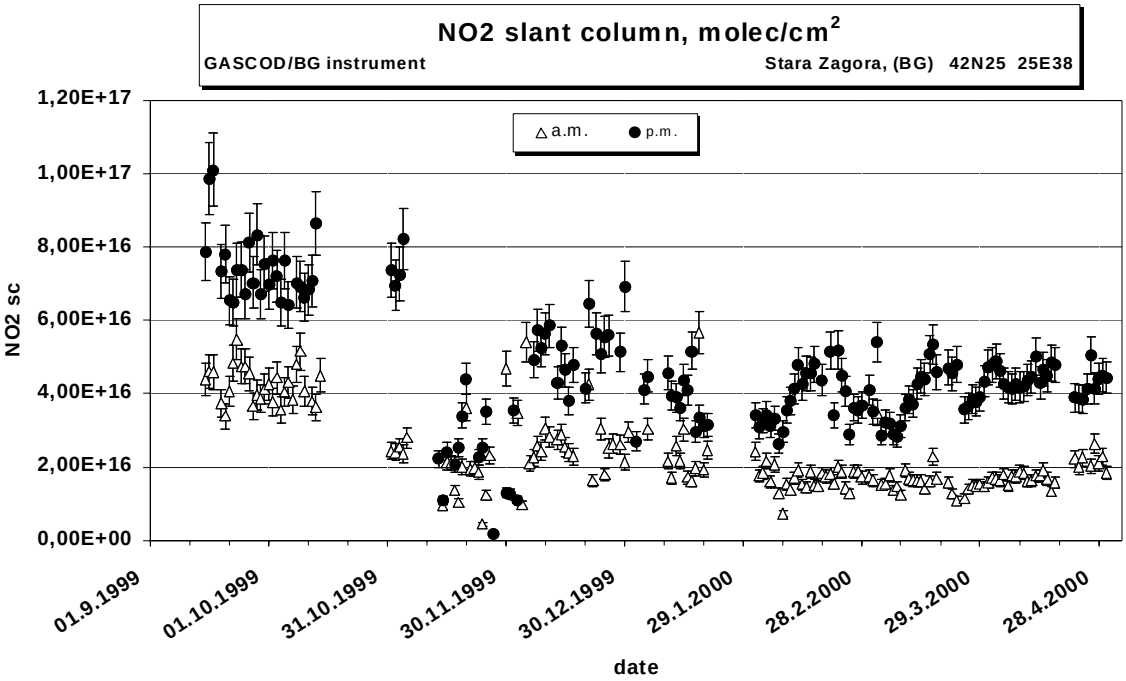

Figure 1. The retrieved NO2 slant column densities for the period of measurements at the Stara Zagora Station.

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