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GEOPHYSICS

Latitudinal Structure of Trends and Effect of Solar Activity in Stratospheric NO_2

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The estimates of linear trends in the total content (TC) of NO_2 as functions of latitude are first presented in this paper. The estimates of trends for several sites of NO_2 observations were obtained earlier in [1–5]. Positive NO_2 trends content (per decade) were reported from the following stations: approximately 5% at Station Lauder, New Zealand [1]; approximately 6% at Station Jungfraujoch, Switzerland [3]; and within 5–7% at Station Issyk-Kul, Kyrgyzstan [4]. These trends are based on the data of observations during 17–21 yr. For a shorter period of measurements (13 yr) at Zvenigorod Scientific Station of the Institute of Atmospheric Physics, Russian Academy of Sciences, large (by module) values of the negative trend in TC of NO_2 (–12% per decade) were obtained [5].

At present, time series of observations of the TC of NO_2 with a duration of ~10 yr and longer were obtained at a number of stations within the Network for the Detection of Atmospheric Composition Change (NDACC). This gives us the possibility to estimate the NO_2 trends for a greater number of stations and distinguish latitudinal peculiarities of the trends.

The data NO_2 TC in the vertical atmospheric column were taken from ftp://ftp.cpc.ncep.noaa.gov/ndacc. It is assumed that the stratosphere is the main contributor to the TC of NO_2. The data of the vertical column NO_2 at Zvenigorod scientific station includes the atmosphere above the surface layer. The information about the stations is given in the table. The results of measurements were subject to statistical verification. Long-term monthly mean values of NO_2 TC and root-mean-square deviations from these were calculated. Data outliers beyond the quadruple root-mean-square deviation respective to the long-term monthly mean values were discarded. This procedure was repeated iteratively. After this, the current monthly mean values of NO_2 content and mean annual cycle of NO_2 were calculated. The monthly mean values of NO_2 content were calculated for the entire period of measurements excluding the data from July 1991 to June 1993, when the stratospheric NO_2 was influenced by products the eruption of the Pinatubo Volcano [1, 4–6].

A model of multiple linear regressions was used to estimate the NO_2 trends:

$$y(t_n) = a_0 + a_1 t_n + a_2 \Gamma(t_n) + a_3 I_{SA}(t_n)$$
$$+ a_4 U_{QBC}(t_n + t_{dQBC})$$
$$+ a_5 I_{SO}(t_n + t_{dSO}) + a_6 V_P(t_n) + a_7 V_{EC}(t_n) + \varepsilon(t_n), \quad (1)$$
$$n = 1, 2, \ldots, N,$$

where $y(t_n)$ is the time series of monthly mean NO_2; t_n is time; N is the number of members in the time series; Γ is the periodically repeated mean annual variations of NO_2; and I_{SA} is the index of solar activity (SA): monthly mean values of spectral density of the solar radio flux F10.7 at a wavelength of 10.7 cm (http://sec/noaa.gov/ftpmenu/indices/old_indices.html); U_{QBC} are monthly mean values of zonal velocity of equatorial stratospheric wind at isobaric surface 50 hPa (http://strat-www.met.fu-berlin.de/research/) used as the index of quasi-biennial oscillation; I_{SO} are the monthly mean values of the index of El Niño–Southern Oscillation (http://www.cru.uea.ac.uk/cru/data); V_P is the index of the stratographic content of aerosol after the eruption of Pinatubo Volcano in June 1991; V_{EC} is the index of the atmospheric content of aerosol after the eruption of El Chichon Volcano in April 1982; t_{dQBC} and t_{dSO} are time delays; $a_0, a_1, \ldots, a_7$ are desirable constants, which have the sense of linear trend (a_1) and regression coefficients ($a_2, \ldots, a_7$); and ε is the residual time series.

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Linear trends in the NO_2 content in the vertical atmospheric column

Station	Latitude	Longitude	Observation period, yr	Trend, %/10 yr	
	degrees			morning	evening
Ny-Alesund	78.92 N	11.93 E	1991, 1993–2003	–3.4 ± 6.4	–3.8 ± 6.1
Scoresbysund	70.48 N	21.95 W	1996–2004	–2.1 ± 6.8	–4.1 ± 6.1
Kiruna	67.84 N	20.41 E	1991–2004	–1.7 ± 3.6	–2.3 ± 2.9
Sodankyla	67.37 N	26.63 E	1995–2004	1.7 ± 5.6	1.5 ± 5.3
Zhigansk	66.79 N	123.35 E	1992–2004	3.9 ± 4.0	**5.5 ± 4.3**
Harestua	60.22 N	10.75 E	1994–2006	0.7 ± 5.6	0.5 ± 4.4
Zvenigorod	55.69 N	36.77 E	1990–2004	**–6.5 ± 3.3**	**–6.7 ± 2.4**
Jungfraujoch	46.55 N	7.98 E	1990–2006	**–9.3 ± 2.5**	**–12 ± 2.3**
Moshiri	44.37 N	142.27 E	1991–2001	**–11 ± 5**	**–6.2 ± 3.8**
Issyk Kul’	42.62 N	76.99 E	1983–2005	**2.6 ± 2.1**	0.6 ± 1.4
			1990–2005	2.4 ± 2.9	**2.4 ± 2.1**
Mauna Loa	19.54 N	155.58 W	1996–2004	–2.0 ± 3.9	–2.5 ± 3.4
Bauru	22.35 S	49.03 W	1996–2004	2.2 ± 4.5	**4.6 ± 3.4**
Lauder	45.04 S	169.68 E	1981–2004	**5.8 ± 1.0**	**5.8 ± 0.9**
			1990–2004	**3.0 ± 1.8**	1.3 ± 1.6
Kerguelen Island	49.35 S	70.26 E	1996–2004	**7.3 ± 4.6**	0.4 ± 4.0
Macquarie Island	54.50 S	158.94 E	1996–2004	**12 ± 6**	**8.0 ± 3.9**
Dumont d’Urville	66.67 S	140.02 E	1988–2004	–1.8 ± 2.5	–1.1 ± 2.2
Rothera	67.57 S	68.13 W	1996–2005	0.4 ± 6.4	–1.5 ± 6.1
Arrival Heights	77.83 S	166.66 E	1991–2004	8.6 ± 9.6	8.4 ± 9.4

The V_P index is presented as

$$V_P(t_n) = 0 \quad \text{at} \quad t_n \le T_P + t_{dP};$$

$$V_P(t_n) = \left(1 - \exp\left(-\frac{t_n}{\tau_{ox}}\right)\right)\exp\left(-\frac{t_n}{\tau_a}\right)(1 + g\gamma(t_n)) \quad (2)$$

$$\text{at} \quad t_n > T_P + t_{dP},$$

where T_P is the moment of the Pinatubo Volcano eruption (June 1991), t_{dP} is the delay in the appearance of the eruption products over a site of NO_2 observations; τ_{ox} is time constant of SO_2 oxidation that characterizes the increase in the concentration of stratospheric aerosol; τ_a is the time constant of aerosol removal from the stratosphere; γ is the mean annual variation of NO_2 normalized by the amplitude; and g is a constant. Index V_{EC} is presented in a similar manner with the exception that the last factor is absent in the expression for this index, and the values of constants of the increase and removal of aerosol were assumed equal to 5.8 weeks and 1 yr, respectively, according to [1].

The use of the mean annual variation Γ in the regression model instead of the set of its harmonics allowed us to decrease significantly the number of variables (by 7 compared to [1]). The introduction of the mean annual variation of NO_2 in the approximating formula of the Pinatubo effect (2) allowed us to take into account the seasonal dependence of the effect [6].

Overdetermined system of equations (1) ($N \gg 8$) was solved using the least squares method at varying parameters t_{dQBC}, t_{dSO}, t_{dP}, t_{dEC} (delay in the appearance of the products of El Chichon Volcano eruption), τ_{ox}, τ_a, and g. The final values of parameters were determined from the condition of minimizing the dispersion of the residual time series. At the values of parameters found using this method, the same model (1) was applied for estimating seasonal linear trends. Figure 1 shows examples of the monthly mean values of the NO_2 TC, their approximation by regression model (1), and residual series for the data of evening measurements at stations Zvenigorod, Lauder, and Dumont d’Urville.

The table contains annual values of trends in the TC of NO_2. Bold type highlights statistically significant values of trends. The estimates of trends for stations Lauder and Issyk-Kul are given for whole and shortened periods of observations. The estimates of NO_2 trends content at Station Lauder for the whole period (~6% per decade) are in good agreement with the esti-

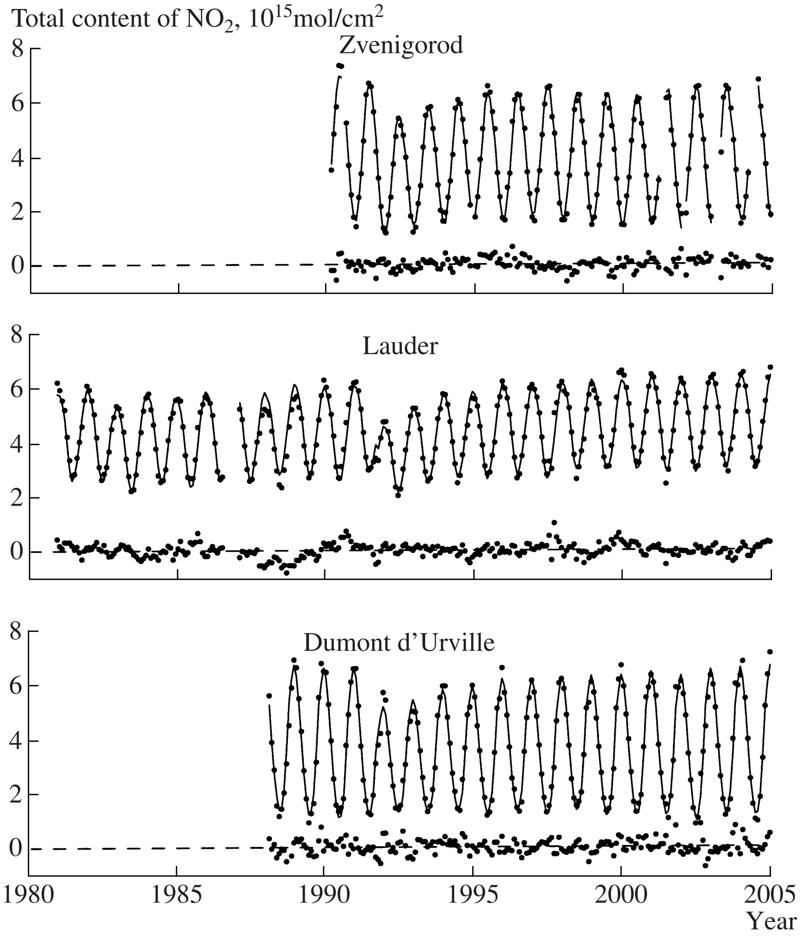

Fig. 1. Monthly mean values of the NO_2 content in the vertical atmospheric column (dots), their approximation by a regression model (curves), and residual time series (dots in the lower parts of the figures) based on the data of evening measurements at stations Zvenigorod, Lauder, and Dumont d'Urville.

mates given in [1], with the account that the authors of [1] distinguished the tendency of trend increase with the increase in the series of observations. A negative trend of about –10% per decade at Station Jungfraujoch, which we obtained for a shorter period of observations than in [3], qualitatively agrees with NO_2 decrease in 1990–2003 in Fig. 4.29 in [3]. Our estimates of the NO_2 trends at Station Issyk-Kul over the whole period of observations quantitatively differ from the estimates obtained in [4]. This difference cannot be explained by the insignificant difference (2 yr) in the length of the time series of observations. The new estimates confirmed the existence of a steady negative NO_2 trend at the Zvenigorod Scientific Station. The update annual estimates of trends of about ~6% per decade are smaller (by module) than the estimates obtained in [5]. This is caused, in particular, by the account of the effect of the solar activity in the regression model.

Figure 2 demonstrates the latitudinal dependence of NO_2 trends. It is characterized by negative values of annual trends at mid-latitudes of the Northern Hemisphere and positive values at mid-latitudes of the Southern Hemisphere. The annual estimates of trends in tropical latitudes are not always statistically significant at the 95% level (but they are usually significant at the 90% significance level). However, we can make a general conclusion that they coincide by sign with the trends at mid-latitudes of the corresponding hemispheres. At high and polar latitudes of the two hemispheres, the annual estimates of the trends are statistically insignificant. We note that the annual estimates of trends at Arctic (Ny-Alesund) and Antarctic (Arrival Heights) stations are presented mainly by the spring and autumn seasons.

The sign of trends at stations Zvenigorod, Jungfraujoch, and Lauder does not depend on the season, although the value of trends changes with the season. At other stations, the values of trends, their statistical significance, and even the sign of trends can change with the season. For example, we recorded in spring a negative NO_2 trend at Station Ny-Alesund (approximately –5% per decade) and a strong positive trend at Station Arrival Heights (~20% per decade) over 10 years.

In the determination of linear trends, it is important to take into account the possible dependence of the NO_2

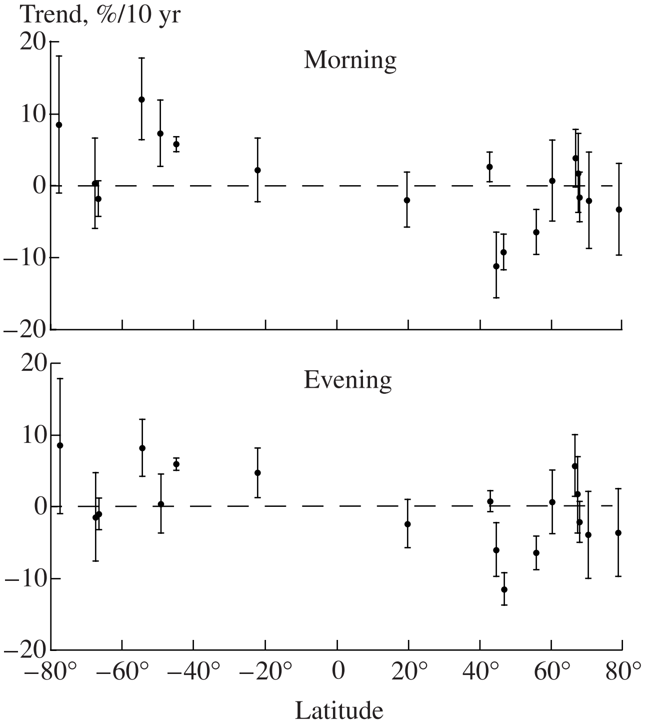

Fig. 2. Annual estimates of the linear trend of the NO_2 content in the vertical atmospheric column (dots) and their 95% confidence intervals (vertical segments) as functions of latitude on the basis of morning and evening measurements.

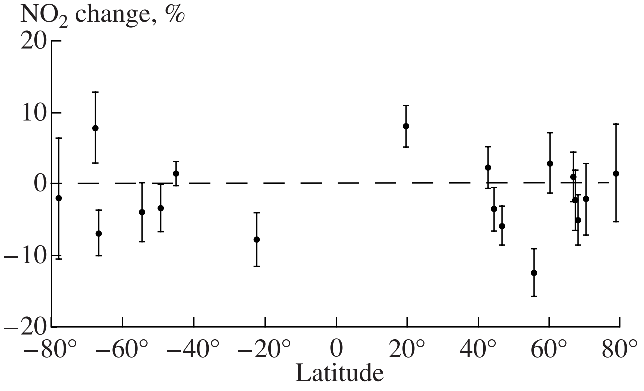

Fig. 3. Changes in the NO_2 content in the vertical atmospheric column (dots) from the minimum phase to maximum phase of SA vs. latitude based on morning measurements. Vertical segments correspond to 95% confidence intervals.

content on the phase of the 11-yr cycle of the SA. Figure 3 presents the estimates of NO_2 variations from the minimum phase to maximum phase of SA for the data of morning measurements. They are calculated as the product of the regression coefficient a_3 by the mean difference of the F10.7 flux values between the maximum and minimum of the SA. We note the qualitative agreement between our estimate and the conclusion in [1] about the insignificant effect of the SA on the NO_2 at Station Lauder. Figure 3 suggests that, at mid-latitudes of the two hemispheres, the TC of NO_2 in the maximum SA period is generally lower than that in the minimum SA period. The difference reaches 12% at the Zvenigorod Scientific Station. The value of the SA effect at mid-latitudes of the two hemispheres decreases with decreasing latitude. In the Northern Hemisphere, it changes the sign to positive near 40° N. A significant positive influence of the SA on the NO_2 content (~8%) was found at tropical station Mauna Loa. On the contrary, the sign of this effect is negative at tropical latitudes of the Southern Hemisphere similarly as at mid-latitudes of this hemisphere.

The negative value of the SA effect on the TC of NO_2 (approximately –7%) was also found at the Antarctic station, Dumont d'Urville, located in one longitudinal sector with the closest mid-latitude station on Macquarie Island (see table). In the opposite longitudinal sector of coastal Antarctica, the sign of the SA effect is positive (Station Rothera). It is likely that such differences within one latitudinal band are caused by a possible regional dependence of the SA effect on the atmospheric composition (see, e.g., [7]).

At high and polar latitudes of the Northern Hemisphere, the effect of the SA on the TC of NO_2 is usually statistically insignificant. However, we can also suppose that a regional dependence of the effect exists here because Station Scoresbysund, for which the effect is statistically significant (approximately –5%), is located in another longitudinal sector as compared to the closest stations in terms of latitude (see table).

According to [1], the observed increase in the tropospheric content of nitrous oxide (N_2O) is the cause of the trends in the stratospheric content of NO_2. If this increase is accompanied by an increase in the stratospheric concentration of N_2O, then the content of NO_2 in the stratosphere should increase as a result of photolysis of N_2O. However, the authors of [2] showed that the observed decrease in the stratospheric ozone and cooling of the stratosphere could result in negative trends in the stratosphere NO_2 down to –5% per decade even if the N_2O content increases. We add that decrease in the stratospheric ozone should provoke increase in the intensity of N_2O photolysis and this should also be taken into account in the consideration of the photochemical mechanisms of long-term variations in the stratospheric NO_2. The calculations using a 2D numerical photochemical model [5] mainly yielded negative trends of the TC of NO_2 at high and mid-latitudes of the two hemispheres and small positive values at low latitudes. Therefore, there are significant discrepancies between the results of the calculations and analysis of observations.

Thus, ground-based column NO_2 measurements have revealed approximately antisymmetric (around the equator) latitudinal distribution of annual estimates in the linear NO_2 trends. Predominantly positive NO_2 trends are characteristic of low and mid-latitudes of the Southern Hemisphere, and predominantly negative NO_2 trends are characteristic of the low and mid-latitudes of the Northern Hemisphere. Along with these trends, significant differences are possible between the values of the NO_2 TC in the maximum and minimum SA periods, with the content of NO_2 at mid-latitudes of the two hemispheres being larger during the SA minimum than during the SA maximum. The effect of the SA on the NO_2 content also has important regional differences.

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REFERENCES

1. J. B. Liley, P. V. Johnston, et al., J. Geophys. Res. **105** (D9), 11633 (2000).
2. A. N. Gruzdev and A. S. Elokhov, Dokl. Earth Sci. **383**, 150 (2002) [Dokl. Akad. Nauk **382**, 678 (2002)].
3. *Scientific Assessment of Ozone Depletion 2002* (WMO, Geneva, 2003).
4. V. P. Sinyakov, V. K. Semenov, et al., in *Proceedings of XX Quadrennial Ozone Symposium* (Athens, 2004), p. 1036.
5. A. N. Gruzdev, A. S. Elokhov, and G. P. Brasseur, in *Proceedings of XX Quadrennial Ozone Symposium* (Athens, 2004), p. 963.
6. A. S. Elokhov and A. N. Gruzdev, Izv. Atmos. Ocean. Phys. **36**, 763 (2000) [Izv. Ross. Akad. Nauk, Fiz. Atmos. Okeana **36**, 831 (2000)].
7. A. N. Gruzdev and G. P. Brasseur, Izv. Atmos. Ocean. Phys. **43**, 344 (2007) [Izv. Ross. Akad. Nauk, Fiz. Atmos. Okeana **43**, 379 (2007)].