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SOIL PHYSICS

Methane Fluxes in Cold Season: Assessment by Closed Chamber Method

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Abstract—The results of field studies of methane emission to the atmosphere from different landscape elements of West Siberian oligotrophic bog (Mukhrino test plot, Khanty–Mansi autonomous okrug) in the cold season are discussed. The statistical parameters of the process are estimated, and the high variability of methane fluxes and their deviation from the normal distribution are shown. From October to May, the mean arithmetic and median values of methane fluxes were equal to 0.06 ± 0.01 and 0.02 mg C/(m^2 h), respectively, with the sampling ranging from –0.3 to 0.5 mg C/(m^2 h). In 22% of cases, the negative fluxes (gas consumption) were observed with the average intensity of –0.03 ± 0.01 mg C/(m^2 h) and the median of –0.01 mg C/(m^2 h). At the same time, a considerable underestimation of emission values cannot be excluded, because of the methodological problems of the routine calculation of fluxes by the linear approximation of trends in the gas concentration dynamics in the chamber. The alternative calculation models are provided, and the possible reasons for the experimentally observed phenomenon of methane sink recorded in the chambers on the snow cover surface, including photochemical processes, are discussed.

Keywords: methane, bog ecosystems, winter observations, emission flows and absorption, diffusive transport, photolysis, mathematical modeling, wetlands

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INTRODUCTION

Methane is the second most important greenhouse gas after carbon dioxide; its relative contribution to the greenhouse effect is estimated at no less than 15% [13]. Wetlands (overmoistened lands) are the main source of methane among terrestrial ecosystems. In recent decades, the studies of methane emission to the atmosphere from bog ecosystems have been intensified [2, 4, 16]. Taking into account that 115 ± 2.3 billion tons or 60% of the world peat resources are concentrated in Russia [6], the acuteness of investigating the methane emission from bogs in Russia becomes evident; this is particularly true for Western Siberia, where wetlands are widespread. Poorly studied methane emission in winter is of particular interest, as its estimation involves certain methodological difficulties. The present work focuses on the results of experimental study of methane fluxes at the boundary of the atmosphere with different elements of bog landscape in winter season; in addition, methodological problems in the estimation of this phenomenon by the routine method of closed chambers are discussed.

OBJECTS AND METHODS

The experimental studies of methane fluxes by the method of closed chambers [13] were conducted in 2010 and 2011 during the vegetation pause from October to May in the middle taiga zone of Western Siberia at the Mukhrino test plot of the Yugra State University (the Khanty-Mansi autonomous okrug, 60°53′20″ N, 68°42′10″ E). Typical elements of bog landscape—forested bog, quaking bog, ridges, and bog pools—were studied. The measuring chambers with squared base ranged in height from 10 to 60 cm and were installed on the metal frame inserted into the snow with a rib from 40 to 100 cm. The gas phase was sampled from the chambers with syringes (4 samples taken at 10- to 30-min intervals), then transported to the stationary laboratory and analyzed on a Crystal chromatograph with the flame-ionization detector. Four portions of the gas were successively injected into the chromatograph from each syringe; the obtained data were then averaged for the given sampling points and sampling times. Overall, 1457 individual samples were taken from 366 sampling points representing different elements of the bog landscape during the 214-day-long cold season. The gas-chromatography accuracy permitted us to detect reliably very low volumetric con-

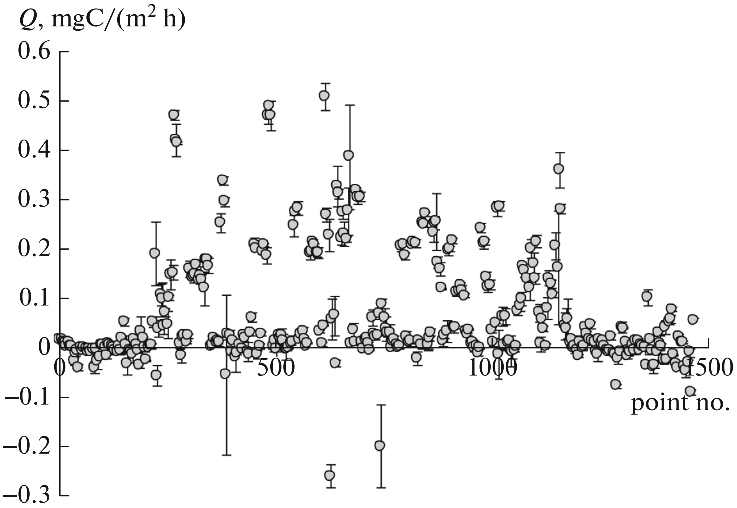

Fig. 1. Methane gas fluxes in the cold season (Mukhrino station, Khanty-Mansi autonomous okrug, October 16—February 22; March 15—May 27); vertical bars stand for the standard deviations.

centrations of methane (about 1 ppm) typical of the gas phase in the natural atmosphere and in the chamber. Simultaneously, the temperature of the environment was measured with programmed sensors DS1921, and the barometric pressure was measured with a portable field meteorological station. The methane concentration in the gas phase (C, g C/m^3) was calculated from the measured volumetric concentration of methane (X, ppm), the absolute temperature (T, K), and the barometric pressure (p, kPa) according to the following equation [13]:

$$C = \frac{0.012Xp}{RT}, \tag{1}$$

where $R = 8.31$ J/(mol K) is the universal gas constant.

The trends of methane carbon concentration dynamics in the chamber ($C(t)$) were approximated by the straight-line equation, the inclination angle tangent of which (a) permitted us to calculate the flux (Q, mg C/(m^2 h)) according to the equation [13]:

$$Q = 1000\frac{dC}{dt}H = 1000aH, \tag{2}$$

where t is the chamber exposure time, h; H is the chamber height above the snow surface, m; and 1000 is the converting coefficient from grams to milligrams.

We applied Statistica 6.1, S-Plot 9, and Microsoft Excel 2003 software with standard function packages and copyrighted macros for statistical treatment of the results, approximation of trends for the gas concentration dynamics in the chamber, calculations of methane fluxes, and graphical plotting.

RESULTS AND DISCUSSION

Figure 1 shows the general results of experimental assessment of methane fluxes during the cold season at the Mukhrino test plot. The high variability of the fluxes should be noted: both positive (emission) and negative (sink) fluxes were observed. The portion of the latter comprised 22% of measurements. Three values sharply differing in their magnitude were preliminarily excluded from the sample: –2.4 ± 0.03, –0.9 ± 0.01, and –0.3 ± 0.2 mg C/(m^2 h). The obtained data were statistically processed. The distribution of fluxes showed a markedly pronounced right-side asymmetry (A = 1.11 ± 0.11) and medium-degree excess (E = 2.59 ± 0.22) [5]. The normal distribution test with the use of two criteria (the criterion of Kolmogorov—Smirnov and χ^2) was negative in both cases. Therefore, we used both the median values and the standard mean arithmetic values. The mean arithmetic value of the flux was equal to 0.06 ± 0.01 mg C/(m^2 h), whereas the median value was 0.02 mg C/(m^2 h) with the sampling span from –0.3 to 0.5 mg C/(m^2 h). As compared to the typical values of methane emission from West Siberian mires in the summer season, which reach about 5—10 mg C/(m^2 h) [2, 16], the obtained value was negligibly small, with its input to the annual emission of no more than 1—3%, even taking into account the long duration of the cold season. This fact is supposedly the specific feature of anaerobic processes, since the winter season contributes significantly (about 30%) to the annual soil respiration (CO_2 emission) and aerobic biodestruction [9, 13, 15]. At the same time, the result obtained may explain a relatively low contribution of West Siberian boreal mires (no more than 2—10% according to [3, 4]) to the global emission from wetlands despite the high pool of the organic matter accumulated in these mires. How-

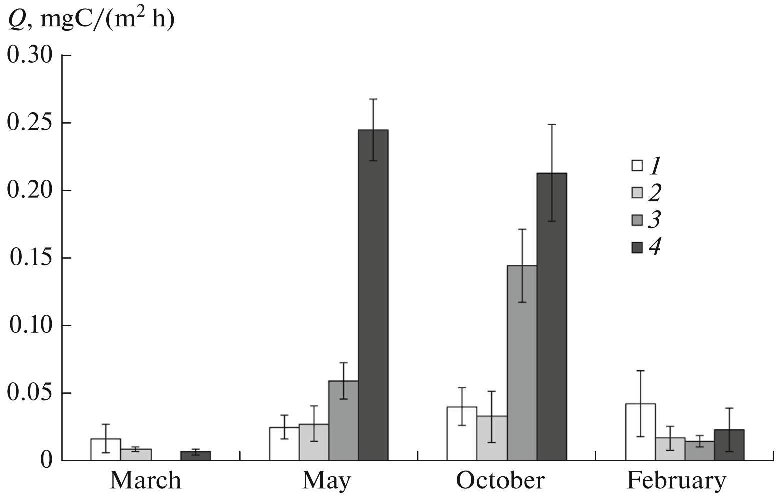

Fig. 2. Dynamics of methane emissions in the cold season from different elements of bog landscape: *1*—ridges, *2*—forested bog, *3*—quaking bog, and *4*—bog pools; hereinafter, vertical bars designate the 95% confidence interval.

ever, the results obtained still cannot be considered indisputable, and there are some methodological grounds (discussed in the final part of this paper) permitting us to increase the obtained estimate of the winter emission of methane by almost an order of magnitude, i.e., to bring it to the level typical of the winter soil respiration.

The high variability of the data with significant asymmetry and excess in the distribution of methane fluxes may result both from the high spatial heterogeneity typical of bog landscapes and from some specific combination of different mechanisms of gas transfer. At the same time, the evident fact of predominately convective flows of methane (vegetative or bubble transport) in the warm season seems to be obscure under conditions of the frozen peat with the snow cover on its surface. Routine gas diffusion should take place in the snow mass, and the differences in fluxes can be related to the emission heterogeneity at the peat bog surface proper with the formation of local concentration gradients. However, it is necessary to explain negative (sink) fluxes recorded in the chambers with the initially increased concentration of methane. A routine hypothesis suggesting that the gas is pressed out from the soil upon installation of the chamber seems to be unsuitable, because the chambers were installed on the snow covering the frozen peat. The deep-soil methane as a lighter (its molecular mass is equal to 16 g/mole) and warmer (as compared to the near-surface air) component may possibly move under the impact of natural convection due to the difference in densities [13]. In this case, there should be some "paths" in the frozen peat mass (fractures, plant stems, etc.). The convective transport is impossible in pure ice without any inclusions, and the diffusive transport tends to zero because of the very low diffusion coefficient. It is known that ice on the river or lake surface is a good isolator, preventing gas exchange with the atmosphere. However, judging from our data, the permeability of the bog for methane is preserved in the cold season.

The analysis of spatial variation in the cumulative emission fluxes from the particular elements of bog landscape during the studied cold season (214 days) proves their growth in the following sequence: forested bog—ridges—quaking bog—bog pools (113 ± 42, 200 ± 41, 265 ± 36, and 495 ± 59 mg C/m^2 per the season, respectively). These data were obtained after the spline approximation of seasonal dynamics trends in positive fluxes of methane and numerical integration of the obtained curves at the studied time span with a step of 1 day.

The emission differed significantly in the months of the cold season (Fig. 2). In February and March, the fluxes did not exceed 0.05 mg C/(m^2 h), being maximum at the ridges. The elevated and, hence, partially drained relief elements were more permeable for methane in peat bog at this time. The mean monthly air temperature was below zero; in February, it was as low as −19 to −20°C; whereas in March, the temperature did not fall below −10 to −13°C. However, the methane emission was higher in February than in March, which casts doubt on the well-known positive relationship between the emission and temperature, which is used in a number of models. We can suppose that the methanogenesis is almost completely suppressed at subzero temperatures; and the gas that has been accumulated in the peat bog in summer is released to the surface. According to the analysis of the constants of interphase equilibrium of methane [12], this release takes place in the adsorbed form rather than in the gaseous phase or in the solution.

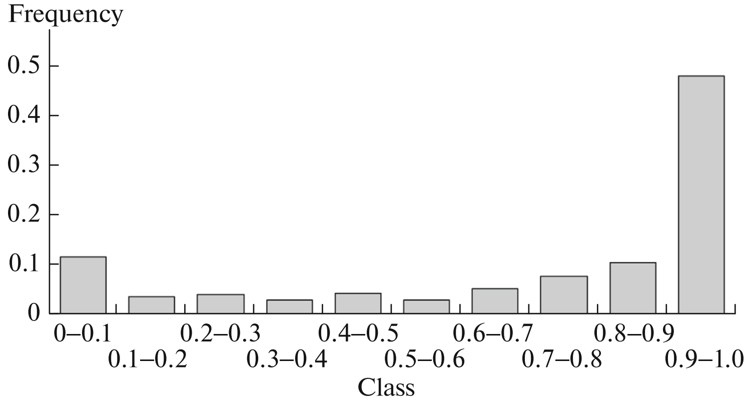

Fig. 3. Frequency distribution R^2 for approximation of methane concentration trends in isolating chambers with the linear model.

The mean monthly temperatures were above zero in October and May; no higher than 3°C (October) and 8°C (May); the snow melting took place at the beginning of May. As a result, the emission fluxes increased to 0.15–0.25 mg C/(m^2 h). The maximum values were recorded not on the ridges (as in February and March), but in the strongly overmoistened elements of the bog landscape (bog pools and quaking bogs), where the methanogenesis was probably more active; in addition, the convective transfer of methane accumulated in the deep soil layers could take place under the pressure of surface floodwater and rainwater.

Let us consider some methodological aspects of the assessment of methane emission by the chamber method. Figure 3 shows the frequency distribution of the reliability of approximation (R^2) of methane concentrations in the chamber by a linear model. Note that the linear character of the accumulation of gas in the chamber is a priori assumption laid in the basis of calculation of the gas flux as a product of the tangent of the slope of the concentration curve (straight line) and the height of the chamber (Eq. (2)). However, as seen from Fig. 3, the R^2 value may exceed 0.9, and the concentration trends are linear only in 50% cases. A considerable portion of the data (about 30%) did not correspond to straight lines at all ($R^2 \leq 0.5$), with extreme functions being noted among them (Fig. 4a). Their presence supports the hypothesis about the convective (fast) predominating fluxes forming a peak in the gas concentration in the chamber, which later may relax to the initial level (probably, because of diffusion). In this case, the flux should be assessed from the concentration peaks rather than from the averaging linear trend. Such an estimation of the trends shown in Fig. 4a gives positive fluxes for points *1, 2,* and *3* equal to 0.01, 0.01, and 0.15 mg C/(m^2 h), whereas the initial calculation by the linear trend models results in negative fluxes equal to –0.02, 0.003, and –0.002 mg C/(m^2 h), respectively. We can see that the discrepancies between these two models are very significant, up to changing the sign of the flux. A reasonable question arises about the duration and the occurrence frequency of these impulse fluxes in order to estimate their total contribution to the emission during a long period (season). Within the framework of our study, it is impossible to answer this question. However, we may indirectly judge the frequency from the portion of the trends with $R^2 \leq 0.5$, i.e., with a probability of about 30%. Note that the researchers of the so-called bubble transport of methane in bogs in summer obtained similar estimates [3, 19]. The three high negative values of methane fluxes excluded from the sample changed their sign after recalculation by the abovementioned method and reached positive values of some tens and even hundreds mg C/(m^2 h). Such phenomena are evidently very rare (the frequency less than 1%). However, as was shown earlier [13], it is the recurrent powerful local convective flows that may be responsible for the main efflux of methane to the atmosphere from bogs via periodical discharge of the gas accumulated in the peat massif.

The flux calculation models alternative to Eq. (2) can be suggested for the monotonous nonlinear trends (Fig. 4b). One of the possible options was first described in [10] upon the physical substantiation of the chamber method of the study of gas fluxes. However, this work contained a number of misprints and disputable items; therefore, in the present paper we try to present a generalized deduction of the equation for the gas concentration dynamics in the closed chamber as applied to the methane measurement problem. For the chamber of volume $V = SH$, where $S = L^2$ is the area of the basement square with side L and H is the height above the surface, which is cut into the soil (snow) to the depth Δz, the following equation for the gas mass (m) balance is valid:

$$\frac{dm}{dt} = QS_1 - qS_2 \pm UV, \tag{3}$$

where Q, q are the gas fluxes into and out of the chamber, g/(m^2 h); S_1 and S_2 are the respective section areas

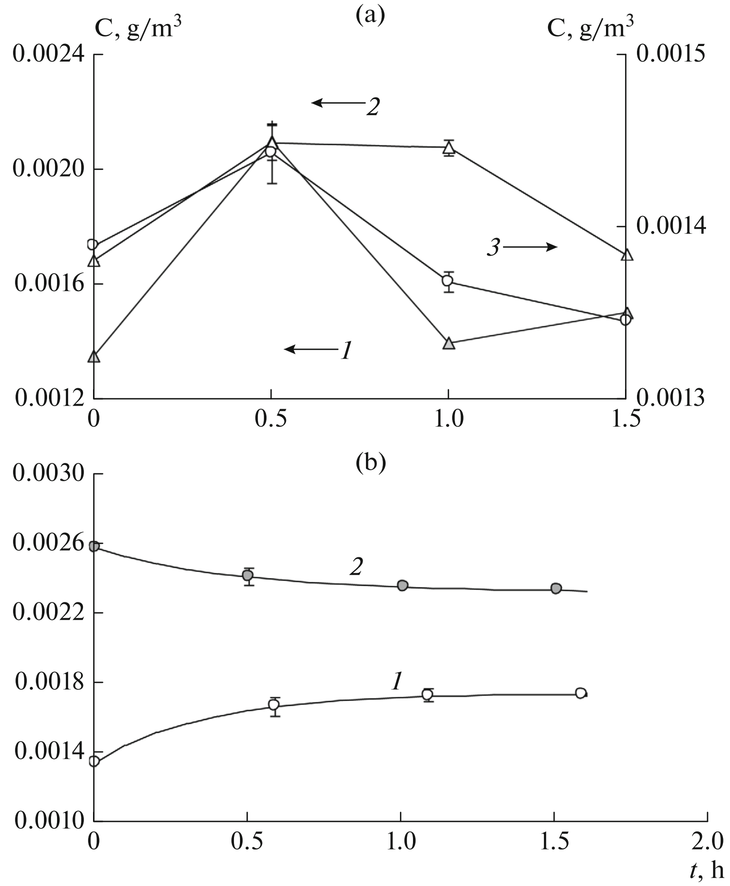

Fig. 4. Examples of trends in methane concentration in the isolating chambers: (a) nonlinear functions with the extremes (*1*—a ridge, May; *2*—a ridge, March; *3*—forested bog, March (ordinate axis on the left)); (b) nonlinear monotonous functions, forested bog, March (*1* – methane accumulation, *2* – methane loss).

for these fluxes, m^2; and U is the source–sink function for the gas inside the chamber, g/(m^3 h). Let $C = m/V$ be the gas concentration in the chamber (g/m^3), depending on time t, h. We take the concentration in the surrounding atmosphere as constant and equal to C_0. Assuming that the gas enters the chamber from the soil (snow) through the entire chamber section ($S_1 = S$) with the rate Q, and diffuses backwards with the permanent diffusion coefficient (D, m^2 h), covering the path Δz through the soil (snow) to the atmosphere with the lateral flows of $q = D\,(C - C_0)/\Delta z$ intensity, and that it also can be absorbed inside the chamber with the first-order kinetics ($U = -kC$), where k is the kinetic constant, 1/h; we can derive the following equation from Eq. (3):

$$\frac{dC}{dt} = \frac{Q}{H} - \frac{DCS_2}{\Delta zHL^2} + \frac{DC_0S_2}{\Delta zHL^2} - kC. \quad (4)$$

In paper [10], it is assumed that $S_2 = S$, although it is not obvious. If the gas is released from the chamber to the atmosphere along the frame by the side walls, the entire chamber section is hardly available to it. The ascending flux comes from the soil through the bulk of this section area; hence, proceeding from the existing gradient, the opposite flux is impossible, otherwise the Fick's law is violated. It appears very difficult to estimate the S_2 value theoretically. Therefore, let us consider two extreme cases. In the first case, we take $S_2 = S$ as is done in [10]. In the second case, we assume that S_2 is equal to the "shadow" of the chamber cutting depth and the diffusive transfer path Δz, i.e., $S_2 = 4L\Delta z$. After the appropriate grouping of Eq. (4) components $A = Q/H + DC_0/(\Delta zH)$ or $A = Q/H + DC_0/(4LH)$ and $b = D/(\Delta zH) + k$ or $b = 4D/(LH) + k$, we obtain:

$$\frac{dC}{dt} = A - bC. \quad (5)$$

The solution to Eq. (5) for the concentration in the chamber at the initial time $t = 0$ equal to C_0 is the following exponential function:

$$C(t) = \frac{A}{b} + \left(C_0 - \frac{A}{b}\right)\exp(-bt). \quad (6)$$

After substitution $y_0 = A/b$ and $a = (C_0 - A/b)$, we approximate the trends of nonlinear monotonous dynamics of concentrations in the isolating chamber with the equation:

$$C(t) = y_0 + a\exp(-bt). \quad (7)$$

From the standard list of functions in the nonlinear regression application Regression Wizard of S-Plot 9 software, we obtain the following equations for calculating the physical parameters of model (4), including the studied fluxes Q:

$$C_0 = y_0 + a, \quad (8)$$

$$k = b - \frac{D}{\Delta z H} \text{ or } k = b - \frac{4D}{LH}, \quad (9)$$

$$Q = (C_0 k - ab)H = ((y_0 + a)k - ab)H. \quad (10)$$

In the absence of gas discharge in the chamber ($k = 0$), in addition to the diffusive mass transfer, Eq. (10) is simplified, and independently of the supposition on the section area size, the flux can be identified directly by the linear regression data as a product of exponent parameters a and b and the chamber height H:

$$Q = -abH. \quad (11)$$

The effective diffusion coefficient in this case is calculated from the equations:

$$D = \Delta z b H \text{ or } D = \frac{bHL}{4}. \quad (12)$$

For the known kinetic constant of gas discharge in the chamber (k), which differs from zero, Eq. (11) acquires the form:

$$D = \Delta z(b - k)H \text{ or } D = \frac{(b-k)HL}{4}. \quad (13)$$

Figure 4b shows the approximation trends for experimental data with Eq. (7). The determination coefficients R^2 were equal to 0.999 for the standard approximation errors of an order of 10^{-6} g/m^3. Note that for the initial linear approximation, R^2 values did not exceed 0.77–0.85 with errors two orders higher. The parameters obtained for Eq. (7) were statistically reliable and for samples *1* and *2* (Fig. 4b), the values were equal to: $y_0 = 1.750 \times 10^{-3} \pm 6.46 \times 10^{-6}$ and $2.327 \times 10^{-3} \pm 2.52 \times 10^{-6}$ g/m^3, $a = -3.969 \times 10^{-4} \pm 8.83 \times 10^{-6}$ and $2.529 \times 10^{-4} \pm 2.95 \times 10^{-6}$, $b = 2.807 \pm 0.21$ and 2.122 ± 0.68, respectively.

Initially, the fluxes were calculated by the simplified Eq. (11) proceeding from the idea [10] about the only possible mechanism of partial methane discharge from the chamber to the atmosphere by diffusion. The following estimates were obtained in this case. For sample *1* (the methane accumulation trend), flux $Q = 0.11$ mg C/(m^2 h) (which is 5–6 times higher than in the linear model). The diffusion coefficients $D = 0.042$ (m^2/h) ($S_2 = S$) and $D = 0.028$ m^2/h ($S_2 = 4L\Delta z$). These values are lower than the diffusion rates in the atmosphere $D = 0.068$ m^2/h, which proves indirectly the validity of both assessment methods according to the suggested eqs. (12).

For sample *2* (the methane discharge trend), the calculated flux $Q = -0.054$ mg C/(m^2 h) turned out to be negative for the corresponding diffusion coefficients $D = 0.032$ and 0.021 m^2/h. This means that the mechanism of diffusive efflux of gas from the chamber to the atmosphere considered in the model (4) according to the concept [10] cannot provide for the actual decrease in methane concentration (discharge) observed in the experiment. Therefore, *some additional mechanism* operates along with the diffusive methane discharge, which is responsible for the methane efflux in the isolating chamber atmosphere.

Supposing that its kinetics corresponds to the first-order reaction as is preset in the full variant of model (4), we come up with the respective kinetic constant $k = 0.245$ 1/h for the zero flux from the soil ($Q = 0$). For the known k, assuming that this discharge process is also valid for the sample *1* (the accumulation trend), and having calculated the respective diffusion coefficients from eqs. (13), we may calculate the corrected flux Q, taking into account the potential methane absorption in the chamber in addition to the diffusion mechanism. This flux (Q) was equal to 0.15 mg C/(m^2 h), which was 1.3 times higher than the initially obtained estimate (0.11 mg C/(m^2 h)) and 7 times higher than in the case of the routine estimate according to linear model (2). The calculated diffusion coefficients were in this case equal to 0.038 and 0.026 m^2/h, respectively.

A reasonable question arises about the nature of the additional methane flux.

The biological factor should be probably ruled out due to the subzero temperatures and a low probability of the snow surface colonization by methanotrophic organisms. For soils, there are sporadic data on the activity of microorganisms at temperatures below –10 to –15 °C; however, there are grounds to consider these data as speculative [11]. Moreover, if such processes are possible in the snow cover, the entire paleoreconstruction of the atmosphere state and climate based on the gas composition of the ice cores becomes doubtful. The supposed methane adsorption by the snow surface also seems hardly probable, since the corresponding interphase equilibrium should be already achieved upon the gas movement from the soil source. As for the quick convective mass transfer, which forms the elevated concentration in the chamber as compared to the atmosphere, the subsequent additional adsorption may occur, with the kinetics of this process fitting the first order [13].

At the same time, the chemical reactions favoring the methane discharge in the isolating chamber atmosphere cannot be excluded, although the authors not being experts in the given topic may be mistaken in the following narrative. For example, we may suppose that methane interacts with the organic matter of the isolating chamber, as field observations attest to a decrease in the decreasing CH_4 concentration upon the sample transportation and storage in the hermetically sealed plastic syringes. However, in our opinion, another mechanism, i.e., the photochemical oxidation of methane is more probable. Photolysis in the atmosphere equal to about 490 Tg/year with the estimate ranging from 375 to 835 Tg/year [1, 13] is known to be the principal global mechanism of methane loss from the atmosphere. Having divided this value by the Earth's surface area (5.1×10^{14} m^2), we obtain the tentative estimate for the corresponding flux equal to 0.11 mg/(m^2 h), and recalculated for the daylight time (12 hours, roughly), it becomes two times higher.

These are small fluxes that can hardly be revealed in the warm season against the background of the high emission values. According to [3], the median of difference between the methane emission fluxes in the dark and transparent chambers constituted 0.11 mg C/(m^2 h) for 38 measurement pairs, which is a negligibly small value against the typically observed emission value equal to 6.1 mg C/(m^2 h). However, this value is very close to the estimate obtained above for the photolysis in the atmosphere (the discrepancy in the measurement units may be neglected because the molar mass of methane is close to that of carbon). It is interesting that in the study by Naumov [8], who was probably the first to notice the difference between methane emission values in the dark and in the light, the investigated typical fluxes, and that the photolysis process could be seen against this background, although the author explained the observed phenomenon by the hypothesis of methane uptake by photochemotrophic organisms.

In general, photolysis may be characterized by the first-order kinetics with the respective constant k [17]. For methane, photolysis is represented by a chain of numerous reactions starting with the interaction with OH-radicals. Therefore, in general, the photolysis constant occurs in a close to linear relationship with the concentration of OH-radicals. In the range typical of the troposphere (note that in negligibly low concentrations, $0.5 \times 10^6 < OH^{\bullet} < 6 \times 10^6$ molecules/cm^3), it varies from 1×10^{-5} to 2.5×10^{-5} 1/s [18]. Even the upper boundary of this range, equal to $k = 0.09$ 1/h, is nearly three times lower than the obtained experimental estimate of the methane discharge trend (Fig. 4b). The calculation by the known value of the global photolysis (490 Tg/year) for the atmosphere methane mass of 4600–5000 Tg (according to [1]) results in an even lower k value (2.4×10^{-5} 1/h). Short-wave ultraviolet (<310 nm) causing the ozone decomposition into O_2 and active atomic oxygen (under the impact of which OH-radicals are produced from water molecules) should not enter the near-surface atmosphere layer. However, in this layer, the quicker photodissociation of nitrogen dioxide should probably occur under the influence of longer-wave irradiation (<420 nm), which is amplified by the reflection from the snow, with the formation of atomic oxygen and, then, OH-radicals. The characteristic period of photochemical reactions for the nitrogen cycle constitute minutes rather than hours, i.e., these processes are rather quick, developing evidently in the surface layer near the potential sources of nitrogen oxide and dioxide [7]. The production of somewhat higher than 6×10^6 molecule/cm^3 concentrations of OH- radicals may perfectly increase the photolysis constant according to [18] and make it close to the experimentally obtained value of 0.245 1/h.

In general, it appears impossible now to either accept or reject the hypothesis about the photochemical loss of methane in the surface atmosphere layer as the mechanism of an additional-to-diffusion decrease in this gas concentration in the isolating chamber. Note just one point, which is well-known in the physics and chemistry of the atmosphere, though being still ignored in soil science upon the study of tiny gas fluxes at the atmosphere boundary. This is the phenomenon of the so-called "dry fallout" of gaseous admixtures from the atmosphere to the surface of soil or water (snow) as a complex process of immobilization of gaseous substances in the thin active surface layer, which is not subject to turbulent diffusion, under the impact of gravity, adsorption, chemical reactions, or other factors. A substantial correction of the methodology of studying minor gas fluxes at the atmosphere boundary might be required in the future. For the cold season with the snow cover, the gradient flux estimation from the profile distribution of gas concentrations in the snow mass is suggested as an alternative to the chamber method [14]. The theoretical substantiation of different variants of this estimate and their practical application for the investigated objects is a subject for a separate publication.

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