Estimation of methane emissions in the St. Petersburg, Russia, region: An atmospheric nocturnal boundary layer budget approach

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[1] The aim of the study is quantitative estimation of methane emissions in the area of St. Petersburg and its suburbs based on observations at the Voeikovo station. The approach is based on formulation and regularized solution of an inverse problem. The effect of methane accumulation in the nocturnal boundary layer is used by the formulation of the problem. The emission field is not homogeneous. The mean flux density on the urban territory is 1 ± 0.3 g km^{-2} s^{-1}. The total methane flux from the urban territory and its suburbs is estimated to be 60 kT year^{-1}. These emissions estimates refer to nighttime conditions in summer; they do not include emissions through tall chimneys. The proposed technique of data processing allows, in principal, for locating unknown sources of emissions. It is the first experience in getting emission estimates from the large industrial region in Russia on the basis of atmospheric measurements. This work shows that national statistical self-assessments of methane emissions can be verified using independent atmospheric measurements. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1610 Global Change: Atmosphere (0315, 0325); 1694 Global Change: Instruments and techniques; *KEYWORDS:* Methane, emissions, top-down, ill-posed, inventories, verification

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1. Introduction

[2] In the physical view water vapour, carbon dioxide, nitrous oxide, methane and ozone are the primary greenhouse gases (GHG). Climate change, in UN Framework Convention on Climate Change (FCCC) usage, is a change of climate, which is attributed to human activity that alters the composition of global atmosphere (www.ipcc.ch). In such view, as a contributor to climate change, methane is second only to carbon dioxide (www.epa.gov/ghginfo). Since the beginning of the industrial era the concentration of carbon dioxide in the atmosphere has increased by nearly 30%, of methane by about 150% and of nitrous oxide by about 15% (www.ipcc.ch). Highly populated and industrialized regions are a major source of methane. Aggregated estimates of methane emissions from Russian anthropogenic sources have been obtained from statistical compilations [*SNC*, 1998]. Radically new studies have showed that the methane emission inventories of urban areas require validation and maybe revision based on atmospheric observations [*Levin et al.*, 1999; *Lowry et al.*, 2001].

[3] The focus of this study is measurement of methane concentration in ambient air and an indirect estimation of methane emissions in the urban area (St. Petersburg, Russia). Methane (CH_4) is measured using a gas chromatograph. Data processing is based on the regularized solution of the inverse problem. In doing so, the stable (nocturnal) atmospheric boundary layer (ABL) is used as a collector and integrator of emissions. For chemical inert atmospheric species, the change over time in concentration within the boundary layer should reflect the magnitude of surface emissions. The ABL budget approach seems to be promising for large area flux estimates, which are otherwise very difficult to evaluate. For nighttime accumulation during 8 hours the catchment area for such atmospheric approach is in the order of 10^3 km^2. The nighttime concentration increase can be used to estimate CH_4 emissions if the height of the accumulation layer is known. In this study the height is determined using radiosonde data as the base.

[4] To determine the height of the accumulation layer, several other techniques could be used. This information could be derived theoretically from micrometeorological parameters. Several variants of tracer techniques can also be used. For example, the Radon 222 (^{222}Rn) tracer is widely used [*Levin et al.*, 1999; *Kuhlmann et al.*, 1998]. ^{222}Rn is a radioactive soil-born noble gas. Its exhalation from soil turned out to be rather homogeneous, that is why radon emission rate can be derived from chamber measurements more accurately than CH_4 fluxes [*Levin et al.*, 1999; *Kuhlmann et al.*, 1998]. Assuming constant and homogeneous ^{222}Rn and CH_4 exhalation rates, one can use the diurnal cycle of ^{222}Rn activity and CH_4 concentrations to calculate the ratio of flux density of these two gases.

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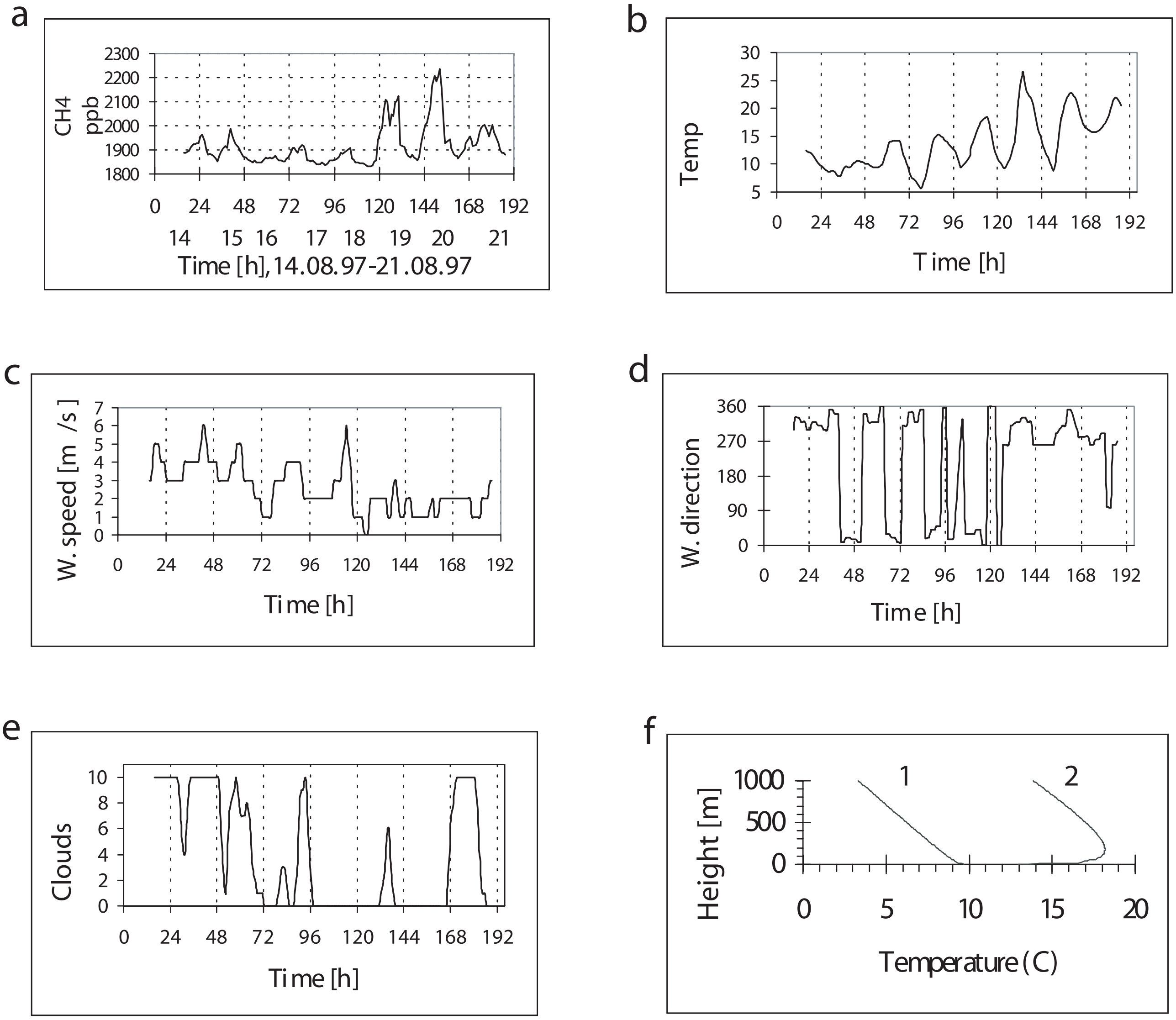

Figure 1. Records of methane concentrations and meteorological elements observed at Voeikovo 14–21 August 1997. (a) Methane concentration. (b) Near surface (2 m) temperature. (c) 10 m level wind speed. (d) Wind direction. (e) Sky coverage by low clouds. (f) Smoothed early morning (04 h LT) temperature profiles in the first - 1 (16 August) and the second - 2 (20 August) half of the period under investigation.

Atmospheric ^{222}Rn is usually measured with the static filter method [*Levin et al.*, 1999]. In fact the α-decay of ^{222}Rn daughters which are attached to aerosols and collected on filter is counted. At St. Petersburg soils are very transformed and the air is polluted by aerosols these may involve difficulties with the use of the radon tracer technique.

[5] A different tracer technique was used to evaluate London methane emissions [*Lowry et al.*, 2001]. As a matter of fact, two ratios have been estimated: a ratio of the total CH_4 emissions to CH_4 emissions due to natural gas leaks from London gas distribution network, and a ratio of the total CH_4 to the total CO_2 emissions. Gas leaks and CO_2 emissions statistics were supposed to be known. Thus, this method is in part statistical. Such technique could not been used either for St. Petersburg because of lack of adequate information.

[6] Several important challenges stand in the way of successful application of ABL budget approach, not least are the instability of the inverse problems and the existence of horizontal concentration gradients leading to advection errors. Errors can be increased with data processing. Such situation is typical for inverse problems since they are ill posed. The regularization technique is used here for solving the problem [*Tikhonov and Arsenin*, 1977].

2. Experiment

2.1. Sampling Site and Methane Measurement System

[7] The methane concentration measurements were carried out in Voeikovo (59°57′N, 30°42′E, 72 m above sea level). Voeikovo is located east of St. Petersburg, 12 km far from its administrative frontier on a smoothed hill. The Voeikovo vicinities are hilly and covered by the mixed forest. In the northwest-southwest quadrant there is a highly populated territory. The sector with low population is the

northeast-southeast quadrant where lowland is up to lake Ladoga at about 20 km to the east. The industrial zone of St. Petersburg extends in the direction range from 200 to 310 degrees. The sector from zero to 200 degrees is relatively free of the industrial activity. The local wind system in Voeikovo is dominated by west, southwest flows. There are meteorological and radiosonde stations operated at Voeikovo, it is extremely important for measurement interpretations because enables us to determine atmospheric boundary layer parameters (about the use of this information see section 3.2 and Appendix B).

[8] Since 1996 an automated gas chromatographic (GC) system has been used for measurement of CH_4 in ambient air. The time interval between single measurements is 10 minutes. The air is collected from an inlet line located on the roof of the observatory building, about 6 m above local ground. Semicontinuous GC measurements have been carried out during one week of each month 24 hours a day. An automated Russian-made GC system (TZVET 500M) has been used for CH_4 concentration measurements in the ambient air [*Smetanin et al.*, 2000]. The GC is equipped with flame ionization detector (FID). Sampling loop volume is 2 ml. The sample is ejected on the GC column using N_2 as a carrier gas. CARBORUS carbon molecular sieve is used in the chromatographic column. CARBORUS consists of the seeds made of solid inert support base, covered by a layer of an active carbon in solid stationary phase. The retention time for CH_4 is less than one minute when using chromatographic column filled with CURBORUS with grains size of 0.12–0.16 mm and the thickness of the active carbon solid stationary phase of 0.02 mm. One routine measurement needs as minimum 4 minutes including one standard and one ambient air.

[9] Calibration of the GC system has been performed against the standard gas (dry air with the CH_4 concentration of 2025 ppb) provided by laboratory from Institute für Umweltphysik (IUP), University of Heidelberg, Germany. The relative random measurement error is 0.2%, as estimated using the measurements of the standard gas concentration. As a long-term stability control check the "target gas" (one and the same air from a cylinder) was analyzed in performing every weekly measurement series. Regular registration of a "target gas" is recommended in WMO TD No. 980 to provide control of the system stability. From December 1996 to January 2001 standard deviation of this gas was 4 ppb with no significant drift or concentration change so that the system was stable during the all period of investigation.

[10] To check the equipment and method, the intercomparison between our GC system and IUP laboratory has been carried. High-pressure tanks (150 atm) filled with the ambient Voeikovo air, have been analyzed using the GC systems of the two laboratories. The concentration differences did not exceed 6 ppb. The mean and standard deviations of the differences were 0.5 ppb and 2.4 ppb, respectively. Methane mixing ratios are given on NOAA/CMDL scale in parts per billion (10^9) by volume (ppbv).

2.2. Observational Data: Examples and Generalization

[11] Concentration of CH_4 can increase in Voeikovo at calm nights up to more than 2800 ppb. Figure 1 shows

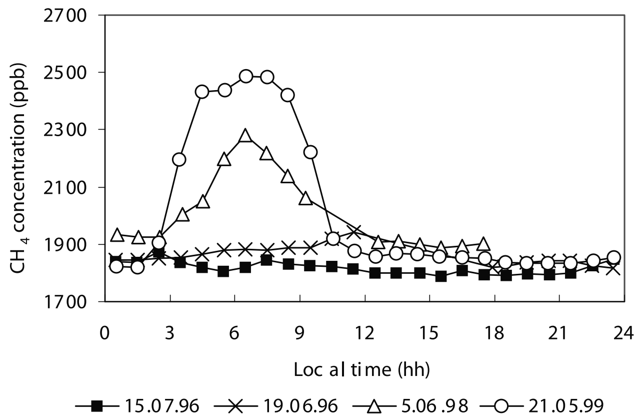

Figure 2. Typical diurnal cycles of CH_4 concentration observed at Voeikovo. 15 July 1996: Transport from the industrial zone, absence of inversion (mean nocturnal wind direction and wind speed are 200° and 4 m s^{-1}); 19 June 1996: Transport from the clear sector, inversion (145° and 1.5 m s^{-1}); 5 June 1998: Transport from the industrial zone, inversion (200° and 1 m s^{-1}); 21 May 1999: Transport from the industrial zone, inversion (210° and 1 m s^{-1}). The daytime weather conditions were in all cases convective with approximately the same wind directions as at nights but higher wind speeds.

examples of typical CH_4 and the basic meteorological parameters records in Voeikovo in summer (14–21 August 1997). General weather situation changed on 18 August. During the period from 14 August to 17 August, there was cyclonic synoptic situation, warm front nearby with overcast conditions. In the period of 18–20 August, there was anticyclonic situation with clear nights and fair-weather cumulus clouds at the afternoon. On 21 August, there was backside of anticyclone, cold front nearby. The situation with strong north wind during 14–18 August changed to the situation with moderate and low west wind during 19–20 August on 18 August. The patterns of CH_4 changed from weak diurnal variations on 14–18 August to strong diurnal variations with large concentration increases during the nights on 19 and 20 August. In Figure 1 the change from low to higher diurnal cycle of concentration variability proceeded in parallel with changing of two important meteorological factors: a switch from north to west wind directions (that is from "clear" to "urban" sector) and the beginning of nocturnal inversion period. Figure 2 demonstrates the influence of wind directions and temperature stratification separately. Examples for 15 July 1996, 5 June 1998, and 21 May 1999 differ mainly in stratification character. The presence of methane sources in the direction of 200°–210° can be concluded from the higher growth of concentration under inversion (5 June 1998, 21 May 1999). However, if there was no inversion (15 July 1996), there were only slight methane variations with amplitude of 20–30 ppb. Direction of wind alone may have a profound effect on the diurnal cycle of methane concentration. Figure 2 shows the event on 19 June 1996 when there was strong surface inversion but advection was from "clean" sector, as a result, no significant growth of concentration was observed. Thus wind from a distinct sector and inversion are both necessary for significant concentration

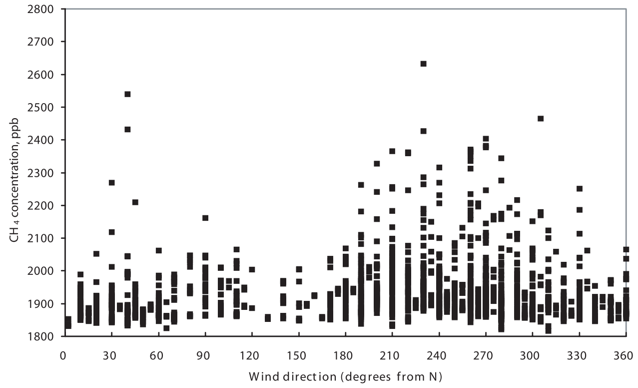

Figure 3. CH_4 concentration at Voeikovo depending on wind direction.

growth. The results of measurements and their analysis show that methane emissions were not spatially uniform. Figure 3 presents the methane concentration dependence on wind direction. Higher concentration values are seen in the sector 190°–330°. This sector is of the highest interest since the methane growth in this case is most probably related to the influence of the city zone. Higher concentrations have also appeared in the narrower sector of 30°–60°. All the events of higher methane concentrations in this sector have been due to the diurnal variations observed for 5 days during the whole measurement period (1996–2000). The fact that the sector is narrow can witness to a closely located emitter of a small extension. Waste treatment plant located about 1 km far from the sampling site is a potential source of a higher methane emission at this sector. The results of the observations can be generalized as follows: (a) In summer the diurnal cycles are the main contributors to the variability of CH_4. (b) The concentrations recorded for diurnal cycle consist, as usual, of three main components: a background value for well mixed air entering the region, a signal resulting from regional emissions, and noise caused by local sources and turbulence. (c) The suppression and enhancement of the upward transport of CH_4 related to the nocturnal inversion layer and the daytime thermal convection are important factors in the diurnal variations of the CH_4 concentration in the boundary layer. (d) The nocturnal increase in CH_4 concentration may delay by up to a few hours in relation to the sunset (see Figure 2), CH_4 concentration continues increasing after sunrise until convective mixing breaks up the shallow surface layer. (e) Anticyclonic conditions are conducive to great amplitude of diurnal variations of CH_4 concentration. Events with inversion at night and convection in the daytime often occur in warm seasons. If the sampling site is downwind from the admixture sources such events lead to a pronounced diurnal methane variation. (f) Pronounced methane concentration growth were observed in Voeikovo under wind velocities less than 3 m/s at night and wind direction from the sector close to that of the angular frontiers of St. Petersburg. The nocturnal concentration growth usually lasts 5–10 hours and has amplitude of the order of several hundred ppb. The distances for the air masses to travel during the accumulation time are from 30 to 60 km. These distances are assumed to be the radius of the region of influence for the nighttime data. (g) The methane emissions are not homogeneously distributed in the region under consideration. Figure 2 and Figure 3 have given evidence of the influence of advection direction on nocturnal accumulation of methane. The scale of the regional square source is not less than the distance of air mass to travel during the nocturnal accumulation period (see (f)). (h) Similar in outline diurnal patterns caused by nighttime inversion situations have been observed at various sampling sites and for various trace substances both in urban regions [*Levin et al.*, 1999; *Lowry et al.*, 2001] and in the sites where emissions were caused by wetlands and other natural sources [*Kuhlmann et al.*, 1998; *Nakazawa et al.*, 1997]. The greatest amplitudes of diurnal CH_4 variations were observed in suburbs of London [*Lowry et al.*, 2001]. The amplitudes in Voeikovo are less than near London but greater than in the urban region of Heidelberg (Germany) [*Levin et al.*, 1999].

3. Theory

3.1. ABL Diurnal Cycle

[12] In warm seasons the atmospheric boundary layer (ABL) in high pressure regions over land consists of three major parts: a very turbulent convective boundary layer (CBL) (mixing layer in the day-time), a less-turbulent residual layer (RL) containing former mixing-layer air, and a nocturnal (stable) boundary layer (NBL) [*Stull*, 1988]. During the day solar heating causes thermal turbulence, mechanical turbulence is caused by air motion over the rough surface of the Earth. A radiative temperature inversion forms at night and burns off during the morning. As a result of the strength of buoyant production of turbulence, the daytime CBL often reaches 1000 m or more in-depth. On the other hand, the depth of the NBL is typically of the order of a few hundred meters. It must take some time for the ABL to adjust from a deep CBL at radiation sunset to a shallow shear-driven NBL at night. This time is proportional to the dissipation time of the largest eddies in the system. The scaling argument and numerical modeling results provide a consistent estimate of this time: approximately 3–4 h is necessary for turbulence within a typical CBL to completely dissipate within RL after radiation sunset and it takes up to 6 hours for final nocturnal equilibrium to be reached [*Benkley and Schulman*, 1979]. The first order local diffusion approach to the treatment of the vertical turbulent mixing usually applies to the NBL because the length scale of largest turbulent eddies is smaller than the size of domain over which the turbulence extends. For convective conditions the largest transporting eddies may have a size similar to the depth of CBL itself. In this unstable case the vertical transport of heat and chemical species can have a strong nonlocal character [*Holtslag and Boville*, 1993; *Wang et al.*, 1999]. Nonlocal schemes for CBL have been developed [*Holtslag and Boville*, 1993]. The flux of any scalar −q can be described as

$$\left(\overline{w'q'}\right)_c = -K_c\left(\frac{\partial q}{\partial z} - \gamma_c\right), \tag{1}$$

where γ_c reflects the nonlocal transport due to large eddy motion in the CBL. Typical K_c values can range between

100 and 400 $m^2\ s^{-1}$ [*Wang et al.*, 1999]. For the developed NBL the flux is typically taken as

$$\overline{w'q'} = -K\frac{\partial q}{\partial z},\ K = l^2 S\, f(Ri), \tag{2}$$

where *l* is a length scale, S is the vertical wind shear, and *Ri* is the gradient Richardson number [*Wang et al.*, 1999]. Typically values of K are much smaller than K_c.

3.2. Mathematical Model for Solving the Inverse Problem

[13] The general equation for mass budget of chemical species in turbulent atmosphere serves as the basis for the calculations:

$$\frac{\partial q}{\partial t} + v_i\frac{\partial q}{\partial x_i} = -\frac{\partial}{\partial x_i}J_i + I(x_i, t), \tag{3}$$

where q(x, y, z, t) is concentration of the admixture (CH_4), I = 1, 2, 3, J_i are the i-axial turbulent fluxes of the admixture, v_i are the i-axial average wind speed components, and *I* is a function describing bulk sources and sinks of the admixture.

[14] Coordinate system related to the wind direction (the horizontal axis O_x is opposite to the wind direction and passes throw the site of measurements; the horizontal axis O_y is perpendicular to the wind; the axis O_z has an upward direction) will be used further. The equations will be written for the plane x-z (q(x, z, 0, t)).

[15] The following assumptions have been adopted: (a) Bulk sources and sinks in the atmosphere do not significantly affect the admixture (i.e., $I(x_i,\ t) = 0$). (b) In the region under consideration there are many minor sources. The sources are located near the underlying surface. The set of these sources may be treated as a large square steady state source, which can be described by the use of its flux density E(x, y). (c) This square source is not homogeneous on the whole, but locally (within several km) it is, however, suggested to be homogeneous enough to neglect horizontal diffusion in the cross-sectional to the wind direction, so that $\frac{\partial J_y}{\partial y} \ll v_x\frac{\partial q}{\partial x}$. It is suggested also that $\frac{\partial J_x}{\partial x} \ll v_x\frac{\partial q}{\partial x}, \frac{\partial J_z}{\partial z} \gg v_z\frac{\partial q}{\partial z}$.

[16] With this assumption equation (3) is simplified:

$$\begin{gathered}\frac{\partial q}{\partial t} + v_x\frac{\partial q}{\partial x} = -\frac{\partial}{\partial z}J_z,\\ J_z\big|_{z=z_1} = E(x)\end{gathered} \tag{4}$$

where z_1 is a level of sampling within the surface layer.

[17] Accumulation takes place within the layer 0 < z < $Z_i(t) \leq$ H, were H is the lowest level within the ABL where the following condition is valid:

$$O(|J_z(H)/E|) \ll 1 \text{ for } t_0 \leq t \leq t_0 + T, \tag{5}$$

where *O* is the symbol of the order of magnitude, t_0 is the beginning of the period of admixture accumulation within NBL, T denotes the duration of the period of nighttime accumulation. Let Q be the gas burden in the layer $z_1 < z < H$: $Q(x,t) = \int_{z_1}^{H} q(x,z,t)dz$ and $V = \frac{1}{H}\int_{z_1}^{H} v(z)dz = \text{const} < 0$.

[18] Appendix A contains justification and detailed derivation of the following Volterra integral equation of the first kind for the sampling point ($x = x_{sp}$) using equation (4) as the base:

$$\begin{gathered}\int_{t_0}^{t} K(t,\tau)u(\tau)d\tau = F(t), t_0 \leq t \leq t_0 + T, T = -\frac{L}{V}\\ F(t) = Q_{sp}(t) - Q_0\big(x_{sp} - V(t - t_0)\big), Q_{sp}(t) = Q\big(x_{sp}, t\big)\\ u(\tau) = E\big(x_{sp} - V(\tau - t_0)\big), K(t,\tau) = 1 \textit{ for } \tau \leq t\end{gathered} \tag{6}$$

[19] F(t) should be known from observations, u(t) is a required function, this function gives the emission flux density:

$$E(x) = u\Big(t_0 + \frac{x_{sp} - x}{V}\Big),\ x_{sp} \leq x \leq x_{sp} + L. \tag{7}$$

[20] If we obtain F(t) for various advection directions we shall be able to determine the two-dimensional field of surface emissions.

[21] Equation (6) has a unique solution but this solution is unstable so that the problem is ill-posed [*Tikhonov and Arsenin*, 1977]. We use the variational method for solving ill-posed problems based on Tikhonov regularization technique [*Tikhonov and Arsenin*, 1977] (see Appendix A).

[22] Appendix B adapts the proposed inverse technique to use data of observations at a single point and estimates associated error. The idea of adapting is that under a distinct diurnal cycle the nocturnal growth of the methane concentration at our sampling point is determined basically by emissions in the nighttime catchment area rather than by horizontal gradient of initial distribution ($Q_0(x)$). Equation (6) is made serviceable (see Appendix B):

$$\int_{t_0}^{t} u(\tau)d\tau = [q_s(t) - q_s(t_0)]h(t),\ t_0 \leq t \leq t_0 + T, \tag{8}$$

where $q_s(t)$ is the near ground methane concentration at the sampling point, h(t) is the effective thickness of accumulation layer at the sampling point. The values of h for every accumulation event have been fitted on the basis of the morning (04 LT) radiosonde profile data at Voeikovo and the empirical formula derived from observations on the 300-m meteorological tower at Obnisk (Russia) [*Sedunov*, 1991] (see Appendix B).

[23] Equation (8) is mathematically similar to the general equation (6) but unlike equation (6), equation (8) refers only to the data of observations at the single point. Appendix B indicates that we are able to select weather conditions (see section 4) when the horizontal gradient of Q_0, which forms in the late afternoon, is small enough. Equation (B3) gives criterion of application for equation (8). Theoretical arguments of Appendix B are supported by examination of observations. The view has been presented in the literature that samples taken in the late afternoon, when convective mixing is well developed, are mostly representative for an area with spatial scale of some hundred kilometres [*Levin et al.*, 1999; *Worthy et al.*, 1998]. Experimental results in

Table 1. Methane Emission Estimates for St. Petersburg (in this investigation), London, and Heidelberg Regions[a]

Regions	Flux Density, G km^{-2} s^{-1} (CH_4) = [kg m^{-2} s^{-1}] × 10^9	Total Flux, kT year^{-1}	Total Flux Per Million of Population, kT year^{-1} mln^{-1}
St. Petersburg and its south industrial suburbs (2000 km^2) (Atmospheric approach)	1.0 (1 ± 30%)	63	14
East agricultural suburbs of St. Petersburg (Atmospheric approach)	0.2 (1 ± 50%)	–	–
London[b,d]	2.3–2.2	186–177	23–22
London[c,d]	3.8–3.6	297–283	37–35
London (Atmospheric approach)[e]	3.1–3.9	240–310	39–33
Heidelberg (4,409 km^2)[f,g]	0.57	79.8	–
Heidelberg (36 km Radius) (Atmospheric approach)[h]	0.24 ± 0.05 (20%)	30	–

[a] Root-mean square errors (RMSE) are presented.
[b] [DETR99].
[c] [DETR98].
[d] DETR emission data, The UK National Air Quality Archive, Greenhouse gas emissions, www.aeat.co.uk/netcet/airqual/.
[e] *Lowry et al.*, 2001.
[f] [CORINAIR90].
[g] CORINAIR 90/94, European Air Emissions, www.aeat.co.uk/netcet/corinair/.
[h] *Levin et al.*, 1999.

favour of this view for the Voeikovo site have been obtained [*Lowry et al.*, 1999]. Using our measurements as experimental foundation, the authors have conducted a sector analysis of 96-hour back trajectories for air masses arriving at the Voekovo station. The daily minimum concentrations were used for the assessment of each sector through which the air mass passed. The lowest methane concentrations were recorded in NW air streams; the highest in air masses coming from the SE, especially those coming from the region around Moscow. Generally, the influence of the St. Petersburg urban-scale source was masked. The variations caused by air mass changes are lasting generally 2–5 days. At Voeikovo this variations in methane concentrations were over the range 1820 to 1920 ppb [*Lowry et al.*, 1999] (see examples in Figure 2 also). Diurnal variations, observed in summer, have larger amplitude and shorter period (see Figure 2). In Figure 2 the daytime concentrations for different examples differ because the examples are dated from various periods of time with various air masses. The daytime weather conditions for these examples were convective with higher wind speed (see Figure 1).

[24] The errors by the inversion process have been estimated with the use of Monte-Carlo technique, its values are given in Table 1. Examples of Monte-Carlo process are presented in section 5. Two main categories of errors have been taken into account: errors in concentration records (due to high-frequency stochastic natural variability and inaccuracy of measurements) and errors caused by the inaccuracy of the model. These two categories of errors have been simulated through variations of observed concentrations and effective height of accumulation layer (h). This approach is close to the way of taking into consideration inaccuracy of model and noise that was used by the inversion process [*Haas-Laursen et al.*, 1996]. The prescribed absolute root-mean square error (RMSE) for concentration is ±20 ppb, the prescribed relative RMSE for effective height of accumulation layer is ±75% for the first three hours of accumulation and ±50% for the rest accumulation period. The errors of concentration in series are assumed to be independent, the errors in h values are assumed to be independent only when various instruments were used to obtain radiosonde data.

[25] Appendix B argues that we can select weather conditions when it is not necessary to know ABL height over the whole area. Nevertheless uncertainties in ABL height for the sampling point remain the main contributor to the total error of emissions estimates. This problem is not specific for the proposed inverse technique. The ABL height is a fundamental parameter in many air pollution models. It was found that the comparison between calculated and measured characteristics of ABL is generally not straightforward [*Seibert et al.*, 2000]. For inverse oriented modeling, unlike forecast oriented modeling, the vertical profiles of methane concentration and wind within the nocturnal ABL can be found directly, for example, by tall tower measurements.

4. Data Selection

[26] Practically the calculations could be performed with fair accuracy if the selected data sets satisfy the following conditions: (a) A fairly large concentration growth during the night should take place (we handled the data with the growth no less than 200 ppb). (b) The weather conditions are anticyclonic, there are no fronts nearby, that is, air mass has homogeneous structure in a free atmosphere. Under such condition q(H) is approximately constant with time during one nocturnal accumulation period. (c) Days with mainly clear sky were preferred. On days with clear sky, except for the short winter days, daytime warming results in afternoon temperatures high enough to allow significant vertical mixing.

[27] To determine q_{s0} average concentration over 15–18 LT is calculated, to determine t_0 the following condition is used: $q_s(t_0 + \Delta t) - q_s(t_0) \geq 30$ppb, where Δt is the time step (1 h).

[28] The appropriate events of methane build-up under nighttime inversions have been chosen from the observational data (16 events in warm seasons for 1996–2000).

5. Test of Regularization

[29] To check the solution algorithm validity and select an optimal value for regularization parameter (α), a numerical simulation experiment has been carried out. Function E(x) was given, function Q(t) was calculated by solving the forward problem and random perturbations were introduced in the calculated values of Q(t). Using the perturbed function $\tilde{Q}$(t) the given function is retrieved ($\tilde{E}_\alpha(x)$) for varies values of random perturbations and regularization parameter (α). In this numerical experiment the accuracy of retrieval of the assumed function has been studied.

[30] As an example, function E(x) has been given in the interval $x_{sp} \le x \le x_m$ as follows:

$$E(x) = A \sin\left(\pi \frac{x - x_{sp}}{x_m - x_{sp}}\right), \tag{9}$$

where A is the assumed maximal emission flux density.

[31] For solving the forward problem, equation (6) is rearranged to (see Appendix A):

$$Q_{sp}(t) = Q_0 + \frac{1}{V} \int_{x_{sp}-V(t-t_0)}^{x_{sp}} E(s)ds, \tag{10}$$

where we assume that Q_0 = const.

[32] Substitution of the assumed equation (9) into equation (10) yields an analytical solution of the forward problem for the sampling point:

$$\Delta Q(t) = Q_{sp}(t) - Q_0 = \frac{A}{V}\frac{x_m - x_{sp}}{\pi}\left[\cos\left(-\pi\frac{x(t) - x_{sp}}{x_m - x_{sp}}\right) - 1\right]$$
$$x(t) = x_{sp} - V(t - t_0) \tag{11}$$

[33] From the ΔQ(t) we get $\Delta q_s(t) = q_s - q_{s0} = \Delta Q(t)/h(t)$. In thus obtained values for Δq_s random perturbations are introduced: $\Delta\tilde{q}_s(t_i) = \Delta q_s + \varepsilon_i$, where ε_i is the normally distributed random value, $M(\varepsilon_i, \varepsilon_J) = \delta_{ij}\sigma^2$, M is autocorrelation function, δ_{ij} is the Kroneker symbol, σ is the standard deviation of $\Delta\varepsilon_i$. The following values are adopted in the simulation: $A = 10^{-9}$ kg m^{-2} s^{-1} = 1 g km^{-2} s^{-1}, V = −1 m s^{-1}, H = 150 m, T = 10 h, $x_m - x_{sp}$ = 36 km, $t_0 - t_1$ = 3 hour (about t_1 see Appendix B). Calculations have been performed by a time step of 1 hour. Numerical results are presented in Figure 4.

[34] Figure 4a presents comparison of the "exact" curve, calculated by the equation (11), for the concentration growth and the perturbed "real" curve imitating experimental data. Figure 4b shows how the attempt to retrieve E(x) using the real curve without regularization (for α = 0) leads to impermissibly great errors. Meanwhile the regularized solution is in a reasonable agreement with the assumed function E(x). Figures 4c and 4d show the influence of the parameters α and σ on the accuracy of E retrieval. The metrics of Chebyshev space: dE = max $|E(x) - \tilde{E}_\alpha(x)|$ is used as a measure of precision. Figure 3c shows that the mean retrieval error reaches its minimum at α = 1.2, this error being almost insensitive to small changes of α in the neighborhood of this value. From Figure 4d it follows that without regularization the retrieval error is almost zero for "exact" data, but rapidly grows with their errors. The error in the regularized retrieval is not a zero for "exact" data, but it grows much more slowly with increasing data random errors.

6. Results of Emissions Estimations

[35] The proposed technique of data processing allows, in principal, to construct the map of emission distribution over the region and to locate unknown sources of emissions. However, now the data and the model are not accurate enough for such task. Only the mean values of emissions for St. Petersburg and its south dense populated industrial suburbs and for the agricultural zone in the close vicinity of Voeikovo are given in Table 1. The obtained emission estimates refer to a warm nonheating season and exclude sources with emissions higher than the nocturnal inversion layer.

[36] For comparison, Table 1 gives also the emission values obtained for London and Heidelberg regions. The emissions for St. Petersburg are heavier than for Heidelberg region but lighter than for London region. The program of GHG inventory in the St. Petersburg region has only started. There are only some preliminary results for Leningrad Region (it is the Region around St. Petersburg (former Leningrad), its area is 88,000 km^2, its population is 1.7 mln). The bottom-up statistical assessments of methane emissions for Leningrad Region have given 70 kT year^{-1} in 1990 (67% agriculture, 32% waste treatment), 49 kT for 1995 (53% agriculture, 46% waste treatment), and 42 kT for 2000 (44% agriculture, 53% waste treatment) [*Yasensky et al.*, 2001]. The accuracy of these figures is not given [*Yasensky et al.*, 2001]. The bottom-up assessments for St. Petersburg have not yet been obtained. These figures should not be compared directly with our top-down estimates. The presented bottom-up assessments include only waste produced by population of Leningrad Region in spite of the fact that landfills of the waste originated from St. Petersburg are located on the territory of Leningrad Region in the suburbs of St. Petersburg, these assessments do not include the natural gas leaks.

[37] Waste treatment and leaks from gas distribution system usually give the main part of methane emissions from urban areas (CORINAIR 90/94, European Air Emissions, www.aeat.co.uk/netcet/corinair/, DETR emission data, The UK National Air Quality Archive, Greenhouse gas emissions, www.aeat.co.uk/netcet/airqual/). High precision stable isotope analysis of atmospheric methane can be used to characterize methane sources. The techniques of isotope analysis developed for Heidelberg and London has been used for St. Petersburg [*Lowry et al.*, 1999; *Poss et al.*, 1999]. Some measurements have been done of the air samples from Voeikovo [*Lowry et al.*, 1999; *Poss et al.*, 1999]. The Siberian gas supply, which is isotopically close to landfill methane emissions, dominates in St. Petersburg. This complicates the interpretation of the isotopic measurements, only some preliminary results have been obtained up to now. Methane released from landfills has $\delta^{13}C = -55.4 \pm 1.4‰$ ($\delta^{13}C$ is the δ-notation for $^{13}C/^{12}C$ ratio) at various sites in Europe [*Levin et al.*, 1999]. The measurements of $\delta^{13}C$ for gas from St. Petersburg gas distribution network are in the range (−51.5 to −48.5‰) [*Lowry et al.*, 2001; *Poss et al.*, 1999]. Calculations based on one diurnal set of

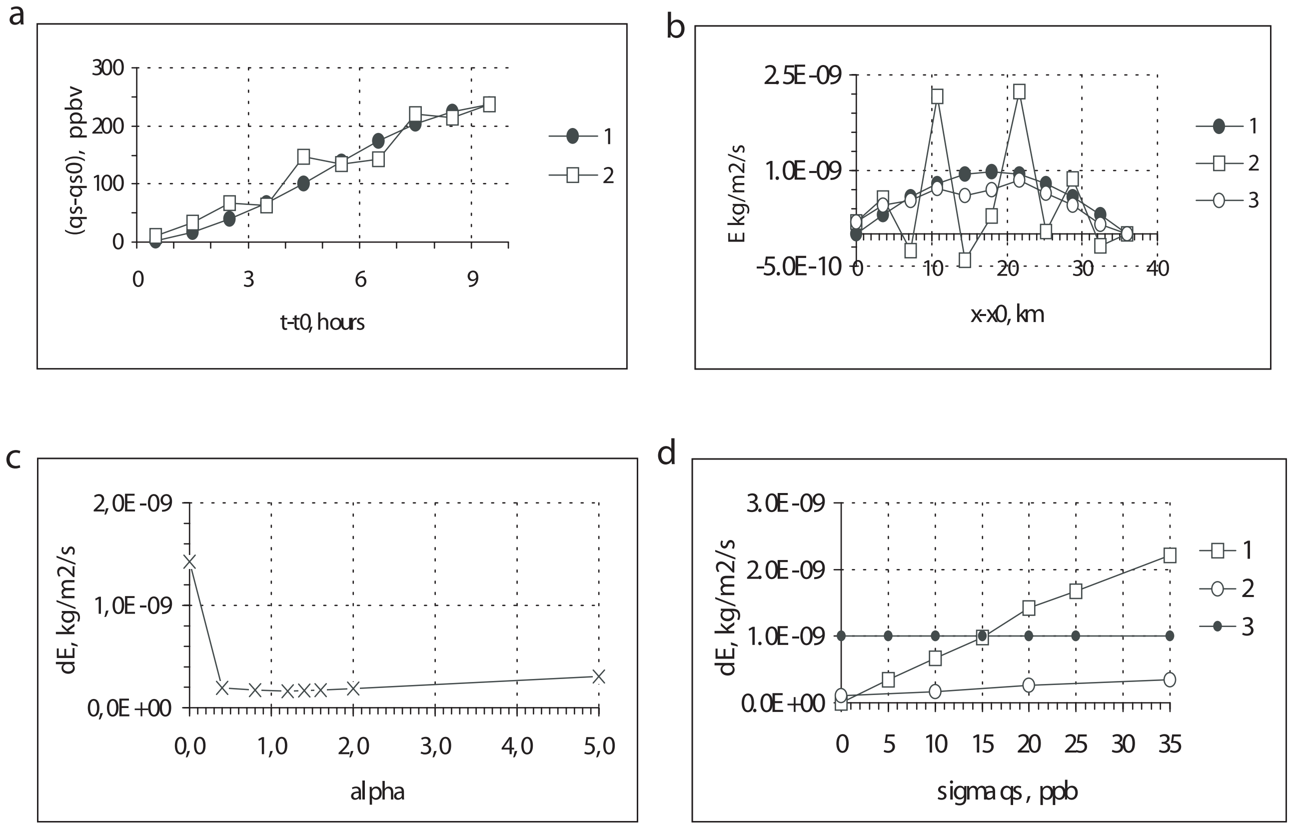

Figure 4. Results from regularization testing. (a) Curve 1 is the excess of the concentration over the initial level as derived from the solution of forward problem (that is, "exact" curve); 2 is the same as 1, but added by the random perturbation ε_i at σ = 20 ppb ("real" curve imitating experimental data). (b) Curve 1 is E(x) retrieved from the "exact" curve at $\alpha = 0$; 2 is E(x) retrieved from the "real" curve at $\alpha = 0$ (without regularization); 3 is the same as 2 but using regularization technique at $\alpha = 1$. (c) Error of E retrieval as a function of regularization parameter α at a fixed σ = 20 ppb. (d) Error of E retrieval as a function of σ at different α: 1 is in line with $\alpha = 0$ (without regularization); 2 is in line with $\alpha = 1.2$ (optimal regularization); 3 is the maximum value of the "exact" curve (given for comparison with the errors of retrieval).

sampling at Voeikovo have indicated a group of CH_4 sources with $\delta^{13}C = -50.6 \pm 0.6‰$ positioned in the city. [*Lowry et al.*, 1999]. This suggests the view that the significant sources of emissions at St. Petersburg are gas leaks. In urban regions of West Europe the main anthropogenic methane sources are landfills [CORINAIR, DETR, *Levin et al.*, 1999; *Lowry et al.*, 2001].

7. Conclusions

[38] The method under consideration is based on modeling of the admixture accumulation under nocturnal boundary layer inversion. This method presents the methane emission estimation from the territory adjacent to the sampling site. The total flux averaged over the city (900 km^2) is about 30,000 metric tons per year, but the total city and its suburbs flux is about 60,000 metric tons per year. This shows that the methane sources exist also outside of the city border.

[39] The inventory study of methane emissions has just been started in Russia. The present paper is the first experience in getting emission estimates from the large industrial region in Russia on the basis of atmospheric measurements. This work and the earlier studies [*Levin et al.*, 1999; *Lowry et al.*, 2001] show that national statistical self-assessments of methane emissions can be verified using independent atmospheric measurements.

Appendix A: Mathematical Justification of the Proposed Inversion Technique

[40] Let us assume that during $t_0 \leq t \leq t_0 + T$ (T is a duration of a nighttime accumulation period) the field of an admixture flux density from the ground to the atmosphere (E) is steady state and the direction of advection is constant. Then taking into consideration the assumptions adopted in the sections 3.1 and 3.2 of the main presentation the transport of the admixture within nocturnal ABL is given by two-dimensional diffusion equation:

$$\frac{\partial q}{\partial t} + v_x \frac{\partial q}{\partial x} = \frac{\partial}{\partial z} K_z \frac{\partial q}{\partial z}$$
$$q(H) = q_H,\ J_z(z_1) = -K_z \frac{\partial q}{\partial z}|_{z=z_1} = E(x), \tag{A1}$$

where K_z is the turbulent exchange coefficient, H is the maximum (equilibrium) height of nocturnal (stable) ABL,

z_1 is a level of sampling within the surface layer. The lower boundary condition is obtained from the fact that within the surface layer the vertical flux of a substance is constant with height. The horizontal axis is assumed to be opposite to wind direction. Upon integrating (A1) with respect to z between z_1 and H we obtain the one-dimensional advection equation for the ABL gas burden $Q = \int_{z_1}^{H} q(z)dz$:

$$\frac{\partial Q}{\partial t} + V\frac{\partial Q}{\partial x} = E(x) - J_z(H), \quad \text{(A2)}$$

where $V = \int_{z_1}^{H} v(z)q(z)dz / \int_{z_1}^{H} q(z)dz$. Equation (A2) is nonlinear (V = V(Q)). For simplicity, we shall use the linerized version of (A2) with $V = \frac{1}{H}\int_{z_1}^{H} v(z)dz = const < 0$, then equation (A2) turns into the constant-coefficient advection equation of a passive scalar.

[41] The different formulations of the exchange coefficient are applied. Let us examine the widely used parameterization of K_z for stable and neutral atmospheric conditions which can be used if $w_*/u_* < 2.3$ (w_* is the convective velocity scale, u_* is the friction velocity) [*Holstlag et al.*, 1995]:

$$K_z(z) = \frac{\chi u_* z}{\Phi_H(z, z_0, L_{MO})}\left(1 - \frac{z}{H}\right)^2, \quad \text{(A3)}$$

where χ is the Karman constant, L_{MO} is the Monin-Obukhov length, and Φ_H is the stability function. For very stable conditions H commonly falls in the range between 50 m and 200 m [*Andre*, 1983]. According to equation (A3) the turbulent flux at the top of nocturnal ABL has to vanish.

[42] To complete the problem, we have to add to equation (A2) the initial and boundary conditions. Obviously, we should only give boundary values at the inflow boundary ($x = x_m = x_{sp} + L$ for $V < 0$):

$$\begin{aligned} Q(x, t_0) &= Q_0(x),\ x_{sp} \le x \le x_m \\ Q(x_m, t) &= Q_L(t),\ t_0 \le t \le t_0 + T_L, \end{aligned} \quad \text{(A4)}$$

where x_{sp} is the coordinate of the sampling point.

[43] At the sampling point the solution is determined by the interior solution being advected out. Solution of the advection equation (A2) is determined only by the initial data in the area [*Sundstrom and Elvius*, 1979]:

$$\begin{aligned} x_{sp} \le x \le x_m \\ t_0 \le t \le t_0 + \frac{x - x_m}{V}. \end{aligned} \quad \text{(A5)}$$

[44] For this area the problem equation (A2), equation (A4) has the following analytical solution:

$$Q(x, t) = Q_1(x, t) + Q_2(x, t),$$

$$Q_1(x, t) = Q_0(x - V(t - t_0)),$$

$$\begin{aligned} Q_2(x, t) &= \int_{t_0}^{t} E(x - V(t - \tau))d\tau = \int_{0}^{t - t_0} E(x - V\tau)d\tau \\ &= \int_{t_0}^{t} E(x - V(\tau - t_0))d\tau = -\frac{1}{V}\int_{x}^{x - V(t - t_0)} E(s)ds. \end{aligned} \quad \text{(A6)}$$

[45] The equality of the integrals in equation (A6) can be easily proofed performing the change of variables. Substituting of equation (A6) in the initial condition and equation (A2) shows that they turn into identities.

[46] By using appropriate notation, equation (A6) can be rewritten for the sampling point ($x = x_{sp}$) in the standard form for Volterra integral equation of the first kind:

$$\begin{aligned} &\int_{t_0}^{t} K(t, \tau)u(\tau)d\tau = F(t),\ t_0 \le t \le t_0 + T,\ T = -\frac{L}{V} \\ &F(t) = Q_{sp}(t) - Q_0\big(x_{sp} - V(t - t_0)\big), Q_{sp}(t) = Q\big(x_{sp}, t\big) \\ &u(\tau) = E\big(x_{sp} - V(\tau - t_0)\big), K(t, \tau) = 1\ for\ \tau \le t. \end{aligned} \quad \text{(A7)}$$

[47] F(t) should be known from observations, u(t) is a required function, this function gives the emission flux density:

$$E(x) = u\left(t_0 + \frac{x_{sp} - x}{V}\right),\ x_{sp} \le x \le x_{sp} + L, \quad \text{(A8)}$$

[48] If we obtain F(t) for various advection directions we shall be able to determine the two-dimensional field of surface emissions.

[49] Equation (A8) has a unique solution but this solution is unstable so that the problem is ill posed [*Tikhonov and Arsenin*, 1977]. We use the variational method for solving ill-posed problems based on Tikhonov regularization technique [*Tikhonov and Arsenin*, 1977]. Equation (A7) can be formally rewritten as Fredholm equation of the first kind and as equivalent variational problem. The regularization technique requires incorporating of Tikhonov stabiliser with a tuneable regularization parameter $-\alpha$. This gives the following variational problem:

$$\begin{aligned} &\int_{t_0}^{t+T_0}\left[\int_{t_0}^{t_0+T} K(t, \tau)u(\tau)d\tau - F(t)\right]^2 dt + \alpha\int_{t_0}^{t_0+T}\left[u^2(\tau) + \left(\frac{du}{d\tau}\right)^2\right] \\ &d\tau = \min, t_0 \le t \le t_0 + T \\ &K(t, \tau) = 1,\ for\ t_0 \le \tau \le t \le t_0 + T \\ &K(t, \tau) = 0,\ for\ \tau > \text{t}. \end{aligned} \quad \text{(A9)}$$

[50] Finite difference approximation of Euler equation for this variational problem leads to a set of linear algebraic equations. This set of equations is well posed if parameter α is not too small [*Tikhikonov and Arsenin*, 1977; *Golub and Van Loan*, 1989].

Appendix B: Adapting the Inverse Technique To Use Data of Observations at a Single Point

[51] The basic integral equation (A7) can be rewritten in the equivalent differential form:

$$\frac{dQ_{sp}}{dt} = -V\frac{dQ_0}{dx}\big(x_{sp} - V(t - t_0)\big) + E\big(x_{sp} - V(t - t_0)\big). \quad \text{(B1)}$$

[52] The idea of adapting is that under a distinct diurnal cycle the nocturnal growth of the methane concentration at our sampling point is determined basically by emissions in the nighttime catchment area rather than by horizontal gradient of initial distribution, that is, that $\left|V\frac{dQ_0}{dx}\big(x_{sp} - V(t - t_0)\big)\right| \ll E\big(x_{sp} - V(t - t_0)\big)$.

[53] We shall use the concept of well-mixed daytime convective boundary layer (CBL). Owing to high turbulent mixing, the meteorological variables within CBL are nearly uniformly distributed along the full vertical extend of the CBL, CBL is generally capped by a potential temperature inversion [*Stull*, 1988]. The schematic of well-mixed CBL is applied in numerous models referred to as ‘‘jump’’ models [*Yamada and Berman*, 1979]. Let us put into use the parameters similar to those that have been introduced for the nocturnal period: the daytime gas burden Q_{day} in the layer $z < H_{day}$, where H_{day} is the maximum height of CBL. Q_{day} represents background plus accumulation in the daytime CBL on the other hand Q represents background plus accumulation in nocturnal ABL. By rough approximation that serves only for estimating the orders of magnitudes the equation for Q_{day} is of the same type as that for Q (A2):

$$\frac{\partial Q_{day}}{\partial t} + V_{day}\frac{\partial Q_{day}}{\partial x} = E_{day}, \quad \text{(B2)}$$

where V_{day} is the average wind speed within CBL.

[54] The orders of magnitude of the governing parameters are assumed on the basis of observations: $O(H) = 10^2$ m, $O(H_{day}) = 10^3$ m, $O(V) = 1 \text{m s}^{-1}$, $O(V_{day}) = 10 \text{ m s}^{-1}$ (see section 3.1), $O(E) = O(E_{day})$, the last assumption is valid because it is unlikely that the main sources of methane emissions in an urban region (waste treatment and gas distribution [CORINAIR]) have any significant diurnal variations. Methane emissions from traffic do have diurnal variations but this kind of emissions does not contribute more than about 10% to the total methane emissions [CORINAIR]. The catchment area radius for nocturnal accumulation can be assumed as a distance of an air mass to travel during the period of accumulation. Using the observed nighttime wind velocity of about 1–2 m s^{-1} and the average duration of a nighttime inversion situation of 8 hours, we calculate 30–60 km for L. The similar evaluation for L_{day} gives the values of some hundred kilometers. To the end of a daytime period $\partial Q_{day}/\partial t|_{t=t_0} \approx 0$ because L_{day} is much larger than the urban area source (Figure 2 presents experimental data which confirm this statement) so that from equation (B2) $\partial Q_{day}/\partial x|_{t=t_0} = E_{day}/V_{day}$. The initial condition for equation (A2) is $Q_0(x) = Q_{day}(x, t_0)H/H_{day}$ because CBL is well mixed. Thus the following estimates are valid:

$$\frac{dQ_0}{dx} = \frac{H}{H_{day}}\frac{\partial Q_{day}}{\partial x}\Big|_{t=t_0} = \frac{H}{H_{day}}\frac{E_{day}}{V_{day}}$$
$$O\left(\left|V\frac{dQ_0}{dx}/E\right|\right) = O\left(\frac{H}{H_{day}}\frac{V}{V_{day}}\right) = 10^{-2}. \quad \text{(B3)}$$

[55] Equation (B3) indicates that we are able to select weather conditions when the error associated with adapting the inverse technique to use data of observations at a single point is small enough. Equation (B3) gives the criterion for uses data of observations at a single point. Taking into account the estimate equation (B3) and returning to integral form, equation (B1) can be written as:

$$\int_{t_0}^{t} u(\tau)d\tau = Q_{sp}(t) - Q_{sp}(t_0), t_0 \le t \le t_0 + T. \quad \text{(B4)}$$

[56] Equation (B4) is mathematically similar to the general equation (A7), but unlike equation (A7) equation (B4) refers only to the data of observations at the single point.

[57] Our measurements give the time series of methane concentrations at a fixed level ($q_s(t)$) (see section 2.1). Some parameterization of vertical profile of methane concentration within nocturnal ABL is needed to determine $Q_{sp}(t)$ from $q_s(t)$. Put into use the following designations:

$$Q_{sp}(t) = q_H H + \Delta q_s h,\ h(t) = \int_{z_1}^{H} f_z(z)dz,\ f_z = \frac{\Delta q}{\Delta q_s},$$
$$\Delta q = q - q_H,\ \Delta q_s = q_s - q_H, \quad \text{(B5)}$$

where $f_z(z)$ is nondimensional vertical profile of gas concentration excess in nocturnal ABL, h is the effective thickness of accumulation layer. We suppose that at the beginning of nocturnal accumulation ABL is well mixed ($q_s(t_0) = q_H$) and $\partial q_H/\partial t \ll \partial q_s/\partial t$ then:

$$Q_{sp}(t_0) = q_s(t_0)H, Q_{sp}(t) = q_s(t_0)H + [q_s(t) - q_s(t_0)]h(t)$$
$$\int_{t_0}^{t} u(\tau)d\tau = [q_s(t) - q_s(t_0)]h(t), t_0 \le t \le t_0 + T. \quad \text{(B6)}$$

[58] The values of h for every accumulation event have been fitted on the basis of the early morning (04 LT) radiosonde profile data at Voeikovo and the empirical formula derived from observations on the 300-m meteorological tower at Obnisk (Russia) [*Sedunov*, 1991]. The maximum nocturnal ABL height (H) is searched for as the height of the upper border of the surface temperature inversion in the early morning. The temperature profile has been smoothed by nonlinear approximation. Approximation of surface inversion height as a function of time ($Z_i(t)$) is given by the empirical formula:

$$Z_i(t) = \min\left(a(t - t_1)^b, H\right), \quad \text{(B7)}$$

where a = 42 m $h^{-3/2}$ and b = 2/3 are empirical coefficients, t_1 is the moment of time 1.5 hour before sunset [*Sedunov*, 1991].

[59] To approximate $f_z(z,t)$ we have used the linear distribution from z_1 to Z_i that transforms progressively to uniform distribution throughout the layer of height H by the time when $Z_i = H$ ($f_z(z_1) = 1$, $f_z(Z_i) = Z_i/H$, $f_z(z > Z_i) = 0$). The uniform distribution is used to describe the influence of far removed sources under trapping conditions [*Perkins*, 1974]. The function f_z has to tend to uniform distribution through the nocturnal ABL since the main urban methane sources are situated far from Voeikovo (at the distances more than 10–15 km).

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