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Ground-Based FTIR Measurements of Atmospheric Nitric Acid at the NDACC St. Petersburg Site

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Abstract—Atmospheric nitric acid (HNO_3) has a significant impact on the formation of the ozone layer; therefore, its content is regularly monitored using various local and remote-sensing methods. We use ground-based measurements of solar IR spectra with a Bruker 125HR Fourier spectrometer to derive information on the HNO_3 content at the NDACC St. Petersburg observational site in Peterhof. The HNO_3 time series shows a pronounced seasonal cycle with a maximum in winter and early spring and a minimum in summer and early autumn. The averaged seasonal variations in nitric acid vary from –30 to +60% for the 0–15 km layer, from –25 to +25% for the 15–50 km layer, and from –25 to +30% for total columns. For the 2009–2022 measurement period, no statistically significant trend is found in the time series considered. A comparison of HNO_3 stratospheric columns with independent satellite measurements by the MLS and ACE–FTS instruments shows their qualitative and quantitative agreement; the correlation coefficient between ground-based and satellite measurements totals 0.88–0.93. Time series on the vertical structure of the atmospheric nitric acid measured at the St. Petersburg site can be used both to analyze the state of the ozonosphere and to validate satellite measurements and refine the parameters of atmospheric models.

Keywords: nitric acid, ground-based FTIR method, satellite measurements, atmospheric gas composition change

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1. INTRODUCTION

Nitric acid (HNO_3) plays an important role in the chemistry of stratospheric ozone. It is involved in ozone-depleting catalytic cycles and in heterogeneous reactions on the surface of aerosol particles and polar stratospheric clouds; it is also a reservoir for reactive nitrogen oxides. According to the toxicity level, the HNO_3 pair is classified as moderately hazardous. The HNO_3 content in the atmosphere is regularly measured using various local and remote methods (WMO, 2018). In recent decades, satellite measurements have been used on global and regional scales using various methods and equipment to determine the content of HNO_3 (Vigouroux et al., 2007; Lindenmaier et al., 2012; Wespes et al., 2009; Wolff et al., 2008; Livesey et al., 2011).

The first long-term ground-based IR spectroscopic measurements of the HNO_3 content in the atmosphere at middle latitudes were described in (Rinsland et al., 1991). Similar measurements were also carried out at other stations of the international Network for the Detection of Atmospheric Composition Change (NDACC); see, for example, (Vigouroux et al., 2007; Dammers et al., 2017; Shan et al., 2021). Measurements of the total content (TC) of HNO_3 have been carried out since 2009 at NDACC St. Petersburg site, located on the campus of Saint Petersburg State University in Peterhof (Semakin et al., 2013; Timofeev et al., 2016; Virolainen et al., 2016, 2021). Ground-based IR spectroscopic measurements are used to study spatiotemporal variations in HNO_3, obtaining estimates of long-term trends, a comparison with numerical models of the atmosphere, and the validation of various types of satellite measurements. In (Virolainen et al., 2022), we described a new method for determining the TC and nitric acid content in two layers: in the troposphere and stratosphere, based on spectroscopic measurements of the Bruker IFS 125HR Fourier spectrometer (hereinafter referred to as FTIR).

In this paper, we present the results of an analysis of ground-based measurements of HNO_3 in Peterhof obtained using the new methodology for the period of 2009–2022, estimates of the seasonal cycle and long-term trends, and the results of a comparison of ground-based measurements with satellite data.

2. FTIR MEASUREMENT OF HNO_3 CONTENT IN PETERHOF

To interpret FTIR measurements at the NDACC St. Petersburg station in Peterhof (59.88° N, 29.82° E, 20 m a.s.l.), we used the PROFFIT96 software (Hase

Table 1. Statistical characteristics of HNO_3 measurement datasets, measurement errors, and trend estimates at NDACC St. Petersburg site. Here, x is the average value of the content; σ is its variability; and ε_{rand} and ε_{syst} are the average random and systematic errors, respectively

Layer	$x \pm \sigma$, $\times 10^{16}$ cm^{-2}	ε_{rand}, %	ε_{syst}, %	Trend, % per year
0–50 km	2.2 ± 0.6	3.9 ± 1.9	9.2 ± 1.6	0.23 ± 0.34
0–15 km	0.7 ± 0.4	14 ± 7	15 ± 6	0.25 ± 0.75
15–50 km	1.5 ± 0.3	1.7 ± 0.3	13.0 ± 2.6	0.22 ± 0.22

et al., 2004), which is also used at a number of other NDACC stations. During the day, the number of measurements of solar spectra ranged from 1 to 20. To obtain each spectrum, interferograms were accumulated (up to ten pieces) for 12 min, which were then averaged and converted into a spectrum. All spectroscopic measurements were performed with an optical path difference of 180 cm; nonapodized spectra were used to solve the inverse problem, corresponding to a spectral resolution of 0.005 cm^{-1}.

When processing the spectra, pressure and temperature profiles were set according to the NCEP CPC reanalysis data for each day of measurements (12 UTC) based on satellite and radiosonde measurements. A priori information about the profiles of the content of various gases that affect the transfer of radiation in the spectral ranges under consideration was taken from the data of the numerical model WACCM v.6 (WACCM output).

In 2009–2022, about 6000 spectra were measured in Peterhof during 850 sunny days. Based on various criteria for assessing their quality, 5182 measurements were selected, obtained over 779 days in the specified period. As criteria for assessing the quality of measurements, we used the difference between the measured and calculated spectra, the number of degrees of freedom of the signal relative to the information on the content of nitric acid in spectroscopic measurements (DOFS), etc. Details of the scheme for solving the inverse problem and other features of the analysis of the measured spectra are presented in (Virolainen et al., 2022). The results of measurements of nitric acid at the station St. Petersburg can be found at the (NDACC database). In our work, we used data from version V004.

For the measurement period of 2009–2022, the average DOFS number over the entire dataset was 3.08 ± 0.38, which means that information on three independent parameters of the vertical structure of nitric acid can be extracted from the measured spectra. The minimum of information content falls on the summer period (DOFS = 2.5–2.8), which may be due to the large effect of water vapor on the signal in summer (Virolainen et al., 2022). To make the results consistent with the vertical resolution of the IR method for any season, we divided the atmosphere into two layers, 0–15 km and 15–50 km, and considered the HNO_3 TC in the 0–50 km layer.

3. ANALYSIS OF RESULTS

Table 1 shows the statistical characteristics of the measured values of the content of HNO_3 in three atmospheric layers: x (average) and σ (variability), as well as estimates of measurement errors: ε_{rand} is the average random error and ε_{syst} is the average systematic error. The last column of Table 1 shows an estimate of the linear trend for 2009–2022 according to the method described in (Polyakov et al., 2021) for a confidentiality level of 95%.

The means, variability, and errors remained virtually unchanged compared to the data obtained in (Virolainen et al., 2022) for the period of 2009–2021. When adding an additional year of measurements, the trend estimates changed for the 0–15 km layer (0.25 ± 0.75% per year versus –0.82 ± 0.86% per year) and for the HNO_3 TC 0.23 ± 0.34% per year versus –0.11 ± 0.38% per year, but still remained statistically insignificant. For the 15–50 km layer, the trend estimate remained the same, 0.22% per year, while the confidential interval decreased to the level of the estimate itself. Thus, with the addition of further measurements, one can expect a statistically significant estimate of the increase in the content of HNO_3 in the atmospheric layer 15–50 km above St. Petersburg.

An investigation of HNO_3 TC trends was carried out in (Rinsland et al., 1991) at two high-mountain NDACC observation stations: Jungfraujoch (Alps, altitude 3.6 km, latitude 46.5° N, longitude 8.0° E) and Kitt Peak (altitude 2.1 km, latitude 31.9° N, longitude 111.6° W). For the Jungfraujoch station, ground-based measurements have been used since 1951 using a diffraction spectrometer, as well as a Fourier spectrometer for June 1986 to June 1990. The trend estimates for the period of ~40 years were −0.16 ± 0.50% per year, which indicates the absence of significant trends. Estimates obtained at high-altitude stations and near St. Petersburg differ strongly from long-term trends for Hefei station in China (Shan et al., 2021). Based on an analysis of three years of measurements (2017–2019) at the Hefei station, the HNO_3 TC trend was obtained in (–9.45 ± 1.20)% per year. In (Ossohou et al., 2019), the variability of surface concentrations of HNO_3 is studied in three regions of Africa, and a significant trend is shown only in the Bomassa region (1.07% per year).

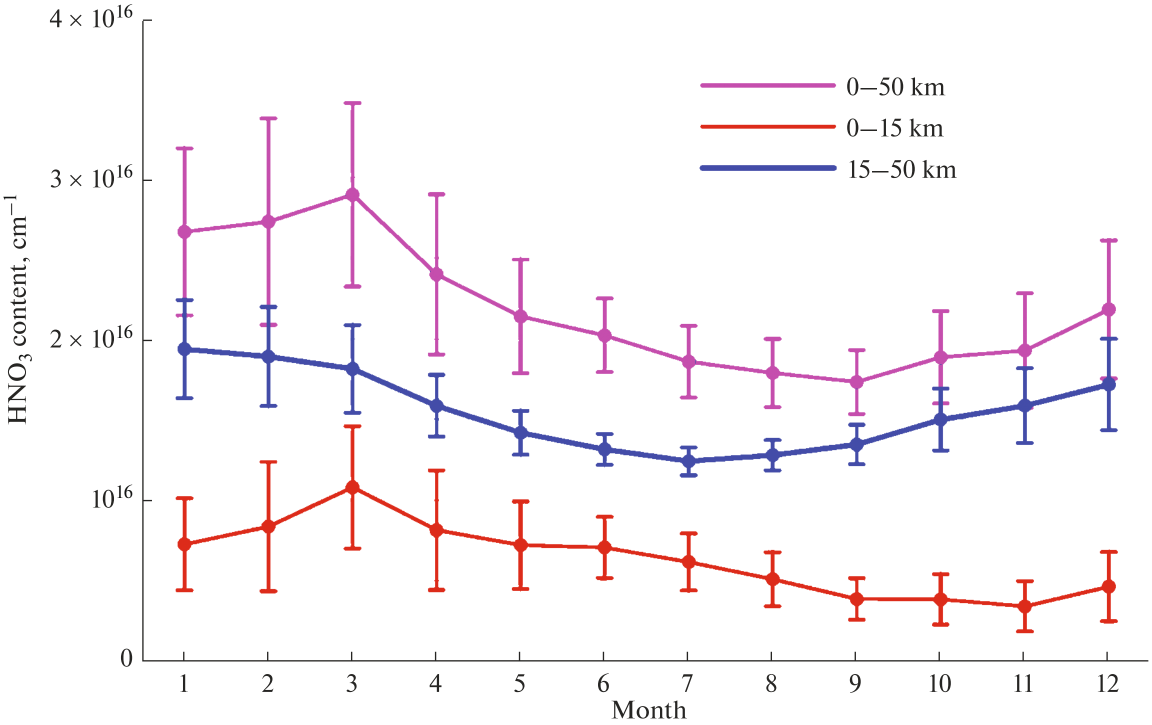

Fig. 1. Monthly averages of HNO_3 content in the 0–50, 0–15, and 15–50 km layers for 2009–2022, as well as their variability, obtained at NDACC St. Petersburg.

The 0–15 km layer contains about a third of the TC of nitric acid, while its natural variability is more than 50%, which may be due to the fact that, depending on the height of the tropopause and taking into account the vertical resolution of the FTIR method in the troposphere (10–15 km), when calculating the content of HNO_3 in this layer, it can also take into account nitric acid from the lower stratosphere (Virolainen et al., 2022). The natural variability of HNO_3 in the 15–50 km layer is about 20%.

Figure 1 shows the annual cycle of the average monthly values of the HNO_3 content in different layers of the atmosphere and their variability at the St. Petersburg station. The maximum values of HNO_3 content in the 15–50 km layer are observed in winter and, in the 0–50 and 0–15 km layers, in early spring. The minimum content in the 15–50 km layer occurs in summer, the TC occurs in early autumn, and the content in the 0–15 km layer occurs in autumn and early winter. Due to the peculiarities of the climate of St. Petersburg and the uneven distribution of sunny days in different months, the number of days over which averaging was carried out varied from 15–20 in November–December to 115–118 in April and May, which can affect the resulting annual variation.

Figure 2 shows the average seasonal cycle of variations in the content of nitric acid in different layers of the atmosphere relative to the average values for the entire period of measurements. The seasonal variation was obtained after subtracting the trend using the method from (Polyakov et al., 2021). Seasonal variations are minimal for the 15–50 km layer (up to 25%), positive for the end of spring, and negative for the middle of summer. For TC HNO_3, the maximum deviation from the average is about +30% in March and about –25% in September. At Hefei station (Shan et al., 2021), similar maxima and minima were recorded for the stratospheric nitric acid content in the 12–40 km layer. The maximum variation in the 0–15 km layer reaches +60% in mid-March and up to –30% in the period from September to December. A significant spring maximum in this layer can be caused by dynamic factors, for example, the horizontal movement of air from polar latitudes rich in nitric acid, or due to changes in the height of the tropopause and the downward movement of air masses at this time of the year.

The seasonal cycle of the HNO_3 TC registered in Peterhof agrees well with measurements at various NDACC stations (Rinsland et al., 1991; Shan et al., 2021; Semakin et al., 2013), in particular, at the high-altitude NDACC Jungfraujoch station (Rinsland et al., 1991). The content of nitric acid in the 0–15 km layer also has a secondary small maximum in the middle of summer. The HNO_3 content in the 15–50 km layer begins to grow from the end of summer; at the same time, the content of HNO_3 in the 0–15 km layer continues to decrease until the onset of winter. Differ-

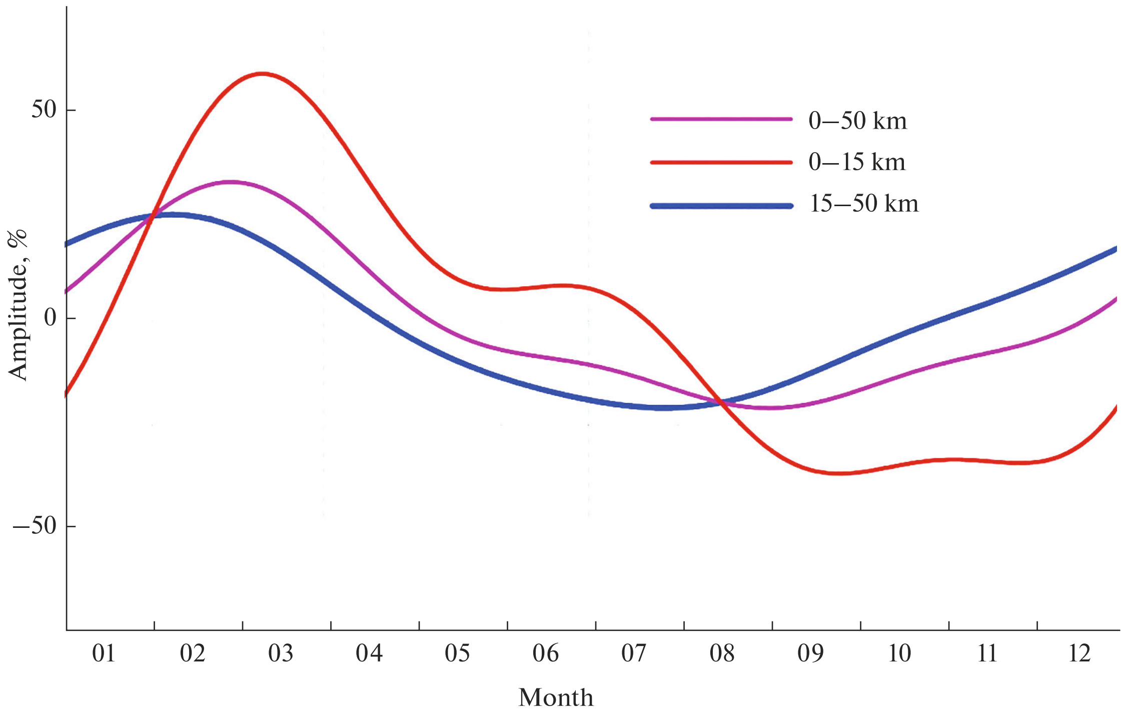

Fig. 2. Seasonal variations in HNO_3 content relative to its average value in different layers of the atmosphere obtained at the NDACC St. Petersburg.

ences in the seasonal course of nitric acid in the two considered layers and their causes require additional analysis and research using modeling data.

4. COMPARISON OF GROUND-BASED AND SATELLITE MEASUREMENTS OF HNO_3 CONTENT

One of the main sources of satellite data on the content of HNO_3 is the Microwave Limb Sounder (MLS) device. It measures the millimeter and submillimeter thermal radiation of the planet's horizon every 24.7 s and provides day and night profiles approximately every 165 km along the suborbital path. The vertical resolution of MLS measurements of HNO_3 content in the pressure range of 1–215 mbar varies from 3.5 to 5 km. The horizontal resolution varies from 250 to 800 km. Estimates of random errors (using the analysis of measured profile variations) are 0.6–1.2 ppbv, and systematic errors are 0.1–2.2 ppbv, depending on altitude (Livesey et al., 2020). For a comparison with HNO_3 measurements in the stratosphere at the St. Petersburg station, we selected MLS profiles at a distance of no more than 500 km away. To obtain the stratospheric nitric acid content, we integrated the profiles from the lower boundary of 100 mbar, which approximately corresponds to a height of 15–16 km.

The second source of satellite data on nitric acid profiles are instrument data of ACE–FTS. This method is based on measurements of direct solar IR radiation at sunrise and sunset over the planet's horizon. It is characterized by a vertical resolution of 1–3 km and a horizontal resolution of 300–500 km at different heights. The determination of HNO_3 profiles is carried out using solar spectra in the spectral intervals of 867–880 and 1691.5–1728.6 cm^{-1} at altitudes from 5 to 37 km. Systematic measurement errors due to the use of different spectral ranges are 5–11% (Wolff et al., 2008; Sheese et al., 2017). One significant difference between ACE–FTS measurements and MLS measurements is the small number of measurements per day (~30) and the limited spatial coverage of observations. For example, in the vicinity of St. Petersburg, ACE–FTS measurements occur only in certain months; in particular, most measurements occur in the winter, when the number of FTIR measurements is minimal. For comparison with ground-based measurements, we also selected ACE–FTS measurements within a radius of 500 km from St. Petersburg, having obtained the stratospheric content by integrating over heights from 15 to 40 km.

Figure 3 shows the time series of measurements of the stratospheric nitric acid content obtained from the FTIR measurements, as well as satellite measurements selected according to the criteria described above. For comparison with satellite data, we took the average daily values of FTIR measurements in the 15–50 km layer. All measurement data are in good agreement with each other both in absolute values and in the

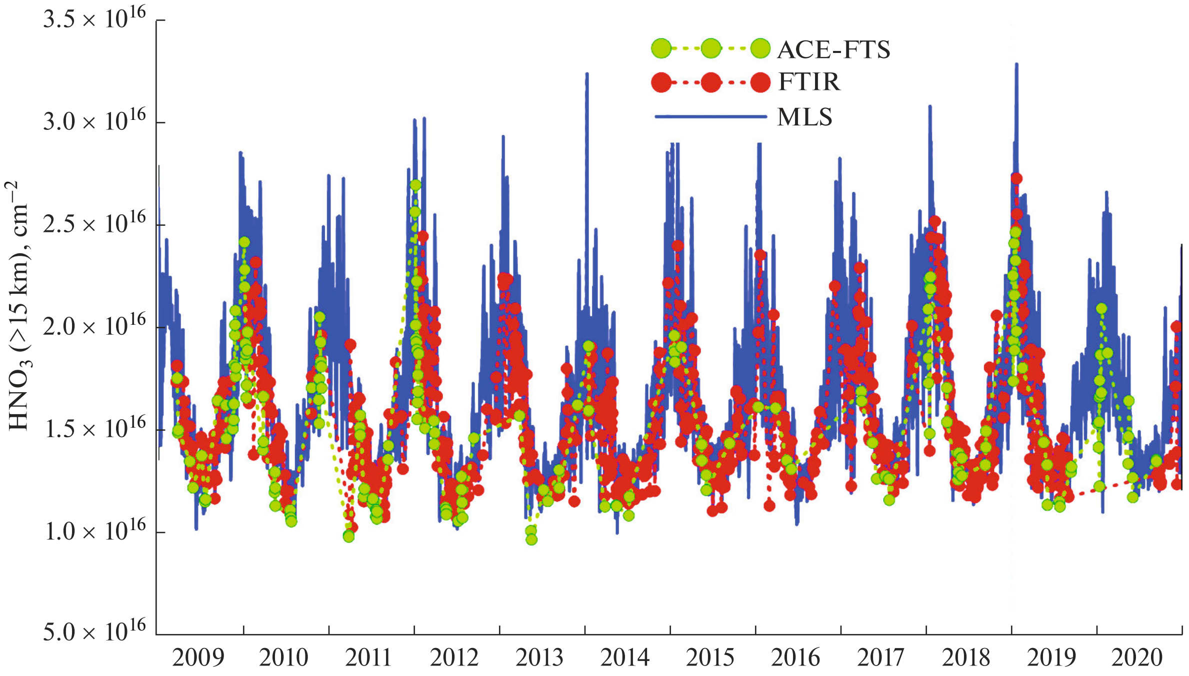

Fig. 3. Time series of the stratospheric content of HNO_3 near the St. Petersburg station according to terrestrial (FTIR) and satellite (MLS and ACE–FTS) data.

description of the temporal variability of the stratospheric HNO_3 content with highs in winter and lows in summer.

Next, we selected the days in which there were simultaneous measurements from both ground-based and satellite data, thus compiling pairs of measurements: ground–satellite. During the period under review, we received 489 FTIR–MLS data pairs and 55 FTIR–ACE–FTS data pairs. Table 2 shows the statistical characteristics of comparing datasets of simultaneous ground-based and satellite measurements of the nitric acid content in the stratosphere layer of 15 km and higher in the St. Petersburg region: the averages, variability, average differences and their standard deviation, and correlation coefficient.

Mean values and natural variations of datasets of ground-based and satellite measurements of HNO_3 matched with each other well. The greatest variability of the measured values of HNO_3 observed for MLS data is about 25%; the variability for other types of measurements does not exceed 20%. This may be due to the different horizontal resolution of the methods, when different air masses fall into the scanned area of a particular measurement. The systematic difference between ground-based and satellite data is explained both by the difference in the vertical grid on which the original profiles are obtained (for example, MLS data are shown on a pressure grid, in contrast to FTIR and ACE–FTS data) and by the spatiotemporal difference in measurements. In addition, when solving the inverse problem, various methods used different a priori information about the average profiles of nitric acid. Small values of the standard deviation of the differences (8.5% for FTIR–ACE–FTS pairs and 9.3% for FTIR–MLS pairs), as well as high correlations (0.88–0.93), indicate that the measurements are consistent with each other within the measurement errors,

Table 2. Statistical Characteristics of Comparison of Ensembles of Measurements of Stratospheric HNO_3 according to ground and satellite data in the area of St. Petersburg: x is the mean, σ is the variability of datasets of measurements, and the difference is presented as the mean difference and standard deviation of the differences. All relative values are taken in relation to FTIR measurements

Device (layer)	Number of pairs	$x \pm \sigma$, $\times 10^{16}$ cm^{-2}	Difference, %	Correlation coefficient
FTIR (15–50 km)	489	1.51 ± 0.30	-5.4 ± 9.3	0.933 ± 0.006
MLS (15–50 km)		1.60 ± 0.37		
FTIR (15–50 km)	55	1.49 ± 0.27	5.7 ± 8.5	0.88 ± 0.03
ACE–FTS (15–40 km)		1.40 ± 0.25		

taking into account the spacetime mismatch, and also equally describe the variability of the stratospheric content of nitric acid.

In (Shan et al., 2021), the data of FTIR measurements at the Hefei station were compared with the data of MLS satellite measurements for different years from 2017 to 2019. The systematic discrepancy between data on the stratospheric content of HNO_3 was 8–9%; the standard deviation of the differences was 11–13%. Dimension mappings of ACE–FTS with the MLS and MIPAS satellite measurements (Sheese et al., 2017) at altitudes below 30 km showed agreement on average within 10% and a standard deviation of ~7% near the maximum HNO_3 content and about 25% at lower altitudes. Above 30 km, ACE–FTS data exceeds MIPAS data by 10–20%.

4. MAIN RESULTS AND CONCLUSIONS

To obtain information on the content of nitric acid in different layers of the atmosphere, we used ground-based measurements of the spectra of solar IR radiation with a high spectral resolution using a Bruker 125HR Fourier spectrometer (FTIR measurements) at NDACC St. Petersburg site in 2009–2022.

(1) The random error of FTIR measurements of HNO_3 in the layers of 0–15 km (conditional troposphere), 15–50 km (conditional stratosphere), and 0–50 km is 14, 2, and 4%, respectively. The 0–15 km layer contains approximately one-third of the total HNO_3 content.

(2) The variability of the nitric acid content in the considered layers is 57, 20, and 27% for the troposphere, stratosphere, and total content. The large variability in tropospheric HNO_3 content is associated with higher measurement errors, as well as vertical motions of air masses, when air rich in nitric acid from the lower stratosphere enters the 0–15 km layer.

(3) Maximum values of HNO_3 content in the 15–50 km layer are observed in winter; they are observed in early spring in the 0–50 km and 0–15 km layers. The minimum content in the 15–50 km layer occurs in summer, the TC in early autumn, and the content in the 0–15 km layer occurs in autumn and early winter. Variations in the average seasonal course vary from –30 to +60%, from –25 to +25%, and from –25 to +30% for the troposphere, stratosphere and HNO_3 TC.

(4) For 2009–2022, there are no statistically significant trends in the content of HNO_3 over St. Petersburg in the considered atmospheric layers.

(5) A comparison of FTIR measurements with data from satellite measurements by the MLS and ACE–FTS instruments showed that the measurements are consistent with each other within their errors, taking into account the spatiotemporal mismatch. All measurement data equally describe the variability of the stratospheric content of nitric acid. The standard deviation of the differences is 8.5% for FTIR–ACE–FTS pairs and 9.3% for FTIR–MLS pairs; the correlation coefficient is 0.88 and 0.93, respectively. The systematic difference between ground-based and satellite data of 5–6% is explained by the methodological aspects of carrying out various measurements and their analysis.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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