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Ground-Based Spectroscopic Measurements of the Total Nitric Acid Content in the Atmosphere

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Abstract—The results of the first ground-based spectroscopic measurements in Russia of the total content (TC) of nitric acid in the atmosphere near St. Petersburg over the period April 2009–October 2011 are presented. These measurements show a substantial seasonal trend of the HNO_3 TC with maximal values in the winter period and early in the spring and minimal values in the summer time. The seasonal trends and variations in the daily mean values of HNO_3 TC near St. Petersburg in the winter and spring periods agree well with observations at the Kiruna station of the international NDACC network.

Keywords: atmospheric composition, gas constituents, HNO_3 content, ground-based measurements, Fourier spectrometer

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INTRODUCTION

In spite of its small concentration in the stratosphere, nitric acid plays an important role in the processes controlling the destruction of stratospheric ozone [1, 2]. Thus, nitric acid is the main reservoir for odd-nitrogen compounds participating in the catalytic reactions of ozone destruction [3]. In addition, HNO_3 plays the main role in the processes of activation and deactivation of chlorine and bromine compounds and, therefore, indirectly controls the intensity and duration of ozone-destruction processes [4].

The spectra of solar radiation with the identification of HNO_3 absorption bands were measured for the first time in 1951 [5, 6]. Subsequently, numerous ground-based, airborne, and balloon measurements have been conducted with the use of various remote methods; later satellite measurements were added to them. These measurements made it possible to study the basic spatial and temporal variations in the HNO_3 content. In recent decades, the total content (TC) of HNO_3 has been regularly measured with the use of ground-based spectroscopic methods at some stations of the international NGACC (Network for the Detection of Atmospheric Composition Change) network [7].

In this work we present the results of the first ground-based measurements of the HNO_3 TC in Russia by a spectroscopic method.

METHOD OF MEASUREMENTS

Ground-based measurements of spectra of direct solar radiation in the IR region with a spectral complex based on the high-resolution Bruker IFS-125HR Fourier spectrometer [8] have been conducted since January 2009 at the Faculty of Physics, Department of Atmospheric Physics, St. Petersburg State University (in Staryi Petergof, about 35 km southwest of the center of St. Petersburg (59°88′ N, 29°83′ E)). Examples of determinations of the TCs of different gases with the aid of the spectral complex are given in works [9–13]. In this work we present the results of determining the HNO_3 TC over the period April 2009–October 2011.

In the process of solar-radiation measurements, series of ten interferograms measured over ~15 min were averaged and used for obtaining the solar-radiation spectrum. The signal-to-noise ratio in the spectral interval was in the range from ~300 to ~1500, depending on conditions of solar-radiation measurements. From 1 to 15 of such measurements were conducted daily (depending on the presence of clouds), which in some cases made it possible to study daily variations in the HNO_3 TC.

The spectral interval 867.5–870.1 cm^{-1} was chosen on the basis of an analysis of data presented in atlas [14] and the numerical analysis of errors in the inverse problem solution for measurements in different spectral intervals for a determination of the HNO_3 TC (the same spectral interval was used for these purpose at the NDACC stations). The HNO_3 TC was determined with the aid of the SFIT software developed by a group of authors [15] for the NDACC network of stations. The HITRAN 2004 spectroscopic database was used as a source of information about the parameters of the fine structure of molecular-absorption lines [16]. The contents of water vapor, CO_2, and OSC were determined as "intervening" parameters for reconstructing the HNO_3 TC. A priori relative variations in the mixing ratio of HNO_3 were specified in the range from

Monthly mean values of the HNO_3 TC and amplitudes of variations in daily mean values Δ ($\times 10_{16}$ mol/cm^2)

Year/month	2009	Δ	2010	Δ	2011	Δ
April	2.21	0.44	2.21	0.40	2.02	0.42
May	1.72	0.05	2.05	0.34	1.96	0.22
June	1.76	0.25	1.96	0.20	1.62	0.37
July	1.67	0.21	1.54	0.13	1.52	0.18
August	1.58	0.19	–	–	1.41	0.20
September	1.69	0.34	–	–	1.73	0.14

27% (0 km) to 12% (80 km) in accordance with current data on its variability [6, 17]. Daily data of radio sounding of the atmosphere at the Voeikovo station, located at a distance of about 40 km from the observation place, were used for a determination of the HNO_3 TC. The quality of the inverse solution to the problem was controlled by the rms deviation between the measured transmission functions and those calculated after the HNO_3 TC determination. In most cases, the rms values were 0.2–0.6%, which agreed with the signal-to-noise ratio during the solar-spectra measurements. Random errors of a single HNO_3 TC measurement did not exceed 1–1.7%, depending on the conditions of solar-radiation measurements (estimates are obtained by calculating the matrix of errors of the method of the optimal estimation realized in the SFIT program). According to the estimates presented in work [17], systematic errors caused by different factors can reach 7%.

To estimate the state of the atmosphere and the stability of operation of the instrumentation in the process of measurements, we analyzed interferograms and variations in the obtained values of the HNO_3 TC. In particular, measurements and individual days with

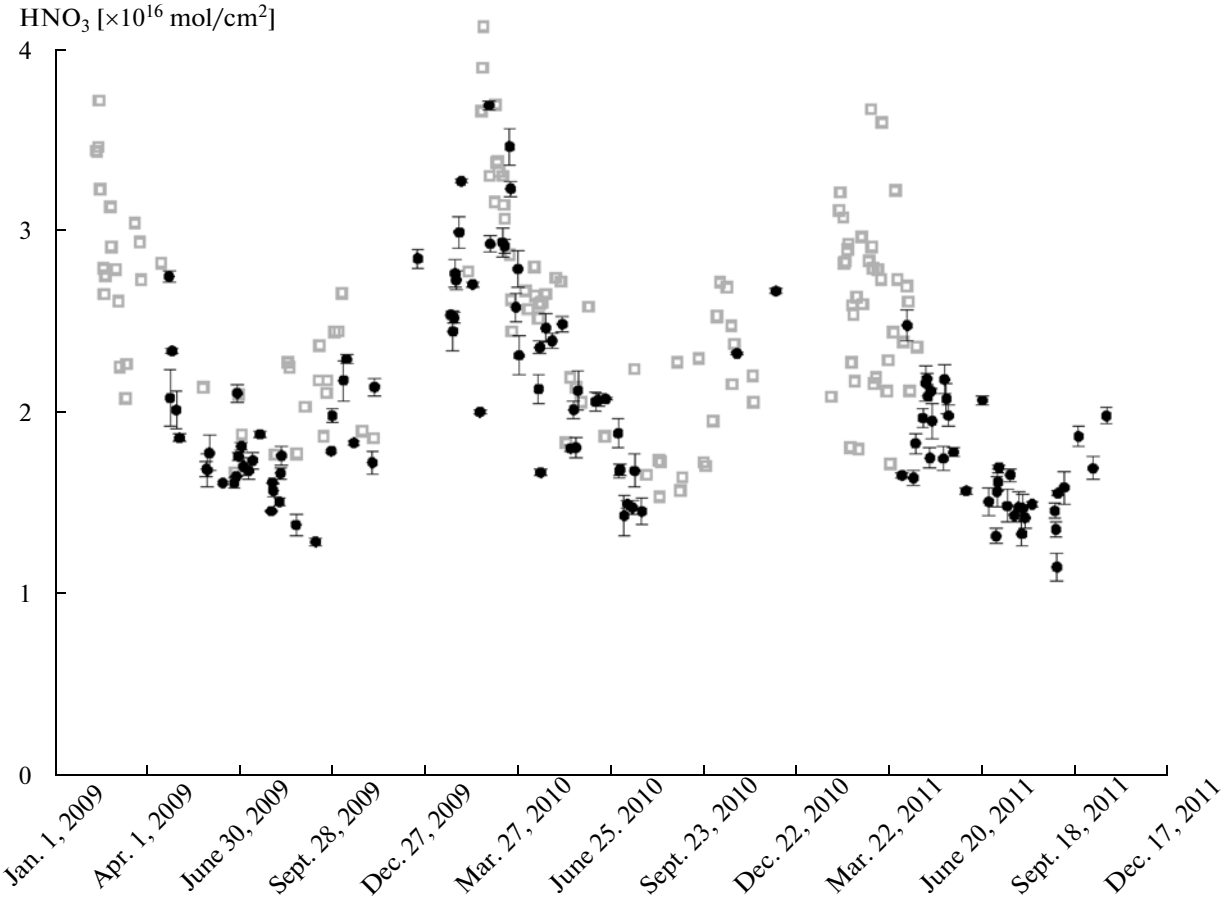

Fig. 1. Time variations in daily mean values of the HNO_3 TC: bold dots with daily variations shown as vertical bars indicate St. Petersburg State University; gray crosses show Kiruna.

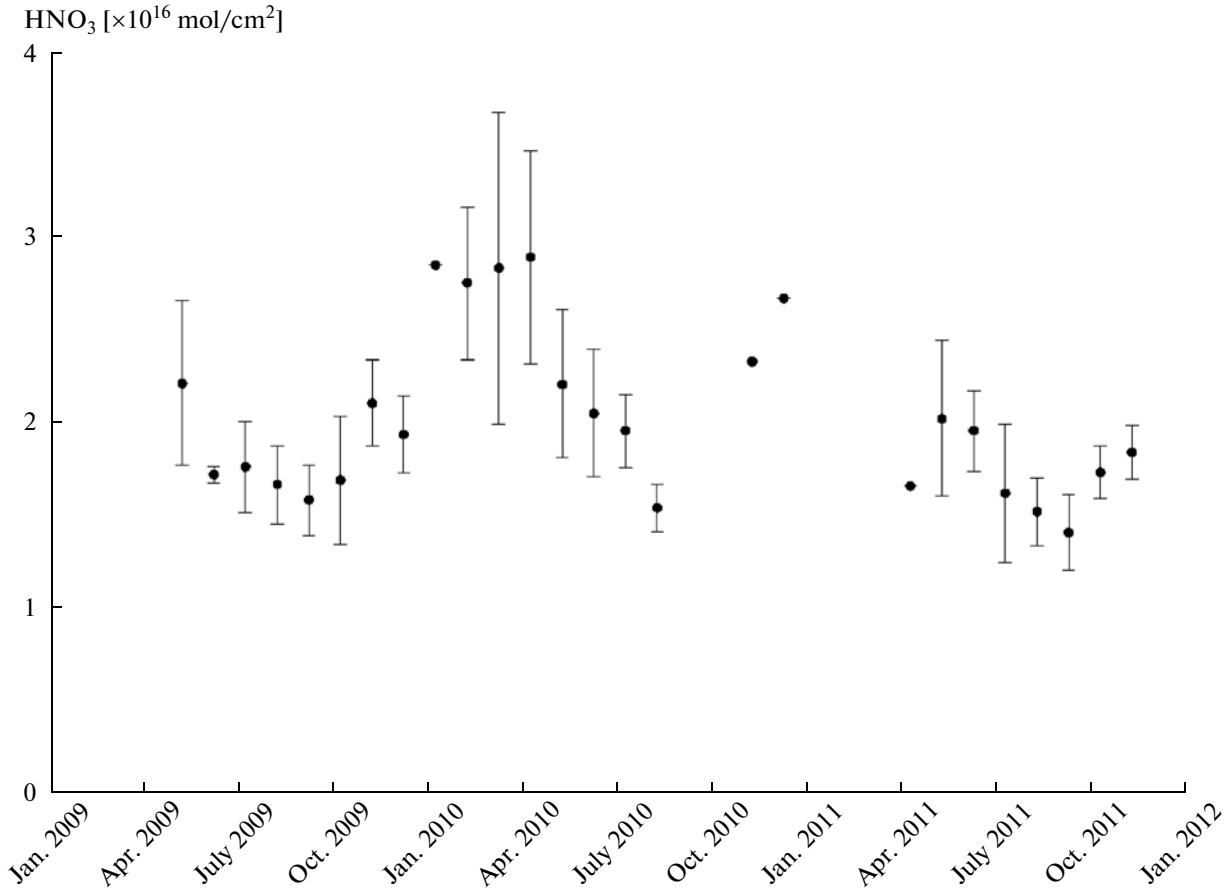

Fig. 2. Monthly mean values (dots) and variations in daily mean values of the HNO_3 TC (vertical bars).

HNO_3 TC variations exceeding 10% were excluded from analysis at this stage. Supposedly these measurements will be analyzed in the future with the invocation of additional information.

RESULTS OF MEASUREMENTS AND ANALYSIS

Figure 1 shows the temporal trend of daily mean values of the HNO_3 TC near St. Petersburg in different days of measurements, as well as daily TC variations shown by vertical bars. The absence of vertical bars means that only one measurement was conducted during that day. Daily variations in the selected set of solar-radiation spectra did not exceed 5%. In the seasonal trend of the HNO_3 TC, maximal values are observed in the winter period and minimal values are observed in summer. The maximal value of the daily mean TC (3.71×10^{16} mol/cm^2) was observed on February 24, 2010. High TC values were also observed in January 2010 (3.09×10^{16} mol/cm^2) and in March 2010 ($\sim 3.5 \times 10^{16}$ mol/cm^2). The minimal value of the daily mean TC (1.12×10^{16} mol/cm^2) was observed on August 28, 2010. Low values of daily mean TCs ($1.29-1.34 \times 10^{16}$ mol/cm^2) were observed at the end of June–July 2011. Figure 1 also shows the results of HNO_3 TC measurements at the Kiruna NDACC station (68° N, 20° E), which agree well with the measurements near St. Petersburg [18].

Figure 2 shows the monthly mean values of the HNO_3 TC, as well as daily mean variations (vertical lines) for most months of the period of observations. The absence of daily mean variations in the HNO_3 TC for some months means that the daily mean HNO_3 TC value measured in that month was a single. Figure 2 demonstrates the same seasonal features of the HNO_3 TC: maximal TC values in the winter period or early spring (for example, in March 2010) and considerable variations in the daily mean HNO_3 TC values in the same periods. Thus, in February 2010, the amplitude of variations in daily mean values was 30%. In the summer period, relative variations usually did not exceed 10–15%.

The monthly mean values and amplitudes of daily mean variations (Δ) for some months over 3 years are given in the table. Relatively large variations in the HNO_3 TC were observed in April and June 2011.

CONCLUSIONS

The results of the first ground-based spectroscopic measurements in Russia of the nitric acid TCs near St. Petersburg over the period April 2009–October 2011 are presented. The seasonal trend of the HNO_3 TC is observed with maximal values in the winter period and at the beginning of spring and with minimal values in the summer time. The minimal TC value (1.12×10^{16} mol/cm^2) was recorded on August 28, 2010, and the maximal value (3.71×10^{16} mol/cm^2) was recorded on February 24, 2010.

Substantial variations in daily mean values of the HNO_3 TC were detected in the winter and spring periods, which is probably caused by the penetration of air of the polar eddy with a high HNO_3 content into the region of observations. The seasonal variations in the HNO_3 near St. Petersburg agree well with the ground-based observations at the Kiruna station of the international NDACC network.

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