Three decades of remote sensing of NO₂ vertical distribution and column content at the A. M. Obukhov Institute of Atmospheric Physics

A N Gruzdev and A S Elokhov

A. M. Obukhov Institute of Atmospheric Physics, Pyzhevsky per. 3, 119017 Moscow, Russia

E-mail: a.n.gruzdev@mail.ru

Abstract. The paper reviews the results of 30-year spectrometric measurements of vertical distribution and column content of NO₂ at the Zvenigorod Scientific Station (ZSS) of the A. M. Obukhov Institute of Atmospheric Physics and presents analysis of NO₂ long-term trends and interannual variations. The station is located in the western Moscow region. It is part of the Network for the Detection of Atmospheric Composition Change (NDACC). Measurements are done in the morning and evening twilight by zenith-scattered visible solar radiation. Vertical NO₂ profiles are retrieved and column NO₂ contents are calculated by profile integration. Long term trends and inter-annual variations of NO₂ are analysed by multivariate regression method taking into account autocorrelation of data in a wide range of time scales. Seasonally dependent estimates of NO₂ trends and interannual variations due to the quasi-biennial oscillation, El Nino–Southern oscillation, North Atlantic Oscillation, and the 11-year solar cycle are obtained. Most pronounced (in per cent units) trends and circulation and solar cycle effects are peculiar to the winter–spring period of the year. Mutual influence is assessed between the estimates of the trend and the solar cycle effect in stratospheric NO₂.

1. Introduction

Nitrogen oxides play a key role in the photochemical balance of atmospheric ozone in the stratosphere and troposphere [1, 2]. Nitrogen oxide, NO, and nitrogen dioxide, NO₂, are major contributors to nitrogen oxides. NO and NO₂ are generally in quick photochemical equilibrium between each other, and their ratio depends mainly on ozone content and light intensity. However their sum is more conservative and can be a tracer of atmospheric motions. In fact, stratospheric TO₂ serve as a good indicator of large-scale dynamic processes in the atmosphere [3].

NO₂ has diffusive absorption band in visible spectral range and can be measured remotely. Background NO₂ concentrations provide quite weak absorption of solar radiation, and stratospheric NO₂ measurements are usually done during twilights when differential absorption by NO₂ is maximal due to slant solar ray geometry [4].

Regular remote spectrometric NO₂ measurements at the Zvenigorod Scientific Station (ZSS) started in 1990. The station is a part of the Network for Detecting Changes in the composition of the atmosphere (NDACC). Three decades of NO₂ measurements at the station give possibility to analyze, along with inter-annual variations, also long term changes in NO₂.
2. Measurement method shortly

Zvenigorod station is located in a rural area 50 km west to Moscow. The measurements are carried out by zenith-scattered solar radiation in the visible wavelength range during the morning and evening twilights. The method used allows retrieving the vertical distribution of NO$_2$ and determining the column NO$_2$ content in the atmosphere by integrating the profile. The method of observations and retrieval of NO$_2$ contents from measured spectra are described in detail in a few works [5–7].

Figure 1 shows examples of vertical NO$_2$ profiles obtained under conditions of clean and polluted surface layer of the atmosphere. The values above the surface level are the NO$_2$ contents in 5-km thickness layers while the value at zero altitude is the NO$_2$ content in the near-surface layer, the thickness of which is a priori unknown. Note that the horizontal axis is broken. Figure 1 shows that the NO$_2$ content in the atmospheric surface layer (ASL) during pollution episodes can be an order of magnitude larger than the total column content in the stratosphere. The NO$_2$ content of the ASL under unpolluted conditions is close to zero.

![Figure 1. Examples of vertical NO$_2$ profiles and their standard deviations measured under polluted (black) and unpolluted (gray) near-surface layer. The horizontal axis is broken.](image)

3. Measurement data

Figure 2 shows altitude-time distributions of monthly mean concentrations of NO$_2$ above the ASL in morning and evening and the evening–morning difference. The difference reflects only a part of the NO$_2$ diurnal cycle [5]. Strong annual and diurnal variations are evident in figure 2 which are related mainly to photochemical processes. Interannual variations are also seen. The NO$_2$ decrease just after 1992 are due to heterogeneous chemistry on stratospheric aerosol particles generated after the Mt. Pinatubo eruption.
Daily values of the column NO\textsubscript{2} content above the ASL and the NO\textsubscript{2} content in the ASL are shown in figure 3. The column NO\textsubscript{2} content is mainly contributed by stratospheric NO\textsubscript{2} since the NO\textsubscript{2} abundance in the troposphere is small (Figure 1). Stratospheric NO\textsubscript{2} in evening is typically larger than in morning (Figures 2c and 3a). This is not always a case for near-surface NO\textsubscript{2} since the NO\textsubscript{2} abundance in the ASL is often perturbed by pollution episodes (Figure 3b).

**Figure 2.** Altitude-time cross-sections of (a) the morning (a) and (b) evening monthly mean NO\textsubscript{2} concentrations and (c) the evening–morning difference of the NO\textsubscript{2} concentration. Units are 10\textsuperscript{8} molecules/cm\textsuperscript{2}.

**Figure 3.** (a) Column NO\textsubscript{2} content above the atmospheric surface layer and (b) NO\textsubscript{2} content in the atmospheric surface layer in morning (red) and evening (blue).
4. Analysis method
Analysis is done with a multivariate regression method. The regression model includes as predictors the following proxies of long term and interannual variability: the free member, the linear term (linear trend), the quasi-biennial oscillation (QBO), the El Nino–Southern Oscillation (ENSO), the 11-year solar activity cycle, the North Atlantic Oscillation (NAO), and stratospheric aerosol.

The NAO proxy is presented by the NAO index (http://www.cru.uea.ac.uk/cru/data/nao/). Aerosol proxy is presented as atmospheric aerosol optical depth (AOD) for the northern hemisphere Studies (http://data.giss.nasa.gov/modelforce/strataer/).

The oscillating predictors, that are the indices of the QBO, solar activity, and Nino 3.4, are presented by two indices: by actual one and by an orthogonal index obtained from the actual index by shifting forwards in time. A pair of orthogonal predictors of the same proxy allows us to describe and estimate a lagged response of a dependent variable [8].

The QBO proxy in the model is presented by the zonal velocity of the stratospheric equatorial wind at 40 hPa level (http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html) and by the same velocity but shifted forwards by six months. The solar cycle proxy is presented by the solar radio flux at wavelength 10.7 cm, F10.7 (https://www.spaceweather.gc.ca/solarflux/sx-5-mavg-en.php), and by the same index but shifted forwards by 37 months. The ENSO proxy is presented by the index of sea surface temperature anomaly in the Nino 3.4 region in the equatorial East Pacific (https://www.esrl.noaa.gov/psd/data/climateindices/list/) and by the same index but shifted forwards by ten months. The above shifts provide orthogonality of the indices in the pairs for the period of NO2 observations at the ZSS.

All regression coefficients in the regression model are expanded into Fourier pairs corresponding to the annual and semi-annual harmonics in order to account for seasonal dependence of trends and other effects on NO2.

To solve the system of the regression equations, the method is used taking into account the serial correlation (autocorrelation) of the residual on long time scales [9]. The serial correlation is due to memory in a system and affects confidence intervals of regression estimates [10].

5. Results of analysis
First results of analysis of interannual variations and trends in NO2 vertical distribution were reported in [8]. The new features of the analysis in this, conference, paper are as follows. First, the series of NO2 measurements in this work is slightly longer. Second, the Nino 3.4 index is now presented by the averaged temperature itself, but by normalized anomaly of sea surface temperature in the equatorial East Pacific. And third, and most important, is that, in this paper, two sets of the NO2 trend estimates are obtained and compared to each other, which are the trends estimated with taking into account the solar cycle influence on NO2 and the trends estimated when ignoring the solar influence. The reason is that the maximum of the last solar cycle was very low, and the F10.7 index as well as the sunspot number have negative linear trend for the period of the NO2 observations. Therefore, the solar activity index and the linear term in the regression model are not statistically independent, and regression estimates of the linear trend and the solar cycle effect in NO2 can mutually influence each other. Below we show primarily the results obtained with accounting for the solar cycle effect. Its influence on linear trend estimates is outlined in the end of the paper.

Figure 4 shows linear trends in morning and evening NO2 concentrations as functions of month and altitude above the ASL. Trends in near-surface NO2 are not depicted in figure 1 because of their peculiar character that could make it difficult to perceive the cross-section in figure 1. Trends in the near-surface NO2 content at the ZSS are analyzed in [11] together with trends in near-surface aerosol concentration.

The trends in stratospheric NO2 above about 25 km altitude are negative, and the trend below this level in the summer period is positive (Figure 4). The tropospheric trends in winter and spring are negative.
The evening trend in tropospheric NO$_2$ has positive values in late spring and summer (Figure 4b). The probable cause is vertical (turbulent, convective) mixing, which leads to the spread of nitrogen oxides from the polluted ASL into the overlying layers of the troposphere. Such an effect is not detected in morning (taking into account the statistical significance) (Figure 4a) due to the fact that the boundary layer of the atmosphere is statically more stable in the morning than in the evening. We note that the trend in near-surface NO$_2$ at the ZSS is generally positive (see [11] and Figure 5a).

**Figure 4.** Altitude-month cross-sections of the linear trend in (a) morning and (b) evening NO$_2$ contents above the atmospheric surface layer. Units are 10$^7$ molecules/cm$^3$ per decade. Areas of a statistically significant trends are not darkened.

**Figure 5.** Vertical profiles of the annual estimates of (a) the linear trend and (b) the QBO effect in morning (gray) and evening (black) NO$_2$ concentrations.

Figure 5a shows altitude profiles of the annual trend estimates derived from morning and evening measurements. Note that figure 5 also includes the ASL. The morning and evening annual trends are close to each other (in per cent values) above 20 km and in the ASL. However the tropospheric trends are fundamentally different, in accordance with the features of the altitude-seasonal distributions in figure 4.
Figure 5b shows altitude profiles of the annual estimates the QBO effect on NO$_2$. The phase lag of the effect relative to the QBO in the 40 hPa stratospheric zonal wind velocity (not shown) is 1–3 months. The magnitude of the QBO effect is the range of NO$_2$ oscillations when the equatorial QBO changes between its westerly and easterly phases. The magnitude of NO$_2$ oscillations due to the QBO is 2–5% in the middle stratosphere. There the maxima (minima) of the NO$_2$ oscillations follow, with the lag, the maxima of the westerly (easterly) wind velocity at the 40 hPa level in the equatorial stratosphere.

Figure 6. (a) Annual (dots on the left side), monthly (curves in the middle), and seasonal (curves on the right side) estimates of the QBO (black), solar cycle (red), and Nino 3.4 (blue) effects on the morning column NO$_2$ content above the ASL and their 95% confidence intervals. The QBO and solar cycle effects are magnitudes of associated NO$_2$ changes. The Nino 3.4 effect is a NO$_2$ response to change in the Nino 3.4 index by one standard deviation. The lags of the effects are specified in the text. (b) Annual (dots on the left side), monthly (curves in the middle), and seasonal (curves on the right side) estimates and associated 95% confidence intervals of morning (red) and evening (blue) linear trends of the column NO$_2$ content above the ASL. Closed dots and solid curves correspond to the estimates derived with taking into account the solar cycle effect, while open dots and dashed curves correspond to estimates derived without taking into account the solar cycle effect. The confidence intervals are only shown for trends derived with taking into account the solar cycle effect.

The magnitude of the QBO effect in the tropopause layer (~10–12 km) and in the troposphere is negative, and only evening estimates of the tropospheric effect are statistically significant. The magnitude of the QBO-related oscillations in the evening NO$_2$ concentrations is of 10–20% (however oscillations in absolute units are weak because of small NO$_2$ concentration, see Figure 1), and the maxima (minima) of the NO$_2$ oscillations there follow, with the lag, the maxima of the easterly (westerly) equatorial wind velocity 40 hPa.

Figure 6 presents annual, monthly, and seasonal estimates of linear trends and quasi-cyclic variations in the column NO$_2$ content above the ASL. We note that, due to small NO$_2$ concentration in the troposphere, Figure 6 reflects mainly changes in stratospheric NO$_2$. According to figure 6, the morning and evening trends as well as the QBO, solar cycle, and ENSO effects in column NO$_2$ maximize (in per cent units) in the late winter–early spring period.

The annual estimate of the QBO effect on the morning column NO$_2$ contents is statistically significant throughout the year (Figure 6a). The effect lags the 40 hPa equatorial QBO by a few months in summer and leads it in autumn through spring. The magnitude of the column NO$_2$ oscillations, in relative units, is about 10% in early spring. However, in absolute units, the oscillations are larger in summer than in winter because of the strong seasonal variation with summer maximum (Figure 3a).

Variations in morning column NO$_2$ due to the ENSO-related variations in sea surface temperature in the equatorial east Pacific, which lag by ten months after the Nino 3.4 index, are most pronounced
and statistically significant in winter (Figure 6a). The negative sign of the effect denotes that column NO\textsubscript{2} decreases approximately in a year after El Nino episodes and increases after La Nina episodes.

The solar cycle effect in NO\textsubscript{2} is statistically significant in the winter–spring period when it is approximately antiphase to the 11-year solar cycle (Figure 6a). The solar-related changes in column NO\textsubscript{2} in this period is of order of 10\% according both to morning and evening NO\textsubscript{2} data. The column NO\textsubscript{2} contents during solar cycle maxima are, on average, less than during solar minima.

The NAO effect on NO\textsubscript{2} is most pronounced in spring (not shown). The amplitude of the associated inter-annual variations of the spring column NO\textsubscript{2} contents is about 2\% per one standard deviation of the NAO index, and column NO\textsubscript{2} decreases at positive phase of the NAO, that is when the surface air pressure gradient and, as a consequence, zonal wind in the North Atlantic is strengthened.

The linear trends in column NO\textsubscript{2} are negative throughout the year, and the strongest (in relative units) trends are observed in the winter–spring period (Figure 6b). If the possible influence of the 11-year solar cycle on NO\textsubscript{2} is taken into account, the strongest, February, trend is –6\% + –8\% per decade (see solid curves in Figure 6b). If the solar cycle influence is ignored, the winter–spring trends diminish (see dashed curves) but are confidently determined. The summer trends as well as annual trends do not undergo noticeable changes.

The comparison analysis of the NO\textsubscript{2} trends with and without accounting for the solar cycle effect shows that although, due to the presence of a linear component in solar activity for a few past solar cycles, the solar cycle effect can probably induce a long term NO\textsubscript{2} trend, this influence does not have a defining value. Along with this, one could allow influence of the linear trend on estimates of the solar cycle effect. Comparison of figures 6b and the “solar” curve in figure 6a shows that the decadal NO\textsubscript{2} changes in winter–spring associated with the solar cycle are significantly larger than the decadal trends. Therefore the solar cycle effect in this period cannot be essentially induced by the linear trend. However we cannot exclude such an influence in summer when a solar cycle effect has not been detected in column NO\textsubscript{2}. We can assume that the solar cycle might actually affect stratospheric NO\textsubscript{2} in summer.

6. Discussion and conclusions

The effects of the QBO, ENSO, NAO, and the s11-year solar cycle on the stratospheric NO\textsubscript{2} are generally most pronounced in late winter and/or early spring. For the same season, the most significant (in per cent units) negative trend in stratospheric column NO\textsubscript{2} has been obtained, due to a decrease in the NO\textsubscript{2} concentration in the middle and upper stratosphere. This common seasonal feature indicates the important role of circulation mechanisms in the interannual and long-term changes in NO\textsubscript{2} during this period. In particular, the changes in the NO\textsubscript{2} content can occur as a result of the large-scale evolution of the stratospheric polar vortex. The beginning of spring is characterized by the final stratospheric warming, accompanied by the weakening and destruction of the polar vortex, and a rapid photochemical increase in the stratospheric NO\textsubscript{2} content. Therefore, the NO\textsubscript{2} content during this period may be particularly sensitive to factors affecting the stratospheric vortex.

Comparison of stratospheric NO\textsubscript{2} trends estimated with and without accounting for solar cycle influence on NO\textsubscript{2} as well as comparison of magnitudes of the trend and the solar cycle effect on NO\textsubscript{2} show some interplay between estimates of the trend and the solar cycle effect. However the interplay does not affect critically the trend and the solar cycle effect. One important conclusion from the comparison analysis is that both the linear trends and the solar cycle effect in column (stratospheric) NO\textsubscript{2} are actual.

Acknowledgments

Equatorial stratospheric wind velocities are provided by Freie Universität Berlin. Solar 10.7 cm flux data are provided by the Natural Resources Canada. Data of the Nono3.4 index are provided by the NOAA Physical Sciences Laboratory. NAO data are available at the site of the Climate Research Unit, University of East Anglia. AOD data are prepared by the NASA Goddard Institute for Space.

This work was supported by the Russian Foundation for Basic Research, project No, 20-05-00274.
References
[1] Brasseur G P and Solomon S 2005 Aeronomy of the Middle Atmosphere (Dordrecht: Springer)
[2] Gradeel T E and Crutzen J P 1993 Atmospheric Change. An Earth System Perspective (New York: W. H. Freeman and Company)
[3] Gruzdev A N, Kropotkina E P, Solomonov S V, and Elokhov A S 2017 Winter–spring anomalies in stratospheric O₃ and NO₂ contents over the Moscow region in 2010 and 2011 Izvestiya, Atmos. Oceanic Phys. 53 195–203
[4] Noxon J F, Whipple E C, Hyde R S 1979 Stratospheric NO₂. 1. Observational method and behaviour at mid-latitude J. Geophys. Res. 84 5047–5065
[5] Elokhov A S and Gruzdev A N 2000 Nitrogen dioxide column content and vertical profile measurements at the Zvenigorod Research Station Izvestiya, Atmos. Oceanic Phys. 36 763–777
[6] Gruzdev A N and Elokhov A S 2010 Validation of Ozone Monitoring Instrument NO₂ measurements using ground based NO₂ measurements at Zvenigorod, Russia Int. J. Remote Sens. 31 497–511
[7] Gruzdev A N and Elokhov A S 2011 Variability of stratospheric and tropospheric nitrogen dioxide observed by visible spectrophotometer at Zvenigorod, Russia Int. J. Remote Sens. 32 3115–3127
[8] Gruzdev A N and Elokhov A S 2021 Changes in the column content and vertical distribution of NO₂ according to the results of 30-year measurements at the Zvenigorod Scientific Station of the A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences Izvestiya, Atmos. Oceanic Phys. 57 91–103
[9] Gruzdev A N 2019 Accounting for autocorrelation in the linear regression problem by an example of analysis of the atmospheric column NO₂ content Izvestiya, Atmos. Oceanic Phys. 55 65–72
[10] Draper N R and Smith H 1998 Applied Regression Analysis (New York: John Wiley & Sons)
[11] Gruzdev A N, Isakov A A, Elokhov A S, and Anikin P P 2021 Submicron aerosol and nitrogen dioxide in the atmospheric near-surface layer at the Zvenigorod Scientific Station of the A.M. Obukhov Institute of Atmospheric Physics RAS: Thirty years of measurements IOP Conf. Ser. Earth Environ. Sci. This issue