ISSN 1064-2293, Eurasian Soil Science, 2015, Vol. 48, No. 8, pp. 823–830. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.V. Smagin, N.A. Shnyrev, 2015, published in Pochvovedenie, 2015, No. 8, pp. 943–951.

SOIL PHYSICS

Methane Fluxes during the Cold Season: Distribution and Mass Transfer in the Snow Cover of Bogs

A. V. Smagin[a, b, c] **and N. A. Shnyrev**[a]
[a] *Faculty of Soil Science, Moscow State University, Moscow, 119991 Russia*
e-mail: smagin@list.ru
[b] *Institute of Ecological Soil Science, Moscow State University, Moscow, 119991 Russia*
[c] *Institute of Forest Science, Russian Academy of Sciences, Uspenskoe, Moscow oblast, 143030 Russia*

Received July 4, 2014

Abstract—Fluxes and profile distribution of methane in the snow cover and different landscape elements of an oligotrophic West-Siberian bog (Mukhrino Research Station, Khanty-Mansiisk autonomous district) have been studied during a cold season. Simple models have been proposed for the description of methane distribution in the inert snow layer, which combine the transport of the gas and a source of constant intensity on the soil surface. The formation rates of stationary methane profiles in the snow cover have been estimated (characteristic time of 24 h). Theoretical equations have been derived for the calculation of small emission fluxes from bogs to the atmosphere on the basis of the stationary profile distribution parameters, the snow porosity, and the effective methane diffusion coefficient in the snow layer. The calculated values of methane emission significantly (by 2–3 to several tens of times) have exceeded the values measured under field conditions by the closed chamber method (0.008–0.25 mg C/(m^2 h)), which indicates the possibility of underestimating the contribution of the cold period to the annual emission cycle of bog methane.

Keywords: mathematical simulation, emission, diffusion, convective transport, winter observations.
DOI: 10.1134/S1064229315080086

INTRODUCTION

Gas exchange with soil is presently considered as one of the most significant factors regulating the composition and state of the atmosphere, and its disturbance by anthropogenic impact can be a reason for global climatic changes. At the same time, mechanisms responsible for the gas function of soils with respect to the atmosphere are insufficiently understood, which in turn complicates the adequate quantification and simulation of this phenomenon [4]. Of special interest is the poorly-studied emission of methane—the second most important greenhouse gas—in winter, the assessment of which is methodologically difficult. It was shown earlier [6] that there is a principal possibility for the quantitative estimation of methane fluxes in the cold season from the data on the profile distribution of CH_4 in the snow layer on the basis of analytical solutions of the corresponding models for diffusive gas exchange under stationary conditions. This is confirmed by the analysis of available foreign publications [8, 10–12], the authors of which, unlike the Russian authors, used the common differential form of the Fick law with the calculation of fluxes from the concentration gradients and the effective gas diffusion coefficients; only Solomon and Cerling [11] used numerical integration methods for nonstationary and stationary problems of diffusive mass transfer. At the same time, experiments indicate nonlinear profile distributions of methane in the snow layer, the stationary form of which cannot be explained by the model of diffusion with constant coefficient. The aim of the current work is the generalized quantitative description of the nonlinear and linear distributions of methane in the snow cover of bogs on the basis of simple and physically substantiated models combining different mechanisms of mass transfer and a source of constant intensity on the soil surface in relation to the assessment of the emission fluxes of this gas during the cold season.

OBJECTS AND METHODS

The object of quantitative study and simulation was the profile distribution of methane in the snow layer on the surface of typical elements of a bog landscape (ryams, hummock ridges, swampy hollows, mires) in relation to the assessment of the gas emission during the cold season. Experimental studies were carried out at the Mukhrino Research Station of the Yugra State University in the middle-taiga zone of Western Siberia (Khanty-Mansiisk autonomous district, 60°53′20″ N, 68°42′10″ E) during the period from October 2010 through May 2011. They included the measurements of methane fluxes from the snow surface to the atmosphere by the chamber method [4], the thickness and bulk density of the snow layer [1], and the vertical distribution of methane in the snow cover. Samples of gaseous methane were thoroughly taken from the snow at a specified depth with 20-mL syringes with an elongated needle (IMP, USA; SFM, Germany) in 3–10 replicates, sealed, and transported to the station laboratory. The concentration of methane in the samples was determined on a Kristall-5000.1 gas chromatograph (Khromatek, Russia) with flame ionization detectors. Three air samples were successively injected into the instrument from each syringe (individual sample); the standard deviation of repeated measurements did not exceed 0.03 ppm. The snow temperature at different depths was recorded with DS1922 programmable sensors (Dallas Semiconductor, USA). The meteorological station measured the air temperature and humidity (at a height of 1.5 m) with a HygroClip S3 probe (Rotronic, Switzerland); the atmospheric pressure was measured with a Baro-Diver DI500 sensor (Schlumberger Water Services, the Netherlands). The concentration of methane in the gaseous phase (C, g/m^3) was calculated from the following equation [4]:

$$C = \frac{0.012X_{\text{ppm}}p}{RT}, \quad (1)$$

where X_{ppm} is the measured volumetric content of methane, ppm; p is the atmospheric pressure, kPa; T is the absolute temperature, K; and R is the universal gas constant equal to 8.31 J/(mol K).

The statistical processing of measurements, the approximation of the profile distribution data, the mathematical calculation of methane fluxes, and the drawing of graphics were performed using S-Plot 9 and Microsoft Excel 2003 with standard function packages and its own macros. The mathematical simulation of the emission and transport of gaseous methane through the snow layer was also used as a separate method of study. The models are partial differential equations with the corresponding boundary and initial conditions. From the obtained analytical solutions of the stationary model versions, the source intensity (emission flux) of methane from the peat bog soil occurring under snow in winter was calculated. The numerical solution of the complete model version was found using MATLAB-7 environment [2].

RESULTS AND DISCUSSION

The emission (positive) fluxes of methane measured by the conventional chamber method strongly varied among the observation dates and the bog landscape elements (Fig. 1). The negative flux values (methane adsorption from the chamber), which made up 22% of the measurements, were preliminarily excluded from the data set. Their genesis is not very clear, but it may be related to the physicochemical mechanisms of methane adsorption by the snow layer under nonequilibrium conditions, as well as to the activity of methanotrophic microorganisms in the thawing snow and on its solid-phase inclusions in spring and fall. In general, the studied positive values were low and rarely exceeded 0.2 mg C/(m^2 h). The minimum values were typical for of the coldest months (February, March): from 0.008 ± 0.004 to 0.017 ± 0.004 mg C/(m^2 h) for ryams, from 0.017 ± 0.012 to 0.043 ± 0.019 mg C/(m^2 h) for hummock ridges, from 0.007 ± 0.003 to 0.024 ± 0.013 mg C/(m^2 h) for swampy hollows, and 0.015 ± 0.006 mg C/(m^2 h) for mires. In the warmer months (May, October) with sporadic positive air temperatures, the emission of methane was higher: from 0.026 ± 0.015 to 0.033 ± 0.020 mg C/(m^2 h) for ryams, from 0.020 ± 0.005 to 0.043 ± 0.014 mg C/(m^2 h) for hummock ridges, from 0.249 ± 0.026 to 0.213 ± 0.042 mg C/(m^2 h) for swampy hollows, and from 0.060 ± 0.014 to 0.140 ± 0.046 mg C/(m^2 h) for mires. In the warm months, the methane fluxes from the waterlogged elements (mires, swampy hollows) were higher than those from hollow ridges and ryams (0.15–0.25 mg C/(m^2 h)) by an order of magnitude.

Compared to the characteristic values of methane emission from West-Siberian bogs in summer of about 5–10 mg C/(m^2 h) [7], the above estimates obtained for the winter period are insignificantly low, and their contribution to the total annual emission does not exceed 1–3% even with consideration for the dominance of the cold period. However, there are some reasons to consider these values underestimated. To solve the issue, let us turn to an alternative assessment procedure with the use of snow survey, which records the traces of methane emission from peat bogs as the corresponding distributions of methane concentrations in the snow cover.

Typical methane distributions in the snow cover are given in Fig. 2. According to the profile shape, they can be subdivided into three main types: (A) linear, (B) nonlinear concave, and (C) nonlinear convex ones. Type A is most frequently common to ryam parcels, and types B and C are usual in swampy hollows and on hummock ridges. The shapes of distributions reflect the processes of their formation and dynamics; therefore, the quantification of the process rates by the inverse problem method from stationary distribution models is feasible in some cases [3, 4]. Analogous physically substantiated models giving linear, concave, and convex profiles for methane distribution in an inert porous layer should be developed for this purpose.

Let us formulate the theoretical concept of the dynamics of gaseous methane in the snow layer on the surface of a peat-bog soil. We consider the elementary snow layer of thickness Δz on a unit area S. The balance of the gas mass (Δm) in this layer the time period (Δt is determined by the input (q_1) from the lower boundary (from the soil) and the output to the upper layer (q_2) according to the equation $\Delta m = (q_2 - q_1)S\Delta t$.

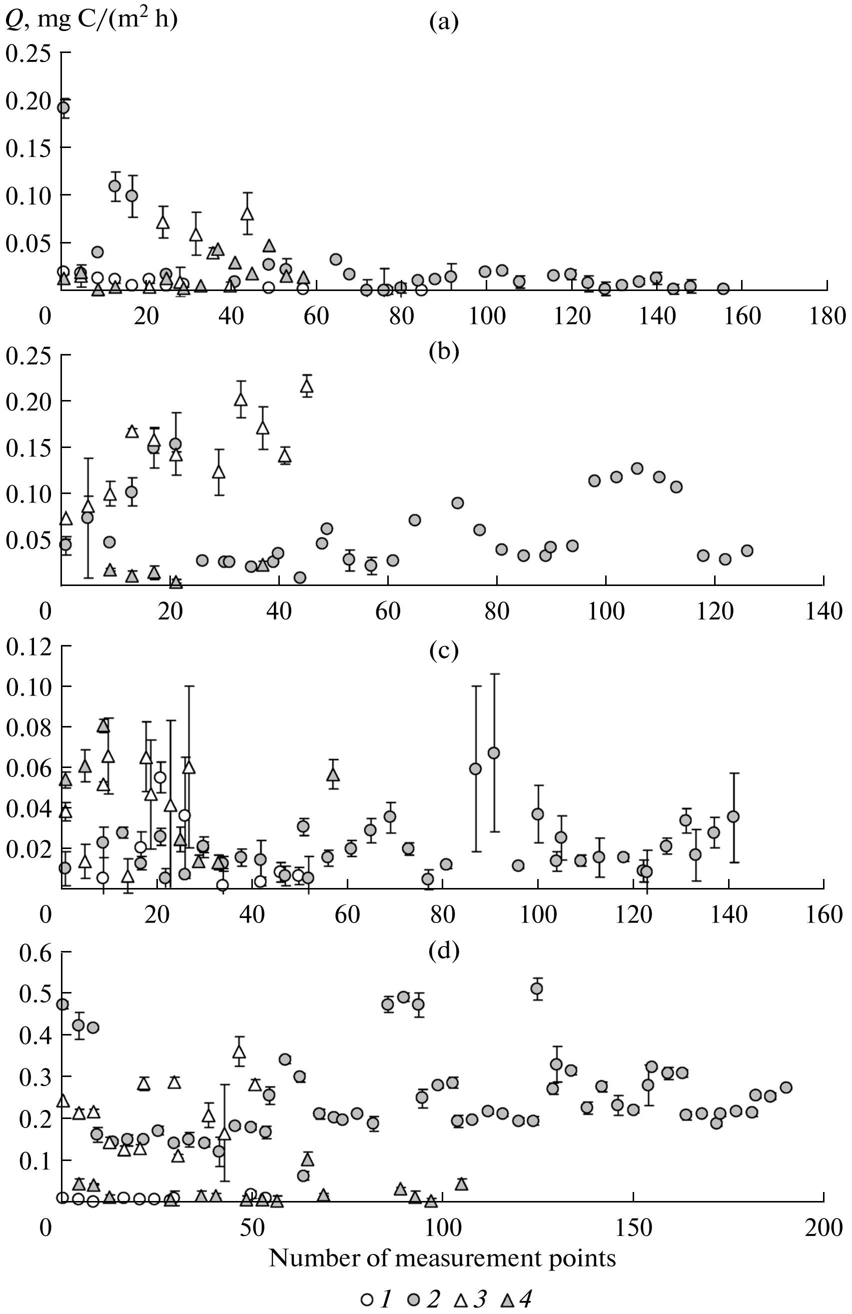

Fig. 1. Methane emission fluxes in different elements of a bog landscape during the cold season (estimation by the chamber method): (a) ryams; (b) mire; (c) hummock ridges; (d) swampy hollows; (*1*) March; (*2*) May; (*3*) October; (*4*) February; (vertical bars) standard deviations.

The volume of the elementary layer is $V = S\Delta z$, and the total gas concentration in the layer is $C_t = m/V$, the coordinate z being directed upwards from the soil surface to the atmosphere; therefore, the material balance law at $\Delta z, \Delta t \to 0$ can be described by the equation of continuity

$$\frac{\partial C_t}{\partial t} = -\frac{\partial q}{\partial z}. \qquad (2)$$

The experiments measure the content of gas in the gaseous phase (pore space) of the snow, rather than in its total volume; therefore, we substitute the total concentration (C_t) in the model (2) by the concentration in the gaseous phase (C) with consideration for the proportion of pores in the total snow volume (porosity P): $C_t = CP$. We take that the leading mechanism of gas mass transfer in the snow layer is molecular diffusion with the corresponding flux (Fick law): $q = -D_{\text{ef}}\, dC/dz$, where D_{ef} is

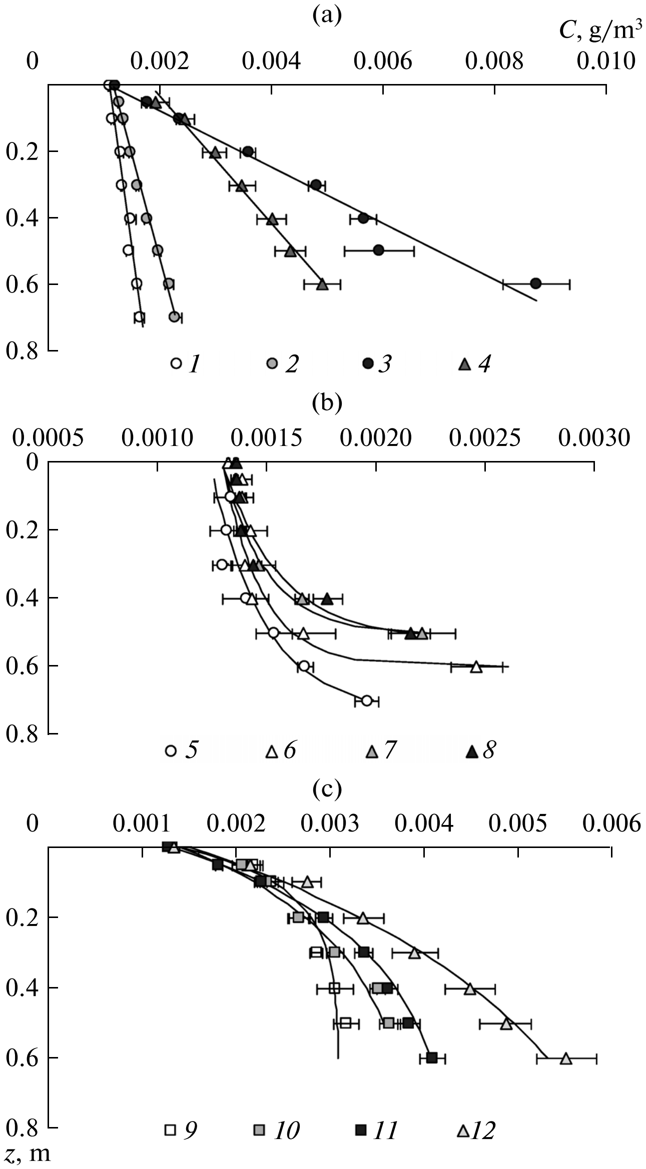

Fig. 2. Profile distributions of methane concentration in the snow layer (March 10 to March 21, 2011): (a) linear; (b) concave; (c) convex; (*1, 2, 3, 5*) ryams; (*4, 6, 7, 8,* 12) swampy hollows; (*9, 10, 11*) hummock ridges.

the effective gas diffusion coefficient as a function of porosity, pore sinuosity, atmospheric pressure (p), and absolute temperature (T). The snow is a macroporous environment; therefore, in a first approximation, the diffusion coefficient can be determined from the Penman equation with corrections for temperature and pressure [4]

$$D_{\text{ef}} = 0.66PD_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right). \tag{3}$$

Substituting Eq. (3) to Eq. (2) and reducing P in the expression, we obtain a simple model for the distribution of methane in a homogeneous inert snow cover incapable of retaining (adsorbing) the gas and transforming it to any other chemical compounds

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}, \tag{4}$$

where z is the vertical coordinate, m; t is the time, h; C is the concentration of methane in the gaseous phase of the snow layer, g/m^3; and $D = D_{\text{ef}}/P$ is the effective diffusion coefficient normalized to the constant P value.

Model (4) has the following obvious boundary conditions. On the soil surface ($z = 0$), the Cauchy boundary condition (methane emission flux of intensity Q, mg/(m^2 h)) is used. With consideration for the diffusional mechanism of methane transport in the snow layer, this condition is formalized as follows:

$$-D_{\text{ef}}\left.\frac{dC}{dz}\right|_{z=0} = Q. \tag{5}$$

At the upper boundary, the absolute index of which is the snow layer depth (H), it is advisable to select the constant methane concentration in the atmospheric air as a suitable condition:

$$C\big|_{z=H} = C_0. \tag{6}$$

Model (4) with boundary conditions (5) and (6) describes the dynamics of gas profile in the snow layer. After a time period specified from the gas emission and diffusion rates, the gas concentration profile becomes invariant (stationary). The shape of the stationary profile can be obtained by equating the left part of Eq. (4) to zero

$$\frac{d^2C}{dz^2} = 0. \tag{7}$$

Integrating Eq. (7) over depth (z), we have

$$\int\frac{d^2C}{dz^2} = \frac{dC}{dz} = A, \tag{8}$$

where A is the integration constant. Comparing Eqs. (8) and (5), we obtain from the first boundary condition that

$$\frac{dC}{dz} = A = -\frac{Q}{D_{\text{ef}}}. \tag{9}$$

After the integration of Eq. (9) over z, we obtain, in the general form, the gas concentration as a function of the vertical coordinate

$$\int\frac{dC}{dz} = C_{(z)} = \int -\frac{Q}{D_{\text{ef}}}dz = -\frac{Q}{D_{\text{ef}}}z + B, \tag{10}$$

where B is the integration constant. Using second boundary condition (6), we determine constant B and the final function of the stationary methane profile in the snow layer

$$C_{(z)} = \frac{Q}{D_{\text{ef}}}H + C_0 - \frac{Q}{D_{\text{ef}}}z. \quad (11)$$

Function (11) is a linear equation

$$C_{(z)} = -az + b, \text{ where } a = \frac{Q}{D_{\text{ef}}}, \ \ b = \frac{Q}{D_{\text{ef}}}H + C_0. \quad (12)$$

Therefore, after the approximation of the methane profile in the snow layer by linear relationship (12), the target emission flux (Q) can be calculated from the line slope (a), effective gas diffusion coefficient (D_{ef}), and porosity (P). Another method of calculation is based on the values of residual term (b), effective gas diffusion coefficient, porosity, snow layer thickness (H), and methane concentration in the atmosphere (C_0). The corresponding equations are as follows:

$$\begin{gathered} Q = -aD_{\text{ef}}, \\ Q = (b - C_0)\frac{D_{\text{ef}}b}{H}. \end{gathered} \quad (13)$$

In a macroporous environment, effective diffusion coefficient is linearly related to porosity (Eq. (3)). Substituting this equation to Eq. (13), we obtain the corresponding formulas for Q

$$Q = 0.66aPD_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right), \quad (14)$$

or

$$Q = 0.66P\frac{D_{st}}{H}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right)(b - C_0). \quad (15)$$

It can be supposed that snow is not completely inert with respect to methane and can adsorb it when going from the peat surface to the atmosphere. Microbial oxidation (methanotrophic filter) in the bulk snow in winter is apparently excluded because of low temperatures. As we showed earlier [6], the introduction of the concept of equilibrium adsorption by interphase distribution with the Henry constant in the model has no significant effect on the linear distribution shape and can be accounted for by a new diffusion coefficient (D'_{ef}), which includes the Henry constant (K_{H})

$$D'_{\text{ef}} = D_{\text{ef}}/(1 + (1/P - 1)K_{\text{H}}). \quad (16)$$

By physical sense, $0 < P < 1$; then, the expression $(1 + (1/P - 1)K_{\text{H}})$ cannot be lower than 1 at any $K_{\text{H}} > 0$. Consequently, at the equal parameters a and b of the linear profile distribution of methane in the snow layer, the new calculation gives the values of fluxes (Q) similar to or lower than those obtained from Eqs. (14) and (15). Thus, in formal terms, the supposition about the presence of equilibrium gas adsorption in the snow layer is adequate to the decrease in diffusion rate ($D'_{\text{ef}} < D_{\text{ef}}$) and, hence, the decrease in the calculated source intensity (Q).

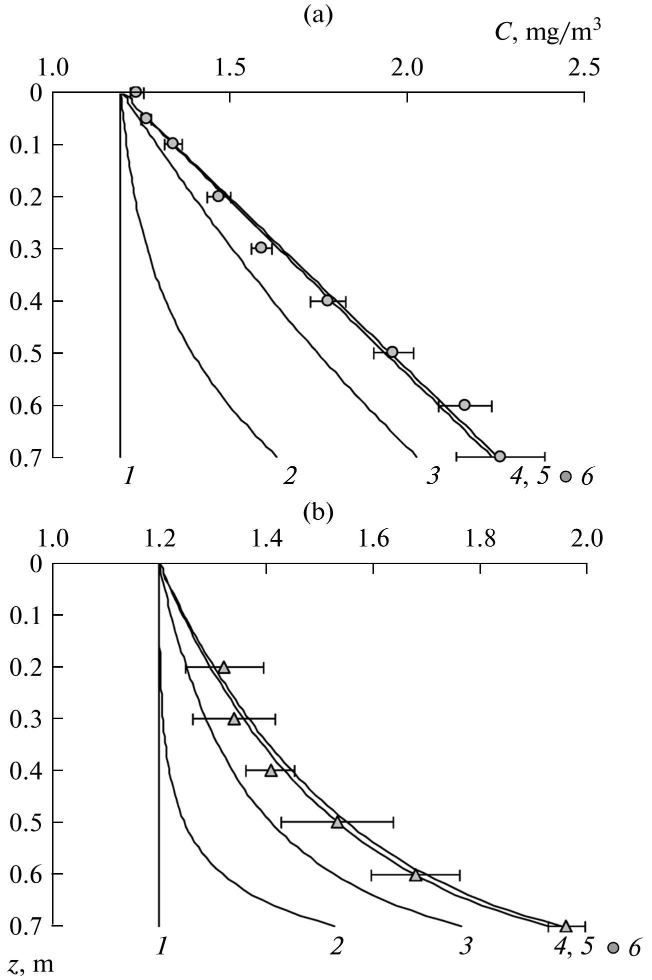

Fig. 3. Simulation of methane distribution dynamics in the snow cover: (a) linear stationary distribution (model (4)); (b) concave stationary distribution (model (17)); (*1*) initial (atmospheric) concentration; (*2*, *3*, *4*, *5*) concentration profiles after 2, 8, 24, and 48 h, respectively; (*6*) actual data (stationary distributions).

We have considered the simplest linear profile of methane concentrations (Fig. 4a). Are similar models possible for nonlinear profile distributions (Figs. 4b–4c)? It may be supposed that the obtained experimental nonlinear profiles are steps towards reaching a stationary state. However, as will be shown below, the characteristic formation time of stationary gas profiles in a snow layer 60–80 cm thick under the studied conditions does not exceed a few days. Hence, a more probable hypothesis is that the nonlinear profiles are also stationary. We attempt to reveal the physical principles of their appearance. First, we consider the concave profile (type B).

The initial model (4) supposed that the snow layer is homogeneous and has similar values of effective diffusion coefficient throughout the profile. However, the analysis of snow density (ρ) revealed its linear increase with depth ($\rho_{(z)} = 0.282z + 0.084$, $R^2 = 0.93$) and the corresponding decrease in porosity. Experimental proof for the relationship between the convex shape of concentration profile and the linear increase of snow density with depth can also be found in [8]. According to the Penman function for diffusion in macroporous environments (Eq. (3)) used in our work, the coefficient of diffusion will also linearly decrease with depth at the linear decrease of porosity. We formalize this statement as follows. Given the diffusion coefficients D_0 on the surface and D_H at the lower boundary of the porous layer (H), the relationship between diffusivity and depth has the form $D_{(z)} = D_0 - (D_0 - D_H)z/H$. Substituting it, together with the phenomenological expression for the diffusion flux, to continuity equation (2) and differentiating with respect to z, we obtain

$$P\frac{\partial C}{\partial t} = D_0\frac{\partial^2 C}{\partial z^2} - \frac{(D_0 - D_H)}{H}z\frac{\partial^2 C}{\partial z^2} - \frac{(D_0 - D_H)}{H}\frac{\partial C}{\partial z}. \quad (17)$$

The stationary version of Eq. (16) is as follows:

$$\frac{\partial^2 C}{\partial z^2}(1 - mz) - m\frac{\partial C}{\partial z} = 0, \quad (18)$$

where $m = (D_0 - D_H)/(HD_0)$.

The solution of Eq. (18) is the simple logarithmic function $C_{(z)} = C_1\ln(1-mz)/m + C_2$, where C_1 and C_2 are the integration constants determined from the boundary conditions. Under the condition of the constant gas concentration in the atmosphere (C_0) and emission flux from the soil (Q), we obtain the following expression for the stationary profile distribution of methane in the snow layer:

$$C_{(z)} = C_0 - \frac{Q}{D_0 m}\ln(1 - mz). \quad (19)$$

This equation successfully describes the concave distribution (type B). The physical sense of the obtained picture is that the diffusion permeability is low in the denser lower layers; therefore, the gas concentration is increased. When the distance from the snow cover surface decreases, the diffusion is facilitated, and methane can be easily released to the atmosphere, which in turn decreases the gas concentration and the corresponding gradient.

The approximation of experimental data on the concentrations of methane in the snow layer by the nonlinear regression equation $C_{(z)} = C_0 - a\ln(1 - mz)/m$, where $a = Q/D_0$, using S-Plot 9 software gives a simple expression for the calculation of emission flux from the diffusion coefficient analogous to Eq. (14).

The concave shape of the stationary profile in the inert snow layer is easy to describe in physical terms, but the diffusion model without the source/sink function is insufficient to explain the convex distributions (type C). At the same time, the inclusion of convective mass transfer mechanism with velocity υ (m/h) allows obtaining similar profile distributions. From the physical point of view, these can be mechanisms of forced convection, e.g., under the effect of wind on the snow surface, or natural convection of the local accumulations of methane, which is lighter than the atmospheric air. The simple convection without diffusion obviously results in the linear vertical concentration distribution ($C_{(z)} = Q/\upsilon$) in the stationary state. Such profile distributions were sporadically observed for the hummock–ridge complex and mire. However, the flux from the soil Q cannot be determined from these values without knowledge of the convection rate, and the theoretical assessment of this mechanism is impossible, as distinct from diffusion. At the same time, the combination of diffusion and convection allows such assessment from the stationary profile distributions, which have a convex shape (type C) and occupy an intermediate position between two extreme lines: an inclined line (diffusion) and a vertical line (convection).

Substituting the combination of diffusional and convective fluxes with constant coefficients normalized to aeration porosity $D = D_{ef}/P$ and $q = \upsilon/P$, respectively, to continuity equation (2), we obtain the following model:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} + q\frac{\partial C}{\partial z}. \quad (20)$$

The stationary version of Eq. (20) has the form

$$\frac{\partial^2 C}{\partial z^2} + \frac{q}{D}\frac{\partial C}{\partial z} = 0, \quad (21)$$

from which, after the first integration over z at the boundary condition of equality of the total diffusional and convective fluxes to the emission from the soil ($DdC/dz + qC = Q/P$ at $z = 0$, $z = H$), we have

$$\frac{\partial C}{\partial z} = \frac{Q}{PD} - \frac{q}{D}C. \quad (22)$$

Then, using the substitution of variables $u = Q/(PD) - qC/D$, we reduce Eq. (22) to the form $\partial\ln u/\partial z = -q/D$, the integration of which gives the function $u = B\exp(-qz/D)$, where B is the integration constant. Returning to variable C and using the boundary condition of constant concentration in the atmosphere (C_0) (hence, $B = Q/(PD) - qC_0/D$), we obtain the final equation for the stationary concentration profile in model (21) combining diffusion and convection

$$C_{(z)} = \frac{Q}{Pq} + \left(C_0 - \frac{Q}{Pq}\right)\exp\left(-\frac{q}{D}z\right). \quad (23)$$

This function describes a convex profile (type C), which approaches a vertical line $C_{(z)} = Q/(Pq)$ at the high velocities of convective mass transfer and an inclined line (Eq. (11)) when diffusion prevails. Approximating the actual profile distribution by a nonlinear regression equation $C_{(z)} = y_0 + a\exp(-bz)$ (where $y_0 = Q/(Pq)$, $a = C_0 - Q//(Pq)$, $b = q/D$ using S-Plot 9 software, we find expressions for calculating the rate of normalized convective flux (q) and methane

Approximation parameters of the profile distributions of methane in the snow layer (Fig. 2)

Model (12) $C_{(z)} = -az + b$						
No.	Parcel	a, g/m^4	b, g/m^3	C_0, g/m^3	R^2	Q, mg C/(m^2 h)
1	Ryam	0.0008	0.0017	0.0012	0.97	0.03
2	Ryam	0.0016	0.0023	0.0012	0.99	0.05
3	Ryam	0.0114	0.0081	0.0012	0.97	0.38
4	Swampy hollow	0.0057	0.0051	0.0012	0.97	0.19
Model (19) $C_{(z)} = C_0 - a\ln(1 - m\,z)/m$						
No.	Parcel	a, g/m^4	m, m^{-1}	C_0, g/m^3	R^2	Q, mg C/(m^2 h)
5	Ryam	0.0003	1.353	0.0012	0.97	0.01
6	Swampy hollow	0.0003	1.666	0.0013	0.99	0.01
7	Swampy hollow	0.0004	1.981	0.0013	0.99	0.02
8	Swampy hollow	0.0005	1.923	0.0013	0.96	0.02
Model (23) $C_{(z)} = y_0 + a\exp(-bz)$						
No.	Parcel	a, g/m^4	b, m^{-1}	y_0, g/m^3	R^2	Q, mg C/(m^2 h)
9	Ridge	0.0031	0.0017	8.722	0.97	1.02
10	Ridge	0.0040	0.0026	3.641	0.98	0.55
11	Ridge	0.0044	0.0031	3.750	0.99	0.62
12	Swampy hollow	0.0069	0.0054	2.060	0.99	0.54

emission (Q) from the known values of porosity (P) and normalized effective diffusion coefficient ($D = D_{\text{ef}}/P$)

$$q = bD = 0.66bD_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right), \tag{24}$$

$$Q = y_0qP = 0.66y_0bPD_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right), \tag{25}$$

or

$$Q = (C_0 - a)qP = 0.66(C_0 - a)bPD_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{p}\right). \tag{26}$$

We illustrate the above theoretical considerations with practical results. All the lines in Fig. 4 are results of the approximation of experimental data for the distribution of methane in the snow layer by stationary profile equations (12), (19), and (23). The reliability values and approximation parameters are given in the table. It can be seen that high values of R^2 (0.97–0.99) at the minimum standard errors (10^{-4} to 10^{-5}) and statistically significant parameters for a significance level of 0.05–0.001 were obtained in all the cases, which indicates adequacy of the models. Using the approximation parameters and the corresponding equations for calculating Q (Eqs. (14), (15), (25), and (26)), the emission fluxes can easily be estimated. The standard diffusion coefficient D_{st} was taken equal to 0.072 m^2/h [4], and the maximum porosity of snow P calculated from the experimental data on the density in the upper layer was 0.9. The comparison of the tabulated data with the emission fluxes measured by the chamber method (Fig. 1) for the studied period (the first 20 days of March) shows that they strongly differ, the higher values being always obtained by the gradient method. The differences vary from 3 to 47 times for the linear trends (diffusion model with a constant coefficient), from 2 to 3 times for the concave distributions (diffusion model with the coefficient decreasing with depth), and from 33 to 77 times for the convex distributions (model of diffusion and convection with constant coefficients). Hence, the difference can be of almost two orders of magnitude in the last case, and this is a direct result of more intensive convective transport of methane to the atmosphere. The velocity of convective mass transfer $\upsilon = qP$ was estimated from Eq. (24) at 0.08 m/h (swampy hollows) to 0.14–0.33 m/h (hummock ridges). Note that for the almost vertical distributions parallel to the ordinate, which are observed in the hummock–ridge complex and mire, the values of $C_{(z)} = Q/\upsilon$ v vary in the range 1–3 mg/m^3; given the above estimate for the convective transfer velocity, this also gives relatively intensive emission fluxes of 0.1 to 1 mg C/(m^2 h).

In conclusion, we consider the dynamics of the profile distribution of methane. How inert is the gas profile in the snow layer, or how rapidly is the stationary distribution of methane established? This question may be answered by using the numerical simulation in

MATLAB-7 environment on the basis of complete models of methane dynamics in the form of differential equations (3), (17), and (20) with boundary conditions of constancy of the flux from the soil (Q) and the concentration in the atmosphere (C_0). The procedure of calculation was described in detail [2]. For the numerical experiment, we used the calculated values of methane flux $Q = 0.05$ mg C/(m^2 h) (model (4)) and $Q = 0.01$ mg C/(m^2 h) (model (17)) estimated from the stationary profiles, the initial concentration equal to that in the atmosphere $C_0 = 1.2$ mg/m^3, and the effective diffusion coefficient $D = 0.033$ m^2/h (model (4)) and $D_0 = 0.038$ m^2/h at $m = 1.35$ L/m (model (17)). The results of the numerical simulation of gas profile dynamics are shown in Fig. 3. It can be seen that a stationary equilibrium almost identical to the distributions obtained under field conditions is established after 24 h. This means that the proposed method of gradient estimation is quite sensitive and gives the value of methane flux from the snow-shielded bog soil averaged over several days.

In general, it can be concluded that the assessment of methane fluxes from bog soils is a difficult methodological problem. The chamber method can underestimate the gas emission [9]; in bog landscapes with potential fast local (preferential) convective fluxes, its use is a priori problematical [4], because it is almost impossible to predict the place and time of local convective discharge of bog gas to the atmosphere, during which the gas reserve accumulated in the zone of active methanogenesis in the unsaturated peat layer can be removed almost instantaneously [4, 5]. On this background, the method of area-averaged gas profiles, including the snow survey considered in this paper, gives a more objective estimate.

ACKNOWLEDGMENTS

We thank E. V. Shein and M. V. Glagolev (Faculty of Soil Science, Moscow State University) for valuable advices and remarks during the preparation of the manuscript.

REFERENCES

1. A. F. Vadyunina and Z. A. Korchagina, *Methods to Study Physical Properties of Soils and Grounds* (Vysshaya Shkola, Moscow, 1973) [in Russian].
2. M. V. Glagolev and A. V. Smagin, *Implementation of the MATLAB Software for Solving Numerical Problems of Biology, Ecology, and Soil Science* (Mosk. Gos. Univ., Moscow, 2005) [in Russian].
3. A. V. Smagin, "Kinetic models of the organic profile of soils," Vestn. Mosk. Univ., Ser. 17: Pochvoved., No. 3, 3–7 (2001).
4. A. V. Smagin, *Gas Phase of Soils* (Moscow State University, Moscow, 2005) [in Russian].
5. A. V. Smagin, "Soil-hydrophysical support of the studies of gas function of West Siberian mires in relation to the problem of greenhouse effect," Ekol. Vestn. Sev. Kavk. **3** (3), 46–58 (2007).
6. A. V. Smagin, N. A. Shnyrev, and V. G. Vityazev, "The theory of profile-gradient method of methane emission by mires during winter," Ekol. Vestn. Sev. Kavk. **7** (2), 23–29 (2011).
7. N. A. Shnyrev and M. V. Glagolev, "Data bank on methane emission from Russian soils," in *Proceedings of the Fifth Scientific School "Mires and Biosphere"* (Center of Scientific-Technical Information, Tomsk, 2006), pp. 283–286.
8. M. A. Mast, K. P. Wickland, R. T. Striegl, and D. W. Clow, "Winter fluxes of CO_2 and CH_4 from subalpine soils in Rocky Mountain National Park, Colorado," Global Biogeochem. Cycles **12** (4), 607–620 (1998).
9. J. M. Norman, C. J. Kucharik, S. T. Gower, D. D. Baldocchi, P. M. Crill, et al., A comparison of six methods for measuring soil-surface carbon dioxide fluxes," J. Geophys. Res. **102** (24), 28771–28777 (1997).
10. N. S. Panikov and S. N. Dedysh, "Cold season CH_4 and CO_2 emission from boreal peat bogs (West Siberia): Winter fluxes and thaw activation dynamics," Global Biogeochem. Cycles **14** (4), 1071–1080 (2000).
11. D. K. Solomon and T. E. Cerling, "The annual carbon dioxide cycle in a montage soil: Observations, modeling, and implications for weathering," Water Resour. Res. **23** (12), 2257–2265 (1987).
12. S. A. Zimov, G. M. Zimova, S. P. Davidov, A. I. Davidova, Y. V. Voropaev, Z. V. Voropaeva, S. F. Prosiannikov, O. V. Prosiannikova, I. V. Semiletova, and I. P. Semiletov, "Winter biotic activity and production of CO_2 in Siberian soils: a factor in the greenhouse effect," J. Geophys. Res.: Atmos. **98** (3), 5017–5023 (1993).

Translated by K. Pankratova