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SPECTROSCOPIC REMOTE SENSING OF NO_2 LEVELS IN URBAN AIR

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We present the instrumentation and results of spectroscopic remote sensing of atmospheric NO_2 levels based on recording spectra of visible solar radiation scattered from the zenith sky, carried out in the central part of St. Petersburg in 2009–2016. The data obtained qualitatively agree with the results of simultaneous analogous measurements in a suburb of St. Petersburg (Petrodvorets), and also with data from the closest satellite measurements.

Keywords: *nitrogen dioxide, differential spectroscopy, anthropogenic emission, spectroscopic remote sensing.*

Introduction. Nitrogen dioxide NO_2 and nitrogen monoxide NO are included in the NO_x group of nitrogen oxides, playing an important role in atmospheric chemistry, especially in the lower troposphere [1]. In industrially developed and densely populated regions, we observe elevated NO_2 concentrations due to high-temperature burning of fuel during operation of motor vehicles and various industrial plants [2]. Accordingly, the problem of air pollution by nitrogen oxides is important for all big cities with heavy vehicular traffic. High NO_2 concentrations in near-ground level air poses a direct threat to human health and environmental conditions [2, 3].

In most big cities, a network of automated stations is used to monitor urban air quality, in particular making direct measurements of near-ground level NO_2 (NO_x) concentrations. Mainly chemiluminescent gas analyzers are used for this purpose, which are complex instrumentation requiring routine calibration and technical maintenance. Furthermore, such measurements are strictly local and characterize the air pollution level at the air intake point.

Along with direct measurements, there are methods for ground-level remote sensing of the atmosphere, allowing us to determine the integrated NO_2 content in a vertical column of the troposphere. These methods are based on zenith measurements of the spectrum of scattered solar radiation in the visible range. The familiar technique of differential optical absorption spectroscopy DOAS is used in this approach [4], combined with numerical modeling of radiation transport in the atmosphere. Although such measurement methods have not been widely applied in routine monitoring of urban air basins, recently papers have appeared that are focused on practical implementation of this observational technology (see, for example, [5–9]). Compared with direct measurements, its advantages include relative simplicity and broad spatial sweep. This work demonstrates zenith DOAS measurements of the atmospheric NO_2 level using a spectral system that was periodically set up in the central part of St. Petersburg in 2009–2016.

The Experiment. We used a spectral instrumentation system and an algorithm for interpretation of the measurement data developed and previously tested in implementation of stationary [7, 10] and mobile [11, 12] observations of the tropospheric NO_2 level in the St. Petersburg district. The technique for extraction of information about the tropospheric part of the total NO_2 content in a vertical column of the atmosphere from the results of zenith DOAS measurements has been described in detail in [7, 10]. The measurements presented here were made in different seasons of 2009–2016 from the roof of the observatory building of the Earth Sciences Institute of St. Petersburg State University ("INOZ" in the following) in the central part of St. Petersburg (Vasilyevsky Island) (Fig. 1a). On the map, we also mark the station for analogous measurements at the building of the National Physics Institute of St. Petersburg State University ("NIIF" in the following) in the Petrodvorets district of St. Petersburg, made continuously since 2004.

The measurement system used (Fig. 1b) consists of a compact USB spectrometer (Ocean Optics HR4000) with a holographic diffraction grating and a multielement CCD photodetector, and also a flexible fiber-optic waveguide for recording the solar radiation scattered from the zenith sky. The entrance portion of the waveguide is fixed vertically toward the zenith;

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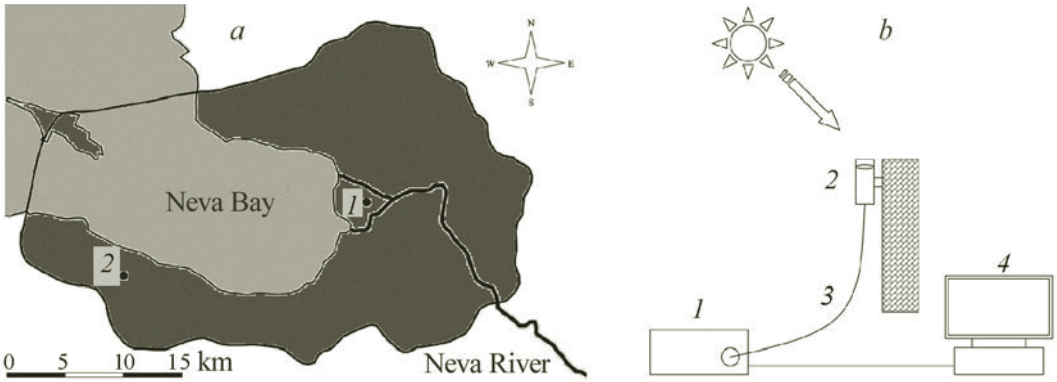

Fig. 1. Map showing the locations at which the DOAS measurements were made in St. Petersburg (a): 1) Earth Sciences Institute (INOZ) in the central part of the city, 2) Physics Research Institute (NIIF) in the Petrodvorets district. Schematic drawing of the spectral system used for the DOAS measurements (b): 1) spectrometer, 2) entrance objective, 3) fiber-optic waveguide, 4) control computer.

a lens is mounted at its end, restricting the angular field of view of the instrument within a 3^o range ($\pm 1.5^o$). The spectrometer allows for measurements of the spectra of the radiation in the interval ~400–610 nm with resolution ~0.6 nm in automatic mode according to a program in the control computer. The spectra of scattered solar radiation are continuously recorded and summed every 60 s (on the average, about 1000 spectra per minute). Correction for the dark current of the spectrometer, inherent to CCD detectors, is made based on the signal from a constantly shaded portion of the array (the first 15 pixels), taking into account the dependence of the dark current for each pixel of the array on the accumulation (exposure) time, as measured in the laboratory. We used the DOASIS software [13] to control the operation of the spectrometer and recording of the measurement data. The spectra were interpreted using the WinDOAS software [14].

Examples of the spectra for the scattered radiation are shown in Fig. 2a: a "reference" spectrum and the spectrum for one of the measurements (in arbitrary units of the readings from the analog-to-digital converter of the spectrometer). The reference spectrum, or the "extraterrestrial" analog, i.e., corresponding to minimum extinction of the solar radiation by the atmosphere, was recorded at the Physics Research Institute (NIIF) (Petrodvorets) at noon on a cloudless day with no air pollution on 15 May 2013. The measured spectra was recorded at the Earth Sciences Institute (INOZ) (St. Petersburg) on 7 July 2013. On both spectra, the solar Fraunhofer lines are quite noticeable (for example, the hydrogen absorption line at ~486 nm and the magnesium absorption line at ~517 nm), used for automatic spectral calibration taking into account shifts and compression/stretching of the CCD pixels. Fig. 2b shows the estimates obtained for the differential optical densities of NO_2 and other gaseous components (ozone O_3, water vapor H_2O, and oxygen dimer O_4) responsible for molecular absorption in the spectral interval of the NO_2 measurements (428–515 nm). Absorption by NO_2 is the most pronounced, which lets us confidently determine its effective content on the propagation path taken by the solar radiation (in this measurement, it was $(43 \pm 3)\cdot 10^{15}$ molecules/cm^2). Contributions from absorption by other components are considerably less pronounced: absorption by ozone in the long-wavelength part of the spectral interval (the Chappuis band), the O_4 band at ~477 nm and the H_2O band at ~500–515 nm (estimates of the effective levels: $(6 \pm 3)\cdot 10^{18}$, $(11 \pm 2)\cdot 10^{42}$, and $(28 \pm 8)\cdot 10^{22}$ molecules/cm^2 for ozone, O_4, and H_2O respectively).

Results and Discussion. Altogether, in different periods from 2009–2016, we recorded about 115 thousand spectra for visible solar radiation scattered from the zenith sky over a period of 456 days from the observatory building of the Earth Sciences Institute (INOZ). The average tropospheric NO_2 level measured in the INOZ area is $(8 \pm 11)\cdot 10^{15}$ molecules/cm^2, which is more than twice the average tropospheric level in the same period according to data from analogous measurements at the Physics Research Institute (NIIF), $(3 \pm 4)\cdot 10^{15}$ molecules/cm^2. It will be more appropriate to do a pairwise comparison of the data from measurements of the daily mean NO_2 level (±2 hours from local noon) made simultaneously at INOZ and NIIF. Such simultaneous observations were carried out for 370 days. The correlation coefficient between the data for these measurements was 0.48, and the measurement data at St. Petersburg (INOZ) were higher than the measurement results at Petrodvorets (NIIF) by $4\cdot 10^{15}$ molecules/cm^2 on the average. A fragment of the comparison as a time series for the daily mean tropospheric NO_2 levels in the St. Petersburg district in the period from 14 January through 5 February 2016

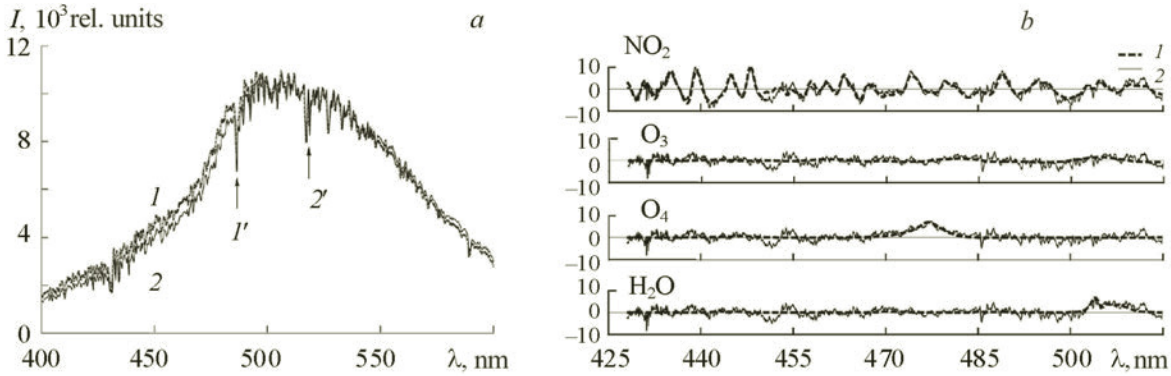

Fig. 2. Examples of spectra of scattered radiation (a): 1) reference spectrum (Physics Research Institute (NIIF), Petrodvorets, 15 May 2013), 2) spectrum for one of the measurements (Earth Sciences Institute (INOZ), St. Petersburg, 07 July 2013). The solar Fraunhofer lines are marked: hydrogen absorption line at ~486 nm (1′) and magnesium absorption line at ~517 nm (2′). b) Calculated (1) and measured (2) differential optical densities ($\times 10^{-3}$) for NO_2, ozone O_3, water vapor H_2O, and the oxygen dimer O_4.

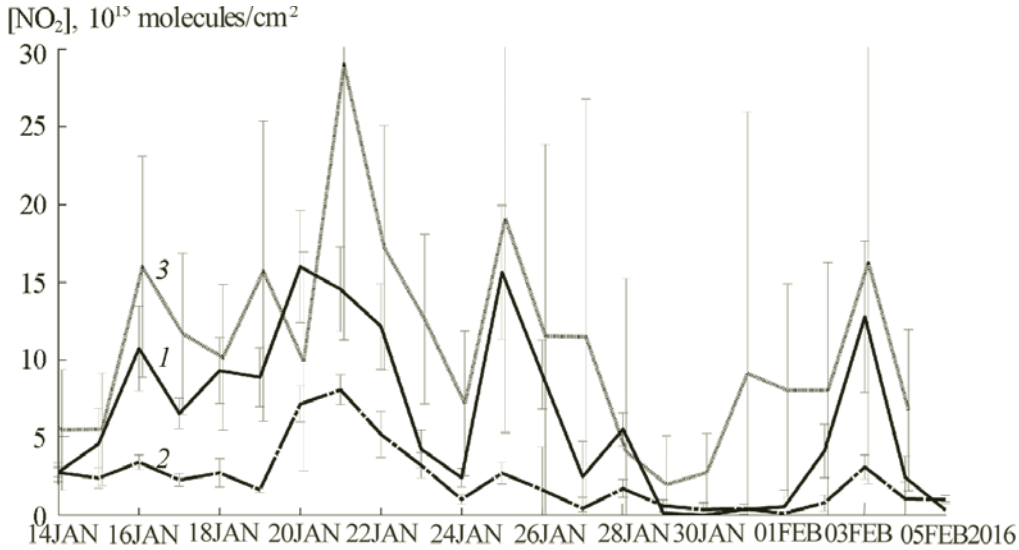

Fig. 3. Time series for daily mean tropospheric NO_2 levels in the St. Petersburg district in the period from January to February 2016: 1) Earth Sciences Institute (INOZ) ground-level measurements, 2) Physics Research Institute (NIIF) ground-level measurements, 3) OMI satellite measurements.

is shown in Fig. 3. For comparison, we show the data from simultaneous spectroscopic measurements by the OMI satellite instrumentation (Ozone Monitoring Experiment [15], AURA satellite). The OMI instrument is a nadir-viewing scanning spectrometer established in a nearly polar solar-synchronous orbit and recording reflected and scattered solar radiation with spatial resolution ~13 × 24 km^2. As in the ground-level observations, for determining the atmospheric NO_2 level from the OMI satellite data we use the DOAS spectroscopic algorithm [4] in the visible region of the spectrum (405–465 nm). The OMI data agree well with the results of simultaneous INOZ ground-level measurements, duplicating the major high NO_2 level episodes (21 January, 25 January, and 3 February), considerably less noticeable in the NIIF ground-level measurement data. We should note the high uncertainties in the satellite measurements: on the average ~100% of the measured tropospheric NO_2 level.

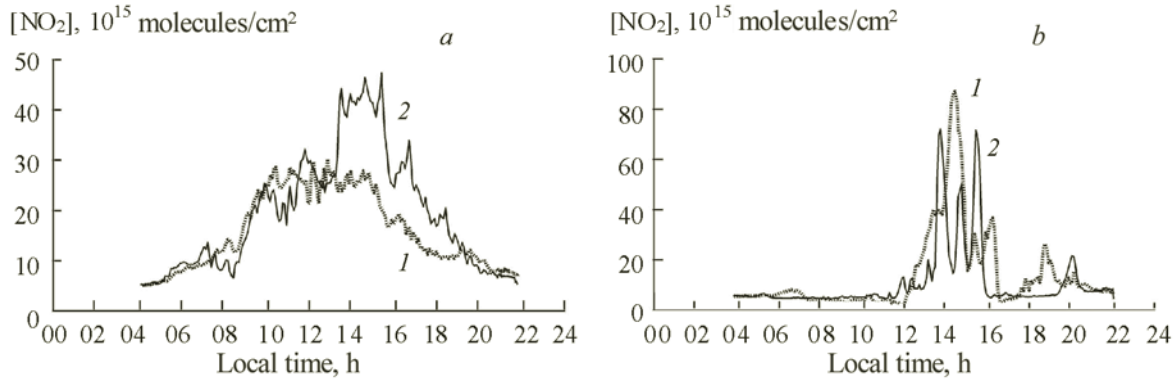

Fig. 4. Examples of daily variations in tropospheric NO_2 levels in the St. Petersburg district on 17MAY2014 (a) and 25MAY2014 (b): 1) Earth Sciences Institute (INOZ) ground-level measurements, 2) Physics Research Institute (NIIF) ground-level measurements.

Examples of daily variations in the tropospheric NO_2 level in the St. Petersburg district, simultaneously recorded in the ground-level measurements at Petrodvorets (NIIF) and St. Petersburg (INOZ), are shown in Fig. 4. For two days (17 May and 25 May 2014), we observe elevated NO_2 due to high pollution of the troposphere by nitrogen oxides (NO_x): up to (30–50)·10^{15} (17 May 2014) and up to (70–90)·10^{15} (25 May 2014) molecules/cm^2. On the first day (17 May 2014), this pollution was associated with prolonged overnight accumulation of anthropogenic air-borne impurities under windless conditions (calm during observations at midnight, 3 am, and 6 am local time [16]) and a near-ground temperature inversion (thickness ~200 m and a temperature jump of ~5^{o}C according to data from the closest radiofrequency sensing at Voeikovo [17]). On the other day (25 May 2014), we observe even higher NO_2 levels, associated with high-temperature dissociation of nitrogen molecules N_2 and oxygen molecules O_2 caused by powerful lightning discharges, followed by formation of NO and NO_2 (the storms occurred between 12:30 pm and 3:30 pm local time [16]).

Conclusions. Spectroscopic measurements of the atmospheric NO_2 level, based on analysis of molecular absorption in the spectra of visible solar radiation (428–515 nm) scattered from the zenith sky, allow us to observe variations in the NO_2 level in the near-ground layer. Using modern fiber-optic spectrometers based on multichannel CCD detectors makes it possible to use a simple scheme for completely automated all-weather measurements. This instrumentation was set up in the central part of the city of St. Petersburg to conduct periodic NO_2 measurements in the near-ground level layer of the atmosphere in 2009–2016. The data obtained qualitatively agree with the results of independent spectroscopic measurements in a suburb of St. Petersburg (Petrodvorets), and also with data from the closest satellite measurements. Further analysis of the collected information and development of this method is of interest for the problem of remote monitoring of air quality near large cities. Such observations can be used for monitoring processes of accumulation and dispersal of anthropogenic air pollution in large cities.

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