Validation of Ozone Monitoring Instrument NO\textsubscript{2} measurements using ground based NO\textsubscript{2} measurements at Zvenigorod, Russia

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Validation of Ozone Monitoring Instrument NO2 measurements using ground based NO2 measurements at Zvenigorod, Russia

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We present the results of comparison between Ozone Monitoring Instrument (OMI) data of NO2 measurements (Collection 3) onboard the NASA EOS-Aura satellite and correlative ground-based twilight measurements at Zvenigorod station in Russia in 2004–2008. Compared quantities are unpolluted column and tropospheric column amounts of NO2 which are standard products of OMI measurements. The NO2 columns observed by our ground-based instrument have been interpolated to the time of OMI measurements using a one-dimensional photochemical model. According to our comparison, the OMI unpolluted NO2 columns underestimate ground-based measurements by \((0.084 \pm 0.025) \times 10^{15}\) molecules/cm², or \((3.2 \pm 0.9)\%\). The correlation coefficient between the OMI and ground-based unpolluted NO2 columns is 0.92. The tropospheric NO2 columns derived from OMI measurements are on average by \((1.8 \pm 0.5) \times 10^{15}\) cm⁻², or approximately 40%, less than those derived from ground-based measurements. The correlation coefficient between these data is about 0.3. Reasons for this discrepancy are discussed.

1. Introduction

Nitrogen dioxide (NO2), together with other nitrogen oxides, plays an important role in atmospheric ozone chemistry. Remote measurements of the atmospheric NO2 content are carried out by spectrometric methods from the Earth’s ground and from satellites, which allow determination of the NO2 content in the vertical atmospheric column. The number of ground-based stations doing such measurements is not large. Therefore the information on global distribution of NO2 obtained from satellite platforms is very important. Instruments and methods of NO2 measurements at ground-based stations included in the Network for the Detection of Atmospheric Composition Change (NDACC, former NDSC – Network for the Detection of Stratospheric Change) have been verified in international comparisons and, therefore, NO2 measurements at these stations can be used for validation of satellite NO2 measurements.

The EOS-Aura satellite was launched by NASA on 15 July 2004. Among the instruments aboard the satellite is the Ozone Monitoring Instrument (OMI) designed for study of gaseous and aerosol composition of the atmosphere. The OMI allows determination of column NO2 amounts. Moreover, a special method of analysis and

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data processing allows also estimating NO$_2$ amounts in the polluted atmospheric boundary layer and in the tropospheric column.

Results on validation of OMI stratospheric NO$_2$ columns using measurements at ground-based stations were presented recently by Celarier et al. (2008), Ionov et al. (2008) and Gruzdev and Elokhov (2009). Tropospheric NO$_2$ columns derived from OMI measurements were compared with data of independent (ground-based, satellite, or aircraft) measurements by Boersma et al. (2008), Brinksma et al. (2008), Buscema et al. (2008), Celarier et al. (2008), Kramer et al. (2008), Wenig et al. (2008), and Gruzdev and Elokhov (2009). This validation activity is a part of a general validation campaign, and we should also note works on validation of OMI ozone measurements presented by Balis et al. (2007), Shavrina et al. (2007), Kroon et al. (2008), McPeters et al. (2008), and Williams et al. (2008). We would also like to mention the most recent, before the EOS-Aura mission, validation efforts on NO$_2$ and ozone measurements on-aboard the ENVISAT satellite launched in 2002 (see, for example, Sussmann et al. 2005, Cortesi et al. 2007).

The aim of the present study is validation of OMI NO$_2$ measurements in October 2004 to May 2008 using collocated ground-based observations at the station of Zvenigorod in Russia. Unlike our previous work (Gruzdev and Elokhov 2009) where OMI NO$_2$ data of Collection 2 for shorter period were used, in the present study we use Collection 3 data. The data are publicly available at http://avdc.gsfc.nasa.gov (accessed June 2008).

2. Ground-based and OMI NO$_2$ measurements

Let us describe the main features of NO$_2$ data obtained from OMI and ground-based measurements at Zvenigorod, which should be taken into account under validation.

2.1 Ground-based measurements at Zvenigorod

Zvenigorod Research Station (55.7° N, 36.8° E) of the A.M. Obukhov Institute of Atmospheric Physics is located in a rural area 50 km west to Moscow. Observations of NO$_2$ are done in the 435–450 nm spectral range by zenith viewing monochromator MDR-23 with spectral resolution of 0.7 nm. Measurements are carried out during morning and evening twilight at solar zenith angles 84–96°. The principles of the method used at present for determination of NO$_2$ contents were described in detail by Elokhov and Gruzdev (2000) and Gruzdev and Elokhov (2005). However the method has improved since that time. An outline of the main features of the method follows.

Given measured transmittance spectra, NO$_2$ contents in slant atmospheric column are calculated as a function of the solar zenith angle. A slant column content is the weighted average integral content of NO$_2$ along trajectories of propagation of the solar radiation registered by the instrument. Slant NO$_2$ columns are calculated with the differential optical absorption spectroscopy (DOAS) technique taking into account absorption of NO$_2$, O$_3$, water vapour, and O$_2$–O$_2$ dimer, molecular and aerosol scattering, and the Ring effect (partial filling in of solar Fraunhofer lines). As a reference spectrum, the transmittance spectrum is used measured at high elevation of the sun under conditions of stable unpolluted atmosphere. The instrument and the method of determination of slant column NO$_2$ were validated in 1997 during the international intercomparison at Zvenigorod under the aegis of the NDSC (see more detailed information on http://www.ndsc.ncep.noaa.gov/data/madir).
Values of slant NO$_2$ columns are averaged within solar zenith angle ranges of 0.5° width. The obtained mean values and associated mean square root deviations are input parameters in an inverse problem. A solution to this problem is the vertical profile of NO$_2$ presented by NO$_2$ contents in 10 layers of 5-km thickness and in a thin boundary layer of *a priori* unknown thickness (Elokhov and Gruzdev 2000). The kernel of the inverse problem consists of air mass factors for these NO$_2$ layers, which are calculated with the help of a spherical single-scattering model accounting for refraction and a one-dimensional photochemical model. The scattering model takes into account the seasonal variations of air density and temperature. The photochemical model is used for accounting for photochemical changes in the NO$_2$ concentration during twilight measurements. The model takes into account basic photochemical processes important for nitrogen oxides, including the oxygen, hydrogen, nitrogen, and chlorine photochemical cycles. Vertical distributions of air temperature and pressure as well as vertical profiles of ozone, methane, nitrous oxide, water vapour, nitric acid and long-living chlorofluorocarbons are seasonally and latitudinally dependent in the models and are taken from the empirical reference models or observations (if available) for the dates of NO$_2$ observations. Using the photochemical model, slant NO$_2$ columns measured during a concrete twilight are put to a uniform time (to one zenith angle, for example 90° or 84°). Figure 1 shows the calculated diurnal variation of the stratospheric NO$_2$ column content as function of time and solar zenith angle for the dates of the equinoxes and solstices. The figure shows that the NO$_2$ content undergoes most quick changes during measurements at solar zenith angles 84–96°. In daytime, the NO$_2$ content changes much slower.

When solving the inverse problem, values of slant NO$_2$ columns are varied randomly within experimentally estimated variance around experimentally determined mean values. Using an ensemble of solutions (400 profiles), a statistically mean NO$_2$ profile and its left and right mean square root deviations for all layers are calculated. These deviations characterize random errors of retrieval of a NO$_2$ profile. Figure 2 shows examples of NO$_2$ vertical profiles derived from measurements under conditions of clean (evening of 16 June 2007) and strongly polluted (morning of 23 June 2007)
boundary layer. It is seen that the NO₂ content in the relatively thin boundary layer
during pollution episodes can be as large as multiple integral NO₂ content in the
stratosphere and troposphere above a polluted layer.

Comparison of NO₂ profiles retrieved from our measurements with satellite SAGE II and CRISTA-2 profiles showed sufficiently good agreement between ground-based and satellite profiles in the neighbourhood of the NO₂ stratospheric maximum (Elokhov and Gruzdev 1998, 2000, Gruzdev and Elokhov 2005).

Summation of NO₂ contents in appropriate layers gives NO₂ contents in tropospheric (0–10 km), stratospheric (10–50 km), and total (0–50 km) columns.

Absorption cross sections of NO₂ in visible spectral range depend on temperature (Vandaele et al. 1998). We used the cross sections at fixed temperature 220 K presented by Vandaele et al. (1998). For ozone, water vapour, and O₂–O₂ dimer, we used the absorption cross sections suggested by Bogumil et al. (2000), Harder and Brault (1997), and Hermans et al. (1999), respectively.

Let us estimate the effect on derived NO₂ contents, which is related to not accounting for temperature dependence of NO₂ cross sections. The values of NO₂ contents derived with the use of the absorption cross sections at 294 K and 220 K provided by Vandaele et al. (1998) differ approximately by 20% (for spectral range 435–450 nm), with larger value for larger temperature. According to the empirical reference model (Barnett and Corney 1985), the typical stratospheric temperature in the NO₂ maximum layer (~30 km) at the latitude of Zvenigorod is about 220 K in winter and 235 K in summer. Therefore, due to the temperature dependence of NO₂ cross sections, stratospheric NO₂ contents are, on average, underestimated in summer by about 4%, or approximately by $0.15 \times 10^{15}$ molecules/cm². Analogously, boundary layer NO₂ contents are, on average, underestimated approximately by 14% in winter (at −10°C) and 17% in summer (at 10°C).
On the other hand, since the radiative transfer (scattering) model does not take into account multiple scattering, lower tropospheric NO$_2$ contents are overestimated. Our NO$_2$ measurements using zenith-scattered and direct solar light have shown that the overestimation is about 45% under cloudless conditions. The overestimation can be larger under cloudiness conditions.

The total error of retrieval of stratospheric column NO$_2$, which has a random character, includes a few parts. One is the random error of the retrieval itself that is between $0.1 \times 10^{15}$ cm$^{-2}$ and $0.3 \times 10^{15}$ cm$^{-2}$ depending on conditions of measurements (atmospheric variability, cloudiness, etc). Next is the systematic error of determination of the NO$_2$ amount in the residual spectrum, which is equal to about $0.1 \times 10^{15}$ cm$^{-2}$. Since the sign of this error is unknown, this error also contributes to the total random error. Third is the uncertainty in stratospheric temperature due to day-to-day variability, which results in uncertainty in NO$_2$ cross sections. The associated error in an NO$_2$ column is about $0.02 \times 10^{15}$ cm$^{-2}$ in winter and $0.1 \times 10^{15}$ cm$^{-2}$ in summer. Fourth is the uncertainty in calculated air mass factors due to day-to-day variability, which is about 1%, resulting in uncertainty in an NO$_2$ column of about $0.05 \times 10^{15}$ cm$^{-2}$. Therefore the total error of unpolluted NO$_2$ columns, which has a random character, is within $(0.3–0.6) \times 10^{15}$ cm$^{-2}$.

The total random error of determination of boundary layer NO$_2$ is contributed mainly by the random error of the retrieval which varies significantly depending on conditions of measurements and is typically within 5–100%. For example, the error is usually small for stable atmospheric conditions with large NO$_2$ amount trapped under a near-surface inversion and large for small NO$_2$ amounts in the boundary layer.

### 2.2 OMI measurements

The Ozone Monitoring Instrument is an imaging spectrometer with a two-dimensional CCD array detector measuring UV and visible solar radiation scattered by the Earth’s atmosphere. The OMI spectral resolution for NO$_2$ measurement is $\sim 0.5$ nm, and the spatial (horizontal) resolution is $13 \times 24$ km$^2$ in nadir direction (Boersma et al. 2002, Celarier et al. 2008). Wavelength range 405–465 nm is used for determination of NO$_2$ contents. Spectra of direct solar radiation are used as reference spectra.

A slant NO$_2$ column content is determined directly from measurements. A vertical NO$_2$ column content is determined by division of the slant NO$_2$ column content by a NO$_2$ air mass factor that depends on a number of parameters including geometry of observations, surface albedo and shape of vertical profile of NO$_2$. It is important that the profile shape and, correspondingly, the air mass factor change substantially in presence of boundary layer pollution.

Primary estimates of NO$_2$ vertical columns, $V_{\text{init}}$, are determined by dividing slant NO$_2$ columns by NO$_2$ air mass factors calculated for a NO$_2$ profile in absence of lower troposphere pollution. The shape of the profile is obtained using a stratospheric photochemical model. A resultant horizontal NO$_2$ field is used for revealing polluted areas on the presumption that the spatial scale of changes in tropospheric NO$_2$ is significantly less than the scale of changes in stratospheric NO$_2$ (Boersma et al. 2002, Celarier et al. 2008). Then, in the obtained horizontal distribution of primary estimates of NO$_2$ columns, areas are selected with typically (according to a tropospheric model) large tropospheric NO$_2$ contents. Over the rest area, smoothing (averaging) of the NO$_2$ field is implemented within latitude belts of $10^\circ$ width along near-zonal
direction taking into account the configuration of stratospheric planetary waves. The obtained smoothed field of NO\textsubscript{2} columns, $V_{bg}$, is considered as background. Localities with primary NO\textsubscript{2} contents larger than the background contents by more than a mean square root deviation are supposed to be polluted. The NO\textsubscript{2} contents for these areas are recalculated using air mass factors calculated with accounting for the estimated profile of tropospheric NO\textsubscript{2}.

In such a way, the following quantities are determined: the background NO\textsubscript{2} column content, $V_{bg}$, the proper NO\textsubscript{2} column content (in unpolluted regions it is identical to the background content), and the NO\textsubscript{2} content, $V_{pol}$, in the polluted layer as difference between the NO\textsubscript{2} column content and the background content. Additionally, the NO\textsubscript{2} content in tropospheric vertical column, $V_{trop}$, is estimated, which consists of the NO\textsubscript{2} content in the polluted layer and the tropospheric NO\textsubscript{2} column content on the presumption of unpolluted profile (of prescribed shape).

In OMI NO\textsubscript{2} measurements, the NO\textsubscript{2} cross sections at 220 K provided by Vandaele et al. (1998) are used. The temperature dependence effect of the cross sections on derived NO\textsubscript{2} is accounted for via the introduction of a correction in the air mass factor (Wenig et al. 2008). This correction is related to the seasonal variation of temperature, not to day-to-day variations.

The random error of stratospheric (and unpolluted) column NO\textsubscript{2} measurements is estimated to be of about $0.2 \times 10^{15}$ cm\textsuperscript{-2} and $0.8 \times 10^{15}$ cm\textsuperscript{-2} under clear sky conditions in unpolluted and polluted cases, respectively (Boersma et al. 2002). According to Boersma et al. (2002), the relative errors in tropospheric NO\textsubscript{2} column estimates are $\sim 30\%$ and $60\%$ under clear and cloudy conditions, respectively, while Wenig et al. (2008) estimated this error under clear sky conditions to range in most cases from 40 to 80\%.

3. Comparison of ground-based and OMI data

3.1 Comparison methodology

Data of observations used for the comparison should as much as possible be collocated in location and time of observations. High spatial resolution of the OMI and sun-synchronized polar orbit of the satellite have allowed the receipt of a big sample of actual daily NO\textsubscript{2} measurements in the close neighbourhood of Zvenigorod station. We have used the data of OMI measurements in the 45-km neighbourhood of the station presented by the Aura Validation Data Center.

Existence of the diurnal cycle in NO\textsubscript{2} means that the data under comparison should be put to the same time. Therefore the results of ground-based observations were interpolated in time to moments of satellite observations. The great bulk of OMI NO\textsubscript{2} data have been obtained in daytime. Figure 1 shows that the photochemically determined NO\textsubscript{2} change is sufficiently slow at that time and can easily be accounted for with the use of a photochemical model. Such a change implies, other things being equal, that an NO\textsubscript{2} increase occurs during the daytime. Furthermore, according to figure 1(a), the NO\textsubscript{2} change is quasilinear during the period between the morning and evening values of solar zenith angle equal to $84^\circ$.

However, multiyear observations at Zvenigorod show that the NO\textsubscript{2} content undergoes significant day-to-day variations, in particular in winter, due to dynamical processes in the atmosphere (Elokhov and Gruzdev 1998, 2000, Gruzdev and Elokhov 2005). This circumstance can result in cases when an evening NO\textsubscript{2} content is smaller than morning content.
The method of interpolation of data of ground-based measurements to the time of OMI measurements is as follows. The NO$_2$ contents from morning and evening ground based measurements for the period of OMI measurements were obtained for solar zenith angles 84°. Morning and evening NO$_2$ values from ground-based measurements for the same day as the day of OMI measurements were interpolated linearly to the time of OMI measurements. Then using results of photochemical model calculations for that calendar day, the calculated morning and evening NO$_2$ values corresponding to solar zenith angle 84° were linearly interpolated to the same time of day (see the dotted line in figure 1(a)). The difference between accurate and interpolated values of calculated NO$_2$ for this time moment was then calculated (denoted by $\delta$ in figure 1(a)). Finally, this difference was added to the NO$_2$ value obtained by interpolation of experimental results. The resultant NO$_2$ value is considered as the result of ground-based measurements corresponding in time to the result of OMI measurements.

3.2 Results of comparison and their discussion

We present results of comparison of ground-based and OMI measurements for two NO$_2$ variables measured by OMI: $V_{bg}$ and $V_{trop}$. We compare the $V_{bg}$ value to the NO$_2$ content in the vertical atmospheric column above the boundary layer retrieved from ground-based measurements (this content includes the NO$_2$ contents in two tropospheric and eight stratospheric layers of 5-km thickness). This value characterizes the ‘unpolluted’ part of the total NO$_2$ column content and mainly contributed by stratospheric NO$_2$. We compare the $V_{trop}$ value to the NO$_2$ content in the vertical tropospheric column retrieved from ground-based measurements, which includes the NO$_2$ contents in two tropospheric layers of 5-km thickness and the NO$_2$ content in the boundary layer.

Figure 3(a) shows unpolluted column amounts of NO$_2$ while figure 3(b) shows tropospheric NO$_2$ column contents according to OMI measurements as well as to morning and evening ground-based measurements at Zvenigorod station. Data in the

![Figure 3](image)

Figure 3. (a) Unpolluted and (b) tropospheric NO$_2$ column contents over Zvenigorod derived from OMI (green squares) and ground-based morning (red triangles) and evening (blue triangles) measurements.
plots are only given for days when both results of OMI and ground-based measurements are available. Discontinuities in data in the plots are due to interruptions of ground-based measurements. According to figure 3(a), the unpolluted column NO$_2$ contents derived from OMI measurements are, on the whole, between the morning and evening NO$_2$ contents derived from ground-based observations. Generally speaking, the same cannot be said about tropospheric NO$_2$ amounts (see figure 3(b)). The spread of tropospheric NO$_2$ from ground-based measurements is three times as much as that for OMI data and approaches values of an order of $10^{17}$ cm$^{-2}$. Because of insignificant NO$_2$ concentration in the near-surface layer (and in the troposphere, on the whole) under unpolluted conditions, non-zero NO$_2$ in figure 3(b) can be considered as a result of pollution of the lower troposphere by nitric oxides. A significant part of tropospheric NO$_2$ values derived from ground-based measurements have been obtained in the absence of pollution or under relatively weak pollution. This is a most probable situation at Zvenigorod station (Gruzdev and Elokhov 2004). Conversely, tropospheric NO$_2$ columns derived from OMI measurements are affected by pollution in the majority of cases. These differences between the OMI data and ground-based measurements of tropospheric NO$_2$ are firstly explained by significant inhomogeneity of the NO$_2$ concentration field in polluted area, which results in dependence of measured tropospheric NO$_2$ on the degree of spatial averaging (which is larger for satellite observations). Another reason for the differences is a typically significant temporal variability of pollution NO$_2$, which diverges data measured at different time.

Figure 4(a) compares the unpolluted column NO$_2$ contents derived from OMI measurements and those obtained by interpolation of the ground-based data to the

![Figure 4(a)](image)

Figure 4. (a) Unpolluted NO$_2$ column contents over Zvenigorod derived from OMI measurements (green squares) and obtained from ground-based data interpolated to the time of OMI measurements (violet diamonds). (b) Difference between these data (OMI minus ground-based) for a complete dataset (red circles) and for data corresponding to dates with OMI tropospheric NO$_2$ column values less than $2 \times 10^{15}$ cm$^{-2}$ (blue circles of smaller size).
moment of OMI observations. On the whole, the data of ground-based measurements are superimposed expressly on the OMI data; however the OMI data are more dispersed. Figure 4(b) shows the difference between the OMI and ground-based data (OMI minus ground-based), and table 1 presents values of the mean and square root mean differences as well as the coefficient of correlation between results of satellite and ground-based measurements. Figure 4(b) shows that in 2006–2008 the difference exhibits a seasonal variation with typically negative values in late winter and positive values in summer. Taking into account the temperature dependence of NO₂, cross sections would decrease the difference values in warm period (by about 0.15 \(10^{15}\) cm\(^{-2}\) in summer, see §3.1) thus decreasing the seasonal variation of the difference. A similar seasonal variation of the difference between stratospheric column NO₂ contents derived from OMI and ground based measurements at middle and high latitude stations was also noted by Celarier et al. (2008) and Ionov et al. (2008). However Gruzdev and Elokhov (2009) using Collection 2 data reported an opposite annual variation of the difference at Zvenigorod.

Table 1 shows that the mean difference of unpolluted NO₂ columns is \(-0.084 \times 10^{15}\) cm\(^{-2}\), or about –3% relative to the average (over all ground-based and OMI data) value. The mean square root difference is about \(0.5 \times 10^{15}\) cm\(^{-2}\), or 18% relative to the average NO₂ value. Taking into account the temperature dependence of the NO₂ cross sections in ground-based observations would probably shift the mean difference by about \(0.075 \times 10^{15}\) cm\(^{-2}\) (by half of \(0.15 \times 10^{15}\) cm\(^{-2}\), see §2.1), i.e. to \(-0.16 \times 10^{15}\) cm\(^{-2}\). Therefore, on the whole, OMI unpolluted NO₂ columns underestimate ground-based measurements; however, the mean difference is well within the precisions of OMI and ground-based measurements (see §2). It is worth emphasizing that the mean difference obtained in this work is significantly smaller than those reported by Celarier et al. (2008), Ionov et al. (2008) and Gruzdev and Elokhov (2009). The mean square root difference is less by 20% than that reported by Gruzdev and Elokhov (2009). The coefficient of correlation between the results of OMI and ground based measurements of unpolluted NO₂ columns is 0.92 (see table 1) and is very close to the 0.9 reported earlier (Gruzdev and Elokhov

### Table 1. The mean difference (OMI minus ground-based (GB)), \(\Delta\), and its 95% confidence interval, mean square root difference, \(\sigma\), and coefficient of correlation, \(R\), between results of OMI and ground-based NO₂ measurements.

<table>
<thead>
<tr>
<th>No</th>
<th>Variable</th>
<th>(\Delta) ((10^{15}\text{ cm}^{-2}))</th>
<th>(\Delta) (%)</th>
<th>(\sigma) ((10^{15}\text{ cm}^{-2}))</th>
<th>(\sigma) (%)</th>
<th>(R)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unpolluted NO₂ column (all data)</td>
<td>(-0.084 \pm 0.025)</td>
<td>-3.2 ± 0.9</td>
<td>0.48</td>
<td>18</td>
<td>0.92</td>
</tr>
<tr>
<td>2</td>
<td>Unpolluted NO₂ column (GB tropospheric column (\leq 1 \times 10^{15}) cm(^{-2}))</td>
<td>(-0.105 \pm 0.034)</td>
<td>-3.6 ± 1.1</td>
<td>0.43</td>
<td>15</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>Unpolluted NO₂ column (OMI tropospheric column (\leq 2 \times 10^{15}) cm(^{-2}))</td>
<td>0.032 \pm 0.030</td>
<td>1.4 ± 1.3</td>
<td>0.41</td>
<td>17</td>
<td>0.94</td>
</tr>
<tr>
<td>4</td>
<td>Tropospheric NO₂ column (distance (\leq 45) km)</td>
<td>(-1.8 \pm 0.5)</td>
<td>-43 ± 11</td>
<td>8.8</td>
<td>210</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>Tropospheric NO₂ column (distance (\leq 10) km)</td>
<td>(-1.8 \pm 0.7)</td>
<td>-42 ± 16</td>
<td>8.4</td>
<td>200</td>
<td>0.42</td>
</tr>
<tr>
<td>6</td>
<td>Monthly mean tropospheric NO₂ column (distance (\leq 45) km)</td>
<td>(-2.1 \pm 1.5)</td>
<td>-50 ± 36</td>
<td>5.1</td>
<td>120</td>
<td>0.28</td>
</tr>
</tbody>
</table>

*All correlation coefficients are statistically significant at the 0.95 level.
This correlation coefficient is, as a rule, larger than those for stratospheric NO$_2$ columns at mid- and low latitude stations but smaller than those at higher latitudes (Celarier et al. 2008). The correlation coefficient of 0.87 at the station of Issyk-Kul is close to ours (Ionov et al. 2008). It should be emphasized that the Issyk-Kul station is located in remote region and much less exposed to pollution than Zvenigorod.

Figure 5(a) shows a scatter plot of the unpolluted NO$_2$ columns derived from OMI and our ground-based measurements, while table 2 presents values of linear regression parameters. The statistical relation between results of OMI, $V_{bg}$, and ground-based, $V_{Zv}$, measurements is described by linear regression equation, $V_{bg} = 0.87V_{Zv} + 0.26 \times 10^{15}$. Furthermore, figure 5(a) shows that the dispersion of the data around the regression line is larger at large NO$_2$ contents (i.e. in summer) than at small NO$_2$ contents (in winter).

The accordance between the ground-based and OMI data of tropospheric NO$_2$ columns is much worse than the accordance between the data of unpolluted columns (see tables 1 and 2 and figure 5(b)). The correlation coefficient is about 0.3 if data of

![Image](image.png)

Figure 5. Scatter plots of the (a) unpolluted and (b) tropospheric NO$_2$ columns derived from ground based and OMI measurements. Symbols and dash line of grey colour in plot (b) correspond to monthly mean NO$_2$ values. The regression analysis parameters are given in table 2.

<table>
<thead>
<tr>
<th>No</th>
<th>Variable</th>
<th>Regression coefficient, $k$</th>
<th>Free term, $a_0$ (10$^{15}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unpolluted NO$_2$ column (all data)</td>
<td>0.87 ± 0.02</td>
<td>0.26 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>Unpolluted NO$_2$ column (GB tropospheric column $\leq 1 \times 10^{15}$ cm$^{-2}$)</td>
<td>0.88 ± 0.02</td>
<td>0.27 ± 0.07</td>
</tr>
<tr>
<td>3</td>
<td>Unpolluted NO$_2$ column (OMI tropospheric column $\leq 2 \times 10^{15}$ cm$^{-2}$)</td>
<td>0.90 ± 0.02</td>
<td>0.28 ± 0.05</td>
</tr>
<tr>
<td>4</td>
<td>Tropospheric NO$_2$ column (all data)</td>
<td>0.16 ± 0.02</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>Monthly mean tropospheric NO$_2$ column</td>
<td>0.10 ± 0.5</td>
<td>2.7 ± 0.7</td>
</tr>
</tbody>
</table>
OMI measurements within 45-km neighbourhood of Zvenigorod are used (see data line 4 in table 1). The mean difference is large (–1.8 × 10^{15} \text{cm}^{-2} or about –40%), with a mean square root difference of 210%, and there are no essential changes in these values under contraction of the neighbourhood (line 5 in table 1). This points at strong inhomogeneity of the NO\textsubscript{2} horizontal distribution in a polluted layer at scales smaller compared with horizontal resolution of OMI.

One may expect an improvement of the correspondence between tropospheric NO\textsubscript{2} columns after averaging the compared data over a specific time interval (e.g. for monthly means). However such an improvement does not come about, as follows from bottom lines in tables 1 and 2. One probable reason is that the statistics of NO\textsubscript{2} contents in pollution episodes at Zvenigorod is far from the Gaussian statistics and is characterized by relatively large probability of episodes of strong pollution (Gruzdev and Elokhov 2004). Under such statistical characteristics an average (over time) value is sensitive to presence of anomalies (see, for example, Davis et al. 1996).

It is interesting to estimate the sensitivity of parameters of correspondence between OMI and ground-based values of unpolluted NO\textsubscript{2} columns to the amount of tropospheric NO\textsubscript{2}, i.e. to the degree of pollution of the lower troposphere. If data of ground-based measurements obtained under conditions of clean or weakly polluted boundary layer are only used, the values of the mean and mean square root differences as well as the coefficients of linear correlation and regression do not change significantly (cf. lines 1 and 2 in table 1 and lines 1 and 2 in table 2). Taking into account that the ground-based and OMI values of tropospheric NO\textsubscript{2} columns are poorly correlated, these unchanged parameters indicate indirectly that boundary layer pollution does not affect, on the whole, the NO\textsubscript{2} contents above a polluted layer derived from ground-based measurements.

If data of OMI measurements are only used with relatively small tropospheric column NO\textsubscript{2} (< 2 × 10^{15} \text{cm}^{-2}), the values of the mean and square root mean differences of unpolluted columns are diminished (cf. lines 1 and 3 in table 1; see also figure 4(b)). However there is not any strengthening of a statistical relation between the tropospheric NO\textsubscript{2} columns, and the correlation coefficient is close to zero. The reason is that, given small tropospheric NO\textsubscript{2} columns measured by one instrument, tropospheric NO\textsubscript{2} columns measured by another instrument vary within a wide range.

An important question is an effect of cloudiness on characteristics of comparison. Figure 6 shows the mean difference and the coefficient of correlation between OMI and ground-based data as function of cloud fraction, for unpolluted and tropospheric NO\textsubscript{2} columns. The mean difference of unpolluted NO\textsubscript{2} columns decreases (by module) with decreasing cloud fraction, more rapidly at smaller cloud fraction values (figure 6(a)). Since under conditions of rare cloudiness twilight ground-based measurements are predominantly done under cloudless zenith, this cloud fraction dependence is most probably associated with OMI observations. The coefficient of correlation between unpolluted NO\textsubscript{2} columns diminishes as well with decrease in cloud fraction except at low values of cloud fraction of 0–0.1 where the correlation coefficient is constant. Such a decline of statistical relation between OMI and ground-based data with decrease in cloud fraction is unclear at present.

Unlike for unpolluted NO\textsubscript{2} columns, the correlation coefficient for tropospheric NO\textsubscript{2} columns increases with decreasing cloud fraction, except at cloud fraction values within 0–0.1 where the correlation coefficient diminishes with decrease in cloud fraction (figure 6(b)). As for unpolluted NO\textsubscript{2} columns, the mean difference between
the tropospheric NO₂ columns has a weak dependence on cloud fraction in interval 0.4–1. However at smaller values of cloud fraction the mean difference increases significantly (by module). Therefore both unpolluted and tropospheric NO₂ column values derived from OMI measurements are sensitive to cloud fraction, and the sensitivity is stronger at lower values of cloud fraction.

4. Summary and conclusions

Comparison of results of ground-based and satellite OMI measurements of NO₂ over Zvenigorod station have revealed that the unpolluted column NO₂ contents derived from OMI measurements are, on average, by $(0.084 \pm 0.025) \times 10^{15}$ molecules/cm$^2$, or $(3.2 \pm 0.9)\%$, less than those derived from ground-based measurements, with a mean square root difference of about $0.5 \times 10^{15}$ cm$^{-2}$. If only the part of data are compared for which the tropospheric NO₂ column contents estimated from OMI measurements are less than $2 \times 10^{15}$ cm$^{-2}$, the difference decreases (by module, with change of sign) down to $(0.032 \pm 0.030) \times 10^{15}$ cm$^{-2}$, or $(1.4 \pm 1.3)\%$. The coefficient of correlation between the results of OMI and ground-based measurements of the unpolluted NO₂ columns is 0.92 and 0.94 for these two cases, respectively.

The obtained mean difference is smaller than the precisions of OMI and ground-based measurements, while the mean square root difference is of an order of the precision of ground-based measurements but larger than the precision of OMI measurements. There are factors affecting characteristics of the comparison. These are the differences in spectral range and spectral resolution of ground-based and OMI measurements, the differences in methods of measurements which, in particular, result in different spatial resolution (smoothing) of measurement results, different sensitivities to tropospheric pollution and cloudiness.

The tropospheric NO₂ columns estimated from OMI measurements are, on average, by $1.8 \times 10^{15}$ cm$^{-2}$, or 40%, less than those estimated from ground-based measurements, with a mean square root difference of about 200% and a correlation coefficient of about 0.3. This significant discrepancy seems to be primarily due to
significant spatial (horizontal) inhomogeneity and temporal variability of boundary layer NO₂ during pollution episodes, which result in different estimates of lower tropospheric NO₂ content because of different spatial resolution of ground-based and satellite measurements. Nevertheless, we could outline a way of further, more detailed, analysis in this direction – by comparing results of measurements taking into account the geometry of ground-based measurements, which is different for morning and evening observations. An obvious success in this direction was achieved, for example, with the use of the MAX-DOAS technique (Brinksma et al. 2008, Kramer et al. 2008).

On the whole, for more comprehensive validation of OMI NO₂ measurements, a more detailed study is necessary of the effects of lower tropospheric pollution.

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