REMOTE SENSING OF ATMOSPHERE, HYDROSPHERE, AND UNDERLYING SURFACE

Validation of TROPOMI Satellite Measurements of the NO_2 Content in the Troposphere and Stratosphere with Ground-Based Measurements at the Zvenigorod Scientific Station of A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences

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Abstract—Results of measurements of the tropospheric and stratospheric NO_2 columns with the TROPOMI (Tropospheric Monitoring Instrument) aboard the Copernicus *Sentinel-5P* satellite in 2018–2020 are compared with the results of ground-based measurements at the Zvenigorod Scientific Station (ZSS) of A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences. The correspondence between the satellite and ground-based measurements is characterized by the difference between them, the linear correlation coefficients, and the regression coefficients. The dependences of these parameters on the season, cloud conditions, and the height of the atmospheric boundary layer are derived.

INTRODUCTION

Nitrogen oxides NO and NO_2 play an important part in the photochemical balance of atmospheric ozone [1, 2]. They significantly contribute to anthropogenic pollution of the atmospheric boundary layer (ABL) in large cities and industrial regions and harmfully impact the human health [3]. Nitrogen oxides appear in the stratosphere as a result of the photolysis of nitrous oxide N_2O [1, 2], and in the lower troposphere due to vehicle and thermal power plant emissions [4].

The absorption of solar radiation by NO_2 molecules allows remote (from the Earth's surface and from satellites) spectrometric measurements of the content of impurities in the atmosphere. Several ground-based NO_2 measurement stations are included in the Network for the Detection of Atmospheric Composition Change (NDACC). Among them is the Zvenigorod Scientific Station (ZSS) of the A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences. The instruments and techniques for measuring the NO_2 content used at the NDACC stations have been verified in international comparison campaigns.

Significant progress in satellite measurements of the NO_2 content in the atmosphere is associated with the Ozone Monitoring Instrument (OMI), which has been operating on board the *EOS-Aura* satellite since 2004 and provides information on the global NO_2 field with a high horizontal resolution (13×24 km^2 at nadir) [5].

A new Tropospheric Monitoring Instrument (TROPOMI) began to operate aboard the Copernicus *Sentinel-5P* satellite in 2018. It measures the NO_2 content with a higher horizontal resolution [6]. The first results of the validation of TROPOMI data were published in [7–12], including on the basis of the measurements of the stratospheric NO_2 content at ZSS [12].

TROPOMI data on NO_2 are currently widely used in solution of different problems related to the pollution of the troposphere with nitrogen oxides [13–18] mainly for assessing and refining anthropogenic emissions [13–17].

Results of measurements of the tropospheric and stratospheric NO_2 columns and the total column NO_2 were compared with the ground-based measurements with different instrument types and techniques used at different stations in most detail in [12]. The agreement between satellite and ground-based data was quite good in many cases. However, a weak correlation ($R < 0.5$) between the tropospheric NO_2 column according to TROPOMI data and the ground-based measurements was noted at certain stations. On average, TROPOMI underestimates tropospheric NO_2 by 20–50% or more

as compared to ground-based measurements. The average difference between satellite and ground-based values at several stations is 37–74%.

The correlation between the measurements of stratospheric NO_2 turned out to be generally much higher: $R \sim 0.8$–0.98 at 21 stations out of 26 [12]. On average, TROPOMI slightly underestimates the stratospheric NO_2 column (by about 1%) as compared to ground-based measurements.

The previous works on the comparison between OMI data on the NO_2 content and ground-based measurements [19–21] have shown that the degree of agreement between them depends on the season, cloudiness, and the level of pollution of the lower troposphere with nitrogen oxides. We assume that these factors can also affect the degree of agreement between the ground-based measurements and TROPOMI data.

This work is aimed at validation of the TROPOMI measurements of the NO_2 content in the stratosphere and troposphere with the results of ground-based spectrometric measurements at ZSS when the satellite is flying over the region of ZSS.

1. MEASUREMENT DATA AND TECHNIQUES

The TROPOMI orbital spectrometer was launched aboard the *Sentinel-5 Precursor* (S-5P) research satellite of the European Space Agency in October 2017. The satellite is in a low Earth orbit; its mission is to provide information on air quality, climate, and the ozone layer. TROPOMI measures solar radiation scattered by the atmosphere in a wide spectral range. Based on the measurement results, the atmospheric contents of several gases, including NO_2, and aerosol are retrieved once a day over most of the Earth's surface. The swath width is 2600 km. The resolution (and therefore the size of the "primary pixel") varies depending on the gas, angular coverage, and swath. The astronomical (solar) time of measurement over each site is approximately 13:30. The standard measurement products are the NO_2 contents in the troposphere and the stratosphere and the total column NO_2. The horizontal resolution of the nadir measurements is about 7×7 km². It was improved to 5.5×3.5 km² in August 2019 [6].

For the validation, we use the data on the NO_2 content retrieved from measurements of zenith-scattered solar radiation of visible spectral region at ZSS (55.7° N, 36.8° E). The station is located in a forested countryside in the Moscow region, about 50 km west of the center of Moscow and 40 km away from the Moscow Ring Road. The NO_2 measurements are performed at ZSS in morning and/or evening twilight at sunrise and sunset in the solar zenith angle range 84°–96° with an MDR-23 automated scanning monochromator [22].

The measured spectra of zenith-scattered solar radiation scattered are used to determine the so-called slant NO_2 content, and the vertical distribution of NO_2 is retrieved from it by means of solution of the inverse problem with photochemical simulation of its daily variation. The values of the NO_2 content are put to the time corresponding to a solar zenith angle of 84°.

The tropospheric (0–10 km) and stratospheric (10–50 km) NO_2 columns and the total column NO_2 are calculated from its vertical distribution. The separation between the tropospheric and stratospheric NO_2 contents is especially important under the conditions of anthropogenic pollution of the ABL, which repeatedly affects the station due to its proximity to Moscow [23]. The weight functions which characterize the vertical distributions of the contributions of the NO_2 content in the stratosphere and the ABL to the slant NO_2 content in zenith twilight measurements (the so-called averaging kernel) do not practically overlap [24]. Therefore, the stratospheric and tropospheric contents of NO_2 we calculate can be considered independent.

During ground-based zenith twilight observations, the horizontal resolution of the tropospheric data is mainly determined by the field of view of an instrument. Since the main contribution to the tropospheric content of NO_2 is made by the ABL during pollution episodes [23], the horizontal resolution of these data is no worse than several hundred meters, i.e., the data refer to a small vicinity of the station. The horizontal resolution of the stratospheric NO_2 column is ~400 km in the direction of rising or setting sun azimuth [21].

At ZSS, the monochromator is mounted on the roof of a building at an altitude of ~8 m above the ground. Hence, the tropospheric NO_2 column measured by us does not include the NO_2 content in this lower layer.

The NO_2 absorption cross sections in the visible region depend on the temperature. The NO_2 data measured at ZSS and used for the validation are calculated on the basis of NO_2 absorption cross sections at a temperature of 220 K [25], which corresponds to the winter (January) temperature in the layer of the stratospheric NO_2 maximum above ZSS. However, it differs from the temperature of the lower troposphere and the summer temperature of the stratosphere. Due to the neglect of the temperature dependence of the NO_2 absorption cross sections, the NO_2 content in the stratosphere is underestimated at ZSS by about 4% in July, and in the troposphere, by 11% in January and 18% in July, on average [21].

Since multiple scattering is ignored when retrieving the NO_2 content from the slant NO_2 abundance [22, 26], the NO_2 content in the lower troposphere is overestimated as compared to values which could be derived if multiple scattering is taken into account. The overestimation can be up to 45% in clear sky con-

ditions and higher under cloudy conditions and a high albedo of the underlying surface.

The random errors in the stratospheric NO_2 column over ZSS are tenths of 10^{15} molec/cm^2. Their monthly mean absolute values are of $0.1-0.3 \times 10^{15}$ molec/cm^2, and the monthly mean relative errors vary within $4-12\%$ with the season [21]. Random errors in the NO_2 content in the lower troposphere ranges from 5 to 100% depending on the conditions. In particular, the relative error is small under stable conditions with high NO_2 content and large under low NO_2 content in the surface air layer [10, 11, 21].

2. DATA PREPARATION FOR COMPARISON

2.1. TROPOMI Data

The *Sentinel-5P* OFFL L2 NO_2 data product (OFFL processing type means that archived data have been preliminarily filtered) is used in this work (https://sentinels.copernicus.eu/web/sentinel/data-products). For an external user, level 2 (L2) is the primary level, where 15 NetCdf files (the number of satellite orbits per day) corresponds to one measurement day [6, 12]. TROPOMI OFFL L3 (level 3) NO_2 data (converted to one daily file) are currently unavailable. Therefore, each research team independently prepares L3 data or uses L2 data, information about several variables (parameters) related to nitrogen dioxide is contained, including: nitrogen-dioxide_tropospheric_column (*TrC*), nitrogen_dioxide_stratospheric_columns (*StC*), cloud_fraction_crb (*crb*), quality assurance value (*qa*) (the data quality parameter), and other georeferenced and related (without coordinate referencing and connecting with the computational algorithms used) variables.

To analyze orbital data (primarily TROPOMI data), we have developed special software tropomi_tools, which allows us to collect TROPOMI L2 data and then convert them into L3 data by means of combining 15 NetCdf files into a single daily .mat file with preservation of any georeferenced variables, the initial data resolution, and location of primary orbital pixels. In addition, based on L3 data from several orbital spectrometers (MODIS/Terra/Aqua, AIRS/Aqua, and TROPOMI/Sentinel-5P), the software allows calculating and mapping the spatial distributions of the fields of contents of several pollutants over an arbitrarily given area and with a certain spatial resolution. The software provides for the daily distributions and distributions averaged over a set of arbitrarily specified dates (including annual average distributions), and any georeferenced parameters for an arbitrarily specified spatial region contained in the source data with a possibility of filtering by selected variables and threshold values. Thus, the daily values of the tropospheric and stratospheric TROPOMI OFFL NO_2 columns over ZSS were calculated.

For the validation of TROPOMI OFFL NO_2 *TrC* and *StC* data, we used $0.1° \times 0.1°$, $0.25° \times 0.25°$, and $0.5° \times 0.5°$ averaging areas with simultaneous data filtering by cloud parameters and *qa*. The former are contained in the variable *crb*, which varies from 0 (no clouds) to 1 (maximum possible cloud amount).

The TROPOMI data were prepared for the comparison with measurements at ZSS as follows. The NO_2 content corresponding to one day and falling into the vicinity of ZSS with boundaries determined by the resolution specified was averaged. For example, the averaging area $0.1° \times 0.1°$ is an approximately rectangular area with ZSS at the center. The boundaries of this area are 5.5 km north and south from ZSS and 3.1 km west and east; Moscow does not fall into the cell. Moscow does not fall in the cells $0.25° \times 0.25°$ and $0.5° \times 0.5°$ as well. The typical number of NO_2 values averaged is $2-3$, $5-10$, and $12-20$, respectively, for cells $0.1° \times 0.1°$, $0.25° \times 0.25°$, and $0.5° \times 0.5°$.

The software described was used in [27] for the analysis of the distributions of the total CO content retrieved from AIRS orbital spectrometer measurements and in [28] when constructing the averaged distributions of the total column CO and the tropospheric NO_2 column for the Moscow megalopolis in the case of sampling by calm days.

Designers of the TROPOMI spectrometer advise using data with $qa > 0.75$ when analyzing the tropospheric NO_2 column data. In their opinion, this makes it possible to exclude the data acquired at $crb > 0.5$, over the snow or ice surface, and part of the erroneous calculations [6]. For the stratospheric NO_2 column, $qa > 0.5$ is advised.

During the preliminary stage (the stage of assessing the quality of initial satellite data), we studied the variability of *crb*. Primary pixels with $crb < 0$ and $crb > 1$ were found for the ZSS region (about 9% of the total number with $qa > 0.75$). These values have no physical sense and testify to the imperfection of the TROPOMI cloud parameter processing algorithms.

Thus, in this study, we used the quality parameters advised ($qa > 0.75$ for the troposphere and $qa > 0.5$ for the stratosphere), and additionally excluded from the analysis all primary pixels with $crb > 1$ and $crb < 0$.

2.2. TROPOMI Data Sampling Depending on Cloudiness and ABL Height

The TROPOMI data samples corresponding to cloud conditions specified were prepared based on the *crb* parameters contained in the initial TROPOMI OFFL L2 level. As mentioned above, the tropomi_tools software allows processing any variable with simultaneous filtering by several parameters related to any variables. In calculations with different spatial resolutions, we used $0 \leq crb \leq crb_{max}$, where crb_{max} took the values 0.05; 0.1; 0.2 etc. up to 1.0. The restrictions $qa > 0.75$ for the tropospheric and $qa > 0.5$ for the

stratospheric content of NO_2 were always imposed, as well as the condition $TrC > 10^{10}$ molec/cm^2, to exclude satellite artifacts (negative values of NO_2 content and emissions due to features or errors of the primary algorithms for orbital data retrieval).

Another approach was applied to the TROPOMI data sampling by the ABL height, since this parameter is not included in the TROPOMI data. We used the ABL heights calculated from meteorological fields from the Global Data Assimilation System (GDAS) database. The spatial resolution of these data is $1° \times 1°$ and the temporal resolution is 3 h. The description of the meteorological fields can be found on the NOAA ARL website; the data are available through the ARL FTP server (https://www.arl. noaa.gov/). In our work, we used the values of the ABL height at the time point the closest to the satellite flyover time, i.e., 09:00 UTC, which corresponds to 12:00 Moscow time.

The TROPOMI data were sampled depending on the ABL height h by the condition $h \geq h_{min}$, where the lower threshold h_{min} varied from 0 to 1000 m with a step of 100 m, and it took values of 1200 and 1500 m above 1000 m.

2.3. Ground-Based Data

The observation data intended for the comparison should maximally match in terms of site and time of observations. The NO_2 content strongly varies during the day; therefore, the ground-based observations of NO_2 were interpolated to the time of satellite observations. The photochemically determined diurnal variations in the NO_2 content are relatively slow and can be taken into account quite simply using the daily NO_2 variation calculated.

The technique for putting ground-based data to the time of satellite measurements is described in detail in [19, 21]. If both morning and evening ZSS data were available for the day of satellite measurements, then they were linearly interpolated to the time of satellite measurements. The interpolated stratospheric NO_2 column was supplemented with a (small) correction calculated with the use of the photochemical model and caused by the nonlinearity of the daily NO_2 variation. If only morning or only evening ground-based data were available for the day of satellite measurements, then the stratospheric content of NO_2 from ZSS data was extrapolated to the time of satellite measurements using the photochemical calculations. The tropospheric content of NO_2 from ZSS data was assigned to the time of satellite measurements as a fixed value, neglecting photochemical variations.

3. RESULTS AND DISCUSSION

The comparison between TROPOMI and ZSS data is performed with the use of the technique suggested in [21] for validation of OMI data on the tropospheric and stratospheric NO_2 content measured in a neighborhood of ZSS within a radius of 10 km. Here, the comparison is performed for measurements from mid-2018 to mid-2020 depending on the season, cloud conditions, and ABL height (this part is absent in [21]). In [21], the dependence has been revealed of the characteristic of comparison on the level of pollution of the lower troposphere with nitrogen oxides. This dependence is not considered in this work because of insufficient statistical coverage of severe pollution conditions.

3.1. General Characteristics of Comparison

The tropospheric and stratospheric NO_2 columns in the vicinity of ZSS according to the TROPOMI and ground-based measurements at ZSS are shown in Figs. 1a and 1b. Here, the TROPOMI data are bounded by an area of $0.1° \times 0.1°$ centered at ZSS. The correlation between the satellite and ground-based data is the best in this area as compared to larger areas.

The annual variation in stratospheric NO_2 is characterized by a minimum in January ($\sim 1 \times 10^{15}$ molec/cm^2) and a maximum in July ($\sim 4 \times 10^{15}$ molec/cm^2); it is shown in both the ground-based and satellite measurements (Fig. 1b). The values of the tropospheric NO_2 column according to the data of both instruments are scattered over a wide range from zero to values exceeding the stratospheric NO_2 column by an order of magnitude; the agreement between them is much worse than in the case of stratospheric column (Fig. 1a). The reasons for this may be the spatial (horizontal) inhomogeneity of the NO_2 field and the large temporal variability of the NO_2 fields in the atmospheric layer subjected to anthropogenic pollution.

The difference between the values of NO_2 content measured from the satellite and from the ground is shown in Figs. 1c and 1d for the troposphere and stratosphere, respectively. According to Fig. 1c, the tropospheric NO_2 column from the TROPOMI data is generally higher by about 10^{15} molec/cm^2 ($\sim 36\%$ of the TROPOMI data) than from the ZSS measurements; at the same time, the difference has no pronounced seasonal variation.

The difference in the stratospheric values varies around zero with an amplitude of about 0.3×10^{15} molec./cm^2 with the mean over the period of comparison of -0.2×10^{15} molec./cm^2 when averaged over an area of $0.1° \times 0.1°$. According to TROPOMI data, the stratospheric NO_2 column is generally a little higher in winter and lower in summer than the ZSS values. This difference cannot be due to ignorance of the temperature dependence of NO_2 absorption cross sections in the ground-based data. If this dependence were taken it into account, then the summer NO_2 content derived from the ground-based
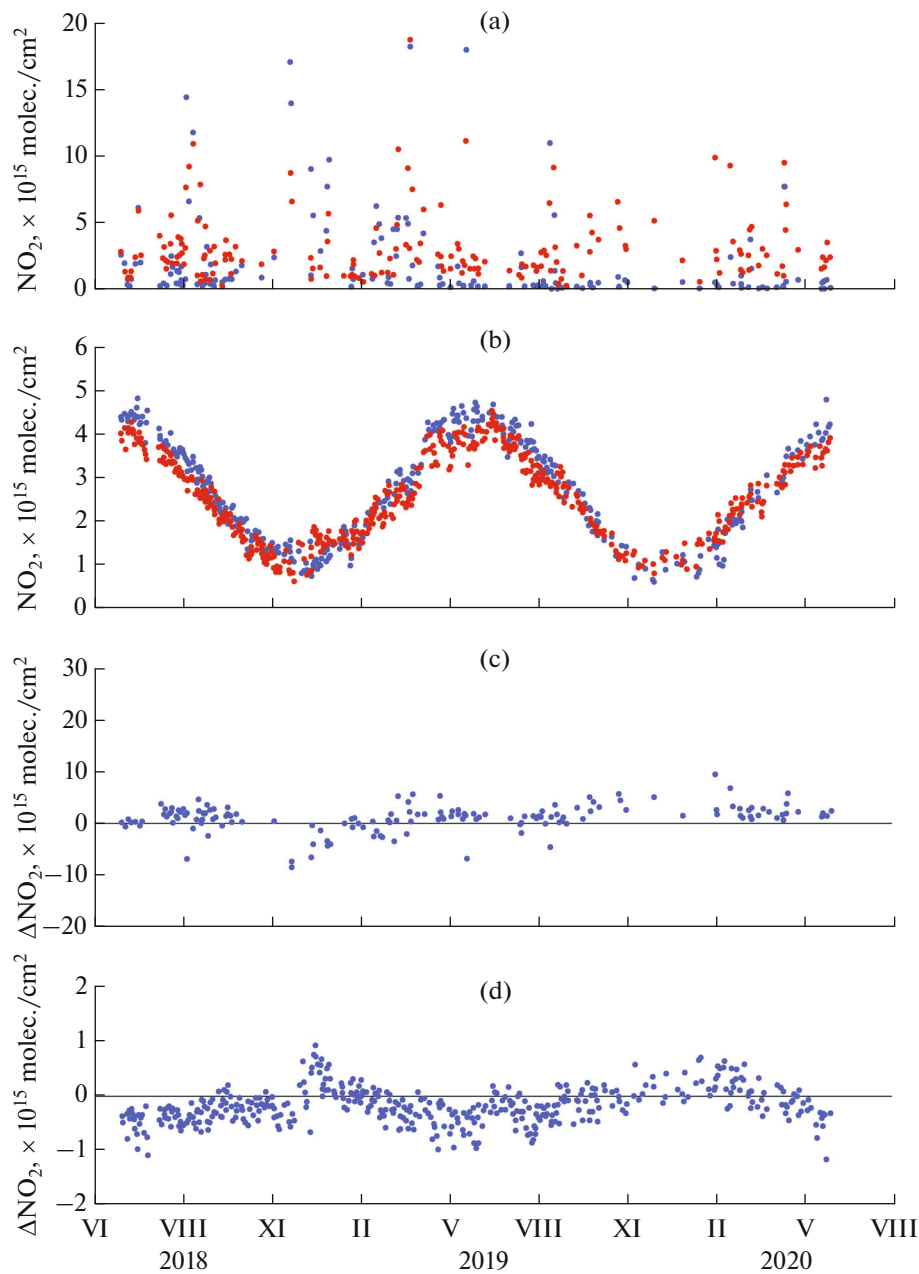
Fig. 1. (a) Tropospheric and (b) stratospheric NO_2 column in a vicinity of ZSS according to the TROPOMI satellite measurements (red dots) and ground-based measurements (blue dots); the difference between satellite and ZSS data on the (c) tropospheric and (d) stratospheric NO_2 column. The satellite data correspond to an area of $0.1° \times 0.1°$ and $qa > 0.75$ for the troposphere and $qa > 0.5$ for the stratosphere. The data with $crb < 0$ and $crb > 1$ have been excluded from the analysis.

measurements would increase by approximately 4% on average ($\sim 0.15 \times 10^{15}$ molec./cm^2 in July) [21] and, hence, the absolute difference would also increase.

The tropospheric NO_2 column from ZSS data can be underestimated on average due to the temperature dependence of the absorption cross section. In the surface layer, the underestimation can be $\sim 10\%$ in January and $\sim 20\%$ in July, on average [21].

Let us estimate the correlation between the TROPOMI and ZSS data using a linear regression.

Figure 2 shows the correlation diagrams of the tropospheric and stratospheric NO_2 columns in the vicinity of ZSS from the ground-based and satellite measurements, as well as the regression equations which describe the dependence of the NO_2 content from TROPOMI data on that from the ground-based measurements, R, and the number of pairs of comparisons (N). The diagrams for the tropospheric NO_2 content in Figs. 2a−2c are shown for three TROPOMI data samples for a vicinity of ZSS of $0.1° \times 0.1°$,
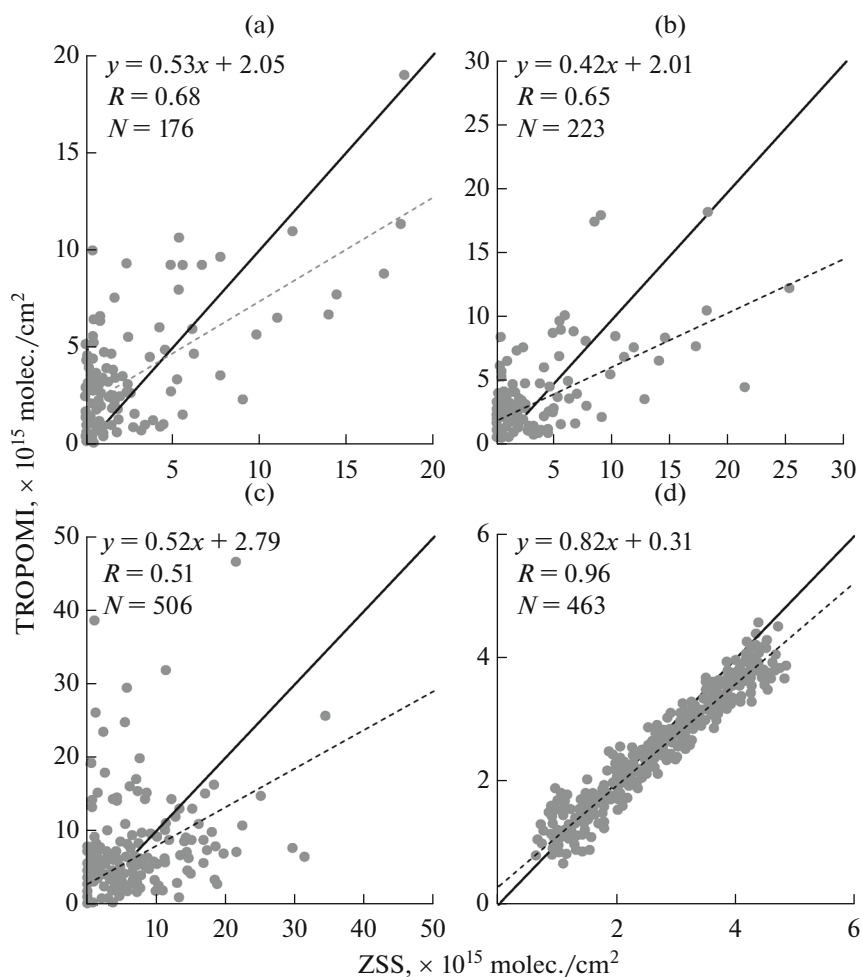
Fig. 2. Correlation diagrams of the (a–c) tropospheric and (d) stratospheric NO_2 content in the vicinity of ZSS from the ground-based and satellite measurements; dotted lines show linear regressions of the TROPOMI data on the ground-based data. Regression equations, correlation coefficients, and the number of points N are given. The TROPOMI tropospheric data with $qa > 0.75$ correspond to areas of (a) $0.1° \times 0.1°$, (b) $0.25° \times 0.25°$, and (c) $0.5° \times 0.5°$; (d) the stratospheric data with $qa > 0.5$ correspond to an area of $0.1° \times 0.1°$. The data with $crb < 0$ and $crb > 1$ have been excluded from the analysis.

$0.25° \times 0.25°$, and $0.5° \times 0.5°$ in area, and for stratospheric NO_2, for a sample from a area of $0.1° \times 0.1°$.

The slope of the regression K for the tropospheric NO_2 column is ~0.5 (which corresponds to the results [12]), and the free term is approximately twice the difference between the tropospheric NO_2 columns from the TROPOMI and ZSS data averaged over the entire period of comparison (Figs. 2a–2c). Note that similar ratios were derived from the comparison between long-term OMI measurements of the NO_2 content and ZSS data in [21].

The correlation between the tropospheric TROPOMI and ZSS data deteriorates with an increase in the area of the TROPOMI data sampling (Figs. 2a–2c). The contribution of the variance of the tropospheric NO_2 column according to TROPOMI data to the total variance due to their linear relationship with the ground-based measurements (determination coefficient R^2) decreases from 0.46 for an area of $0.1° \times 0.1°$ to 0.26 for an area of $0.5° \times 0.5°$. The corresponding correlation coefficient R decreases from 0.68 to 0.51. Note that the first of the values is noticeably higher than the correlation coefficient between the ground-based measurements at ZSS and the OMI data in a 10-km neighborhood of ZSS in [21].

The correlation between the stratosphere NO_2 columns from the satellite and ground-based measurements is almost independent of the TROPOMI data sampling area in the vicinity of ZSS. The fraction of the variance of the TROPOMI stratospheric NO_2 column in the total variance due to the linear relationship between the data is 0.93, and $R = 0.96$ (Fig. 2d). The slope of the regression $K < 1$ ($K = 0.82$), which is due to, in particular, the difference in the amplitudes of the annual variations in the stratospheric NO_2 according to TROPOMI and ground-based data (see Fig. 1b). The free term of the regression is positive in Fig. 2d; it is
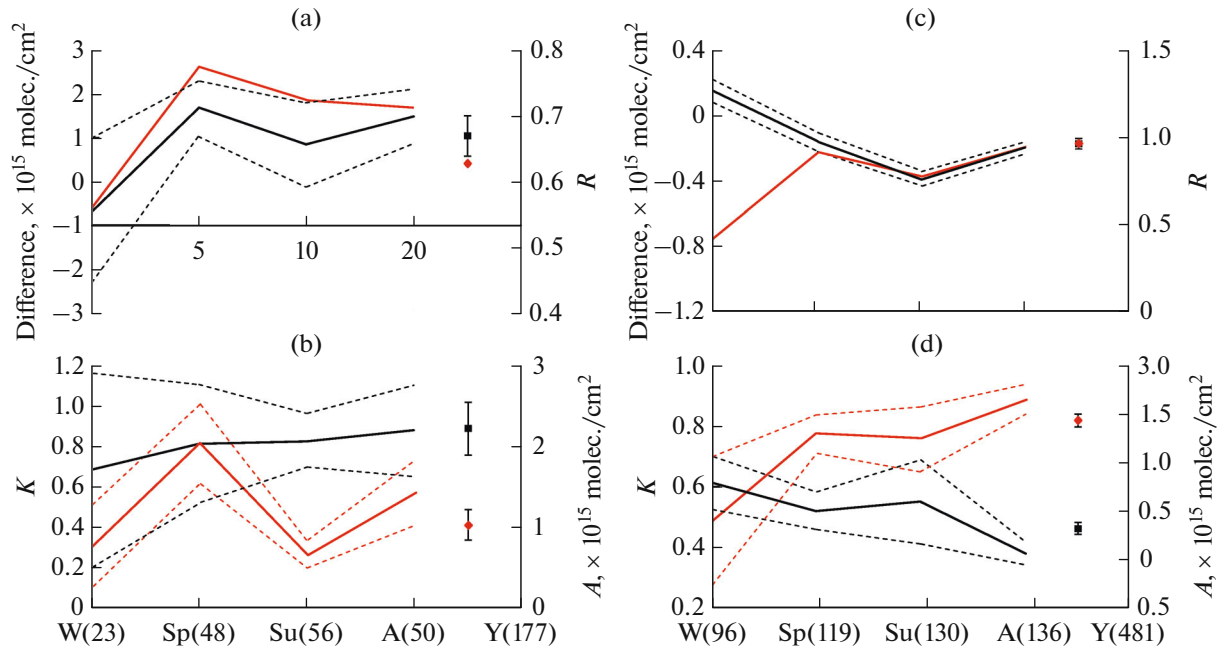
Fig. 3. Seasonal (winter (W), spring (Sp), summer (Su), and autumn (A)) and annual (Y) values of the characteristics of comparison between the TROPOMI and ground-based (ZSS) data: (a) R (solid red curve and diamond) and difference (solid black curve and square) between satellite and ground-based tropospheric NO_2; (b) slope K (solid red curve and diamond) and free term A (solid black curve and square) of the linear regression of the tropospheric TROPOMI data on the ground-based data; (c and d) the same as in (a and b), but for stratospheric NO_2. The number of comparisons for each season is given in parentheses along the abscissa. Dashed curves show the 95% confidence boundaries; the vertical segments are 95% confidence intervals.

opposite in sign to the mean difference (see Fig. 1d) and is 1.5 times higher in absolute value. The presented statistical characteristics of the linear relationship between the values of the stratospheric NO_2 column are close to those derived from the comparison between OMI and ZSS data in [21], as well as to the results of comparison of stratospheric NO_2 measurements from TROPOMI and NDACC stations [12].

3.2. Seasonal Dependences of the Comparison Results

The seasonal dependence of the parameters of comparison between the TROPOMI and ZSS measurements is shown in Fig. 3 by curves, and the symbols in the right parts of the plots show the average values of the corresponding parameters over the entire measurement period. Here and below (Figs. 3–5), satellite data correspond to the $0.1° \times 0.1°$ region centered at ZSS with $qa > 0.75$ for the troposphere and $qa > 0.5$ for the stratosphere; data with $crb < 0$ and $crb > 1$ have been excluded from the analysis.

The seasonal average differences in tropospheric NO_2 columns are positive for most of the year and are maximal in spring and autumn (Fig. 3a). In winter, the difference is close to zero (taking into account the confidence interval). The seasonal dependence of the difference in Fig. 3a is qualitatively the same as in [21] for OMI data, and the average difference over the period of comparison (the annual value equal to

1.05×10^{15} molec/cm^2 in the right part) is close to the annual average in the case of OMI.

Accounting for the temperature dependence of NO_2 absorption cross sections would probably increase the tropospheric NO_2 column according to ZSS data (see Section 3.1). This would increase the small negative difference in winter and decrease the positive difference in other seasons. One could expect an increase in the annual average tropospheric NO_2 columns according to ZSS data by up to 15% and, hence, a decrease in the annual average positive difference between the TROPOMI and ZSS tropospheric data.

Another reason for the tropospheric NO_2 column from the TROPOMI data to be generally higher than from the ZSS measurements is the significant difference in the spatial resolution of both data and the horizontal inhomogeneity of the NO_2 field in the ABL in the vicinity of ZSS. According to [21], the vicinity of ZSS is more polluted by nitrogen oxides than the territory of ZSS; therefore, the field of view of the orbital instrument includes areas more polluted on average than ZSS.

The correlation coefficient between the tropospheric NO_2 content according to the TROPOMI and ZSS data is maximal in spring ($R = 0.77$), like for OMI data [21], though is higher in value. The minimum $R = 0.55$ is noted in winter and is close to the winter value for OMI data in [21]. The seasonal and annual
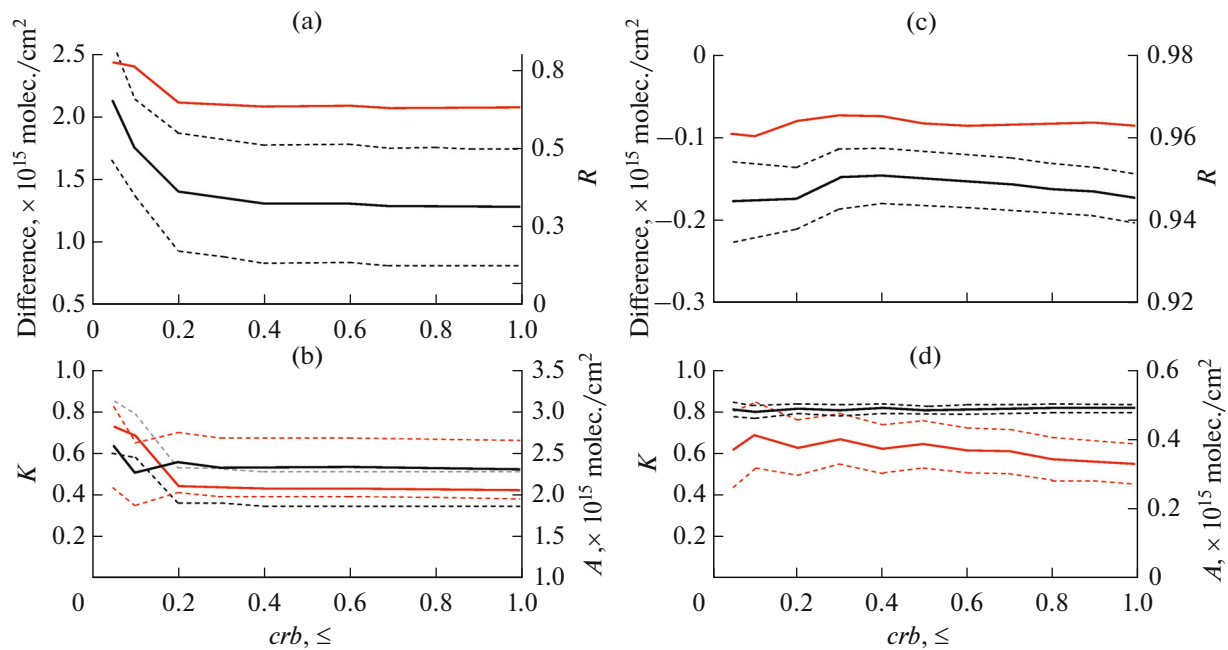
Fig. 4. Parameters of the comparison between the TROPOMI and ZSS data as functions of the upper threshold of *crb*: (a) *R* (solid red curve) and difference (solid black curve) between satellite and ground-based tropospheric NO_2; (b) slope coefficient *K* (solid red curve) and free term *A* (solid black curve) of the linear regression of tropospheric TROPOMI NO_2 on the ground-based data; (c and d) the same as in (a and b), but for stratospheric NO_2. Dashed curves show the 95% confidence boundaries.
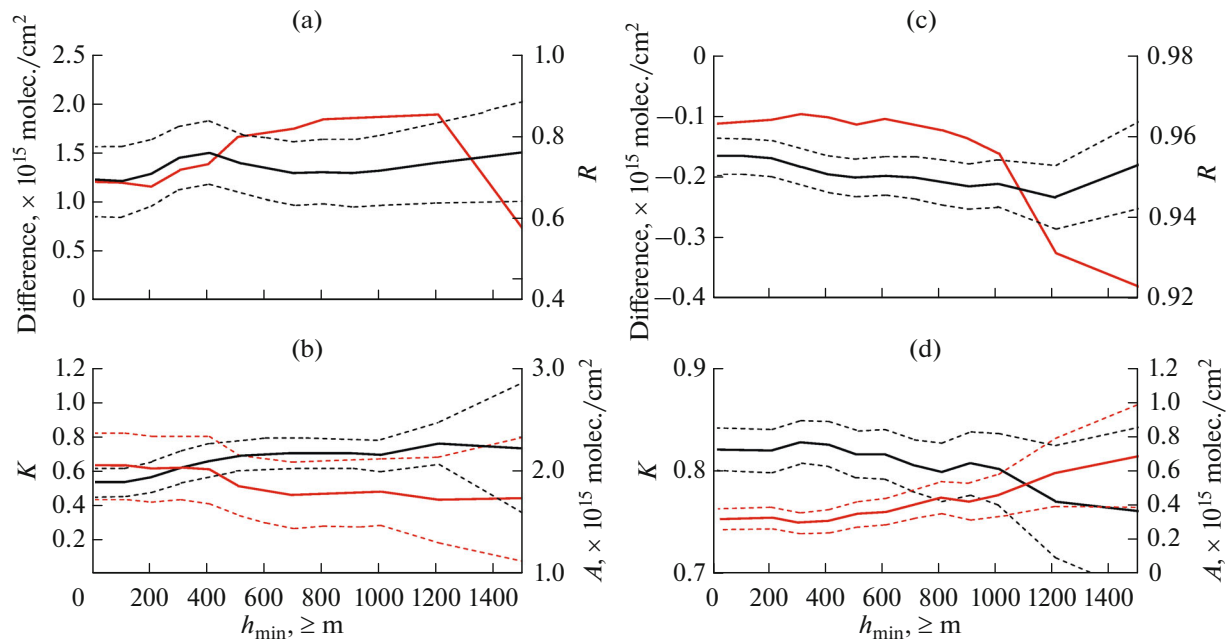

Fig. 5. The same as in Fig. 4, but versus the lower threshold of the ABL height.

values of *R* in Fig. 3a are noticeably higher than in [21]. The most important difference is that a high correlation ($R > 0.7$) between the TROPOMI and ZSS data has been found in summer, while the correlation between OMI and ZSS tropospheric data is weak in summer ($R \sim 0.2$). The reasons for the better correlation with the TROPOMI measurements may be the better horizontal resolution of the satellite data and their smaller localization area in the vicinity of ZSS. These factors are significant in summer, when the atmospheric transfer weakens and the horizontal scale of the NO_2 field inhomogeneities in the ABL decreases.

The regression slope coefficient K for the tropospheric NO_2 column strongly varies with season, from 0.2 in summer to 0.8 in spring (Fig. 3b). The agreement between the TROPOMI and ZSS data in terms of this parameter is better in spring and autumn than in winter and summer. The free term A has approximately the same value in all seasons, but it is characterized by great uncertainty, especially in winter.

The character of variations in the seasonal mean difference between stratospheric NO_2 columns in Fig. 3c confirms the above-noted features of the behavior of the difference in Fig. 1d. The coefficient of correlation between the stratospheric NO_2 columns has approximately the same spring and autumn peaks with $R > 0.9$. This is partly due to the significant annual variation in stratospheric NO_2 with the highest rate of changes in spring and autumn (see Fig. 1b). The minimal value $R \sim 0.5$ is observed in winter, and it is noticeably lower than the coefficient of correlation between the OMI and ZSS winter stratospheric data in [21] ($R = 0.76$). The reason for this discrepancy is not entirely clear, since the statistical coverage of the winter value of R is low in the case of TROPOMI due to the small number of data pairs compared for this season (see Fig. 1c).

The seasonal dependence of K for the stratospheric NO_2 content in Fig. 3d generally follows the seasonal dependence of R in Fig. 3c. The former is somewhat higher than the corresponding coefficient for OMI data in summer and autumn and much lower in winter (see Fig. 3d). The free term of the regression A is smaller than in the case of OMI; the autumn value of A is close to zero.

Thus, based on the difference between the correlation and regression coefficients, a stronger correlation is found of the ground-based measurements at ZSS with the TROPOMI data on the tropospheric NO_2 than with the OMI data. However, we cannot draw the same conclusion about data on the stratospheric NO_2 column based on the amount of measurements available for the comparison.

3.3. Dependence of the Comparison Results on Cloudiness

The dependence of the comparison results on cloudiness is determined with the use of the parameter crb. It is important to remember that the cloud cover over the ground station and in the region of satellite observations can differ due to both the difference in the time of satellite and ground-based measurements and the inhomogeneity of the cloud field. Therefore, we note that twilight zenith ground-based measurements are insensitive to clouds if the cloud conditions in the field of view of the device are stable during a measurement session. The narrow spectral range of the monochromator used at ZSS makes it possible to linearize and eliminate the spectral dependence of absorption and scattering by aerosol and clouds, which is an additional factor which weakens the effect of cloudiness on the ground-based data.

Figure 4 shows the correlation and regression coefficients and the differences between the TROPOMI and ZSS data averaged over the period of comparison depending on the upper crb threshold specified. According to Figs. 4a and 4c, the correlation between the tropospheric NO_2 columns according to the TROPOMI and ZSS data is stronger and between the stratospheric columns is somewhat weaker under low cloud conditions than under cloudy conditions. This corresponds to similar dependences derived in [21] from the comparison between OMI and ZSS data. The average difference (residual) between the tropospheric NO_2 contents from satellite and ground-based measurements increases under low cloud conditions (Fig. 4a).

Thus, the absence of clouds, on the one hand, enhances the consistency (correlation) between satellite and ground-based data, and on the other hand, increases the residual between them.

Variations in K for the tropospheric NO_2 content versus crb in Fig. 4b follow the variations in R in Fig. 4a, while the coefficient A remains approximately constant. The coefficient K for the stratospheric NO_2 content does not change in Fig. 4d, and the coefficient A slightly varies depending on the crb threshold.

3.4. Dependence of the Comparison Results on the ABL Height

The ABL thickness affects the vertical distribution of NO_2 in the lower troposphere. Other conditions being equal, in the presence of surface sources of NO_2 (anthropogenic or natural), the low ABL height contributes to the concentration of nitrogen oxides in the surface air layer, and the high altitude contributes to their transfer to higher layers. The redistribution of NO_2 within the ABL under a change in the height does not affect the results of twilight zenith ground-based measurements at ZSS, but it can affect the satellite data. The NO_2 content in the ABL according to ZSS measurements is one of the values of the vertical profile of NO_2 derived by inverse problem solution. When retrieving the tropospheric and stratospheric NO_2 columns from the satellite data, a priori information about the NO_2 profile is used, the shape of which can significantly vary in the lower troposphere under pollution conditions depending on the ABL height.

The results of comparison between the data TROPOMI and ZSS measurements are shown in Fig. 5 as function of the lower threshold of the ABL height h_{min}. The correlation between the tropospheric NO_2 values is relatively weak ($R \sim 0.65$) at $h_{min} = 200$ m and increases up to ~0.85 as the ABL height range narrows to $h_{min} = 1.2$ km. With a further increase in h_{min}, the correlation sharply weakens. No characteristic

changes in the difference between the tropospheric NO_2 columns are detected (Fig. 5a). The slope of regression K in Fig. 5b gradually increases and the coefficient A decreases with an increase in h_{min}. According to Figs. 5a and 5b, the agreement between the TROPOMI and ZSS data in terms of all the parameters considered is the best at moderate h_{min} within 500−1200 m.

The coefficient of correlation between the stratospheric NO_2 columns from the TROPOMI and ZSS data in Fig. 5c weakly depends on low and medium h_{min} values and drops at $h_{min} > 1$ km. The slope K also changes along with R (Fig. 5d). The difference between the stratospheric NO_2 columns weakly changes and the slope of the regression increases with h_{min}. Thus, the agreement between the stratospheric NO_2 from the TROPOMI and ZSS data is the best when h_{min} is not too high; the optimal range of h_{min} is from 0.5 to 1 km.

Nonmonotonic dependences of R on the lower threshold of the ABL height in Fig. 5 do not follow from the seasonal variation in the ABL height, which increases from winter to summer. According to Figs. 3a and 3c, R insignificantly changes from spring to autumn and sharply decreases in winter. Due to the seasonal variation in the ABL height, the amount of data on NO_2 available for the comparison decreases in winter at high h_{min}, which should not lead to a sharp drop in R in Figs. 5a and 5c.

The reasons for the revealed weakening of the correlation at high ABL can be different. First of all, we note that narrowing the ABL height range reduces the statistical reliability of the comparison results giving rise to greater uncertainty, and the estimates of R at high h_{min} are at the limit of 0.05-level of statistical significance. If this decrease in the correlation is not random, then its cause may be a deterioration in the correspondence of the ABL height simulated to the conditions used by the developers to prescribe a priori NO_2 profile [6] in the ABL when simulating TROPOMI measurements.

CONCLUSIONS

The comparison between the TROPOMI measurements of NO_2 content in the atmosphere in 2018−2020 with the twilight zenith ground-based measurements at the Zvenigorod Scientific Station shows that the data agreement depends on the season, cloud conditions, and the ABL height. The comparison has been made using two products of satellite measurements: the tropospheric and stratospheric NO_2 columns. The difference between the values, the linear correlation coefficient, and the linear regression coefficients are considered as quantitative characteristics of the correspondence between the satellite and ground-based measurements.

The stratospheric NO_2 column according to the TROPOMI data is generally slightly lower than according to the measurements at ZSS throughout the entire period of comparison, and the average difference between the data is an order of magnitude lower than the average stratospheric NO_2 column. The tropospheric NO_2 column in the vicinity of ZSS according to TROPOMI data exceeds the value obtained in ground-based measurements at ZSS. The average difference is ~1×10^{15} molec./cm^2.

The characteristics of the correspondence between the TROPOMI and ZSS data more or less depend on season. The correlation between satellite and ground-based data from spring to autumn is better than in winter. The correlation between the satellite and ground-based tropospheric NO_2 contents is stronger than the correlation between the tropospheric OMI and ZSS data [21] in all seasons (except winter) and for the whole year.

The dependence of the comparison results on cloudiness is revealed. The correlation between the satellite and ground-based values of stratospheric NO_2 is weaker, while the correlation between the values of tropospheric NO_2 is stronger under low-cloud than under cloudy conditions.

The comparison results are found to depend on the ABL height. The coefficient of correlation between the tropospheric NO_2 content according to the TROPOMI and ZSS data turned out to be sensitive to it. The value of R increases with an increase in the lower threshold of the ABL height from 0 to 1200 m. As for the stratospheric NO_2 content, the correlation coefficients are relatively higher at the lower threshold values of the ABL height from 0 to 1 km. The agreement between the TROPOMI and ZSS data on both tropospheric and stratospheric NO_2 is the best at the ABL altitude range more than 0.5−1 km.

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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