ISSN 0001-4338, Izvestiya, Atmospheric and Oceanic Physics, 2011, Vol. 47, No. 6, pp. 739–746. © Pleiades Publishing, Ltd., 2011.
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Time Variations of the Total CO Content in the Atmosphere near St. Petersburg

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Received June 2, 2010; in final form, October 13, 2010

Abstract—We analyzed measurements of the total carbon monoxide (CO) content in the atmosphere in the region of St. Petersburg (59.88°N, 29.83° E; 20 m above sea level) in the period from 1995 to 2009. The average annual behavior for the entire measurement period has a maximum in February–March and a minimum in July with an amplitude of ~20%. In the absence of strong forest fires in the European part of the Russian Federation and Siberia, the annual minimum of the total CO content is usually recorded in August–September. In winter 1995–2009 (November–January), there was a decrease in the total CO content with a gradual shift in the maximum of the annual behavior from January (1995–1999) to February (2000–2004) and March (2005–2009). The total CO content in January–February 2009 was ~20% lower than the multiyear average level. Estimates of the linear trend for the maximum, minimum, and average values for the period of 1996–2009 showed an absence of statistically significant long-term changes in the total CO content. A spectral analysis of data showed that the spectral components with periods of 12, 14, 17, 24, and 46 months are extracted with 80% confidence. It is shown that the irregular component of the time series of the total CO content (calculated for the period from May to September) agrees well with data on the areas of the forest fires and on the volume of the burnt forest and that 1999, 2001, 2005, 2007, and 2009 can be considered "background" years with the least numbers of forest fires.

Keywords: spectroscopic measurements, gas composition, the atmosphere, carbon monoxide.

DOI: 10.1134/S0001433811060090

1. INTRODUCTION

Carbon monoxide (CO) is one of the most important gas constituents, controlling the oxidation capacity of the troposphere (through its reaction with OH). CO is an index of anthropogenic air pollution and affects the ozone concentration in the troposphere [1]. In view of the important role played by carbon monoxide in tropospheric chemistry, the study of CO continues to be an urgent problem. The scientific community implements MOPITT [2], SCIAMACHY [3], and other satellite programs, each with a specific emphasis on measurements of the CO content in the troposphere. CO measurements are in progress in international networks of ground-based stations: NOAA [4] and NDACC [5]. The NOAA network conducts local gas-chromatographic measurements of near-ground concentrations of different gases such as CO. The Network for the Detection of Atmospheric Composition Change (NDACC) has been measuring the characteristics of aerosol and gas composition in the stratosphere and troposphere since 1991. It is noteworthy that NDACC network stations retrieve the total content and elements of the vertical CO distribution using high-resolution spectra recorded with Fourier spectrometers. On the territory of Russia, the Institute of Atmospheric Physics of the Russian Academy of Sciences [6], the Scientific Research Institute of Physics at the Physical Department of St. Petersburg State University [7], and the Institute of Experimental Meteorology [8] carry out spectroscopic measurements of the total CO content in the atmosphere. In 2009, the Scientific Research Institute of Physics at the Physics Department, St. Petersburg State University, initiated measurements of the atmospheric gas composition with a high-resolution Fourier spectrometer [9]. A program for the complex study of the gas and aerosol composition of the atmosphere with the help of the Transportable Observatory for Investigations and Control of the Atmosphere (TROICA) is also underway [10]. Experimental information is used to analyze the spatiotemporal CO variations in the atmosphere, as well as those reasonably assimilated by atmospheric models of different spatial scales and resolutions. A joint analysis of experimental data and simulation results helps identify the most significant factors determining the carbon monoxide variations in the atmosphere and estimate the adequacy of transport-photochemical models and their predictions.

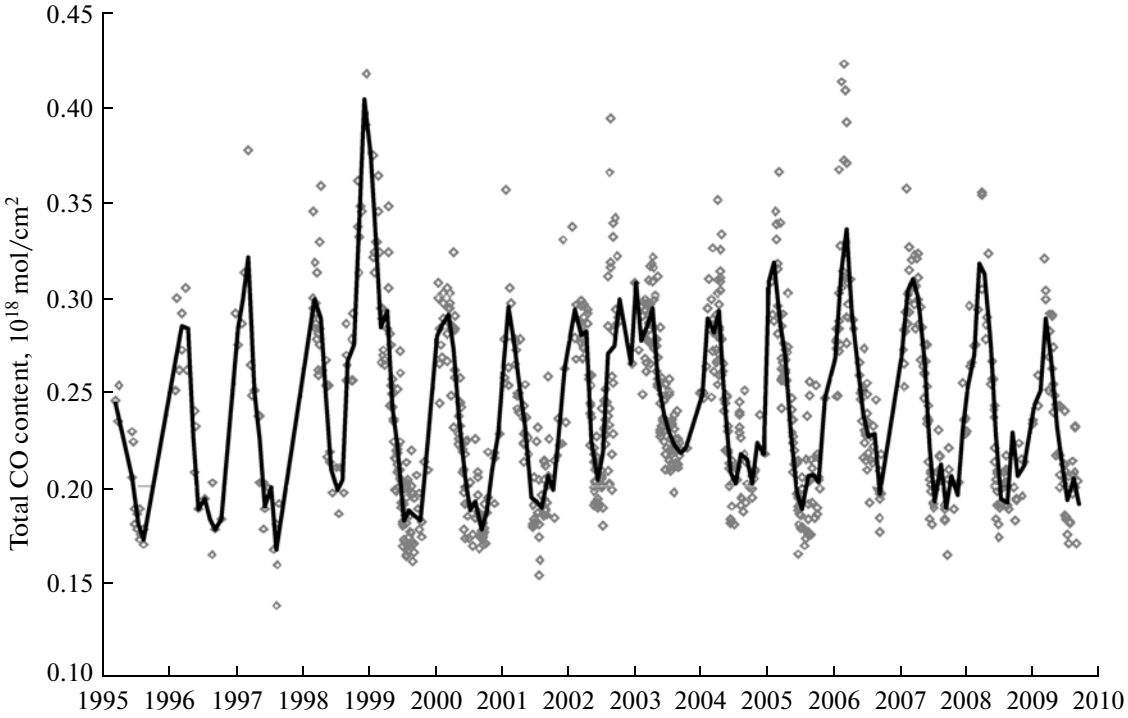

Fig. 1. The diurnally average total CO content in the region of St. Petersburg (gray diamonds) and the monthly average behavior of the total CO content (black line).

2. INSTRUMENTATION AND INTERPRETATION TECHNIQUE

Near St. Petersburg (the Peterhof site, 59.88° N, 29.83° E; 20 m ASL), the spectra of direct IR solar radiation in the CO absorption band (4.7 μm) have been measured since 1995. The spectra in the spectral interval of 2140–2180 cm^{-1} are recorded with a resolution of ~0.4–0.6 cm^{-1} with the help of a diffraction spectrometer with a photoelectric system pointing at the sun. The method of statistical regularization is used to determine the total CO content in the atmosphere from the spectra of direct solar radiation. The instrumentation and the method for interpreting the spectra are described in more detail in work [7].

3. GENERAL CHARACTERIZATION OF CO TIME SERIES

Results of total carbon monoxide measurements include about 1000 diurnally average values of the total CO content. Theses data are presented in Fig. 1; the behavior of the monthly average total CO content is also given. One specific feature of the spectroscopic measurements is their dependence on the weather conditions (clear sky or gaps in clouds are required for observations) and sunshine duration. As a consequence, there are far fewer measurements in the fall–winter period, as can be seen from Fig. 1. The diurnally average value of the total CO content was calculated as a weighted average of single measurements of the total CO content during the day. A value inversely proportional to the root-mean-square discrepancy between the measured and calculated spectra of solar radiation was used as a weighting coefficient for a particular measurement. This value is an objective estimate of the quality of the solution to the inverse problem dealing with determining the total gas content. The random error of a single measurement of the total carbon monoxide content is 4–6% [7]. The error of the diurnally average total CO content is usually 1–3%, depending on the meteorological conditions and the number of spectra recorded.

For the entire measurement period, Table 1 presents the extreme (maximum w_{max} and minimum w_{min}) total, average (w_{avr}), and median (w_{med}) CO contents; the standard deviation (σ); and skewness μa and kurtosis μe. According to 1995–2009 measurements, near St. Petersburg the diurnally average total CO content was minimum in August 1997 and maximum in August 2002 (due to forest fires). If we discard the extreme maximal values, which were obtained during measurements in plumes from forest fires in the summer of 2002, then the largest total CO content for 1995–2009, recorded in March 2006, will be 0.422×10^{19} mol/cm^2.

The total CO content frequency histogram for 1995–2009, presented in Fig. 2, illustrates the statistical characteristics of the time series (the extreme total CO contents that were recorded in periods of forest fires were also used to calculate the statistical charac-

Table 1. The statistical characteristics of the time series of the total CO content for the period of 1995–2009

w_{max}, 10^{19} mol/cm^2	w_{min}, 10^{19} mol/cm^2	w_{avr}, 10^{19} mol/cm^2	w_{med}, 10^{19} mol/cm^2	σ, 10^{19} mol/cm^2	μa	μe
0.629	0.137	0.241	0.234	0.05	1.	3.4

teristics of the time series). The vertical lines in the figures indicate w_{med} and $w_{avr,}$ which are seen to be close in value. A visual inspection of histograms reveals manifestations of multimodality, which arise due to the abovementioned features of the spectroscopic measurements (the multimodality manifestations can be avoided by dividing the entire record into seasons and by plotting the distributions for each season separately). The total CO content is minimal in the summer period; therefore, the distribution has a peak in the region of low values because of more frequent measurements in summer. The positive skewness indicates that the distributions presented in Fig. 2 are shifted toward larger values: the tail in the region of large total CO contents is a consequence of disturbances from different sources. The positive μe value signifies a sharper than normal distribution.

4. ANNUAL BEHAVIOR OF TOTAL CO CONTENT

A bulk of periodic, long-term, and irregular variations determines the time variations in the time series of the total CO content. The most pronounced periodic 12-month component primarily defines the observed annual behavior of the total CO content. It is easily seen in Fig. 1, where the monthly average total CO content is shown by a solid line. Figure 3 shows the annually averaged behavior for four periods, 1995–1999, 2000–2004, 2005–2009, and 1995–2009, thus giving a more detailed pattern of the seasonal variations in the total CO content near St. Petersburg. The annually average behavior over the entire measurement period has a maximum in February–March and a minimum in July with an amplitude of ~20%. In the absence of intense forest fires in the European part of the Russian Federation and in Siberia, the annual

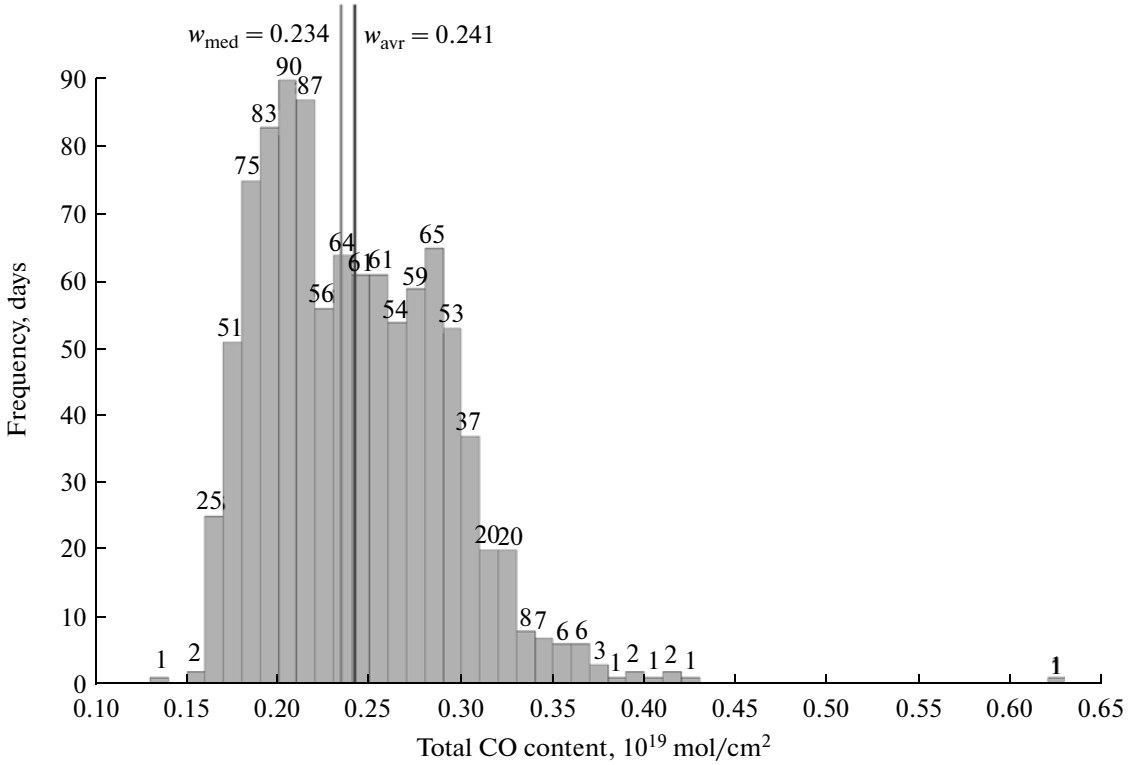

Fig. 2. Frequency histogram of the total CO content for 1995–2009.

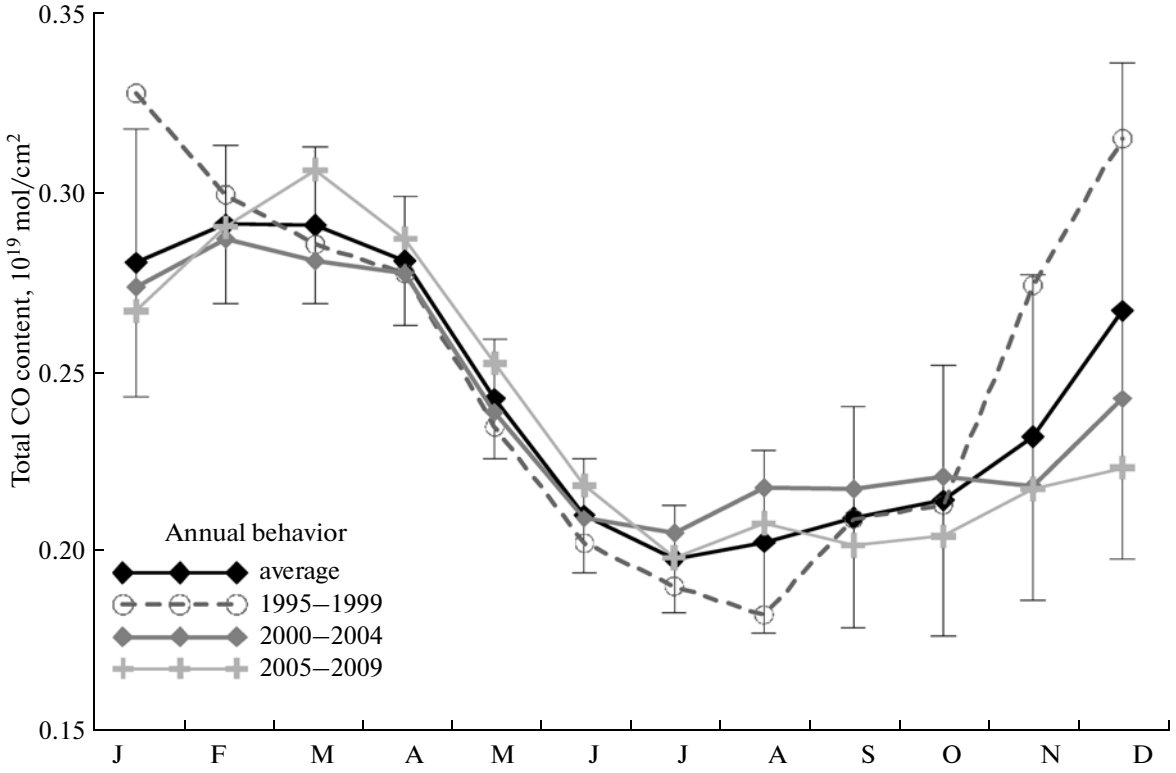

Fig. 3. Annually average behavior for three periods: 1995–2005, 1995–2007, and 1995–2009.

minimum of the total CO content shifts toward August–September, as was the case in 2000. Figure 3 gives an idea of the most marked changes in the character of the annual behavior, which occurred in 1995–2009. The error bars in Fig. 3 (STD) characterize the variations in the monthly average values over the entire observation period (1995–2009) and, together with the annual behaviors for 1995–1999, 2000–2004, and 2005–2009, they indicate the months with substantial variations. The monthly average values of the total CO content are most stable in April, May, June, and July for different years of measurements. In November–January (see Fig. 3), the total CO content tends to decrease, with the maximum of the annual behavior gradually shifting from January (1995–1999) toward February (2000–2004) and March (2005–2009). These features were most pronounced for the period from the fall of 2008 to the spring of 2009, when the March maximum of the total CO content was very sharp against the background of the preceding low total CO content from November 2008 to February 2009. The total CO content for January–February 2009 differed from the multiyear average by ~20%, with the springtime and summertime CO in 2009 being in a good agreement with the annually average behavior. This rapid decrease of the total CO content in winter of 2009 might be due to the global economic crisis, which led to a reduction in fossil fuel consumption (with associated deceases in the anthropogenic CO emissions to the atmosphere).

The observed changes in the character of the annual behavior may be due to the reduction in the fossil fuel consumed to heat buildings (in view of the gradual climate warming), the change in traffic, and the introduction of new standards regarding traffic-exhaust pollutants.

5. LONG-TERM VARIATIONS IN THE TOTAL CO CONTENT

The long-term variations in the total CO content near St. Petersburg were analyzed using extreme and average values of the total CO content for each measurement year from 1996 to 2009 (see Fig. 4). In 1995 the measurements were performed only from March to August; therefore, this year was excluded from consideration. The uppermost curve shows the absolute maxima of the total CO content (max_3) recorded for a specific year, and the curve that is a little lower shows the averages of the three highest values of the annual total CO content (min_3). We note that measurements on September 6, 2002, were performed in the plume of forest fires, and so they were not used in the analysis. Two lower curves were calculated in a similar way and reflect the behavior of the minimum values of the total CO content (max_3 and min_3) for different measure-

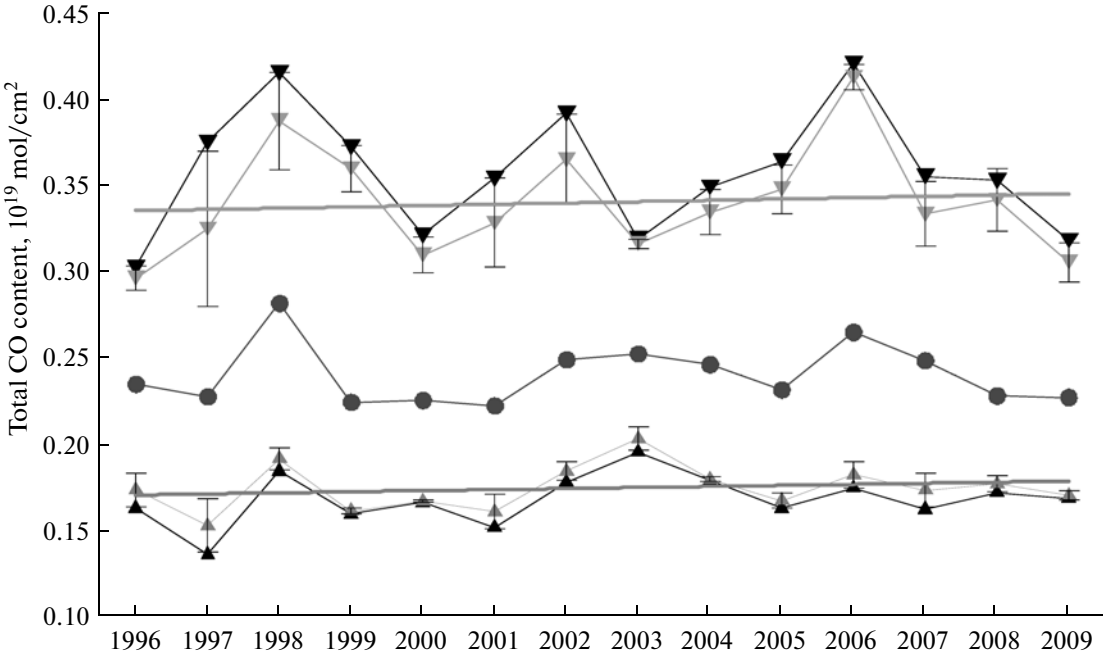

Fig. 4. The annually maximum, average, and minimum total CO contents in the period from 1996 to 2009: maximum total CO contents max and max_3 (upper curves), annually average total CO content avr (middle curves), and minimum total CO contents min and min_3 (lower curves).

ment years. Correspondingly, the middle curves show the annually average values of the total CO content (avr). The linear trend for the period of 1996–2009 was estimated using the max_3 and min_3 values, because they more reliably (with a less probability of erroneous and spurious values) reflect the levels of maximum and minimum values of the total CO content. It can be seen that the extreme values max_3 and min_3 (the boundaries of the "corridor" within which all values of the total CO content fall) exhibited insignificant growth. It is noteworthy that the minimum values describe tendencies characteristic for the background values of the total CO content (observed predominately in the summer period); the maximum values describe those for the conditions of CO accumulation in the atmosphere during the cold season (when intense anthropogenic sources have a strong effect and CO is relatively slowly destroyed). The linear trends and their determination errors for max_3, min_3, and avr were (0.2 ± 1.2)%/yr, (0.4 ± 0.8)%/yr, and (0.0 ± 2.0)%/yr, indicating that there were no statistically significant long-term changes in the total CO content. We note that the maximum values in Fig. 4 show 4-year oscillations with amplitudes of ~10–12% and with peaks in 1998, 2002, and 2006. A visual inspection of the minimum values of the total content (Fig. 4) reveals no such dependence.

6. SPECTRAL ANALYSIS OF TOTAL CO CONTENT

A spectral analysis of the total CO content was performed for time series of the monthly average values for the observation period of 1995–2009. Diurnally mean values were averaged to give average values for each month. It is noteworthy that we used an algorithm of the modified classical Fourier analysis; it is employed to study time series with nonuniform gaps [11]. The results are presented in Table 2, and the general view of the periodogram for the time series of the monthly average total CO content (St. Petersburg) is presented in Fig. 5. We identified the spectral components with periods of 12, 14, 17, 24, and 46 months with an 80% confidence probability and one harmonic with a period of 12 months with a 95% confidence probability. The annual harmonic of the total CO content is most intense and has an amplitude of ~22% of the multiyear average total CO content. The meteorological time series, as well as the time series of the total content of the atmospheric trace gases, have not only annual periodic components, but also a number of other harmonics with periods of 8, 13–15, and 18 months, as well as quasi-biennial, three- to four-year, and quasi-pentennial oscillations (among others) [12]. Thus, variations with periods of 24 months can be classified as quasi-biennial oscillations, and 46-month periodic variations can be classified as quasi-quadrennial oscillations. The long-period quasi-quadrennial oscillations (46 months or 3.8 years), whose amplitude

Table 2. Main results of the spectral analysis of the total CO content

Period, month	Amplitude in % (10^{19} mol/cm^2)
12	22 (0.053)
14	6 (0.015)
17	6 (0.014)
24	6 (0.015)
46	8 (0.019)

is 8% (next in amplitude to the annual behavior), are well discernible in Fig. 4. As was already noted above (during an analysis of long-term variations in the total CO content), this periodic component was distinctly seen in the record of maximum annual values of the total CO content with a close amplitude of 10–12%.

7. ANALYSIS OF THE IRREGULAR COMPONENT OF THE TIME SERIES OF THE TOTAL CO CONTENT

We process the time series of the total CO content to remove the annually average behavior (no long-term trend was detected in our case) by dividing the monthly average values of the total CO content by the values of the average annual behavior corresponding to this month. The obtained value (an_{CO}), which characterizes the irregular variations in the total CO content (see Fig. 6), depends on the variations in the intensity of CO sources [13]. It is well known that the main CO sources in the atmosphere are anthropogenic emissions from fossil-fuel combustion, the oxidation of atmospheric methane and hydrocarbons, and forest fires. The intensities of the two first sources do not vary significantly from one year to another [1, 13, 14]. Forest fires are the most variable CO sources: their contribution to the total global CO budget may differ by a factor of two for different years [13, 14]. Most fire-produced CO is emitted to the atmosphere in the period of late spring–early fall (the Northern Hemisphere), when anthropogenic CO sources are the most intense. On the hemispherical spatial scales, the periods of the maximal emissions of these two source types are time separated by about a half-year. Figure 6 presents the an_{CO} value averaged over May–September, burnt areas for Russia [15] and Eurasia [16], and the volume of burnt forest for Russia [15]. It is clearly seen that the four curves qualitatively agree. However, we note that the maximum in 2002, which is apparent in the average an_{CO} values, is absent in the data on the forest fires on the territory of Russia. Most probably, this was due to the effect of intense forest fires in southeastern Asia (outside Russia), with an extra contribution from regional-scale fires [15, 16, 17]. In August–September 2002, the forest fires in Leningrad, Pskov, Novgorod, and Moscow regions were located such that the total CO content was mostly measured through plumes from forest fires [17]. It is seen that an_{CO} values and areas of the forest fires agree well (the correlation coefficients are not presented in view of the small amount of data); however, it seems more correct to compare an_{CO} with the volume of burnt forest.

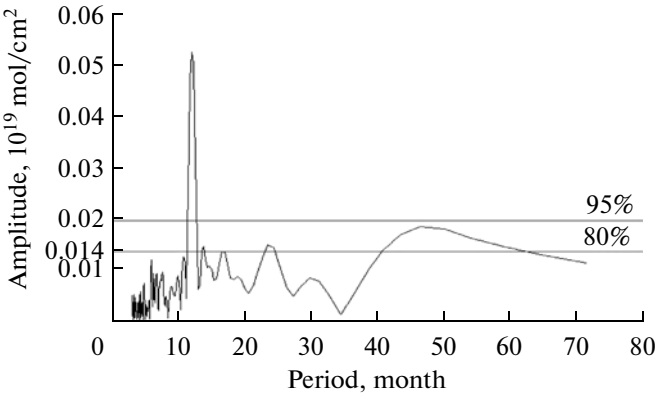

Fig. 5. General view of the periodogram of the record of the monthly average total CO content.

8. CONCLUSIONS

We analyzed the data of ground-based spectroscopic measurements of the total CO content in the atmosphere near St. Petersburg for 1995–2009. The following was found:

(1) In the period of 1995–2009, the total CO content was maximal in March 2006 (if we discard the extremely maximal values measured in plumes from forest fires in summer 2002) and reached 0.422×10^{19} mol/cm^2. The total CO content was minimal in August 1997 and reached 0.137×10^{19} mol/cm^2.

(2) The average annual behavior for the entire period of measurements has a maximum in February–March and a minimum in July, with an amplitude of ~20%. In the absence of intense forest fires in the European part of the Russian Federation and in Siberia, the annual minimum of the total CO content shifts toward August–September. For four periods, namely, 1995–1999, 2000–2004, 2005–2009, and 1995–2009, the annually average behavior shows the most stable monthly average values of the total CO content in April, May, June, and July.

(3) The total CO content tends to decrease in November–January, with the maximum of the annual behavior gradually shifting from January (1995–1999) toward February (2000–2004) and March (2005–2009). The observed changes in the character of the annual behavior may be due to less fossil fuel being consumed to heat buildings (in view of the gradual climate warming), due to change in the traffic, and due to the introduction of new standards regarding traffic-exhaust pollutants.

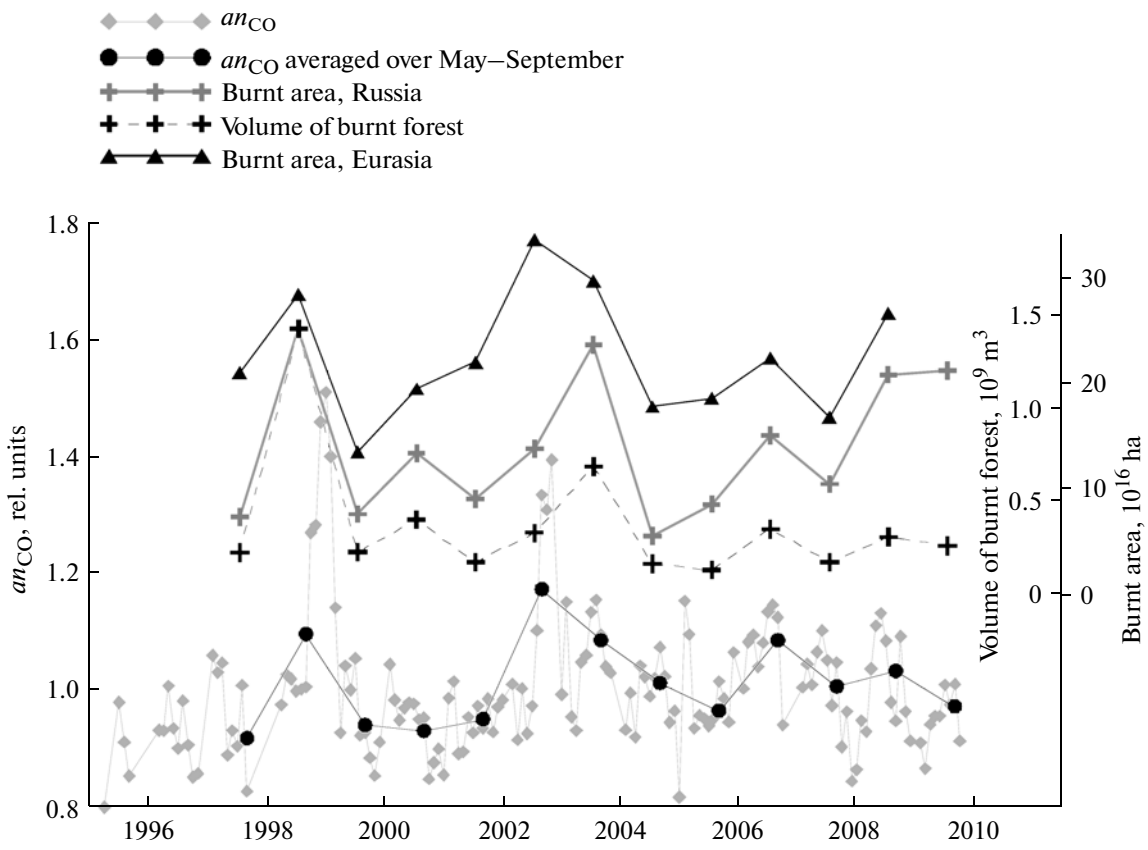

Fig. 6. Burnt areas an_{CO} (Russia and Eurasia) and volume of burnt forest (Russia).

(4) The total CO content in January–February 2009 was ~20% lower than the multiyear averages, with springtime and summertime total CO contents in 2009 being in good agreement with the annually average behavior.

(5) The linear trend of the total CO content for the period of 1996–2009 was estimated at (0.2 ± 1.2)%/yr, (0.4 ± 0.8)%/yr, and (0.0 ± 2.0)%/yr respectively for max_3, min_3, and avr values of the total CO content, indicating no statistically significant long-term variations in the total CO content.

(6) The spectral analysis of ground-based measurements of the total CO content showed that the spectral components with periods of 12, 14, 17, 24, and 46 months are identified with 80% confidence probability. The annual harmonic of the total CO content has the largest (95%) confidence probability, its amplitude being ~22% of the multiyear average total CO content. The long-period quasi-quadrennial oscillations in the total CO content (46 months or 3.8 years) are next in amplitude (~8%) to the annual behavior.

(7) The average values an_{CO} for May–September, which characterize the irregular component of the record of the total CO content, agree well with the data on the areas of the forest fires and on the volume of the burnt forest. We note that the number of forest fires and, correspondingly, the values an_{CO}, were minimal in 1999, 2001, 2005, 2007, and 20091.

ACKNOWLEDGMENTS

This work was partially supported by the Federal Target Program "Scientific and Scientific-Pedagogical Personnel of an Innovative Russia" (State Contract no. P969 as of May 27, 2010) and by the Russian Foundation for Basic Research (through grants 08-05-00857-a, RNP.2.1.1.1138, and RNP.2.2.1.1.3846).

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