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Variations in the Column-Average Dry-Air Mole Fractions of CO_2 in the Vicinity of St. Petersburg

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Abstract—The results obtained from ground-based spectroscopic measurements of column-average dry-air mole fractions of CO_2 in the atmosphere over the St. Petersburg region are given for the period April 2009–October 2011 (~900 measurement runs, 151 measurement days). These results show significant variations in the CO_2 mixing ratio in the atmosphere over the St. Petersburg region. The minimum value of this mixing ratio (373.1 ppm) was observed on April 27, 2011, and its maximum value (420.8 ppm) was observed on February 10, 2010. The typical seasonal behavior of the CO_2 mixing ratio with its summer minimum was observed in 2009. In July 2010 and 2011, the values of the CO_2 mixing ratio increased apparently due to high air temperatures. In 2010 an additional contribution to this increase in the CO_2 mixing ratio could have been made by strong natural fires.

Keywords: atmospheric composition, CO_2 mixing ratio, Fourier transform infrared spectroscopy

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INTRODUCTION

Carbon dioxide is the most important anthropogenic greenhouse gas; its concentration increase is responsible for approximately 80% of radiative perturbation in the earth's atmosphere. The combustion of fossil fuel (coal, oil, and natural gas) and motor transport are the main emissions of anthropogenic CO_2. The concentration level of its mean mixing ratio increased from 280 ppm in the preindustrial epoch to ~390 ppm in 2011 [1]. The annual growth amounted to ~2 ppm/year in 2000–2009. Note that there has been an increase in this rate of growth over the last 40 years.

The regular measurements of the CO_2 column began in 1958 at the Mauna Loa station [2]. At present the regular measurements of the CO_2 column are taken at international ground-based networks of both local and remote measurements and from on board aircrafts, ships, and satellites with different instruments (AIRS, SCIAMACHY, IASI, and GOSAT) for nadir sounding and (ATMOS, CRISTA, TES, ACE, etc.) for limb sounding.

One of the ground-based methods of measuring the total CO_2 column is the method of solar absorption spectroscopy (the spectroscopic method). This method has been used by Russian and Kirgiz scientists at the Issyk Kul station since 1980. A detailed analysis of these measurements is given in [3, 4]. Both daily and monthly means of the height-averaged relative volume concentrations of the CO_2 mixing ratio, the amplitudes of its seasonal variations, long-term trends, distribution functions, etc., are analyzed in [3, 4]. Spectroscopic measurements of the CO_2 mixing ratio are also taken at the NPO Taifun (Obninsk) [5] and were taken in Moscow and Zvenigorod [6, 7]. Data on the CO_2 column in the atmosphere over Moscow are given for a period of 35 years in [8].

MEASURING METHODS

Ground-based measurements of the IR spectra of direct solar radiation with a spectral complex based on an IFS-125HR Fourier spectrometer with a high spectral resolution have been carried out by scientists from the Faculty of Physics, Department of Atmospheric Physics, St. Petersburg State University (Staryi Petergof, approximately 35 km southwest from the center of St. Petersburg, 59.88° N, 29.83° E; 20 m above sea level) since January 2009 [9].

The total column of CO_2 (molecules/cm^2) was determined using the SFIT v3.92 software developed by the authors of [11] for the stations of the Network for the Detection of Atmospheric Composition Change (NDACC). The input data for SFIT v3.92 are the spectra of solar radiation; the standard profiles of the mixing ratios of atmospheric gases (WACCM model [12]), which are used as an initial approximation, and their a priori variations; and the pressure and temperature profile for an observation station (data

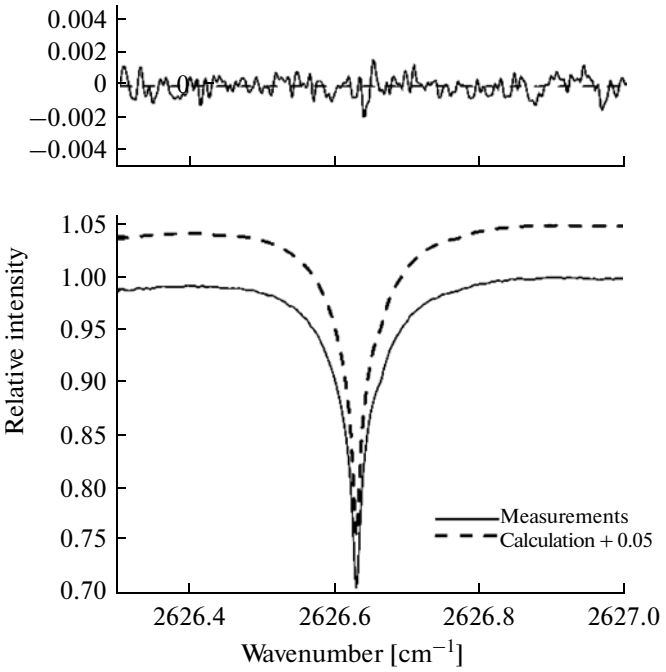

Fig. 1. Comparison between the measured and calculated (after solving the inverse problem) spectra of solar radiation within the spectral interval 2626.3–2627.0 cm^{-1}. Difference between these spectra (at the top).

obtained from radiosounding carried out by scientists from the Main Geophysical Observatory in the village of Voeikovo, about 50 km from Staryi Petergof) [13]. The a priori relative variations in the CO_2 mixing ratio were specified at 5% in the lower troposphere and 3% above the lower troposphere.

On the basis of an analysis of atlas data [10] and a numerical analysis of errors in solving the inverse problem, the spectral interval 2626.3–2627.0 cm^{-1} was chosen to determine the total column of CO_2. The HITRAN 2004 spectroscopic database [14] was used as a source of data on the parameters of the fine structure of molecular-absorption lines. The measured (May 12, 2010) and calculated (SFIT v.3.92) spectra of direct solar radiation within the interval 2626.3–2627.0 cm^{-1} are compared and the difference between these spectra is shown in Fig. 1. As a rule, the difference between these spectra did not exceed 0.2–0.4%, which is in agreement with the values of the signal-to-noise ratio (160–550 for the measured spectral region). The contents of CH_4 and HDO (their spectral lines are also present within the chosen interval) were determined simultaneously with the total column of CO_2. The random errors in a single measurement of the CO_2 column, which were obtained from calculations of the error matrix of the optimum estimation method (used in SFIT v3.92), did not exceed 1% (~4 ppm). When passing from the values of the total CO_2 column to those of column-average dry-air mole fractions of CO_2, radiosounding data were used.

The IR spectra of direct solar radiation were measured under clear skies or breaks in clouds, which were sufficient for recording an interferogram. All in all, 900 spectra were obtained from April 2009 to October 2011. During a day, several (as a rule, no more than four) series of spectra were recorded; the time interval between these series was 1.5–2 h. In this case, one series included three spectra, each of which was obtained from 10 interferograms. The stability of the CO_2 mixing-ratio values obtained for different series and inside one series served as a criterion for the stability of operating instruments and atmospheric state during a day. At this stage, we excluded some series and days of measurements with wide CO_2 mixing-ratio variations (more than 2.5%), which are to be analyzed later using additional information. Under the conditions of a stable atmospheric state, the CO_2 mixing-ratio variations within series and during a day, as a rule, did not exceed 1%.

MEASUREMENT RESULTS AND THEIR ANALYSIS

Data on the CO_2 mixing ratio were obtained throughout 151 days of measurements (45 days in 2009, 42 days in 2010, and 64 days in 2011). Figure 2 gives the daily means of the CO_2 mixing ratio and their errors (which also characterize the CO_2 variability during a day) for the entire measurement period. Thus, for the whole series under analysis, the relative daily variability ranged from 0.1 to 2.2% at its mean 0.7%.

2009. The maximum values of the CO_2 mixing ratio were observed in April (400.7–401.6 ppm) and May (398.6 ppm), and these values started to decrease in the middle of May. The relatively low mixing-ratio values ranged within 376.6–384.1 ppm from late May to early November. Significant variations (with the minimum values ~376–378 ppm) were observed in September–November 2009.

2010. Extremely high values of the CO_2 mixing ratio ~417–420 ppm in combination with its wide variations reaching 40 ppm were observed in February 2010 (the reasons for such variations will be studied later on). The values of the CO_2 mixing ratio were high (394–397 ppm) also in April–May 2010. The minimum values of the CO_2 mixing ratio for 2010 were recorded in June, and they amounted to ~387 ppm.

2011. Relatively high mixing-ratio values were observed in March–June 2011, and these values reached 398.0 ppm. Some individual cases of a rapid mixing-ratio decrease to ~373 ppm (April 27, 2011) and 375 ppm (May 2011) were also recorded. Only in August were the values of the mixing ratio below 390.0 ppm, with its minimum 384.8 ppm (August 5, 2011).

Analysis of seasonal variations in the CO_2 mixing ratio. An analysis of the monthly means of the CO_2 mixing ratio should be made only for months with no less than three days of measurements, which usually happens within the warm spring–fall period. The table

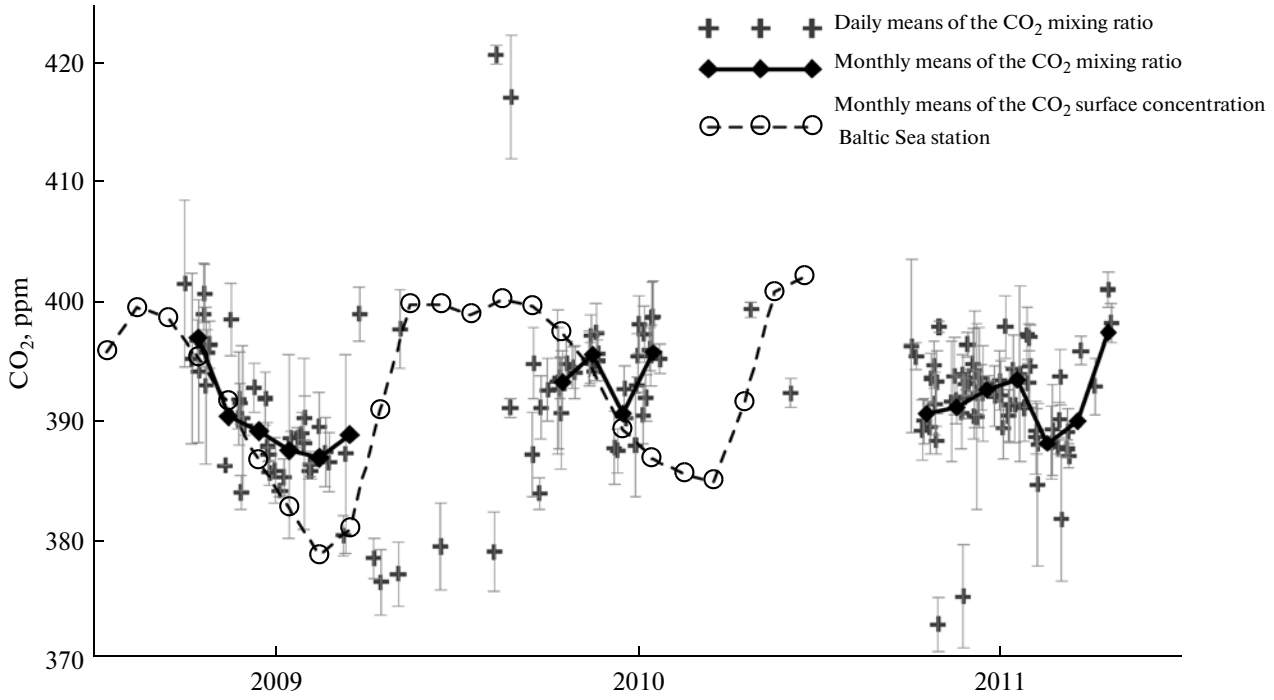

Fig. 2. Daily means of the CO_2 mixing ratio in the vicinity of St. Petersburg; comparison between the monthly means of the CO_2 mixing ratio in the vicinity of St. Petersburg and the CO_2 surface concentration for the NOAA/ESRL Baltic Sea station.

gives the monthly means of the CO_2 mixing ratio from April to September with indicated mixing-ratio variations (Δ) and number of measurements per month (N). The monthly means of the CO_2 mixing ratio (which correspond to those in table) are compared to the surface concentrations of CO_2 for the Baltic Sea station—the (closest to St. Petersburg) station of the NOAA/ESRL regional monitoring of surface CO_2 concentrations, 55.35° N, 17.22° E, 28 m above sea level—in Fig. 2 [15].

In 2009, according to our measurement results, a portion of the seasonal trend of the CO_2 mixing ratio has a characteristic CO_2 decrease from spring to summer [4, 16]. The difference between the April maximum values of the CO_2 mixing ratio and its August minimum values amounted to ~8 ppm, and this difference can be treated as an approximate estimate of the amplitude of its seasonal trend for 2009. The fragment of this seasonal trend that was obtained is in agreement with the results of similar spectroscopic CO_2 mixing-ratio measurements taken at the Issyk Kul monitoring station [4]. According to the results of long-term observations [4], in central Eurasia, maximum and minimum seasonal CO_2 mixing-ratio variations are usually observed in April and August, respectively, and the mean amplitude amounts to (8.0 ± 1.4) ppm.

A comparison of the monthly means of the CO_2 mixing ratio for the St. Petersburg region and the surface concentrations of CO_2 for the Baltic Sea station (see Fig. 2) showed that the 2009 seasonal variations obtained at both stations are of similar character. However, the amplitude of the seasonal variations in the surface concentration of CO_2 (which was calculated also for the April–October period) is approximately two times larger (~15 ppm). This result is in good agreement with the results obtained in [16],

Monthly means of the CO_2 mixing ratio

Year/month	2009	Δ	N	2010	Δ	N	2011	Δ	N
April	397.0	14.6	9	393.4	10.5	9	390.7	6.7	11
May	390.5	8.2	7	395.7	4.8	7	391.3	8.7	10
June	389.3	3.9	6	390.8	6.2	7	392.8	12.6	13
July	387.6	11.3	9	395.9	7.1	9	393.6	11.4	12
August	387.0	5.0	6	–	–	–	388.3	10.9	10
September	389.0	8.8	3	–	–	–	390.1	2.6	4

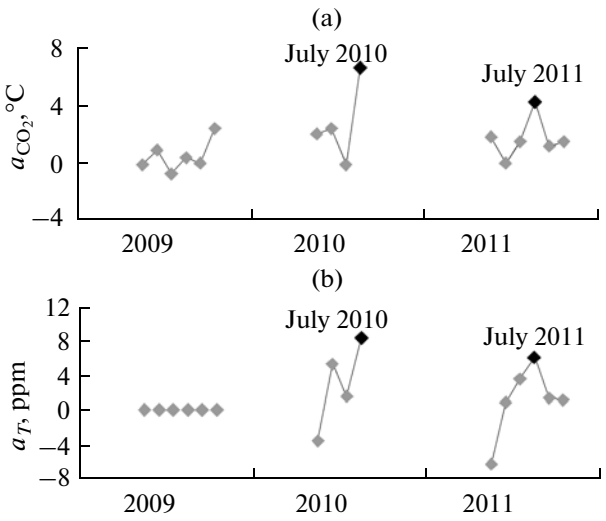

Fig. 3. (a) Monthly mean temperature anomalies (a_T) for St. Petersburg and (b) monthly mean anomalies of the CO_2 mixing ratio (a_{CO_2}) for 2010 and 2011.

where a detailed comparative analysis of the features of time variations in the mixing ratio and surface concentration of CO_2 in the atmosphere was made. In particular, for the Eurasian latitudinal belt (50°–90° N), the mean amplitudes of seasonal variations amount to 22.6 ppm (surface concentration) and 8.31 ppm (mixing ratio) [16]. It is noted also in [16] that the annual extrema for the mixing ratio are usually observed later than those for surface concentrations; moreover, this delay may range from a few days to about 7 weeks.

The lack of measurements in August and September 2010 did not allow us to obtain the characteristics of seasonal variations. Data obtained only for 4 months from April to July are available. According to measurements taken in June 2010, mixing-ratio minima were expected in July. However, this was not supported by the results of measurements taken in July: the mixing-ratio values were high ranging from 391.0 to 398.8 ppm. Thus, the difference in the monthly means between July 2010 and July 2009 amounted to 8.3 ppm. In July 2010, increased values were also observed for surface concentrations (Baltic Sea station); however, their difference between July 2010 and July 2009 was significantly smaller than that for the mixing ratio and amounted to 4.1 ppm.

In 2011 the monthly mean of the CO_2 mixing ratio was minimal in August and its seasonal increase began in September–October. In July (similarly to 2010), the monthly mean exceeded that in 2009 by 6 ppm. The July values of the CO_2 mixing ratio were high in both 2010 and 2011, probably due to very hot weather conditions which affected the cycles of the photosynthesis and breathing of plants. For our latitudes, if the air temperature is higher than optimal (20–25°C), the photosynthesis intensity rapidly decreases and the intensity of plant breathing increases simultaneously, which results in a decrease in CO_2 absorbed from the atmospheric air [17]. In fact, when comparing the monthly mean "anomalies" of the CO_2 mixing ratio for the warm periods of 2010 and 2011 (a_{CO_2}, calculated with respect to 2009) and the monthly mean temperature anomalies (a_T) for St. Petersburg [18], it is seen (Figs. 3a, 3b) that the maxima of a_{CO_2} and a_T coincide and occur in July. Thus, the July values of a_T amounted to 6.6°C for 2010 and 4.3°C for 2011 [13]. Note that such air-temperature anomalies were not observed in the summer of 2009.

In 2010, strong natural fires accompanied by emissions of a large amount of carbon-cycle gases (CO, CO_2, CH_4, and others) into the atmosphere could additionally contribute to the increase in the CO_2 mixing ratio [19, 20]. This is indirectly supported by the results of our measurements of the total column of carbon monoxide (these measurements were taken simultaneously with the measurement of the CO_2 mixing ratio), which showed that, in May–July 2010, the mean multiyear values for this period were exceeded by ~10%. Available statistical data accumulated over 20 years show that 2010 is the second in burnt-forest volume after the record year of 1998 [21]. Thus, the forest burnt in Russia amounted to 25.4×10^6, 93.1×10^6, and 28.7×10^6 m^3 in 2009, 2010, and 2011, respectively [21].

CONCLUSIONS

The results obtained from the ground-based spectroscopic measurements of the CO_2 mixing ratio in the atmosphere over the St. Petersburg region are given for the period April 2009–October 2011 (~900 measurement runs, 151 measurement days). These results show significant variations in the CO_2 mixing ratio in the atmosphere over the St. Petersburg region. The minimum value of this mixing ratio (373.1 ppm) was observed on April 27, 2011, and its maximum value (420.8 ppm) was observed on February 10, 2010. Such behavior of the CO_2 mixing ratio was probably caused by the influence of anthropogenic CO_2 sources in the megapolis (for example, for Moscow, the observed surface values of the CO_2 mixing ratio amount to ~800–900 ppm [8, 22]). The typical seasonal behavior of the CO_2 mixing ratio with its summer minimum was observed in 2009. Such minimum was almost not observed in 2010, and, in 2011, it began to show itself only in late August. In July 2010 and 2011, the observed increased values of the CO_2 mixing ratio were probably due to high air temperatures that affected the cycles of the photosynthesis and breathing of plants. In 2010 an additional contribution to the increase in the CO_2 mixing ratio could be made by strong forest fires.

The physical reasons for the anomalies in the CO_2 column will be analyzed in the subsequent publication.

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REFERENCES

1. Current data for atmospheric CO_2. http://co2now.org/Current-CO2/CO2-Now
2. Earth System Research Laboratory. http://www.esrl.noaa.gov/gmd/ccgg/insitu.html.
3. F. V. Kashin, V. N. Aref'ev, N. E. Kamenogradskii, et al., "Carbon dioxide column in the atmospheric thickness over Central Eurasia (Issyk Kul Monitoring Station)," Izv., Atmos. Ocean. Phys. **43** (4), 480–489 (2007).
4. F. V. Kashin, V. N. Aref'ev, V. K. Semenov, et al., "Structure of time variations in carbon dioxide in the atmospheric thickness over Central Eurasia (Issyk Kul Monitoring Station)," Izv., Atmos. Ocean. Phys. **44** (1), 90–99 (2008).
5. F. V. Kashin, Yu. I. Baranov, P. P. Tans, and T. J. Conway, "Studies of carbon dioxide, methane and carbon monoxide variations in the air near the ground and in the atmospheric column in the European territory of Russia (Moscow region)," in *Extended Abstracts of the Seventh International Carbon Dioxide Conference*, Boulder, Colorado, September 25–30, 2005), pp. 269–270.
6. N. S. Pugachev, "Spectroscopic measurements of carbon dioxide column in the total atmospheric column over Moscow," Izv. Akad. Nauk, Fiz. Atmos. Okeana **29** (4), 430–432 (1993).
7. N. S. Pugachev, V. I. Dianov-Klokov, and T. N. Doronina, "Measurement of CO_2 column in the total atmospheric column over Zvenigorod using the spectroscopy method," Izv. Akad. Nauk, Fiz. Atmos. Okeana **21** (7), 784–788 (1985).
8. A. I. Khlystov and B. V. Somov, "Results of 35-year studies of CO_2 column ib the Moscow atmosphere by the astrophysical method," Soln.-Zemnaya Fiz. **2** (12), 332–333 (2008).
9. A. V. Poberovskii, "High-resolution ground measurements of the IR spectra of solar radiation," Atmos. Ocean. Opt. **23** (2), 161–163 (2010).
10. A. Meier, G. C. Toon, C. P. Rinsland, et al., "Spectroscopic Atlas of Atmospheric Microwindows in the Middle InfraRed," IRF technical report No. 048 (Swedish Institute of Space Physics, Kiruna, 2004).
11. C. P. Rinsland, B. J. Nicholas, B. J. Connor, et al., "Northern and southern hemisphere ground-based infrared spectroscopic measurements of tropospheric carbon monoxide and ethane," J. Geophys. Res. **103** (D21), 28197–28218 (1998). doi 10.1029/98JD02515
12. R. R. Garcia, D. R. Marsh, D. E. Kinnison, B. A. Boville, and F. Sassi, "Simulation of secular trends in the middle atmosphere, 1950-2003," J. Geophys. Res. **112**, D09301 (2007). Doi 10.1029/2006/JD007485
13. Radiosonde station data. http://weather.uwyo.edu/upperair/sounding.html
14. The HITRAN molecular spectroscopic database. http://www.cfa.harvard.edu/hitran/
15. The World Data Centre for Greenhouse Gases (WDCGG). http://ds.data.jma.go.jp/gmd/wdcgg/index.html
16. S. C. Olsen, J. T. Randerson "Differences between surface and column atmospheric CO_2 and implications for carbon cycle research," J. Geophys. Res. **109**, D02301 (2004). doi 10.1029/2003JD003968
17. N. I. Yakushkina, *Plant Physiology* (Vlados, Moscow, 2004) [in Russian].
18. Hydrometeorological weather forecasts for past months and seasons (St.-Petersburg Center for Hydrometeorology and Environmental Monitoring). http://www.meteo.nw.ru/articles/index.php?id=2
19. N. F. Elanskii, I. I. Mokhov, I. B. Belikov, et al., "Atmospheric gas composition in Moscow in summer of 2010," Dokl. Akad. Nauk **437** (1), 90–96 (2011).
20. E. V. Fokeeva, A. N. Safronov, V. S. Rakitin, et al., "Investigation of the 2010 July–August fires impact on carbon monoxide atmospheric pollution in Moscow and its outskirts, estimating of emissions," Izv., Atmos. Ocean. Phys. **47** (6), 682–698 (2011).
21. Data on forest fires in Russia (Federal State Statistics Service). http://www.gks.ru/free_doc/new_site/business/sx/les2.htm
22. I. M. Kvashnin and I. I. Gurin, On the normalization of air exchange with respect to CO_2 column in ambient and indoor air. http://www.abok.ru/for_spec/articles.php?nid=4046)

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