

Spectroscopic Measurements of the Total Methane Content in the Atmosphere over St. Petersburg

M. V. Makarova, A. V. Poberovskii, and Yu. M. Timofeev

*Research Institute of Physics, St. Petersburg State University,
Ul'yanovskaya ul. 1, Petrodvorets, St. Petersburg, 198904 Russia*

*e-mail: pober@troll.phys.spbu.ru
e-mail: yuriy.timofeev@pobox.spbu.ru*

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Abstract—The results of the ground-based spectroscopic measurements of the total methane content in the atmosphere over St. Petersburg are given. The characteristics of seasonal cycles and the estimates of the rate of increase in the total methane content are obtained for the observation period between 1991 and 1999.

INTRODUCTION

Methane is one of the most important atmospheric gases; its quantitative variations can affect the thermal structure and chemical composition of the atmosphere [1–3]. Intense bands of methane absorption in the IR spectral region make methane the most important greenhouse gas. Methane is also important for both tropospheric and stratospheric chemistries. In the troposphere, the reactions of methane with hydroxyl and ozone are important, and, in the stratosphere, methane serves as a source of water vapor and hydrogen and as a sink of chlorine.

The methane content of the atmosphere has been increasing since the Industrial Revolution. In 1992, the global mixing ratio of CH₄ was equal to ~1714 ppbv [3]. At present, this value is close to 1800 ppbv [1]. It should be noted that a large portion of methane is emitted from anthropogenic sources: at present, their contribution is about 2/3 of the total CH₄ emission. Due to the prevalence of anthropogenic sources in the Northern Hemisphere, the surface methane concentrations in the Southern Hemisphere are 6% lower.

Measurements of the content of methane are mostly the measurements of its surface concentrations. The surface mixing ratio of CH₄ (q_0) is continuously measured at the NOAA/CMDL stations. The results of the measurements show that, in the atmosphere, the trend of q_0 was about 1.2% per year in the 1970s and 0.8% in the 1980s. According to recent estimates, the surface mixing ratio of CH₄ is 0.2% per year for 1996–1997; moreover, for the period of observations since 1940, the rate of q_0 increase was the lowest in 1996–1997 (with the exception of anomalously low values for 1992–1993) [1]. For the prediction of climate changes in the future, it is very important to know the long-term trends of methane in the earth's atmosphere and also space and time variations in atmospheric methane.

The total content (TC) of CH₄ throughout the atmosphere is measured with the aid of a spectroscopic method based on an analysis of ground-based measurements of the spectra of transmission of direct solar radiation. These measurements have been performed over a long period of time not far from Moscow at the Zvenigorod Research Station (ZRS) of the Institute of Atmospheric Physics, Russian Academy of Sciences, at the Jungfrau high-mountain station (Switzerland), and at the Kitt Peak station (United States). The most prolonged series of observations of the atmospheric methane TC are available at the ZRS, where such measurements have been taken since 1970. According to the data obtained at the Jungfrau station, the rate of increase in the CH₄ TC was 0.73% per year in the middle of the 1980s and 0.44% in 1991–1997 [1]. The data obtained at the Kitt Peak station yield the following trends: 1.1% per year for the 1979–1985 period and 1% per year for the 1979–1989 [3].

Thus, the data of different measurements show that the methane content of the atmosphere varies with time, the trend of the methane content of the atmosphere is variable and has different values for different regions of observations. It should also be noted that some differences are observed in the trends of the TC and surface concentrations of CH₄. It is also important that the results of measurements of the CH₄ TC throughout the atmosphere are less affected by local sources of methane as compared to the results of local concentration measurements. In this connection, the methane content trends determined from the results of spectroscopic measurements of the methane TC are, in our opinion, of great interest in studying the current changes in the earth's climate. In this paper, the results of measuring the CH₄ TC are analyzed, and the first estimates are given for the trends of the CH₄ TC in the vicinity of St. Petersburg.

Table 1. Results of measurements of q_0 and the CH₄ TC (w)

Date	q_0 , ppb	q_{sp}^o , ppb	q_{sp} , ppb	w^o , atm cm	w , atm cm
30.11.1998	2071 ± 7	1850	2110	1.47 ± 0.02	1.45 ± 0.02
01.12.1998	1962 ± 4	1820	2080	1.45 ± 0.02	1.44 ± 0.02
22.12.1998	1900 ± 5	1680	1920	1.34 ± 0.01	1.33 ± 0.01
02.02.1999	1968 ± 6	1790	2040	1.45 ± 0.01	1.44 ± 0.01
10.02.1999	1955 ± 3	1690	1930	1.36 ± 0.03	1.35 ± 0.03
11.02.1999	2043 ± 10	1760	2000	1.41 ± 0.03	1.40 ± 0.03
05.03.1999	1914 ± 4	1730	1980	1.37 ± 0.02	1.36 ± 0.02

METHODS OF SPECTROSCOPIC MEASUREMENTS OF THE TOTAL METHANE CONTENT

To study the time variations in CH₄, spectroscopic measurements of the CH₄ TC have been taken over St. Petersburg (59.9° N, 29.9° E, 20 m above sea level) since 1991. The IR spectra of direct solar radiation are recorded in the spectral range between 3.15 and 4.55 μm with a resolution of 0.3–1.0 cm⁻¹ with the aid of a diffraction spectrometer with a photoelectric sun guidance system [4].

The CH₄ TC is determined with the aid of the spectroscopic methods used to interpret the solar IR spectra in the spectral range between 2890 and 2910 cm⁻¹. The random errors in determining single and daily average values of the CH₄ TC are 4–6 and 1–4%, respectively [5].

The reliability of the gas TC values obtained with the aid of the spectral method was verified by comparing the total water-vapor content values retrieved from

the solar spectra and the results of radio sounding [5]. The methods used to measure the CH₄ TC and developed at the Research Institute of Physics; St. Petersburg State University; the Institute of Atmospheric Physics, Russian Academy of Sciences (Moscow); and the Institute of Experimental Meteorology (Obninsk) were intercalibrated at the ZRS in September 1997. The intercalibration results have shown that all these spectroscopic methods allow one to obtain the daily average values of the CH₄ TC that agree within the limits of errors of their determination [6].

The necessity of using an a priori (model) vertical profile of the mixing ratio is an important property of the spectroscopic methods of determining the total contents of atmospheric gases at a moderate spectral resolution. According to the estimates obtained from the numerical simulation of the experiment, the form of this vertical profile of the CH₄ mixing ratio does not introduce a significant error to the CH₄ TC values obtained [5]. However, to compare the CH₄ TC values with the results of measurements of q_0 , it is necessary to use the vertical CH₄ distribution closest to the real one, which is especially important in performing the measurements in the vicinity of large industrial centers. To this end, within a period from November 1998 to March 1999 over a seven day period in the region of Staryi Peterhof, the solar spectra were recorded simultaneously with the surface air sampling. The results of the gas chromatography of air samples and the determination of the CH₄ TC are given in the second column of Table 1.

The spectra were interpreted in accordance with the unified method of [5]; however, two different model profiles of the methane mixing ratio (Fig. 1) were used. Profile 1 corresponds to the case of a uniform distribution of methane and is characteristic of the background state of the atmosphere. Profile 2 has a gradient of the mixing ratio of methane in the lower one-kilometer layer and is characteristic of the regions with local methane sources near the earth's surface. The vertical distribution of $q(z)$ was chosen on the basis of recent data on methane distribution in the troposphere over cities [8] and the results of measurements of q_0 over St. Petersburg (Voeikov Main Geophysical Observatory).

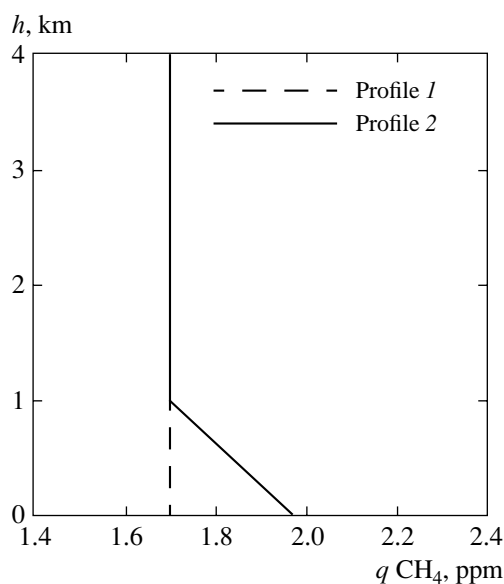


Fig. 1. Vertical methane mixing ratio distributions in the lower troposphere used in determining the CH₄ TC.

Note that, according to direct measurements, the mean value of q_0 is 1970 ± 20 ppb, which is characteristic of urban conditions [7] and significantly larger than the background values (~ 1800 ppb) obtained at the NOAA/CMDL stations for the middle latitudes [1]. A comparison between individual values of the surface CH_4 mixing ratio obtained by direct (q_0) and remote (q_{sp}^0) measurements with the use of the model profile *I* shows that there are significant systematic differences between the results of the two types of measurements (the second and third columns of Table 1). In every case, the spectroscopic values of q_{sp}^0 are systematically smaller than the values of q_0 . Such disagreement averaged over seven cases of comparisons is about 10%, which is certain to be greater than the total errors of the two methods of measurements.

In interpreting the transmission spectra, the use of the model profile 2 (the nonuniform profile of the methane mixing ratio) allows one to obtain a significantly better agreement between the results of the direct (q_0) and spectroscopic (q_{sp}) measurements of the surface methane mixing ratio (the fourth column in Table 1). In this case, the mean deviation is 1.5%. Thus, the use of the model nonuniform profile of CH_4 allows one to obtain a better agreement between the direct and spectroscopic measurements of q_0 . This indirectly confirms the presence of the mixing ratio gradients in the region under study and also the adequacy of the chosen model profile. As noted above, the effect of the type of the model methane profile on the CH_4 TC value obtained with the spectroscopic method is insignificant. This is clearly demonstrated by the data in Table 1. The differences between the CH_4 TC values for the two model profiles are within the errors of spectroscopic measurements [5]. In this case, it should be noted that, when the model nonuniform profile is used, the CH_4 TC values are systematically lower than the corresponding values obtained with the uniform profile.

ANALYSIS OF TOTAL METHANE CONTENT MEASUREMENTS

On the basis of the results obtained above, the CH_4 TC was determined from the whole set of the IR solar radiation spectra obtained in 1991–1999 with the use of the chosen type of the vertical CH_4 profile. In this case, a number of the CH_4 TC values were corrected because of random errors made in processing the experimental data. Figure 2 gives the daily average CH_4 TC values calculated as weighted average values from single measurements of the CH_4 TC during the day. The quantity inversely proportional to the rms difference between the measured and calculated spectra of solar radiation transmission, which is an objective estimate of the quality of the inverse problem solution, was used as a weight of an individual measurement.

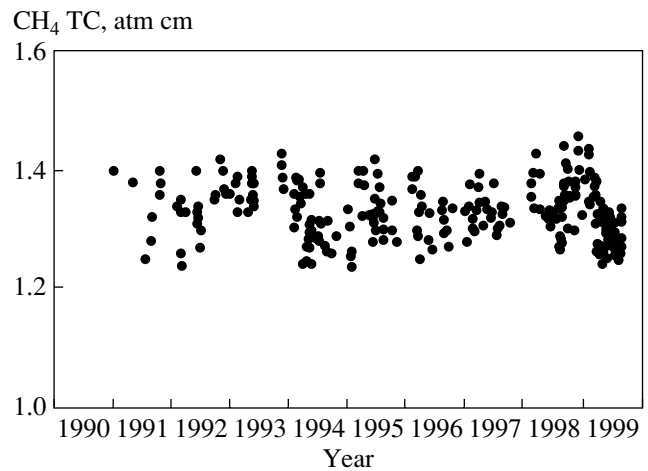


Fig. 2. Daily average values of the CH_4 TC.

An analysis of the data obtained from the measurements of the CH_4 TC over St. Petersburg shows that the minimum daily average value (1.24 atm cm) was observed in March 1992, the maximum value (1.46 atm cm) was observed in November 1998; the average CH_4 TC for the whole period of observations was 1.32 atm cm.

Time variations of the CH_4 TC, which contain cyclic seasonal and long-term variations and also irregular variations, are determined by the time behavior of different (natural and anthropogenic) sources and sinks of CH_4 . To characterize CH_4 TC seasonal variations, Fig. 3a is given, which shows the mean annual cycle (d) for the whole observation period. The values of d are the CH_4 TC deviations from its mean in percent. The interannual variability of the CH_4 TC seasonal cycle is characterized by the rms deviations of the values of d (s_d) given in Fig. 3. The values of s_d for St. Petersburg are smaller for the March–August period than for the fall–winter period (with the exception of December). This may be due to a small number of observation days within the fall–winter period and also due to a higher variability of the CH_4 TC during this period (through an increased intensity of anthropogenic sources in fall and winter). In December, the number of measurement runs is small; however, all the measured values of the CH_4 TC are close to one another.

The average annual cycle of the CH_4 TC obtained for 1991–1999 is characterized by maximum values in November–January and minimum values in June–August. An analysis of the results of our measurements during the 1991–1993 period shows that there are two minima (in February–March and July–August) and two maxima (in May and November–December) in the annual CH_4 TC cycle [4]. Such difference in the character of the seasonal cycle can be explained by a natural variability of the intensity of CH_4 sources and sinks from year to year, which affects the amount of methane in the atmosphere. As an additional example, we can

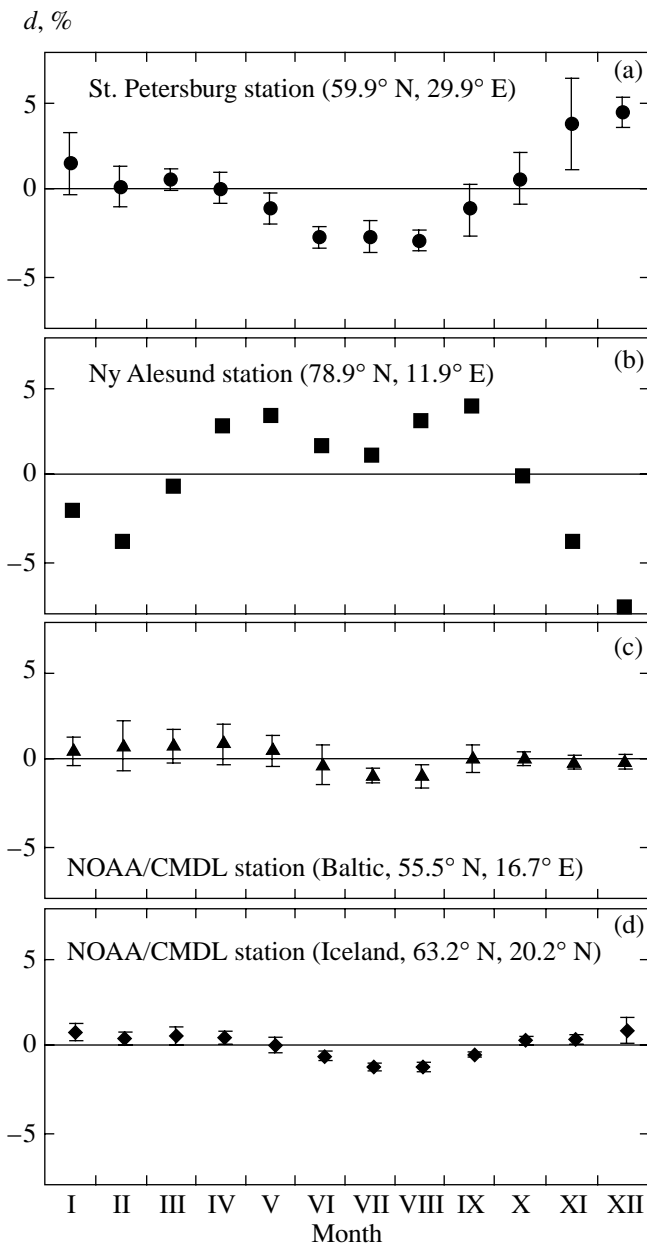


Fig. 3. Annual cycle of atmospheric methane for St. Petersburg (a), the Ny Alesund station (b), and for the two NOAA/CMDL stations (c, d).

use the dry and hot summer of 1999 with stably low values of the CH_4 TC. A decrease of CH_4 emission due to the drying of waterlogged grounds (powerful natural sources of methane in the northwestern region) could be the reason of the low CH_4 TC values observed.

Seasonal variations in q_0 for two NOAA/CMDL stations nearest in latitude (Figs. 3c, 3d) where the mea-

surements of q_0 CH_4 are performed have similar properties of seasonal variations in atmospheric methane [7]. In this case, the amplitudes of the CH_4 TC annual cycle for St. Petersburg are about 4%, while, for the surface mixing ratios obtained at the NOAA/CMDL stations, they do not exceed 2% [9]. The CH_4 TC annual cycle obtained by us can be explained by the seasonal cycles of atmospheric OH concentration [10] and also by a high intensity of anthropogenic sources in late fall and winter. The spectroscopic measurements taken at the Kitt Peak station (32° N, 112° W) did not show seasonal variations in the CH_4 TC [11]. The Kitt Peak Observatory is located at a height of 2.1 km above sea level, and its conditions can be likely considered the background conditions, because the most disturbed and saturated (with methane) atmospheric layer does not contribute to the results of the CH_4 TC measurements.

An analysis of the results of the spectroscopic methane measurements taken at the ZRS (55.4° N, 36.5° E, 200 m above sea level) also did not reveal the CH_4 TC annual cycle [12]. Since, at the NOAA/CMDL stations, the measurements of q_0 are taken in the atmospheric surface layer, one can suppose that, in our case, it is the lower tropospheric layers that mostly determine seasonal variations in the CH_4 TC. On the other hand, Fig. 3b gives an example of reverse seasonal variations (with an amplitude of about 6%) obtained from the results of CH_4 TC measurements taken at the Ny Alesund station (78.9° N, 11.9° E) at Spitsbergen for the Arctic near-polar region [13]. The authors of this paper relate such seasonal variations to the properties of the winter atmospheric circulation in the polar regions. Note that, at the Ny Alesund station, in addition to a deep winter minimum, a decrease in the CH_4 TC is observed in June–July, which appears to correspond to a summer increase in the concentration of the radical of hydroxyl in the atmosphere. One can see that, according to the results of the spectroscopic measurements, the CH_4 TC seasonal variations may have a different character depending on the observation site. On the contrary, the measurements of q_0 taken at the NOAA/CMDL stations show that its seasonal variations, on average, have the same properties for the whole Northern Hemisphere [9]. The relationship between the CH_4 TC variability and the geographical location of the observation site (in particular, its geographical latitude) is studied only in a general way; the dependence on local conditions is of a local character. Therefore, in comparing the results of the long-term CH_4 TC measurements taken at different stations, even though with the instruments of the same type and with the same methods, the agreement of such results must be additionally substantiated. Such sub-

Table 2. Estimates of the rate of increase in the CH_4 TC

	February	March	April	May	June	July	August
r , % per year	1.0 ± 0.8	0.4 ± 0.9	0.02 ± 0.9	-0.1 ± 0.8	0.03 ± 0.7	0.5 ± 1.0	0.3 ± 0.8

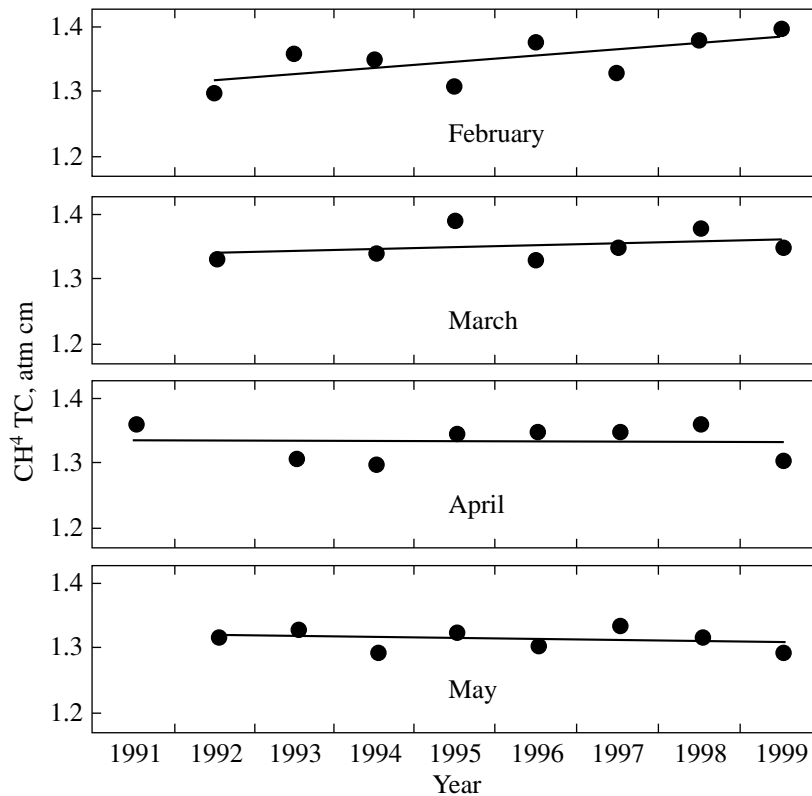


Fig. 4. Monthly average values of the CH₄ TC.

stantiation is much more important when different methods and instruments are used.

To estimate possible long-term changes in the CH₄ TC during the period 1991–1999, the monthly average values of CH₄ TC (w_m) for the months with the maximum number of measurement runs were used. The values of w_m were calculated from the daily average values, with the weights proportional to the number of single measurements taken during that day (see Fig. 4). The rate of increase in the CH₄ TC for each month was estimated with the aid of linear regression (with the weights proportional to the number of measurements taken during each month). These results are given in Table 2.

As seen from Fig. 4, the variations in w_m are different for different months, and the interannual variability of the monthly average values of the CH₄ TC is observed. Thus, in 1997–1999, the monthly average values of the CH₄ TC decrease in April–August and increase in February–March. It is seen from the given values of r that the February value is reliable, and the rest of the values are considered as estimates.

A comparison of the r values with the seasonal variations shows that the largest values of r fall on the months when the CH₄ TC is relatively stable (February–March and July–August).

CONCLUSIONS

An analysis of the results of simultaneous direct and spectroscopic measurements of the surface values of methane mixing ratios shows that there are noticeable systematic differences between the two types of measurements when the uniform tropospheric model CH₄ profile is used in the spectroscopic method. In this case, the spectroscopic estimates of q_0 are systematically lower than the results of direct measurements. The use of the model profile of the CH₄ mixing ratio with the gradient in the lower one-kilometer layer (which is characteristic of the regions subjected to the influence of anthropogenic sources of CH₄ [8]) allows one to obtain a significantly better agreement between the results of the direct and spectroscopic measurements. Thus, the mean deviation has an almost sevenfold decrease and is about 1.5%.

The annual variations in the CH₄ TC for St. Petersburg have been analyzed. In the CH₄ TC annual cycle, the minimum values fall within June–August and the maximum values fall within November–January, which is similar to the seasonal variations in the surface mixing ratio observed at the NOAA/CMDL stations. The amplitude of the seasonal variations in the CH₄ TC is ~4% of its annual average value. A comparison with the data obtained from the CH₄ TC spectroscopic measurements taken at the Zvenigorod Research Station of the

Institute of Atmospheric Physics, Russian Academy of Sciences (55.4° N, 36.5° E), the Ny Alesund station (78.9° N, 11.9° E), and the Kitt Peak station (32° N, 112° W) shows that the character of the CH₄ TC annual cycle is different for the four stations. The amplitudes of the CH₄ TC seasonal variations obtained for St. Petersburg and the Ny Alesund station are significantly higher than the analogous amplitudes of the mixing ratios obtained for the NOAA/CMDL stations. Thus, the observed properties of the CH₄ TC seasonal variations depend on the geographical location of the measurement site and also on the conditions and methods of measurements.

The estimates of the rate of increase in the CH₄ TC obtained for different months from February to August on the basis of the 1991–1999 data are statistically significant only for February ($1.0 \pm 0.8\%$ per year). For the rest of the months (with the exception of May) the values of r are positive; however, they are within the limits of errors in their determination.

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