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

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Abstract. The paper presents results of measurements and trend analysis of the mass concentration of submicron aerosol and the NO₂ content in the atmospheric surface layer at the Zvenigorod Scientific Station of the A. M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences. The station is located in a rural area of the western Moscow region. Aerosol concentration is determined by directional light scattering in a flow nephelometer. The NO₂ content is measured spectrometrically by zenith-scattered solar radiation. Three decades of aerosol and NO₂ measurements give a possibility to analyze long-term trends in near-surface aerosol and NO₂. Seasonally dependent estimates of the aerosol trends are presented for three periods differing in character of aerosol variability: 1991–2002, 2003–2012, and 2013–2020. The common feature of the trends is a general decrease in the aerosol concentration. There are however significant interdecadal differences in the strength of the trends and in their seasonal dependence. The NO₂ content in the near-surface layer undergoes a significant positive trend. The NO₂ increase is likely associated with an increase in the population and human activity resulting, in particular, in the increase in motor traffic in the region. Effects of wind direction on aerosol and NO₂ anomalies are also studied.

1. Introduction
Aerosol and nitrogen oxides are typical gaseous and particulate species of the atmospheric surface layer (ASL). Their concentrations are determined by local (regional) sources and by atmospheric transport from remote sources. Both can also be generated in the atmosphere through photochemical processes.

Measurements of the near-surface concentration of submicron aerosol started at the Zvenigorod Scientific Station (ZSS) of the A. M. Obukhov Institute of Atmospheric Physics in 1991. One year before, in 1990, spectrometric measurements of nitrogen dioxide, a major representative of the nitrogen oxides family - were begun. Three decades of aerosol and NO₂ measurements at the same site give unique possibility to analyze and compare their long-term variability. It is especially interesting since the two species are affected by regional pollution and long range transport to varying degrees.

This paper reviews shortly the results of measurements of the aerosol concentration and the NO₂ content in the ASL at the ZSS and presents analysis of their long-term trends.
2. Site and methods of measurements
Zvenigorod station is located in a rural area in the west Moscow region at ~55 km distance from the Moscow center and 40 km distance from the Moscow ring highway (Figure 1). At distances of 10 km and 13 km to the south of the ZSS are Mozhaiskoe and Minskoye highways, and 17 km to the north is Novorizhskoe highway, which are major highways with heavy traffic.

Near-surface aerosol measurements at the ZNS in 1991–2003 were performed around the clock with a flow nephelometer by V. N. Sidorov [1]. In 2001–2012, measurements were carried out with a spectropolarimeter [2]. Since 2012, measurements were done with a serial FAN nephelometer. Spectropolarimeter and FAN measurements were performed in morning around 9 a.m. local time. Comparison and mutual binding of data obtained with different instruments was done for the overlap intervals of 2001–2003 and 2012.

Values of the mass concentration of aerosol are obtained by multiplying the directional light scattering coefficients measured at an angle of 45° by a factor of 2000. The factor was estimated by comparing our data with the results of PM2.5 measurements at the Mosecomonitoring station located at the ZNS [3]. An uncertainty of application of this coefficient is about 20%.

The NO$_2$ content is measured by the spectrometric method registering zenith-scattered solar radiation during morning and evening twilight [4]. The measurement method allows retrieving the vertical distribution of NO$_2$. The bottom value of the vertical profile characterizes the NO$_2$ content in the atmospheric boundary layer. Under typical conditions, the main contribution to it is made by the ASL [5]. An important feature of the NO$_2$ contents in the ASL determined in our measurements is that it is not a local concentration but the content in the ASL column. This feature makes the ASL NO$_2$ content insensitive to local pollution, for example, due to individual cars.

3. Measurement data
Figure 2a shows a series of daily aerosol concentrations. The period from 2003 to 2012 is characterized by frequent and strong anomalies of large concentration values. Their cause has not yet been fully established, although analysis of the anomalies and their relation to atmospheric transport was done [6].

Figure 2b shows decimal logarithm of the aerosol concentration. It is the logarithm, and not the concentration, that is preferable to use for the trend analysis [3].
According to figure 2 three periods can be distinguished: before 2003, after 2012 with “normal” level of aerosol concentration and variability, and the “abnormal” period of 2003–2012. The three periods will be considered separately.

The NO$_2$ abundance in the ASL according to morning and evening measurements, as well as the corresponding monthly mean values are shown in figure 3. Evening values are generally larger than morning values. This is due to the additional formation of NO$_2$ as a result of the photolysis of N$_2$O$_5$ and more intensive motor traffic during daytime. Monthly averages indicate the presence of the annual variation of NO$_2$ with the winter maximum and the summer minimum. It is due to the fact that the most frequent and strong episodes of ASL pollution by nitrogen oxides are observed in winter. The proportion of days with close to zero NO$_2$ content in the ASL in summer is 30-40%, while it is less than 10% in winter.

**Figure 2.** (a) Mass concentration of near-surface aerosol and (b) its decimal logarithm.

**Figure 3.** (a) Daily and (b) monthly mean values of the morning (red) and evening (blue) NO$_2$ content in the atmospheric surface layer.
Figure 4. 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 linear trends in logarithm of aerosol concentration in (a) 1991–2002, (b) 2003–2012, and (c) 2013–2019.

4. Method of trend analysis

Trend analysis is done with a multivariate regression method. Analysis of NO$_2$ in this paper is a part of the analysis of the long-term trends and interannual variability in the NO$_2$ vertical distribution reported in a paper published in this issue [7]. In this case 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, the sea surface anomaly index for the equatorial east Pacific in the Nino 3.4 region, the solar activity index $F_{10.7}$, the North Atlantic Oscillation index, and the aerosol optical depth. References to these data can be found in [7]. The regression model is applied to monthly mean NO$_2$ contents. Here we keep all these features of the regression model unchanged to be consistent with [7].

In case of aerosol, the regression model includes as predictors a free term, a time-linear term (to describe a linear trend), a quadratic term (to account for a quadratic trend), and variables describing changes in wind direction. The quadratic term is symmetric with respect to the midpoint of the analyzed period. Thus, it does not affect the value of the linear trend. Its purpose is to approximate the domed shape of aerosol course in 2003–2012. The quadratic trend is also kept in the regression model when analyzing data for the other periods (also with centering on the middle of the corresponding period).

The proxies of the wind direction in the regression model are sine and cosine of the angle corresponding to the wind direction. The wind direction is determined from velocities of zonal and
meridional winds at 975 hPa level derived from the ERA-Interim reanalysis data (https://www.ecmwf.int/en/forecasts/datasets/reanalysis-datasets/era-interim).

Technique of estimating statistical significance in the regression problem is mostly applicable when a residual series (error) obeys the Gaussian distribution [8]. This is not the case if the regression analysis is applied to aerosol concentration. We use for the trend analysis the logarithm of aerosol concentration since the residual series in this case follows the Gaussian low [3].

All regression coefficients in the regression model are expanded into Fourier pairs corresponding to the annual and higher harmonics in order to account for seasonal dependence of trends in aerosol and NO$_2$. In case of NO$_2$, two harmonics, the annual and semiannual ones, are used. In case of aerosol, four harmonics are used.

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 [8].

Figure 5. 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 linear trends in the morning (gray) and evening (black) NO$_2$ contents in the ASL.

5. Results of trend analysis

Figure 4 shows the annual, monthly, and seasonal estimates of the linear trends in the aerosol concentration for the three periods. The annual trends are negative for all the periods. The annual trend, linear in logarithm of concentration, is about $-0.6\%$ per year in 1991–2002 and 2003–2012 and $-2.6\%$ per year in 2013–2020. Seasonal dependences of monthly trend estimates in the first two periods have common features. These are the negative trend in the winter–spring season, the absence of trend in summer, the negative trend in autumn (statistically insignificant for the first period), and the change in the trend sign in late autumn to positive value in early winter. Some fragments of this dependence are also characteristic of the third period.

The main feature of the third period is the negative aerosol trend in late spring and summer (Figure 4c). It was discussed in [3] and is presumably associated with a decrease in the summer surface temperature in the region. However, a special analysis is needed to quantify the contribution of temperature to the aerosol trends.

Figure 5 shows the NO$_2$ trends derived from data of morning and evening measurements. The trends are positive and statistically significant in winter and spring, and the evening trend for this period is larger than the morning trend. The NO$_2$ trends in summer are also positive but statistically insignificant. However we would like to note a larger value of the morning trend in this season. The lower evening value of the summer NO$_2$ trend is likely associated with turbulent (convective) transport.
of near-surface NO\textsubscript{2} during daytime to higher tropospheric heights (see trends in the NO\textsubscript{2} vertical profiles in [7]).

The annual estimates of the NO\textsubscript{2} trends are about 15\% per decade in morning and 29\% per decade in evening. The winter trends approach 20\% per decade in morning and almost 40\% per decade in evening.

![Figure 6](image)

**Figure 6.** Probability of (a) low and (b) high values of the aerosol concentration as function of wind direction in 1991–2002 (dashed curves) and 2003–2012 (solid curves) in winter (blue) and summer (red) and for entire year (black).

6. **Effects of atmospheric transport**

Distribution of aerosol and its sources in the ASL is non-uniform [10–13]. Aerosol abundance in the ASL at an observation site is determined by local conditions and atmospheric transport. Changes in transport patterns bring air from various regions with different aerosol content and composition.

Concentration of nitrogen oxides in the ASL near industrial centers and big cities is affected significantly by anthropogenic activity [14]. Changes in wind direction can result in significant fluctuations of the NO\textsubscript{2} content at a measurement site.

Figure 6 shows the probability of low and high aerosol concentrations at the ZSS depending on the wind direction for the first and second periods of measurements in winter, summer, and for the entire year. Low and high values are defined as the concentrations for which their logarithm is out of 1.6 standard deviation (SD) of the logarithm below or over its mean value, respectively. Since the logarithm of the aerosol concentration obeys the Gaussian distribution (see [3]), 90\% of the logarithm values falls within 1.6 SD of the mean, and the low and high values contain each 5\% of the distribution.

According to the diagrams in figure 6a, low aerosol concentrations are usually observed under winds from the western sectors. At north-westerly winds, low concentrations are most probable. For example, probability of low concentrations under the north-westerly wind in summer is about 0.15 (see red diagrams). The probability of low aerosol concentrations in an easterly wind is small, and during the second period is close to zero.

High concentrations of aerosol at the ZSS in winter are most probable at winds with the easterly, southerly, and south-easterly directions (Figure 6b). The probability diagrams for the winter seasons of the 1st and 2nd periods differ significantly. The highest probability, of about 0.15, of high aerosol anomalies was associated with southerly winds in 2003–2012 and with easterly winds in 1991–2002.
The southerly wind in 1991–2002 also often brought high anomalies (with 0.1 probability). In addition, we note that the probability of high anomalies under south-westerly winds in winters of the two periods is not small (about 0.05), which, in combination with the wind rose extended in this direction, provides a significant number of high aerosol concentration values.

The angular diagrams of summer probabilities of high aerosol anomalies for the two periods have the same main qualitative features as the diagrams of winter probabilities (Figure 6b). The summer diagram extends in the eastern direction in 1991–2002 and in the southern direction in 2003–2012. Along with this we note that the winter diagrams for high anomalies are wider than the summer diagrams, and the probability of abnormally high aerosol concentrations in winter is significantly larger than in summer.

Figure 6 shows that high and low aerosol concentrations at the ZSS are usually associated with winds of generally opposite directions. In winter conditions, these directions are oriented toward remote regions with relatively strong and weak sources of aerosol. In summer conditions with slower winds, the role of local conditions and regional transport increases.

The NO$_2$ content in the ASL at the ZSS changes in a very wide range from zero to values, which in order of magnitude are larger than the column NO$_2$ content above the ASL [5, 7]. Zero values mean that the NO$_2$ content in the ASL is less than the detection threshold of the method used. They correspond to background conditions.

Figure 7 shows probabilities of evening NO$_2$ contents in the ASL that are larger than prescribed threshold contents, as function of wind direction, in winter and summer. The threshold values are specified in the legend. We note for information that the threshold value of 2.10$^{15}$ molecules/cm$^2$ is approximately equal to the typical winter value of the column NO$_2$ content above the ASL (see, for example, Figure 3 in [7]).

The probability of the ASL pollution by NO$_2$ at the station decreases with increasing threshold under all wind directions (Figure 7). Pollution is possible at any wind (see diagrams for zero threshold). In winter, easterly and south-easterly winds always bring pollution (probability at zero threshold is equal to 1). Probability of pollution is also very high in winter under winds of north-east, south, and south-west directions.

The strongest pollution is mainly related to easterly winds blowing from Moscow. Sector of winds associated with strong pollution in winter is wider and include also orientations to the north-east, south-east, and south (Figure 7a), i.e. toward the major highways and Moscow suburb (see Figure 1).
Note that strong pollution is not observed in westerly and north-westerly winds. The north-westerly wind direction is the direction of the least pollution probability at all thresholds.

Weak NO\textsubscript{2} pollution, which can be characterized by differences between diagrams for the zero and the closest to it thresholds in figure 7, is observed in winds not blowing from a major highway or large locality. This level of pollution is a feature of “background” parts of the region itself, which, however is also affected by motor traffic and other human activity in the region.

7. Discussion and conclusions

The long-term trends in the near-surface aerosol concentration and in the ASL NO\textsubscript{2} content at the ZSS are, in general, of opposite signs. The NO\textsubscript{2} content in the ASL is most sensitive to human activity and strongly affected by transport from polluted zones. Due to relatively short lifetime of nitrogen oxides, especially in summer, the NO\textsubscript{2} content is primarily affected by transport from a surrounding area. Proximity to Moscow and major highways has defining value to strong and moderate pollution of the ASL by nitrogen oxides. The increase in the NO\textsubscript{2} content reported in this study can be attributed to an increase in population of the megapolis and associated increase in anthropogenic activity, especially to the increase in motor traffic.

Unlike near-surface NO\textsubscript{2}, the mass concentration of near-surface aerosol at the ZSS undergoes a long-term decrease that is not uniform on the interdecadal scale and depends on season but determines most general long-term evolution of aerosol. The negative aerosol trends at the ZNS are consistent with a general decrease in the aerosol mass concentration in West Europe and some other regions of the world\cite{15,16} (see also\cite{3} for more references).

Small aerosol concentrations and small NO\textsubscript{2} contents at the ZSS are associated with winds directions of the north-west and neighbor sectors. In the NO\textsubscript{2} case, this direction is most clean in the sense of absence of significant sources of nitrogen oxides at a distance of up to a few hundred km from the ZSS. In the aerosol case, it orients toward the Baltic region and, farther toward the northern Atlantic since aerosol can be transported over larger distance than chemically active species like nitrogen oxides.

The observed large NO\textsubscript{2} concentrations are related to pollution episodes at the ZSS caused by air transport from the sides of Moscow with its suburb and major highways. The directions associated with high aerosol anomalies are approximately the same. However we do not believe that the location of aerosol sources should be the same. The south-east direction is the orientation toward steppes, which are sources of soil aerosol. In summer, forest fires in Siberia could be also responsible for high aerosol concentrations under appropriate advection conditions. However, high aerosol concentrations are most probable in winter.

It is worth to note a general decrease in the aerosol optical thickness (AOT) over the ZSS reported in\cite{17} for the warm periods of 2007–2017, which is less pronounced, however, than the negative AOT trend over Moscow. The difference is attributed in\cite{17} to opposite long-term tendencies of pollutant emissions at the two sites: an emission decrease in Moscow and an emission increase in the ZSS area. Our results show a very distinctive negative aerosol trend for the spring-summer periods after 2013. We can therefore deduce that local urban emissions do not affect significantly this trend.

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References

[1] Sidorov V N 1999 Seasonal and diurnal variations of the dry fraction content of submicron aerosol in the surface layer Proceed. Conf. “Physics of Atmospheric Aerosol” (Moscow) 356–367 (in Russian)

[2] Isakov A A and Gruzdev A N 2009 Long-period variations in the optical and microphysical
parameters of surface aerosol in a Moscow suburb *Izvestiya, Atmos. Oceanic Phys.* **45** 233–241

[3] Gruzdev A N, Isakov A A, and Anikin P P 2020 Multiyear trends in the mass concentration of near-surface aerosol at Zvenigorod Research Station, A. M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences *Atmos. Oceanic Optics* **33** 274–281

[4] 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

[5] 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

[6] Gruzdev A N and Isakov A A 2021 Anomalies and trends in the mass concentration of near-surface aerosol in the western Moscow region *Izvestiya, Atmos. Oceanic Phys.* submitted

[7] Gruzdev A N and Elokhov A S 2021 Three decades of remote sensing of NO\textsubscript{2} vertical distribution and column content at the A. M. Obukhov Institute of Atmospheric Physics *IOP Conf. Ser. Earth Environ. Sci.* This issue

[8] Draper N R and Smith H 1998 *Applied Regression Analysis* (New York: John Wiley & Sons)

[9] Gruzdev A N 2019 Accounting for autocorrelation in the linear regression problem by an example of analysis of the atmospheric column NO\textsubscript{2} content *Izvestiya, Atmos. Oceanic Phys.* **55** 65–72

[10] Hatzianastassiou N, Gkikas A, Mihalopoulos N, Torres O, and Katsoulis B D 2009 Natural versus anthropogenic aerosols in the eastern Mediterranean basin derived from multiyear TOMS and MODIS satellite data *J. Geophys. Res.* **114** D24202

[11] Chazette P, Raut J-C, Dulac F, Berthier S, Kim S-W, Royer P, Sanak J, Loaëc S, and Grigaut-Desbrosses H 2010 Simultaneous observations of lower tropospheric continental aerosols with a ground-based, an airborne, and the spaceborne CALIOP lidar system *J. Geophys. Res.* **115** D00H31

[12] Taylor M, Kazadzis S, Amiridis V, abd Kahn R A 2015 Global aerosol mixtures and their multiyear and seasonal characteristics *Atmos. Environ.* **116** 112–129

[13] Liu Y, Zhu Q, Wang R, Xiao K, and Cha P 2019 Distribution, source and transport of the aerosols over Central Asia *Atmos. Chem. Phys.* **210** 120–131

[14] Finlayson-Pitts B J and Pitts J N Jr. 2000 *Chemistry of the Upper and Lower Atmosphere: Theory, Experiment, and Application* (San Diego: Academic Press)

[15] Barmpadimos I, Keller J, Oderbolz D, Hueglin C, and Prévôt A S H 2012 One decade of parallel fine (PM\textsubscript{2.5}) and coarse (PM\textsubscript{10}–PM\textsubscript{2.5}) particulate matter measurements in Europe: trends and variability *Atmos. Chem. Phys.* **12** 3189–3203

[16] Wang K C, Dickinson R E, Su L, and Trenberth K E 2012 Contrasting trends of mass and optical properties of aerosols over the Northern Hemisphere from 1992 to 2011 *Atmos. Chem. Phys.* **12** 9387–9398

[17] Zhdanova E Y, Chubarova N Y, and Lyapustin A I 2020 Assessment of urban aerosol pollution over the Moscow megacity by the MAIAC aerosol product *Atmos. Meas. Tech.* **13** 877–891