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Study of the Formation of the Methane Field in the Atmosphere over Northwestern Russia

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Abstract—Major processes of generation of the methane field in the atmosphere over northwestern Russia have been studied on the basis of measured surface concentration and total content of methane in the environs of St. Petersburg, air-mass trajectories, and a three-dimensional regional pollution transport model. It is shown that the contribution of methane emission from an industrial center to the total column amount of methane is no more than 2% of its average value. At the same time, because of this emission, the surface methane concentration in the environs of St. Petersburg varies by as much as 50%. The origin of air masses arriving at the site of measurements influences both the total content and the surface concentration of methane. The air masses that passed over the continental part of western and eastern Europe are characterized by the values of total content and surface concentration of methane that are about 4% higher than those in the air masses formed over the ocean, which come to the region from the northwest. The regional transport model for greenhouse gases satisfactorily describes the results of surface measurements and adequately simulates observed tendencies in the change of total methane content. An estimate of the integral emission of methane into the atmosphere from St. Petersburg and its industrial suburbs is about 100 kt per year.

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INTRODUCTION

One of the main problems in the prediction of possible climate changes is a correct consideration of the spatiotemporal variability of greenhouse and chemically active gases in numerical atmospheric models. This is impossible to carry out without reliable data on the strength of regional sources, gas concentrations, and seasonal and long-term variations of these parameters. Measurements of atmospheric gases, along with three-dimensional regional transport models, provide an opportunity to estimate greenhouse gas emissions from man-made and natural sources, determine the contribution of regional and transboundary air-mass transport, detect the annual cycle of emission, and assess the influence of sources on the gas concentration fields. Such an approach is efficiently used to examine trace gases having a long lifetime, in particular, methane [1].

The goal of this study was to examine the key factors responsible for the formation of the methane field in the atmosphere over northwestern Russia. The study was based on analysis of measurement results [2–4], air-mass trajectories [5], and numerical modeling of the methane concentration fields [1].

Results of gas-chromatographic measurements of surface methane concentrations and spectroscopic measurements of the total methane content (hereinafter, TM) have been used. These measurements provide various characteristics of the gas content in the atmosphere. The use of model simulations for analysis of measurement results makes it possible to examine changes in TM and atmospheric methane concentrations at a qualitatively new level [1, 6]. The field of methane content is simulated using a three-dimensional regional tropospheric transport model of high spatial resolution [1]. Back trajectories of the air masses are calculated using the NOAA ARL HYSPLIT model [5].

The development and evaluation of the latest systems of satellite measurements of trace gases [7] determine the importance of the approach proposed in this paper, because the organization of subsatellite spectroscopic and surface measurements with assimilation of their results into the numerical model makes it possible to qualitatively improve the validation of

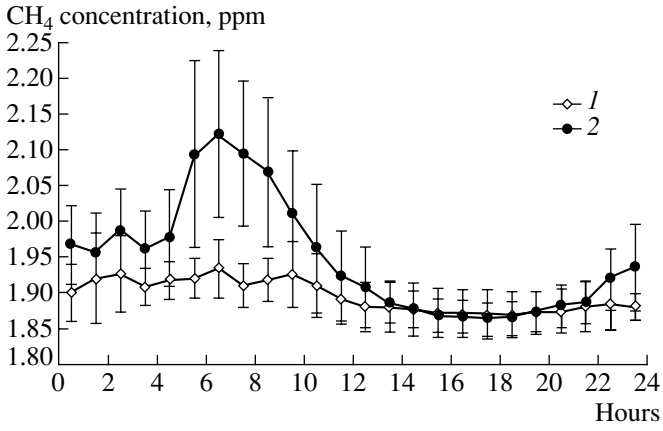

Fig. 1. Daily mean cycle of methane concentration for summer conditions (the sample of measurements at a temperature above 10°C): wind from (*1*) unpolluted (0°–175°) and (*2*) urban (200°–300°) sectors.

the data of remote sensing of the atmospheric gas composition.

1. EXPERIMENTAL DATA

1.1. Measurements of Surface Methane Concentrations

Measurements of the surface methane concentration at the settlement of Voeikovo (59°57′ N, 30°42′ E), located east of St. Petersburg, 12 km from its administrative boundary, have been performed since 1995 [3, 4]. Areas of St. Petersburg and its industrial suburbs are located to the northwest and southwest (200°–300°). In the northeast and southeast directions (0°–175°), sparsely populated waterlogged lowlands extend up to Lake Ladoga. Weekly measurement series were carried out for 24 h approximately once a month. The concentration of methane was measured every 10 min with an error of 0.2% [3, 4]. A detailed description of the instruments is given in [4]. The measurement scale is fixed to the WMO reference by calibration of the equipment against a standard gas. The intercomparisons performed have shown good agreement of the NITsDZA measurements at Voeikovo with results from the leading laboratories of Europe [8].

As shown by the first results of measurements presented in [3], the methane emission in the environs of Voeikovo is inhomogeneous in space. High concentrations (up to 2.8 ppm) are observed when winds blow from the sector 200°–320°, which is close to the sector of the angular boundaries of St. Petersburg [3]. When the air masses come from the unpolluted sector (0°–180° and 330°–360°), the concentrations do not exceed 2.2 ppm.

In this study, regularities in the change in surface methane concentration are examined on the basis of the averaged relationships obtained for the samples from the dataset (1995–2000) comprising over 5000 hourly means of methane concentration with current meteorologic information. The effect of the sources located within 40–50 km from the measurement site (local sources) is most clearly seen in the diurnal cycle of methane concentration under the condition of a significant change in the intensity of mixing processes in the atmosphere during the day. Such situations occur in summer in anticyclonic conditions. The surface temperature inversion that arises in this case generates a stable stratification in the surface layer, thus preventing vertical air exchange and decreasing the mixed-layer height by several times [9]. This results in the nighttime accumulation of methane near the ground. The heating of the underlying surface in the daytime gives rise to developed turbulence. As the surface warms up, a well-mixed layer forms whose thickness increases. In the afternoon, the mixed-layer height may exceed 1000 m [9]. Strong vertical mixing (unstable stratification) leads to a significant reduction in the amount of methane accumulated at night near the surface and substantially diminishes the influence of local sources on the formation of surface concentration.

Distinctions in the summer diurnal cycle of methane between the cases with wind directions from the unpolluted (0°–175°) and urban (200°–300°) sectors are seen in Fig. 1. The concentration in the morning hours is greater than that in the period of intense daytime mixing (17:00–19:00 local time) by 0.05–0.06 ppm when the air masses come from an unpolluted sector and by 0.24–0.25 ppm when winds blow from St. Petersburg. In the unpolluted sector, the only source of methane is the emission from wetland complexes in the summer season. The ratio of the diurnal amplitudes for the samples shown in Fig. 1 indicates that the specific emission of urban origin exceeds the intensity of natural emission by several times. The features of the diurnal cycle not only provide evidence of the presence of emission sources but also give information about their strength. The approach to the estimation of the methane emission from the St. Petersburg area that is based on measurements at Voeikovo and on model simulations of the accumulation rate of methane in inversion conditions is described in [10, 11].

Under conditions of intense daytime mixing, the contribution of local sources to the surface methane concentration is very small. This follows from the coincidence of the concentrations in daytime hours (usually, from 15:00 to 20:00 LT) in the samples shown in Fig. 1 (wind directions from the unpolluted and urban sectors).

Another factor that diminishes the contribution of nearby sources to the formation of surface concentration is the increase in wind speed, because the accumulation of pollutant is proportional to the time it

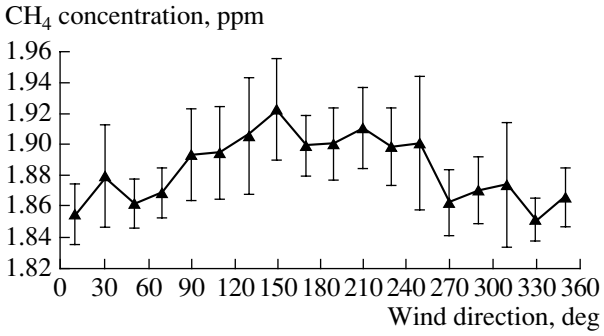

Fig. 2. Methane concentration as a function of wind direction for intense mixing conditions.

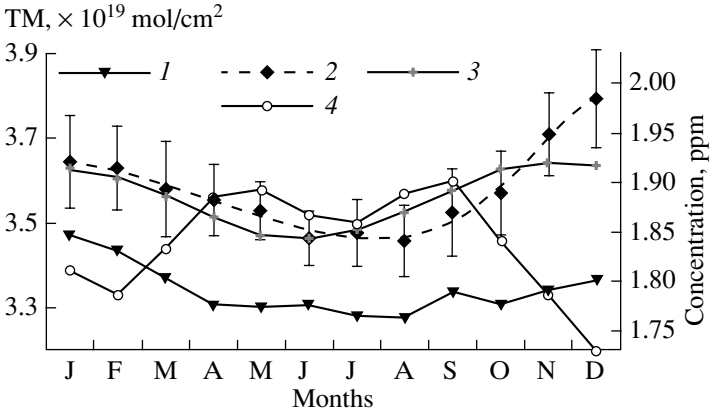

Fig. 3. Annual cycle of total methane and surface methane concentration: (*1*) annual cycle of TM for 1999, (*2*) mean annual cycle of TM for 1991–2003, (*3*) mean annual cycle of surface CH_4 concentration at Voeikovo (1995–2000), and (*4*) mean annual cycle of TM at Ny-Ålesund (1992–1995) [17].

takes for the air mass to travel over the region of influence of the sources. Moreover, the increase in wind speed is accompanied by the intensification of mixing processes and, consequently, by an increase in the mixed-layer height [9]. The results of measurements at Voeikovo show that, if the wind blows from St. Petersburg and its speed exceeds 3 m/s, no high (above 2.2 ppm) surface methane concentrations are observed.

The sample of data for which the contribution of local sources to the surface methane concentration is small was composed of the total dataset according to two parameters: the wind speed should exceed 3 m/s and the time of day should cover the period of intense daytime mixing (from 15:00 to 20:00 LT). The concentration level for the sample thus formed is on average 0.04 ppm greater than the background level. The amount by which the background is exceeded depends on the direction of air-mass transport (Fig. 2). When winds blow from the sector 270°–360°–70°, the concentrations are about 0.02 ppm higher than the background values. The annual means at the nearby Teriberka background station (69°14′ N, 35°06′ E) during the given period (1996–2000) are 1.840 ± 0.005 ppm [12, 13]. With southerly winds (90°–240°), the concentration is 0.06 ppm higher than the background value. Analysis based on the use of not only wind directions but also air-mass trajectories [14] has shown that the passage of air masses over the southern sectors (western and eastern Europe) leads to an approximately 4% increase in the concentration at Voeikovo in comparison with conditions when the air masses move from the unpolluted oceanic regions. This finding agrees with data in Fig. 2. Analysis of the influence of air-mass trajectories on the surface methane concentration at Voeikovo [14] under conditions of a weak effect of local sources was carried out for 1996–1998 by analogy with the analysis described in Section 2.3 for total methane.

Data obtained under conditions of intense mixing in the atmospheric boundary layer and statistically processed using the CCGvu program [15] make it possible to isolate the seasonal cycle of methane concentration, which is shown in Fig. 3 and considered in combination with the annual cycle of TM.

1.2. Spectroscopic Measurements of Total Methane Content

Measurements of TM have been carried out since 1991 at Staryi Peterhof, about 35 km southwest of the center of St. Petersburg (59°83′ N, 29°83′ E) [2]. The angular sizes of the urban boundaries relative to the observation site lie within 40°–130°. The method of determining the total content of atmospheric gases is based on the interpretation of IR spectra of direct solar radiation and provides diurnal measurements of TM with an error within 1–3%. Comparisons of the techniques of ground-based spectroscopic measurements of TM (NIIF SPbGU, IFA RAN, and NPO Taifun) have shown that the results of single measurements agree within the errors of these measurements, about 3–4% [16].

During 1998–2000, measurements of TM and surface methane concentration were simultaneously carried out at Staryi Peterhof from December to May under conditions of intense mixing between 15:00 and 17:00 [2]. A total of 21 pairs of measurements were conducted. The calculation of the correlation coefficient r between the simultaneous measurements of surface concentrations and TM revealed a positive correlation. The correlation coefficient and the standard deviation were found to be $r = 0.75$ and $\sigma_r = 0.095$ ($3\sigma_r = 0.29$), respectively. Statistically significant correlation indicates the presence of common factors that induce variations in TM and surface concentration under conditions of intense mixing. Long-range transport is considered to be one of these factors. This presumption is supported mainly by the consistent results of air-mass trajectory analysis performed for both surface concentration and TM. In 25% of cases, the observed changes in total methane and surface concentration disagree with each other. This disagreement occurs in part because the surface concentration characterizes the amount of methane in the mixed layer, while TM variations are associated mainly with concentration changes above the planetary boundary layer. The difference between air-mass trajectories at different altitudes may also cause the observed disagreement.

The variability of daily mean TM values averages ~3–5% and increases in the cold period. In some cases, however, TM changes of about 10–12% have been observed over two or three days. These observations require an additional explanation. Such changes were observed in April 1999, i.e., during the period used for further combined analysis of experimental data, results of numerical modeling of the methane concentration fields, and air-mass back trajectories.

Throughout 1999 (in particular, in April), lower values of TM were observed (Fig. 3). The pattern of annual changes during some years may considerably differ from the mean seasonal cycle. The mean seasonal cycle of TM for St. Petersburg has a maximum in November–December and a minimum in June–August (Fig. 3). Its amplitude is ~4.5%, or 0.17×10^{19} molecules cm^{-2}. An example of a more complicated annual cycle (with an amplitude of about 6%) derived from the results of TM measurements in 1992–1995 at Ny-Ålesund, Spitsbergen (78.9° N, 11.9° E), is shown in Fig. 3 [17]. The mean annual cycle of TM is different for St. Petersburg and Ny-Ålesund. At Ny-Ålesund, apart from a deep winter minimum, there is a TM decrease in June–July, which appears to be caused by a summer increase in the concentration of hydroxyl radical in the atmosphere. In [17], the observed seasonal cycle of TM is attributed to atmospheric circulation features in the polar region.

The mean seasonal cycle of the surface CH_4 concentration from Voeikovo measurement data is shown in the same figure. The amplitude of seasonal variations of surface methane over St. Petersburg, equal to 2% (or 0.04 ppm), is about twice the background value [13]. The increase in the amplitude of seasonal variations is due mainly to the seasonal behavior of the mixed-layer height and is typically observed in regions where there are methane sources. Seasonal TM changes show a large amplitude. The large amplitude may be caused by seasonal changes in methane concentration above the boundary layer. A summer maximum of the surface methane concentration at Voeikovo is observed in May, not in July as follows from measurements at island stations in the same latitudinal belt [13] and from the mean annual cycle of TM. The cause of the observed shift may be the influence of the methane emission from natural sources, which has a maximum in the second half of summer [18–20].

1.3. Influence of Air-Mass Trajectories on TM

Combined analysis of TM and air-mass trajectories was carried out for the period from January 1998 to December 1999 (a total of 180 measurement days). This period was characterized by sharp irregular TM changes. For each day, 120-h air-mass trajectories [15] were constructed for altitudes 50, 1500, and 3000 m. The air-mass trajectories were calculated for these altitudes because 50 m is the elevation of the measurement site, 1500 m is the top of the atmospheric boundary layer, and 3000 m is the altitude characterizing the dynamics of air masses in the lower troposphere.

The area adjacent to the study region was conditionally divided into five sectors (Fig. 4). These sectors are (1) the Barents Sea and the north of European Russia, (2) the continental part of Russia (southeast of St. Petersburg), (3) Europe, (4) the Baltic Sea, and (5) the north European basin and Scandinavia. Back-

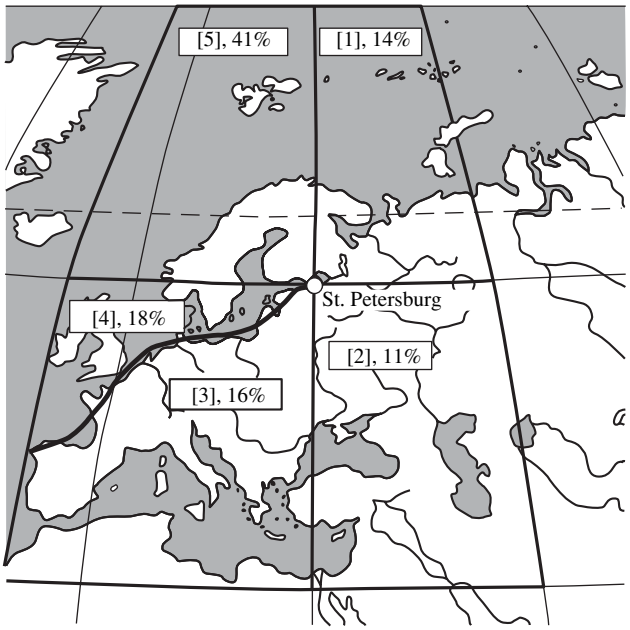

Fig. 4. Division of adjacent regions into five major sectors (percentage of air masses that arrived from each sector over 180 measurement days).

trajectory analysis showed that, during the day before arriving at St. Petersburg, the air-mass trajectories at the indicated altitudes passed through the same sectors in 90% of cases. The air mass was assigned to a given sector if it had existed in this sector for two days before reaching St. Petersburg. The air masses having complicated trajectories and not assigned to any sector were eliminated from analysis. The frequency of arrival of the air masses from each sector, expressed as a percent, is shown in Fig. 4. It can be seen that the transport from the northwest (sector 5) prevails.

The total number of measurement days was insufficient to analyze the influence of air-mass transport in each of the seasons. Distributions of the mean, minimum, and maximum TM values are shown in Fig. 5 for the sectors displayed in Fig. 4. The minimum TM (which is most often observed in summer) can be regarded as a minimum background value for the selected sector in 1998–1999. The maximum values, which are normally observed in the fall–winter period, may be affected by the anthropogenic sources located along the trajectory of the air mass. The air masses with a high content of methane are typical of the continental areas of Russia (sectors 1, 2). The air masses with a relatively low content of methane come from sectors 4 and 5, and the air masses with intermediate TM values arrive from Europe (sector 3). The relative differences between the mean TM values calculated for sectors 4, 5 and 1, 2 may be as large as ~4–5%, i.e., comparable to the amplitude of the annual cycle of TM for St. Petersburg.

Combined analysis of ground-based and spectroscopic measurements shows that the effects of the proposed mechanisms on the formation of the fields of surface concentration and total methane are principally different. The largest variations in surface methane concentration are induced by local sources located within the radius of 50–60 km. The maximum variability of TM is associated with a changing methane

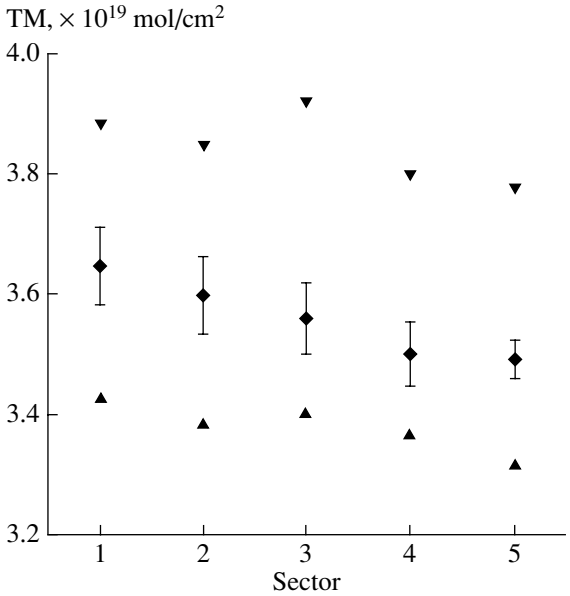

Fig. 5. Distribution of mean, minimum, and maximum TM values by sectors (based on all measurements made during 1998–1999).

concentration in the upper troposphere. At the same time, the common factors that form both fields may be efficient under conditions of intense daytime mixing, when the influence of local sources on surface concentrations is less significant. Long-range pollution transport is one such factor, as evidenced by a statistically significant correlation, obtained from measurements at Peterhof, between the surface concentration and TM. The consistent results of back-trajectory analysis for both the surface concentration and the total content of methane also support this conclusion.

2. MODEL ESTIMATES

2.1. Regional Modeling of Methane Fields

To simulate the methane field over the northwestern part of European Russia (55°–65° N, 20°–40° E), a three-dimensional regional pollution transport model for the troposphere is used with assimilation of direct measurements of surface concentration and total columns of methane made at the Voeikovo and Peterhof stations, respectively. The model has a high spatial resolution (0.5° in latitude and 0.25° in longitude) and includes a block of pollution transport and a parametrization block for the vertical structure of the planetary boundary layer [1]. The model takes into account the distribution of methane sources in an industrial region and provides a sufficiently accurate comparison of measured and simulated concentration values. For the initial meteorological data in the study area, we use the ERA-40 reanalysis of the European Centre for Medium-Range Weather Forecasting [21] with a time step of 6 h and a space step of 2.5°. Simulations are carried out using a spline interpolation of the reanalysis data in time and space to the grid points.

2.2. Methane Emission from the Underlying Surface and Boundary Conditions

To carry out simulations, several versions of the distribution of local natural and anthropogenic methane sources were incorporated into the model and tested. The initial version of the geographic distribution of methane fluxes from the underlying surface was prepared on the basis of maps of natural complexes and soil cover in the Leningrad oblast. In addition, estimates of anthropogenic methane emission from St. Petersburg and its environs from [10, 11] were used as a first approximation. For characteristic values of methane fluxes from natural complexes, we used results of long-term direct measurements of methane concentrations and fluxes from Swedish and Finnish mires [18–20], similar to the Leningrad oblast with respect to conditions of ecosystem formation in wetlands.

The background surface concentration (1.86 ppmv at the southern and eastern boundaries, 1.83 ppmv at the western boundary, and 1.84 ppmv at the northern boundary of the domain up to an altitude of 11 km) was specified on the basis of methane measurements in Finland [19] and at the Teriberka station [12, 13] and by taking into account the minimum methane concentrations measured at Voeikovo for the corresponding wind directions. The methane concentration at the upper boundary of the model domain was taken to be 1.81 ppmv (version 1) or 1.72 ppmv (version 2) (see, e.g., [22]). In the second version, the methane mixing ratio at the western boundary of the domain above 2 km was set equal to 1.66 ppm because preliminary results in subsection 1.3 showed that the air masses with depleted methane arrive from this sector.

Model analysis was carried out for the winter–spring period, when the urban emission of methane has the largest influence on its concentration in the atmosphere. In this period, the main source of methane in the region is the emission from St. Petersburg and, to a lesser extent, from wetland complexes in its environs. Computations were performed for April 1999, when the surface concentration and TM were simultaneously measured and when the air mass changes occurred. For analysis of the methane field and for detection of the most adequate distribution and strength of the regional methane sources affecting the methane concentration at Voeikovo, several versions of specifying the lower boundary condition of the model were developed and tested.

2.3. Simulation of Surface Methane Concentrations

Figure 6 compares measured and simulated methane concentrations at Voeikovo over the period of simultaneous measurements. The measurement data are averaged using 2-h moving means in time. The difference between the modeled and measured surface wind velocities is usually no greater in magnitude and direction than the measurement error. From the preliminary estimates [10, 11], several versions of the specification of the methane emission from St. Petersburg were determined and tested. The modeling results are given for the following three versions of emission intensity: (A) 130 mg $(m^2\ day)^{-1}$; (B) 300 mg $(m^2\ day)^{-1}$; and (C) 600 mg $(m^2\ day)^{-1}$. As follows from Fig. 6, the model with version B adequately simulates surface concentration changes induced by emissions from the urban methane sources. Simulations have shown (Fig. 8b) that the emission from St. Petersburg has some influence on surface methane concentrations as far as 150–200 km from the city. The integral emission from St. Petersburg in the model with version B is ~84 kt/yr (1 kt = 10^6 kg), increasing to 100 kt/yr with the southern industrial suburbs added. Our estimates of

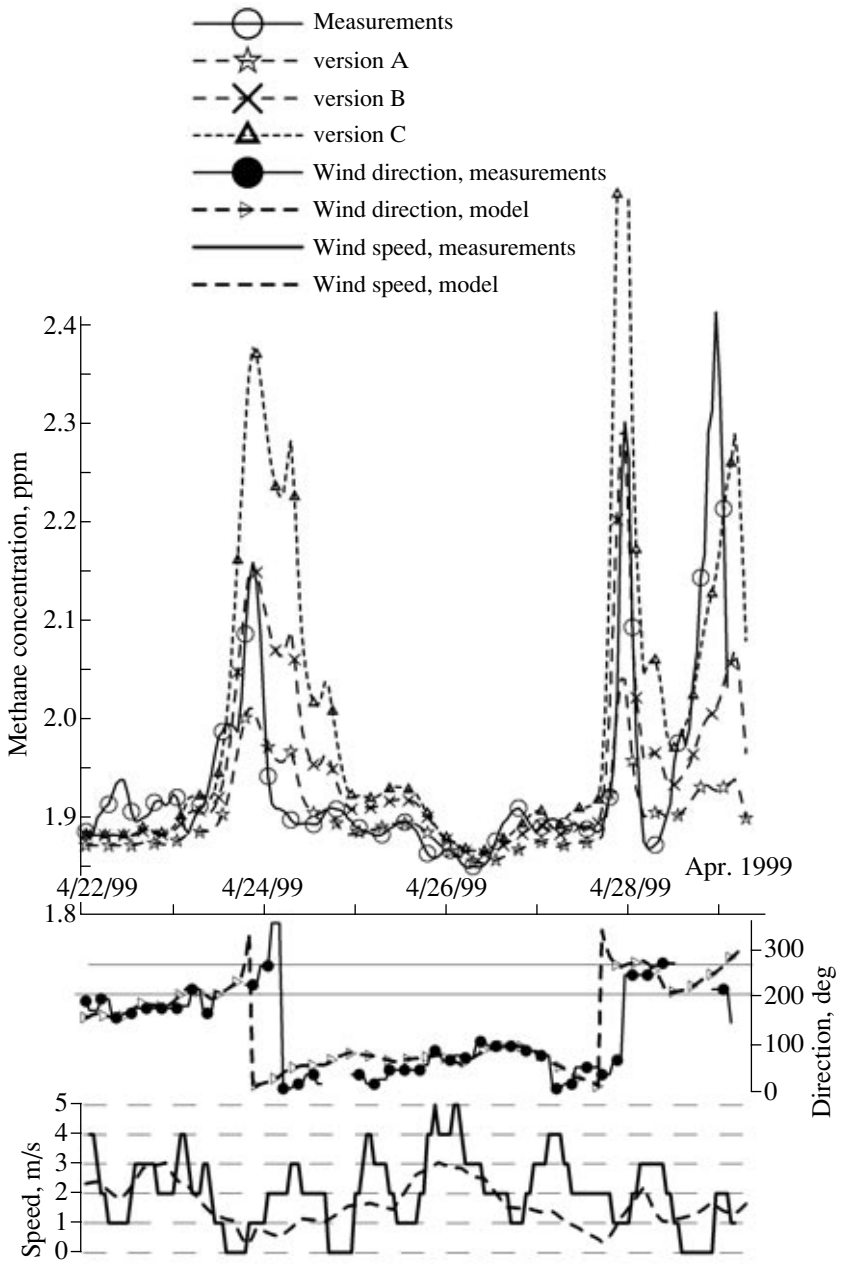

Fig. 6. Comparison of surface measurements and numerical modeling of methane concentration and of surface wind direction and speed (Voeikovo, Apr. 1999).

the integral methane emission from St. Petersburg are about 1.5 times the estimates from the model simulation of a summer methane accumulation under surface temperature inversion. Seasonal emission changes may be a possible cause of this discrepancy because our estimates are calculated for April, when the heating period still continues, while estimates in [10, 11] are made for the summer season. Measurements of the methane isotopic concentration in the air sampled at Voeikovo have shown that gas leaks from the gas distribution network of St. Petersburg are a major source of methane [13]. Analysis of the estimates obtained by different methods is a task for another study; it should be based on the same experimental data and the same meteorologic information and should consider emissions from the same area.

Some differences between the simulated and measured concentration values may be due to interpolation of the meteorologic fields from the 2.5° by 2.5° grid to the 0.5° by 0.25° grid, which inevitably gives fields that are more smoothed in space than the real fields. The appearance of additional false maxima

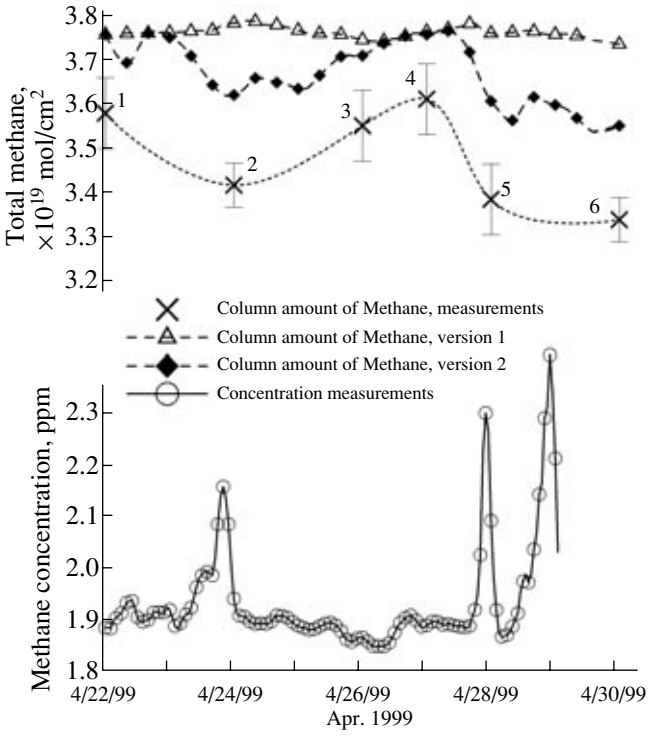

Fig. 7. (Top) Measured and simulated values of methane content in the atmospheric column for two versions of the upper boundary condition and (bottom) measured surface methane concentrations, Apr. 1999.

of the model concentration can be attributed to an underestimation of the model wind speed, thus leading to an inversion that was not actually observed. It is possible that a more detailed distribution of sources is required. For this purpose, a higher spatial resolution of the model and, consequently, a larger volume of data are needed. This requirement may be fulfilled in the following study. At the same time, the refinement of model description is not fundamental to the solution of the problem of the combined interpretation of local and spectroscopic methane measurements.

2.4. Modeling Results and Analysis of Total Methane Content

To understand the processes that control the methane content in the entire atmospheric column, the contribution of different atmospheric layers was estimated and the influence of pressure changes on the measurement results was assessed (see table). The upper boundary of the three-dimensional regional transport model is located at 11 km (about 200 hPa). Therefore, for comparison of the model results with measurements of total methane, the contribution of the layers above 200 hPa has to be estimated. For the northwestern region, the following data were used: (1) three-dimensional methane distribution from the MEZON global photochemical model [23], describing the vertical atmospheric structure from 1000 to 1 hPa, and including the annual cycle of hydroxyl radical, and (2) results of satellite (HALOE) measurements of methane in the stratosphere. In [23], the range of seasonal changes in the contribution of above-tropospheric layers was found to be 7.1×10^{18} molecules cm^{-2} (February to March) to 7.8×10^{18} molecules cm^{-2} (October to December), i.e., no more than 2% of the CH_4 column amount. Computations with the data of [24] (HALOE satellite experiment) have shown that changes in stratospheric CH_4 may lead to 2% changes in TM. A change in the tropopause height may also have some influence on the observed TM variations. This is related to the vertical distribution of methane concentration in the atmosphere, whereas the methane concentration in the troposphere is nearly constant: it begins to decrease rapidly above the tropopause. Computations have shown that varying the tropopause height from 8 to 12 km may change TM by ~1.5%. These estimates and contributions of surface atmospheric layers from 0–1, 0–2, 1–11, and 2–11 km to the variability of the total amount of methane in the atmospheric column are shown in the table for different profiles of methane concentration and different surface pressures. Computations were made with a

Model estimates of the contribution of various factors to the total content of methane in the atmospheric layer

Parameter	Atmospheric layer	Variation range	Relative change in TM compared to its mean, %
Vertical profile of methane concentration (for 1000-hPa surface pressure)	0–1 km	2.8–1.8 ppm^{-1}	~1.8
	0–2 km	2.8–1.8 ppm^{-1}	~3
	1–11 km	1.6 ppm^{-1}–1.8 ppm^{-1}	~ 7
Methane content	>11 km	$7.1–7.8 \times 10^{18}$ molecules cm^{-2}	<2
Tropopause height	–	8–12 km	~1.5
Surface pressure	–	1000 hPa–1030 hPa	2.5

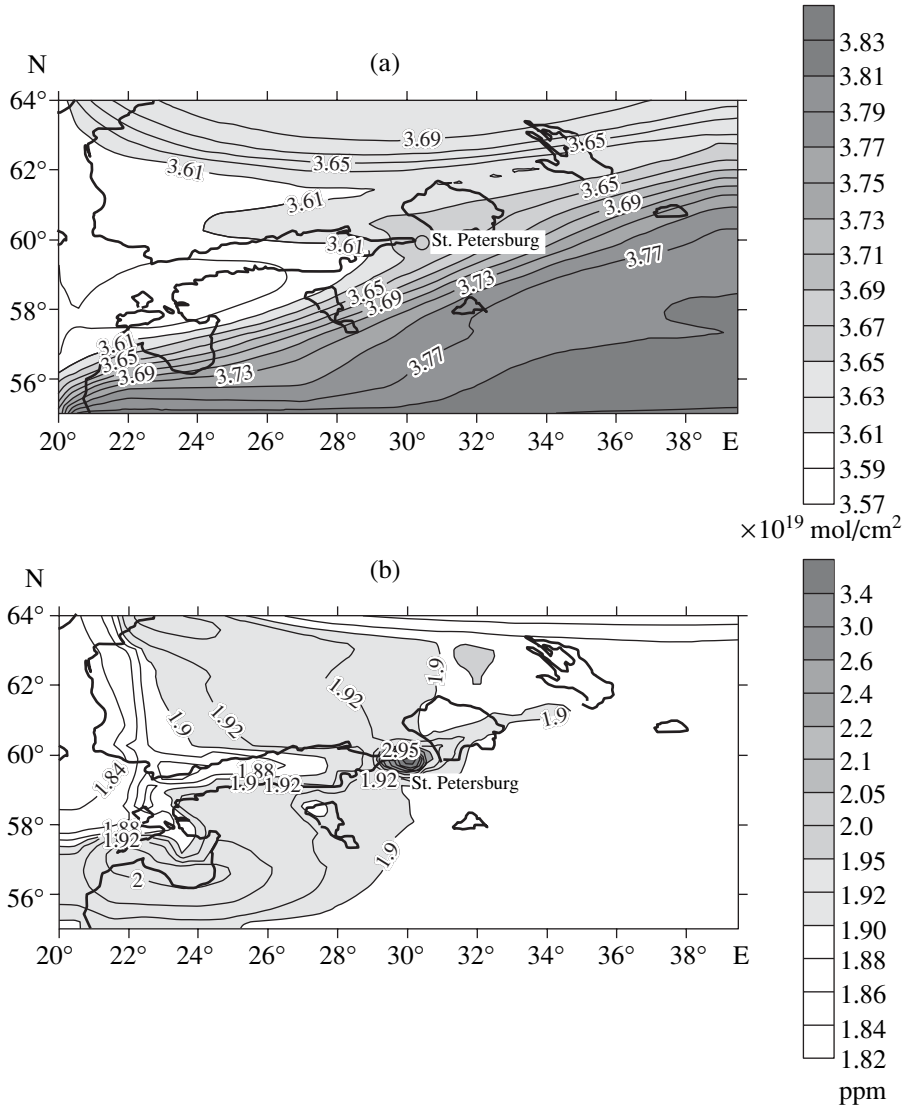

Fig. 8. Model distributions of (a) total methane (molecules $cm^{-2} \times 10^{19}$) up to 11 km and (b) surface concentration (ppm) at a level ~10–15 m in northwestern Russia (Apr. 24, 1999).

one-dimensional model for the atmospheric column. The contributions of the layers from 0–1 and 0–2 km were estimated for the profile of methane concentrations decreasing linearly with height from the mixing ratio of 2.8 ppm at the surface to 1.8 ppm at 1 km (2 km) and then remaining constant to the upper boundary of the model domain (11 km).

Thus, changes in upper-troposphere methane and changes in the distribution of the surface pressure field are the main contributors to variations of TM in the atmospheric column. Measured and simulated (calculated for version B of methane emission) April (1999) column amounts of methane are shown in the upper part of Fig. 7. The model values were obtained for two versions of the upper boundary condition (versions 1 and 2, see subsection 2.2). Methane concentrations measured in the surface layer during the same period are shown in the lower part of Fig. 7. Figure 7 shows that considerable increases in the surface mixing ratio of methane recorded at Voeikovo on April 24 and 28, 1999, manifested themselves neither in measurements of total methane at Peterhof (Fig. 7) nor in the values of this parameter in the model (the differences in TM between the two stations are estimated to be no greater than 1–1.5%). However, the air-mass transformation on April 24 and April 27–28, 1999, induced by a change in the direction of air transport in the troposphere, resulted in a considerable change in total methane.

The TM computations carried out with a spatially constant upper boundary condition (version 1) do not reproduce variations in measured total methane. The

(a)

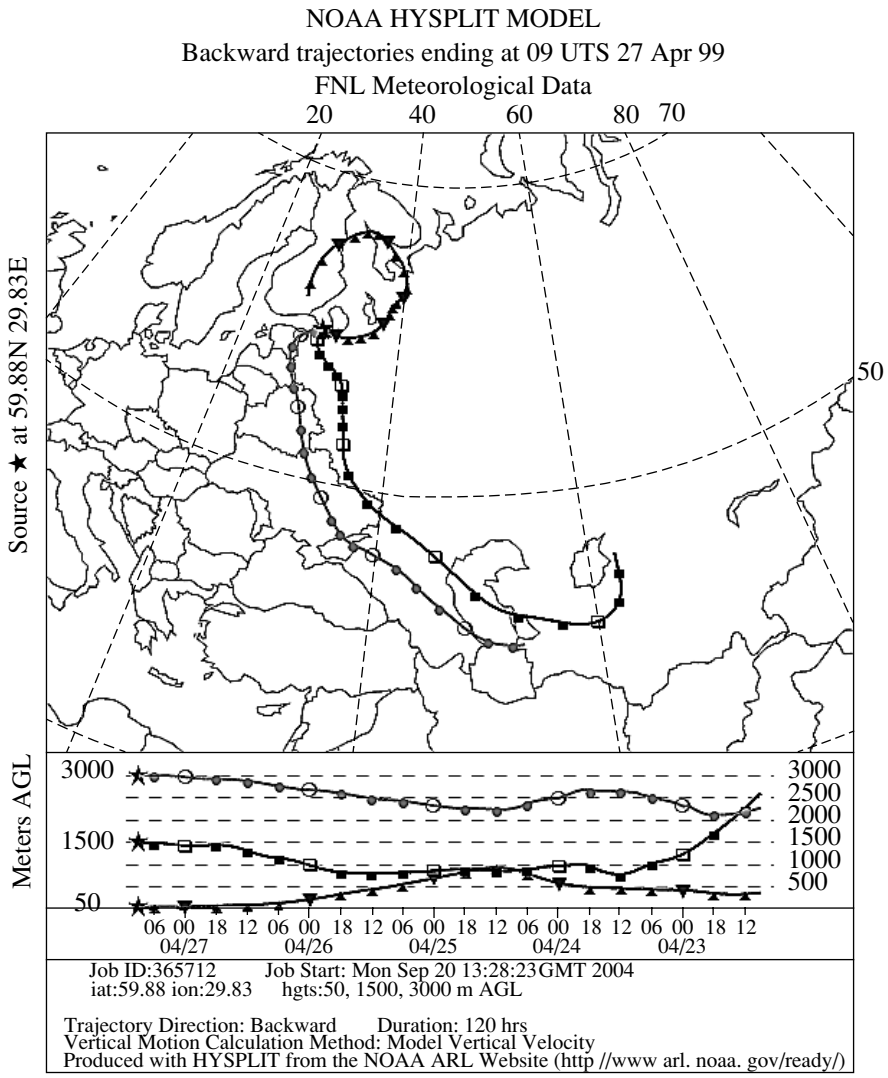

Fig. 9. Air-mass back trajectories on (a) April 27 and (b) April 30, 1999.

TM values obtained from the model with the upper boundary condition given by version 2 with consideration for a lower methane content in the air mass moving from the west (formed over the sea) reproduce variations in the measured value. The measured and model values do not coincide in absolute value. This indicates the necessity of refining both the upper boundary condition and the estimate of the contribution from the higher atmospheric layers to the total methane in 1999, when it was lower than in other years (Fig. 3). It is also possible that the improvement of the technique of spectroscopic measurements is needed. Figure 8a presents the spatial distribution of total methane in the atmosphere over the region for April 24, 1999, calculated with version 2 (see description of the boundary conditions of the model). Version B is used for the intensity of methane emission from the surface. Figure 8b displays the distribution of surface methane concentration for the same day. Figure 8 shows that the TM distribution (Fig. 8a) does not reflect the effect of the city, which is characterized by maximum surface concentrations of methane in the region (Fig. 8b), but the contribution of the air mass coming from regions with a low content of methane is clearly seen. The air mass that originated over the ocean, where there are practically no methane sources, has relatively low amounts of TM. An example is the transformation of air masses on April 27–30, 1999, when the TM content changed from 3.61×10^{19} to 3.34×10^{19} molecules cm^{-2}, or by 8%; meantime, the surface concentration was increasing (Fig. 7). Analysis of back trajectories for April 27–30 showed that the air mass located over St. Petersburg on April

(b)

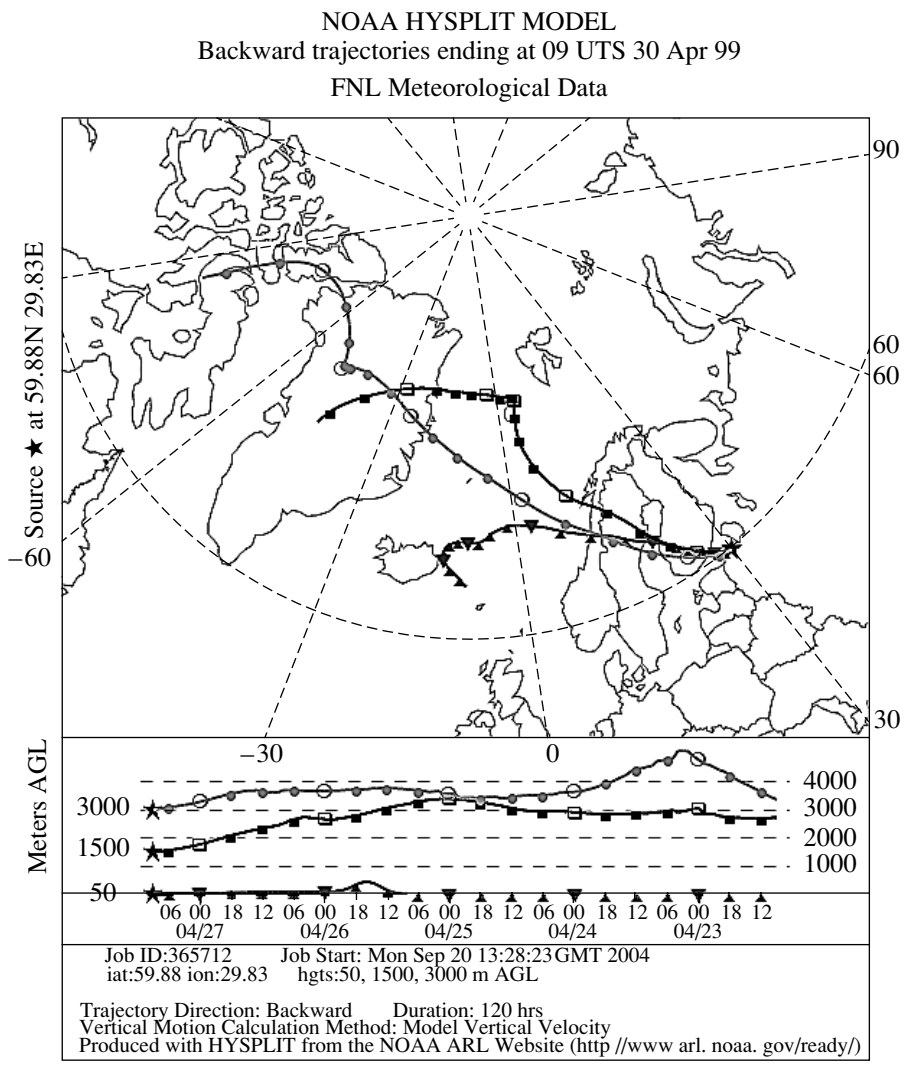

Fig. 9. (Contd.)

27 moved over the continental regions, where intense methane sources are located, during the previous five days. A change in the direction of the air mass started on April 28 and ended by April 30, when a new air mass originated over the ocean had already reached St. Petersburg (Fig. 9). This was accompanied by increases in surface methane concentrations at Voeikovo. The increase in methane concentration was related to the air mass moving from the urban sector. A similar situation was observed on April 22–24, when the air masses that originated over the European continent changed to oceanic air masses.

CONCLUSIONS

The main factor responsible for the variability of surface methane concentration in the environs of St. Petersburg is the emission of methane from the urban area. In the stably stratified boundary layer, this emission results in a concentration increase of up to 1 ppm (or over 50% as against that in the well-mixed layer). The specific methane emission from wetlands is several times as small as that from the urban area. Variations in surface concentration during intense mixing, when the contribution from local sources is small, are determined by the seasonal changes and long-range transport of air masses.

The contribution of urban emission to TM does not exceed 2%. The observed changes in TM depend on the origin of air masses coming to the area where measurements are performed. In the air masses that arrive from the continental part of western and eastern Europe, both the TM content and the surface methane

concentrations are about 4% higher than those in the air masses moving from the northwestern sector.

The proposed three-dimensional regional pollution transport model for the troposphere adequately describes the results of measurements of surface CH_4 concentrations and simulates observed changes in total methane in the atmosphere over northwestern Russia. This model is used to estimate the anthropogenic emission of methane from St. Petersburg. The integral methane emission from St. Petersburg and its industrial environs for the spring season is estimated to be about 100 kt/yr. The influence of the urban emission on the surface methane concentration in the northwestern region of Russia manifests itself as far as 150 km from St. Petersburg.

The three-dimensional regional transport model can be used in investigation of the processes that form the CH_4 fields for description of methane concentration and total methane fields in real time; for estimation of the intensity of regional sources on the basis of comparison of the model values with measurements; for analysis of total atmospheric methane values from ground-based and satellite measurements; and with consideration for the fact that tropospheric layers are most difficult to observe from space, for refinement of the vertical profiles and TM obtained from satellite data.

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