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MEASUREMENTS OF THE TOTAL COLUMN AMOUNT OF NO_2 AT "KISLOVODSK" OBSERVATORY IN 1979-1990

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ABSTRACT

The results of the measurements of the NO_2 total content at the "Kislovodsk" observatory (North Caucasus 2070 m a.s.l.) in 1979-1990 are presented. The measurements were based on the absorption of the direct sunlight in the visible region of the spectrum. The variation of the NO_2 content from the morning to the evening and the seasonal and year to year variations are analyzed.The less amplitude of the daily variations of the NO_2 total content in comparison with the variations of the stratospheric NO_2 content says about the significant insert of the tropospheric and lower stratospheric NO_2 in its total content. The year to year variations of NO_2 and ozone are in antiphase. Their values depends on the regional features of the atmospheric circulation. The quasibiennial oscillations of the total NO_2 content are picked out.

1. INTRODUCTION

The measurements of the NO_2 total amount in the vertical column have being carried out at the observatory "Kislovodsk" since 1979 (Elansky et al., 1986). The observatory is situated in the North Caucasus (43,7 N, 42,7 E, 2070 m a.s.l.), 18 km away to the south from the town of Kislovodsk. In the vicinity of the observatory there is no intensive sources of NO_2. The measurements of the surface NO_2 concentration carried out during about 5 months in 1989-90 have shown, that its daily means did not exceed 1 ppb. The short-term increasings of the NO_2 concentration, connected with the local transport, didn't influence its total amount. More significant variations of the NO_2 concentration up to 3-5 ppb during 1-3 hours were registered when nitric fertilizers have being brought into the surrounding pastures. But such cases happened very seldom and the increasing of the NO_2 concentration had only occurred during the intense sunshine. Some cases (not always coincident with the time of the NO_2 total amount measurements), when the NO_2 concentration was enhanced up to 5-8 ppb for a few houres, were registered. These cases can be bounded up with the long-way transport of the polluted air masses.However, the variations of the total NO_2 content in the vertical column at that time did not come out of the limits of standard deviation for the daily means. Thus we can consider that the conditions at the Kislovodsk observatory are near to the background. This was confirmed by the results of the trace gases measurements (see, for example, Elansky et al., 1992).

2. THE METHOD OF MEASUREMENTS

The measurements of the NO_2 content were based on the absorption of the direct sunlight. In contrast to the measurements of the absorption of the scattered at zenith sunlight (Syed and Harrison, 1980; Solomon et al., 1987) this method gives the total content in the vertical column. The "direct sunlight" method is not sensitive to the variations of the optical parameters of the atmosphere, its aerosol characteristics among them, and does not require of taking into account the Ring- effect and of photochemical modeling of the NO_2 vertical distribution variations in the atmosphere at the transition from its night to day regime. The shortcoming of the "direct sunlight" method is the impossibility of observation in the presence of the clouds.

The calculation of the NO_2 content was made on the base of the absorption of sunlight at 5 wavelengths (see Tabl. 1), the absorption of the ozone taken into account. The spectra within the 430-450 nm region were registered by the spectrophotometer with the spectral resolution 0.4 nm. The observations have been carried out at solar zenith angles 75-87°. The time of the single measurement was 55 s.

Tabl. 1. The absorption crossections

K_{NO2}(10^{-19}cm2) and K_{O3} (10^{23}cm^2).

nm	434.86	437.94	439.06	441.22	442.02
K_{NO2}	6.86	3.21	6.73	3.676	3.376
K_{O3}	6.75	8.35	9.86	14.03	15.74

The technique of the calculation is analogous to that used by Syed and Harrison (1982) and Kerr (1988). The NO_2 (for the temperature 235 K) and O_3 absorption coefficients were taken from the works of Leroy et al. (1987), Johnston and Graham (1976) correspondingly. As these coefficients differ from used by us earlier, the data given in the work of Elansky et al. (1986) have been recalculated.

The O_3 total content have been measured till March 1989 using spectrophotometer IPA (Elansky et al., 1986), later with the help of the spectrometer Brewer N 43. The IPA data are less than Brewer's by 2%.

The random error of the measurements of the NO_2 total amount within the single set under the best conditions is $0.4 \cdot 10^{15}$ cm^{-2}. The values of the NO_2 content that were obtained with the relative random error more than 30% were not included in the monthly means. That is why the data for some summer months are absent.

3. THE RESULTS OF THE MEASUREMENTS

The monthly means of the total NO_2 amount for morning observations are shown in Fig. 1. The amount of observations during the month varied from 5 (in separate spring-summer months) to 25 (in autumn-winter) The number of the measurements at sunset is somewhat less.

The evening NO_2 values are larger than the morning ones. It is connected with the transition of the significant part of NO_2 in N_2O_5 during the night and photodissotiation of N_2O_5 in the daytime. The mean ratio NO_2 evening /NO_2 morning for the different seasons is given in Tabl.2.

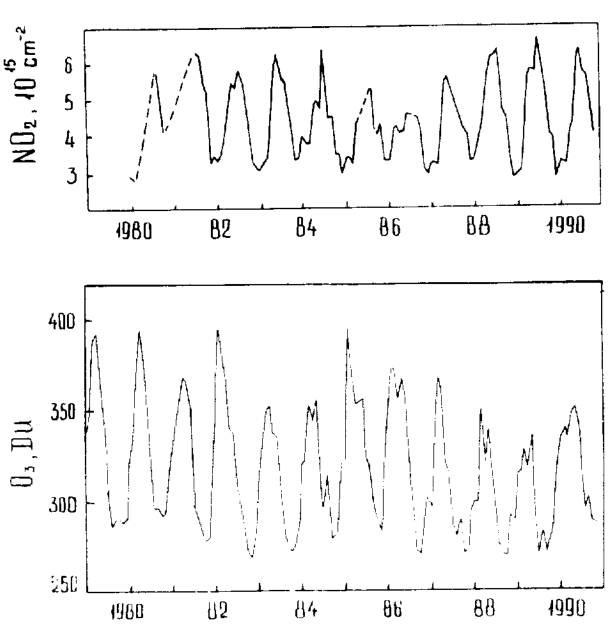

Fig. 1. Monthly mean total NO_2 (a) and ozone (b) content for Kislovodsk, 1979-1990.

Table 2. The ratio $NO_{2\ evn}$ / $NO_{2\cdot morn}$

	winter	spring
$NO_{2\ evn}/NO_{2\ morn}$	1.29±0.03	1.32±0.04

summer	autumn	year
1.34±0.055	1.31±0.03	1.32±0.02

The differences in the values are not big, though the duration of the light part of the day changes within the wide limits. The ratio averaged over the year is 1.32±0.02 what is significantly less than for the stratospheric NO_2 , measured by the zenith skylight method. The presented by Amanatidis et al. (1989) data of such measurements made by different authors give the value 1.5-1.7. Our measurement of the stratospheric NO_2 carried out at the "Kislovodsk" observatory during the autumn of 1990 also give the value 1.5. Evidently, the lower stratosphere and the troposphere, where the transition NO_2 <--->N_2O_5 is weakened, bring in the significant contribution in the NO_2 total content in the column.

In Fig. 2 the seasonal variations of the NO_2 are shown. Averaged over the period 1979-1990 the ratio of the summer and winter values is 1,9 (the maximum value is $6.0 \cdot 10^{15}$ cm^{-2} - in July, the minimum value is $3.1 \cdot 10^{15}$ cm^{-2} - in December). Its value is close to the values got approximately at the same latitudes in Toronto - 2.0 (Kerr, 1989) and in the south hemisphere in New Zealand (McKenzie, 1982) The absolute values of the NO_2 total content at all three stations differ by 20-50%. In addition to the already noted causes of that (Kerr,1989), let's mention two more: 1) the total NO_2 content can significantly exceed its stratospheric part, 2) the NO_2 absorption coefficients, that were used in the present work differ from the coefficients of Johnston and Graham.(1976).

In Fig.3 the 12-month averaged values of NO_2 and O_3 are given. Their variations from year to year have close relative values (within the limits of 7-9%) and are in the opposite phase. This important result shows that the gases are in the

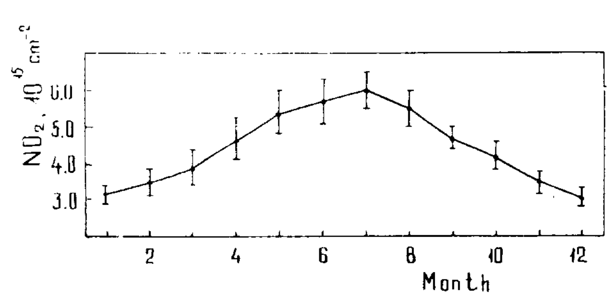

Fig. 2. Average seasonal variation and standard deviations of total NO_2 content for Kislovodsk, 1979-1990.

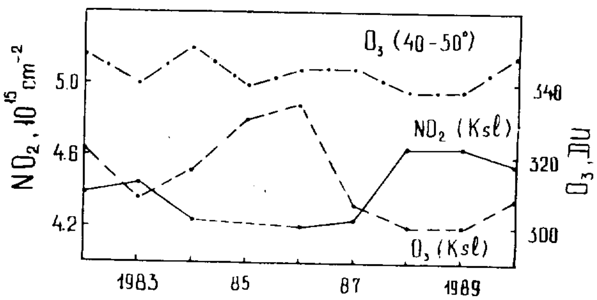

Fig. 3. The 12-month averaged total NO_2 and ozone content for Kislovodsk and latitudional zone 40-50 N.

equilibrium. Taking into account the distinction of the ozone behavior in Kislovodsk from the means for the latitudes 40-50 N (Fig 3) we can suppose that the year to year variations are connected with the influence of the regional dynamic processes. The significant role there plays the migration of the subtropic high-altitude frontal zone. The warming up of the air during the summer months above the deserts of the Near East leads to the

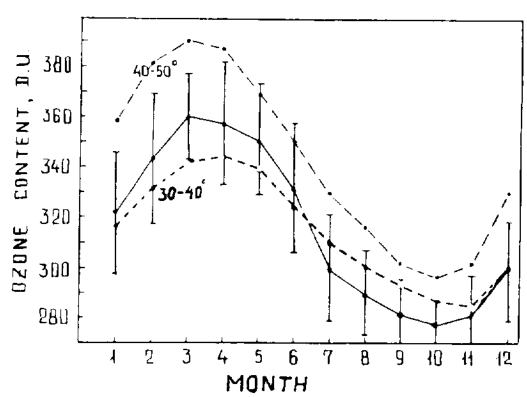

Fig. 4. Average seasonal variation and standard deviations of total ozone content for Kislovodsk (solid line) and for latitudional zones 30-40 and 40-50 N (dashed lines), 1979-1990.

removal of the frontal zone further north than 43 N. The observatory gets then in the region of the high-altitude anticyclone with the ascending motion in the higher troposphere and lower stratosphere and the reduced ozone content. This is confirmed by Fig.4 where the seasonal variations of the ozone content got by the averaging of the data of the Kislovodsk observatory and ozonometric stations, situated between 30-40 and 40-50 N, over the period 1979-1990. Even taking into account the systematic difference in the instrument's readings and the high altitude of the observatories above the sea level (about 2% of the ozone total amount contains within the layer 0-2 km), it is seen that the ozone content over the "Kislovodsk" observatory in summer is sharply reduced.

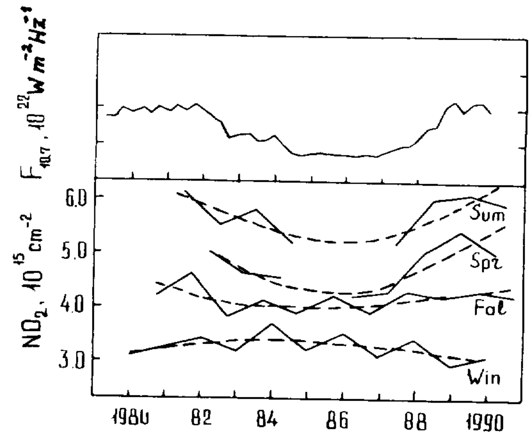

Fig. 5. Solar flux $F_{10.7}$ at wavelenght 10.7 cm as an indicator of solar activity (a), the seasonal averaged total NO_2 (solid lines) and their interpolated values (dashed lines) (b).

Fig. 5 shows, that the yearly NO_2 variations are determined by its variations during the spring-summer period. The smoothed time dependence of the total NO_2 content for these seasons repeat the behavior of the solar activity ($F_{10.7}$). It is possible that the solar activity do determine the long-term NO_2 variability, though not straight through the photochemical processes but through the influence on the circulation of the atmosphere and alteration of the location of the active neareastern part of the subtropical frontal zone. In winter, when the frontal zone is located at 30-35 N, the observatory gets into the midllatitudinal air mass and the NO_2 content experiences less variations from year to year.

If to take into account, that the seasonal variations of the NO_2 content include the 11-year harmonic, then subtracting it out of the time dependence of the NO_2 content we can select the quasibiennial oscillations. In Fig. 6 the deviations

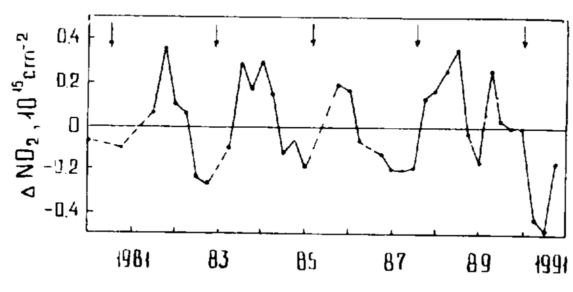

Fig. 6. The deviation of the seasonal averaged total NO_2 content from interpolated values (dashed lines in Fig.5). The arrows show the maximum of west phase of zonal circulation at Singapore at 50-100 mb.

of the seasonal means of the NO_2 content from the smoothed values, given in Fig. 5 by the dotted line, are represented.

The variations with the amplitude of approximately 5% are in the definite correlation with the change of the zonal circulation in the tropical stratosphere. The decreasing of the NO_2 content is going on during the developing of the west phase of the zonal wind at the altitudes 100-50 mb. The similar variations in the ozone content are well known. As the source of the odd nitrogen and, consequently, of NO_2 is localized also in the equatorial stratosphere, the quasibiennial modulation of the meridianal flow of the odd nitrogen can lead to the analogous result. It is possible that the pronounced quasibiennial cycle is connected with the fact, that the source is localized within the limits of the narrow inner-tropical zone of convergation. The significant time variations of the NO_2 content over the Kislovodsk and their obvious connection with the atmospheric circulation give no possibility to estimate the value of the NO_2 content trend. Though the increasing of the NO_2 content by 5% in 1989-90 in comparison with the 1982 is observed at the similar solar cycle phase, it can be the displaying of the regional features of the atmospheric circulation.

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