

# Evaluation of Ozone Content in Different Atmospheric Layers using Ground-Based Fourier Transform Spectrometry

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**Abstract**—For the first time in Russia, using ground-based measurements of direct solar infrared radiation, we derived data on ozone content in different layers of the atmosphere. The measurements were conducted with the help of a Bruker IFS-125HR Fourier spectrometer in 2009–2012 in Petergof, which is 30 km west of the center of St. Petersburg. The errors in determining the ozone content by this method in the troposphere (0–12 km), in the stratosphere (12–50 km), in the layers of 10–20 and 20–50 km, and in the layers of 12–18, 18–25, and 25–50 km were ~4, 3, 3–5, and 4–7% (taking into account the instrumental and methodological errors, as well as the errors in specifying the temperature profile), respectively. The seasonal variation of tropospheric ozone content in the layer of 12–18 km is characterized by a clearly expressed maximum in March and a minimum in November, with amplitudes of 30 and 40%, respectively. For the layer of 18–25 km, the maximum and minimum are reached in the winter–spring period and late summer, respectively; the amplitude of the seasonal variation is ~20%. The amplitude of the annual variation in ozone content in the layer of 25–50 km is around 30%, with a maximum close to the summer solstice and a minimum close to the winter solstice. Over the three years of observations, the growth in the ozone content in this layer was ~10% per year of its value averaged over the time period. Comparisons of ground-based measurements with satellite measurements (by the IASI instrument) of tropospheric ozone revealed a discrepancy of  $(3.4 \pm 17)\%$  for both ensembles. The correlation between the two ensembles is 0.76–0.84 (depending on the season). Comparisons between ground-based and satellite measurements (by the MLS instrument) of stratospheric ozone revealed no systematic discrepancies of the two ensembles. The rms errors were 13, 6, and 5% for the layers of 10–20, 20–50, and 10–50 km, respectively; the coefficients of correlations between the two types of measurements were 0.82–0.94.

**Keywords:** ozone, vertical structure, seasonal variation, Fourier spectrometry

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## INTRODUCTION

Ozone is the main absorber of solar ultraviolet (UV) radiation (largely controlling the UV-illumination of the Earth's surface), a key greenhouse gas, and a gas that affects the photochemistry troposphere. At certain concentrations, ozone is a strong pollutant in the troposphere and significantly affects the environment and human health. Long-term variations in ozone content due to anthropogenic factors have stimulated the continuous monitoring of ozone content in recent decades with the help of different ground-based and satellite measurement methods.

These methods include a ground-based method that has been intensively used in recent years based on the interpretation of measurements of direct solar infrared (IR) radiation spectra with high spectral resolution. The physical basis of measurements of the vertical structure of ozone is that there are substantial dif-

ferences in the altitudinal behavior of absorption coefficients at the centers and wings of Lorentz (or Voigt) spectral lines of ozone [1, 2]. At the line centers, with increasing altitude (decreasing pressure), the absorption coefficients increase, while the wings are characterized by the opposite effect. This feature makes it possible to obtain certain information about the ozone content at different altitudes in the atmosphere.

This method was pioneered in [1, 2]. Later, different methodological aspects of the ground-based IR-method were analyzed in detail in many studies [3–10]. The authors of these studies considered instrumental aspects of the remote measurement method and its informativity for different spectral “windows,” calculated the number of independent parameters of the vertical structure averaging the specific features of the remote method and the errors in determining ozone content for different vertical reso-

lutions, gave examples of comparisons with independent (including satellite and ozonesonde) measurements, investigated the long-term trends of ozone content in different layers of the atmosphere, conducted comparisons with the results of numerical simulations, etc. At present, this method is routinely used at a number of stations of the Network for the Detection of Atmospheric Composition Change (NDACC).

The present paper presents (for the first time in Russia) the results of ozone content measurements at different layers of the atmosphere (up to 4 layers) conducted with help of spectroscopic measurements of direct solar IR-radiation by a high-resolution ( $\sim 0.005 \text{ cm}^{-1}$ ) Bruker IFS-125HR Fourier spectrometer located near St. Petersburg in 2009–2012. The relevant ground-based spectral system was described in [11]. Examples of determining the total content of different gases with the help of this system can be found, for example, in [12–14]. In this paper we analyze the influence of different sources of errors on the error in the calculation of ozone content, investigate the seasonal variations in ozone content in different layers of the atmosphere, and compare the results of ground-based measurements of ozone content with satellite measurements (conducted by IASI [15] and MLS [16] instruments) in different layers of the atmosphere.

## 2. GROUND-BASED MEASUREMENTS OF OZONE CONTENT

The Bruker IFS-125HR Fourier spectrometer operating at the measurement station in Petergof ( $59.88^\circ \text{ N}$ ,  $29.82^\circ \text{ E}$ ) performs routine ground-based measurements of the spectra of direct solar IR-radiation from April 2009. In this study we interpret the IR measurements using the PROFFIT software package [17] developed at the Technological Institute of the University of Karlsruhe (Germany) and used at a number of stations of NDACC. To calculate the vertical profiles of ozone for each day of spectrometric measurements, we used the National Center for Environmental Prediction (NCEP) pressure and temperature profiles based on satellite and radiosonde measurements [18]. A priori data on the profiles of the content of ozone and other gases (the initial approximations) that affect the radiative transfer in given spectral intervals (5 microwindows in the range from 991 to  $1014 \text{ cm}^{-1}$  were used; see [19] for more details) were specified from the results of the Whole Atmosphere Community Climate Model (WACCM) [20]. To solve the inverse problem, we used an algorithm that is based on the Tikhonov–Phillips regularization method [21, 22]. The moisture content in the atmosphere was adjusted preliminarily from the same spectral data in the water-vapor absorption band, which made it possible to reduce the error caused by the uncertainty in specifying the water-vapor profiles. In addition, the microwindows chosen to calculate the

ozone content in the atmosphere are most sensitive to atmospheric ozone changes; i.e., the contribution of water vapor to the radiation in these microwindows is minimized.

To interpret the spectrometric measurements, we had preliminarily restored the vertical profile of ozone content and then integrated it to obtain the gas content in the different layers of the atmosphere. During the day, the number of measurements is from 1 to 18 spectra (typically, 5–6 spectra). To obtain an individual spectrum, we accumulated the interferograms (up to 10) over a period of 12 min, which were then averaged and converted into a spectrum [11]. This paper analyzes the results of measurements of daily-averaged values of ozone content in the atmosphere; i.e., the resulting individual measurements of each individual spectrum were averaged over a day. The measurements of solar radiation were conducted with an optical path depth of  $180 \text{ cm}^{-1}$ . The inversion was performed using spectra obtained with the Norton–Beer medium apodization function [23]; here, the spectral resolution was reduced to  $0.008 \text{ cm}^{-1}$ . The ozone content in the atmosphere was determined on the basis of 1190 spectra for 189 days of measurements in 2009–2012.

A detailed analysis of total ozone content (TOC) obtained from spectrometric measurements with a Bruker Fourier spectrometer located in St. Petersburg can be found in [19, 24]. The authors of [24] compared the TOC data obtained for the same ensemble of measurements as in this work with the results of independent measurements by an M-124 filter ozonometer and a Dobson spectrophotometer (Voikov station at Main Geophysical Observatory), as well as the Ozone Monitoring Instrument (OMI).

Analyzing the possibilities of determining the vertical structure of ozone content, we note that the ground-based measurements of the solar radiation spectra with the Bruker Fourier spectrometer make it possible to determine up to four independent parameters for the main isotope of ozone (the number of degrees of freedom is from 3.5 to 4.5, depending on the measurement day and conditions) (for example, see [3, 5, 8]). Thus, for the whole measurement period (2009–2012), we calculated the ozone content in two, three, and four layers of the atmosphere, as well as estimated its accuracy as a function of given layers. The calculation of errors in the determination of ozone content takes into account the following error sources:

- (i) instrumental (random noise of measurements, errors in the specification of instrument function, the position of the zero signal level, and the tracking system pointing accuracy);
- (ii) methodical (quality of spectroscopic data on different gases and accuracy of specifying the amplitude and spectral positioning of solar lines);
- (iii) uncertainty in specifying the measurement conditions (vertical profiles of temperature).

**Table 1.** Contribution of different sources of errors to the error in the measurement of ozone content in two layers of the atmosphere (0–12 and 12–50 km)

| Source of error               | Magnitude of error                            | Troposphere            |                       | Stratosphere           |                       |
|-------------------------------|---|------------------------|-----------------------|------------------------|-----------------------|
|                               |   | $\sigma_{\text{rand}}$ | $\sigma_{\text{sys}}$ | $\sigma_{\text{rand}}$ | $\sigma_{\text{sys}}$ |
| Shift of baseline of spectrum | 0.5%  | 0.6%                   | 0.6%                  | 0.2%                   | 0.2%                  |
| Temperature profile           | 1 K (<11km)<br>2 K (11–35 km)<br>5 K (>35 km) | 0.2%                   | 0.1%                  | 2.2%                   | 1.0%                  |
| Intensity of lines            | 2%  | –                      | 3.8%                  | –                      | 1.9%                  |
| Half-width of lines           | 5%  |                        |                       |                        |                       |
| Noise of measurements         | From residuals                                | 0.7%                   | –                     | 0.1%                   | –                     |
| Total error                   |   | 4.0%                   |                       | 3.0%                   |                       |

$\sigma_{\text{sys}}$  and  $\sigma_{\text{rand}}$  are the systematic and random errors, respectively.

For the case of two layers (troposphere and stratosphere), Table 1 lists the main errors affecting the error in the determination of ozone content. The contribution of other sources to the total error in ozone content measurements in given layers is less than 0.1%. The errors were calculated on the basis of different weights for contributions of systematic and random components. Specifically, this contribution is 50% for the errors associated with baseline line shift and 30% and 70% for errors in the specification of the temperature profile for systematic and random components, respectively. The total error in the measurement of tropospheric ozone content is around 4% and depends mainly on the systematic error associated with errors in the specification of spectroscopic data (intensities and half-widths of lines). Stratospheric ozone can be measured with an accuracy of around 3%; in this case, the total error is almost equally contributed to by the random component of error due to the uncertainty in the specification of the temperature profile and the systematic component due to errors in spectroscopic data. The random error can be reduced through independent measurements of the temperature profile (or the simultaneous determination of temperature from spectrometric measurements [25]); the systematic errors can be reduced by adjusting the parameters of spectroscopic data.

We note that the calculation of the total error ignores the errors in smoothing of profiles due to the limited vertical resolution of the method; according to different estimates, these errors range from 4% to 9% for the same spectral instruments [3–6, 9, 10]. The smoothing errors are systematic errors for each individual measurement point and can be taken into account when comparing data obtained by different instruments. The quality of measurements by a spe-

cific instrument is mainly estimated on the basis of random errors. In stable atmospheric conditions, the random error in the measurement of tropospheric ozone content in Petergof by the Bruker Fourier spectrometer is 1.0–1.3%, which coincides with the results of other studies [3–5, 9, 10].

Table 2 shows the errors in the determination of ozone content for two and three stratospheric layers; the results of ozone content measurements will be analyzed later. Here, as before, the smoothing error was ignored. It can be seen from Table 2 that the total error is determined mainly by the systematic component at altitudes of up to around 20 km and the contribution of systematic and random components to the total error is almost equal at altitudes above 20 km. In general, one can say that the error in determining the ozone content is 3–5% for two layers of the stratosphere and 4–7% for three layers of the stratosphere.

**Table 2.** Errors in measurement of ozone content in different layers of the stratosphere

| Layer    | Random | Systematic | Total |
|----------|--------|------------|-------|
| 12–18 km | 0.9%   | 3.4%       | 3.5%  |
| 18–25 km | 2.5%   | 2.4%       | 3.5%  |
| 25–50 km | 4.2%   | 5.7%       | 7.1%  |
| 10–20 km | 0.5%   | 3.1%       | 3.1%  |
| 20–50 km | 3.4%   | 3.8%       | 5.1%  |

**Table 3.** Comparison between data on tropospheric ozone measured by Bruker-IASI for the period 2009–2012

| Time period (days)            | Instrument | Mean (variability), DU | $M \pm \sigma$ , DU | Correlation coefficient $r$ |
|-------------------------------|------------|------------------------|---------------------|-----------------------------|
| Winter half-year period (41)  | Bruker     | 50.0 (9.3)             | $-6.7 \pm 9.6$      | $0.78 \pm 0.06$             |
|                               | IASI       | 56.7 (15)              |                     |                             |
| Summer half-year period (116) | Bruker     | 46.1 (7.3)             | $4.5 \pm 4.2$       | $0.84 \pm 0.03$             |
|                               | IASI       | 41.6 (7.6)             |                     |                             |
| Annual total (157)            | Bruker     | 47.1 (8.0)             | $1.6 \pm 7.8$       | $0.76 \pm 0.03$             |
|                               | IASI       | 45.6 (12)              |                     |                             |

These estimates for the error in determining the stratospheric ozone content in several layers is also very consistent with the numerical estimates obtained by other researchers using Bruker Fourier spectrometers (for example, see [4–6]).

### 3. MEASUREMENTS OF TROPOSPHERIC OZONE CONTENT

The data on ozone content in the troposphere (0–12 km) obtained from the interpretation of measurements of solar IR-radiation by a Bruker Fourier spectrometer were compared with data of satellite measurements by the Infrared Atmospheric Sounding Interferometer (IASI) [15]. The IASI instrument was located onboard the MetOp-A polar satellite and designed to measure the radiation of the Earth–atmosphere system in the thermal infrared range of the spectrum using the nadir measurement geometry. The satellite was synchronized with the Sun in such a way that the measurements at each point were conducted at around 9:30 and 21:30 local time. The measured spectra were interpreted using the LISA algorithm [26], which is based on the similar radiative code and algorithms for solving inverse problems as the PROFIT software package used for the interpreting ground-based measurements. For comparison with ground-based measurements, we used all satellite-measured profiles of ozone content within a radius of 2° centered at Petergof, which were then averaged and integrated over height. The number of averaged profiles ranged from 10 to 70, depending on the day.

The two ensembles were compared on the basis of the calculated correlation coefficient  $r$  and the following characteristics of discrepancy of ensembles:

(i) mean discrepancy:  $M = \frac{1}{N} \sum_{i=1}^N (x_i - y_i)$ ,

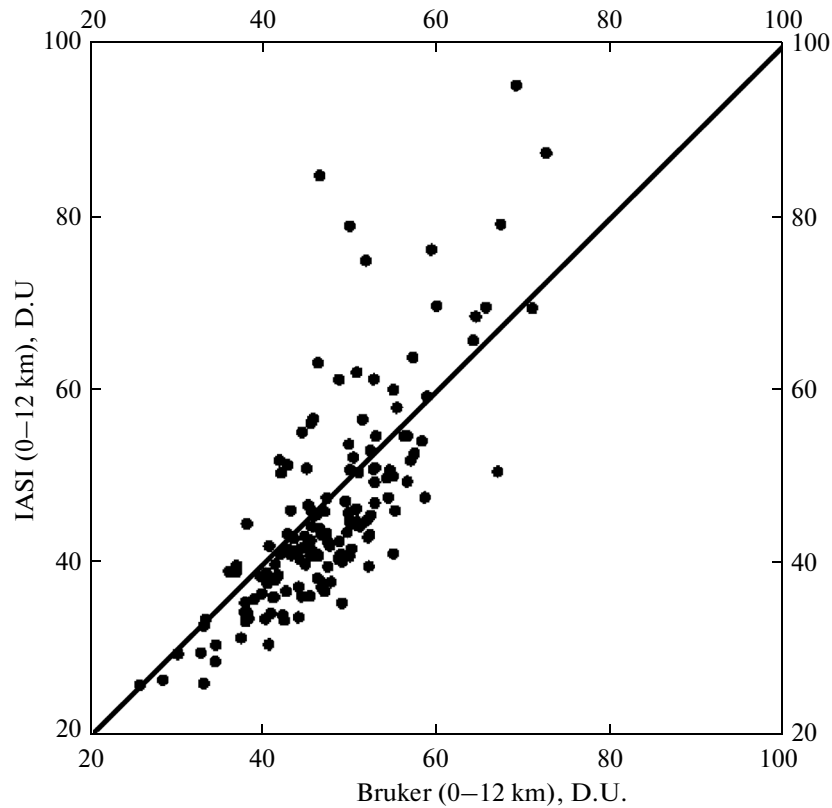
(ii) standard deviation from the mean:

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - y_i - M)^2}.$$

Table 3 shows the statistics of the comparison between the two ensembles: the mean values, variations, and characteristics of consistency of ensembles. In addition to general estimates for the whole period of observations, we also present the data separately for the winter (October–March) and summer (April–September) half-year periods. In the cold period of the year at low surface temperatures, the errors in satellite measurements of tropospheric ozone grow [26]; for ground-based measurements, the errors are also higher in the winter period due to the low sun.

It can be seen from Table 3 that, first, the variability in satellite measurement data is higher than the variability of ground-based measurement data; second, in the winter half-year period with higher values of tropospheric ozone content, the satellite data exceed ground-based measurements and in the summer half-year period with its lower values, on the contrary, the ground-based measurements exceed the satellite. A comparison of IASI data with ground-based measurements by the Observations of Atmosphere by Solar Infrared Spectroscopy (OASIS) in Paris during the summer period also revealed that ground-based measurement data on tropospheric ozone exceed satellite data [27]. The correlations between ensembles are higher during the summer time period, which is caused by both the lower variability of measurements and higher accuracy of both methods. Over the total period of measurements, the ensembles are consistent within  $(3.4 \pm 17)\%$ ; here, the error in determining tropospheric ozone is  $\sim 11\text{--}15\%$  by the IASI instrument [26, 27] and  $\sim 4\text{--}5\%$  by the Bruker Fourier spectrometer. In view of daily variations in tropospheric ozone (we considered daily-averaged measurement data) as well as the spatial discrepancy, the comparison revealed a good agreement between the two measurement ensembles.

Figure 1 shows measurement data on tropospheric ozone by two instruments for the total time period (157 points). One can clearly see the abovementioned



**Fig. 1.** Measurements of tropospheric ozone (0–12 km) by a Bruker ground-based Fourier spectrometer and IASI satellite instrument in the area of St. Petersburg in 2009–2012.

tendency: at medium and low values of tropospheric ozone content, the ground-based measurement values exceed the satellite data, and at high higher values, the satellite data exceed the ground-based measurements. However, it should be noted that the maximum difference between the two ensembles is observed in January–February, which can be caused by both the increased measurement errors in winter and differences in the compared air masses.

#### 4. MEASUREMENTS OF STRATOSPHERIC OZONE CONTENT

Stratospheric ozone is measured by a number of satellite instruments. To compare with ground-based measurement data, we used the results of measurements by the Microwave Limb Sounder (MLS) [16]. This satellite instrument determines the vertical profiles of ozone content by interpreting the microwave radiation of the Earth's horizon from dozens of measurements during the day near St. Petersburg. Specifically, the analysis of MLS instrument data indicated that, over the given time period, there were more than 7000 measurements in a circle of radius of 500 km around Petergof. In each of the coinciding days, the measured ozone vertical profiles that fall into this

range were averaged to obtain a daily profile, which then was integrated in the given atmospheric layer. The two ensembles were compared using the same characteristics as for tropospheric ozone (see the formulas in Section 3).

Table 4 shows the statistical characteristics of the two ensembles of measurements performed in 2009–2012 for the layers of 10–50, 10–20, and 20–50 km. Analyzing this table, it can be seen that all these layers are characterized by almost no systematic discrepancy between ground-based and satellite measurements. The layer of 10–50 km is characterized by similar variability of ensembles; however, when the layer is divided into two layers, the variability of ground-based measurements is slightly higher.

As a whole, the standard deviation from the mean difference is no more than 5% for the entire stratosphere, 6% for the layer of 20–50 km (with a maximum of ozone content), and 13% for the lower stratosphere (10–20 km). In view of the variability of ozone content in the lower stratosphere due to a change in the tropopause height (around 30%) and a high correlation between measurement series ( $r = 0.90$ ), it can be concluded that both ensembles are in good agreement in this high-altitude area as well.

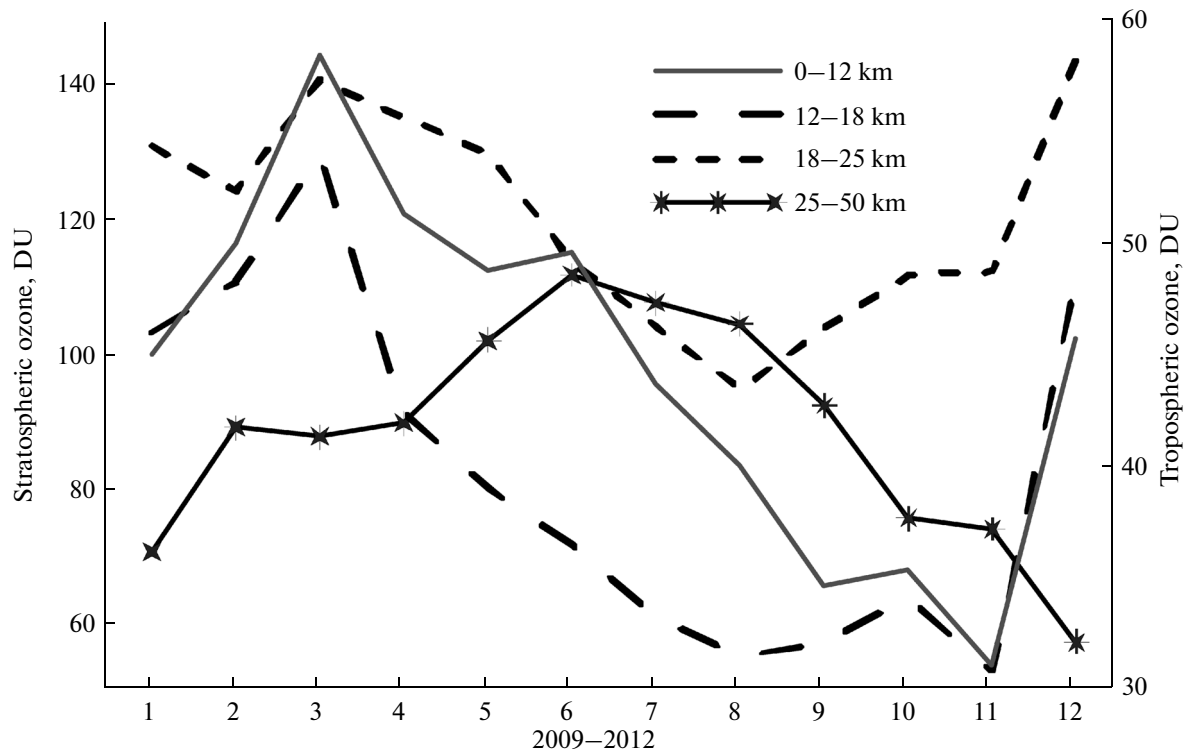


Fig. 2. Annual cycle of monthly averages of ozone content in different layers of the atmosphere in Petegof in 2009–2012.

5. TEMPORAL VARIATION IN OZONE CONTENT IN ATMOSPHERIC LAYERS

We analyze the temporal variation in TOC as well as the ozone content in four atmospheric layers (0–12, 12–18, 18–25, and 25–50 km). These layers were chosen (by our own estimates of the vertical resolution of the method [7]) from the errors obtained in that work, as well as from data provided by other researchers [3, 5, 6]. Figure 2 shows the annual cycle of monthly average values of ozone content in the four atmospheric layers. It can be clearly seen from this figure that the seasonal cycle for lower atmospheric layers (0–12 and 12–18 km) is characterized by a clearly

expressed maximum in March and a minimum in November, with amplitudes of 30 and 40%, respectively. It should be noted that the same cycle is characteristic of the TOC. This seasonal cycle is mainly caused by atmospheric dynamics, synoptic and mesoscale processes, and vertical exchange between the stratosphere and troposphere. The layer of 18–25 km, which accounts for the largest amount of ozone content in the atmosphere, is characterized by a smoother seasonal cycle with an amplitude of around 20%. The minimum of ozone content in this layer falls on late summer, when the Brewer–Dobson circulation slows down and the inflow of ozone-rich air

Table 4. Statistical characteristics of series of measurements of stratospheric ozone content by Bruker Fourier spectrometer and MLS

| Layer    | Instrument | Mean   | Variability | $M \pm \sigma$  | Correlation coefficient $r$ |
|----------|------------|--------|-------------|-----------------|-----------------------------|
| 10–50 km | Bruker     | 310 DU | 14%         | $0.1 \pm 5\%$   | $0.94 \pm 0.01$             |
|          | MLS        | 310 DU | 14%         |                 |                             |
| 10–20 km | Bruker     | 122 DU | 30%         | $-0.3 \pm 13\%$ | $0.90 \pm 0.01$             |
|          | MLS        | 122 DU | 27%         |                 |                             |
| 20–50 km | Bruker     | 188 DU | 11%         | $0.3 \pm 6\%$   | $0.82 \pm 0.02$             |
|          | MLS        | 187 DU | 9%          |                 |                             |

masses from the tropics is reduced. The maximum of ozone content in this layer falls on the winter–spring period. The seasonal cycle of ozone content at high altitudes (25–50 km) is largely affected by photochemical processes of ozone formation; therefore, here we have the opposite pattern: the maximum values are found near the summer solstice and the minimum values are found close to winter solstice. The amplitude of changes in the annual cycle of ozone content in this layer is around 30%.

Now, we turn from an analysis of the annual average course of ozone content in atmospheric layers to an analysis of changes in ozone for the entire observation time since 2009. The trends in ozone content in four atmospheric layers at several NDACC stations located in the Northern Hemisphere were analyzed in [6, 28]. The trends were evaluated over a period of 10–15 years. The most important of these results was the evaluation of positive trends in ozone content in the upper stratosphere for a number of high- and mid-latitude stations. This is explained by both a decrease in the effect of active chlorine on ozone depletion after the Montreal Protocol on the limitation of halogenated hydrocarbon emissions into the atmosphere and changes in the transport of air masses caused, for example, by the Brewer–Dobson circulation, changes in the temperature regime in polar regions, etc.

Because the measurement data obtained by the Bruker Fourier spectrometer in Petergof make it possible to determine the ozone content in the four layers, we attempted to evaluate the possible changes in these layers for 2009–2012. It should be noted that we imply merely an evaluation of possible linear changes rather than the trends due to the smallness of the time sample. To exclude the seasonal cycle of ozone content, the monthly averages for the whole measurement period were deducted from daily average values. Thus, the difference allows us to judge annual changes in ozone content regardless of its seasonal cycle. The results were analyzed by applying the linear regression approximation to the calculated differences in ozone content. The regression-model adequacy was assessed using the determination coefficient  $R^2$ , which indicates which part of the parameter variability is due to namely the equation of linear regression. The significance of regression coefficients was estimated on the basis of Student's  $t$ -test with a 95% confidence interval. As a result, the TOC and tropospheric ozone were found to experience no linear changes over the 3 years under consideration. The changes in the remaining layers are shown in Fig. 3. The bottom (12–18 km) and average (18–25 km) stratosphere is characterized by a decrease in ozone content over the period from 2009 to 2012. However, the determination coefficient here is small ( $R^2 = 0.22$  and  $0.16$ , respectively); i.e., these changes are insignificant. The upper stratosphere (25–50 km) is characterized by a significant increase in ozone content by  $33 \pm 9$  DU for 3 years, which is approximately 10% per year of its average

content for the period ( $88.5 \pm 16.5$  DU). Here, the determination coefficient  $R^2 = 0.56$ ; i.e., the changes in ozone content over this period are mostly caused by its linear increase in the layer. The NDACC stations Kiruna ( $68^\circ$  N) and Harestua ( $60^\circ$  N), which are located in the same latitudinal belt and have similar climatic conditions, are characterized by increased ozone contents in the layer of 1.5% and 3% per year, respectively [6]. On the basis of a 3-year series, we cannot draw certain general conclusions on the trends in ozone content in the St. Petersburg area, especially as we did not take into account many factors that globally affect its variability. We can only claim that the resulting linear increase in ozone content in the upper stratosphere in the St. Petersburg area from 2009 to 2012 is substantial and the Bruker Fourier spectrometer ultimately can be used to monitor the changes in the vertical structure of ozone content.

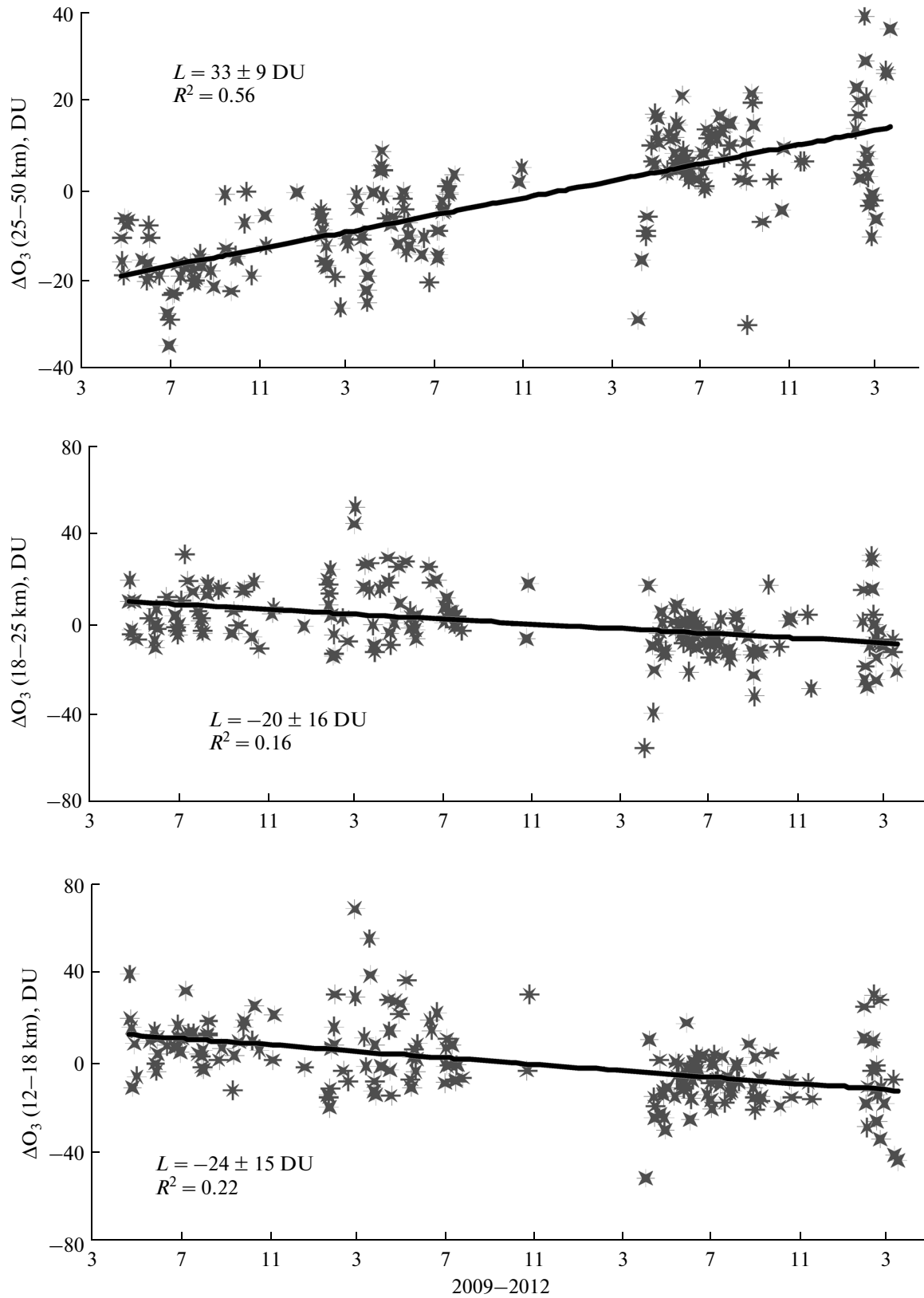
## 6. MAIN RESULTS AND CONCLUSIONS

For the first time in Russia, using ground-based measurements of direct solar infrared radiation, we derived data on ozone content in different layers of the atmosphere near St. Petersburg in 2009–2012. The numerical estimates for the error in determining ozone content in different layers of the atmosphere caused by instrumental and methodological factors, as well as by the errors in specifying the temperature profile, indicated that ozone can be determined with an accuracy of ~4% in the troposphere and 4–7% in the stratosphere, depending on the layer thickness.

The data on ozone content in different layers of the atmosphere obtained by a ground-based Bruker Fourier spectrometer were compared with independent satellite data. The comparisons between ground-based and satellite (IASI instrument) measurements of tropospheric ozone showed that the ensembles agree within  $(3.4 \pm 17)\%$  for the layer of 0–12 km. In this case, the wintertime data of satellite measurements exceed the ground-based data, and, on the contrary, the summertime ground-based data exceed satellite data.

The correlation coefficients between the two ensembles are 0.76–0.84, depending on the season. The comparisons of stratospheric ozone content obtained by the Bruker Fourier spectrometer with MLS instrument data in layers of 10–20, 20–50, and 20–50 km showed that there are no systematic discrepancies between the ensembles. The rms errors are 5–13% and the coefficients of correlation between the two types of measurements are 0.82–0.94, depending on the given layer. On the basis of these data, we can claim a good agreement between the ensembles of independent measurements of tropospheric and stratospheric ozone.

An analysis of temporal variations in TOC and ozone content in the four atmospheric layers (0–12,



**Fig. 3.** Variations in ozone content (daily averages minus monthly averages) in atmospheric layers in Petergof in 2009–2012.  $L$  is the linear change in the content over 3 years and  $R^2$  is the coefficient of determination.



12–18, 18–25, and 25–50 km) allows us to make the following conclusions.

(i) The seasonal cycle for lower atmospheric layers (0–12 and 12–18 km) is characterized by a clearly expressed maximum in March and a minimum in November, with amplitudes of 30% and 40%, respectively.

(ii) The layer of 18–25 km, which accounts for the largest amount of ozone content in the atmosphere, is characterized by a smoother seasonal cycle with an amplitude of around 20%. The minimum of ozone content in this layer falls in late summer, when the Brewer–Dobson circulation slows down and the inflow of ozone-rich air masses from the tropics is reduced. The maximum of ozone content in this layer falls on the winter–spring period.

(iii) The seasonal cycle of ozone content at higher altitudes (25–50 km) is highly affected by the photochemical processes of ozone formation; therefore, the maximum and minimum values of ozone are observed close to the summer and winter solstices, respectively. The amplitude of annual variations in the annual cycle of ozone content in this layer is around 30%.

The data analysis allowed us to reveal a significant increase in ozone content ( $33 \pm 9$  DU) for 3 years in the upper stratosphere (25–50 km). Here, the determination coefficient was  $R^2 = 0.56$ ; i.e., the changes in ozone content over this period can be assumed to be caused by its linear increase in the layer.

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