================================ **SOIL PHYSICS** ================================

Kinetic Assessment of Gas Exchange between the Soil and the Atmosphere by the Static Chamber Method

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Abstract—The method of closed (static) chambers finds wide use in the study of gas and vapor flows at the soil–atmosphere interface. However, it can significantly underestimate the values under study in some cases, depending on the procedure of flux calculation from the experimental data on the dynamics of gas and vapor concentrations in a closed chamber. An original calculation procedure suitable for different (linear and nonlinear) trends in the dynamics of concentrations is proposed. It is based on the tangent equation to the trend line at the starting point of the experiment ($t = 0$). The comparison with the conventional procedure shows that the difference can be from several units to tens of times. The theory of the static chamber method and possible latent reasons for underestimation of gas exchange at the soil–atmosphere interface by this method are discussed.

Keywords: emission, gas absorption, closed chamber method, concentration trends, calculation of gas flows, simulation

INTRODUCTION

Gas exchange with the soil is considered to be one of the main factors regulating the composition and state of the atmosphere and potential climatic changes. The method of closed (static) chambers conventionally used for its study involves the experimental estimation of the increase or decrease in the concentration of a gaseous substance in a closed chamber installed on the soil surface [8]. From these experimental data and the geometric parameters of the chamber, the corresponding fluxes of gaseous substances are calculated as their emission (concentration gain) or absorption (concentration loss) at the soil–atmosphere interface. Numerous publications are devoted to different technological versions of the chamber method, primarily detectors of gases and vapors, as well as to the comparison with other methods for studying gas exchange between the soil and the atmosphere, but only a few works deal with the theoretical substantiation of the closed chamber method [7, 11]. Nonetheless, this method determines the concepts of gas dynamics in the chamber and the methods of gas flux calculation. In this context, the aim of this work was to dissect the theory of the closed chamber method and to substantiate a universal procedure for the calculation of gas fluxes from the data on the dynamics of concentrations in the chamber, including both linear and nonlinear trends.

OBJECTS AND METHODS

In this work, we analyze experimental data on fluxes of carbon-containing gases (CO_2, CO, and CH_4) at the soil–atmosphere interface obtained by the conventional closed chamber method [2, 8] for urbanozems in the Western and Southeastern districts of Moscow and for an oligotrophic bog at the Mukhrino research station of the Yugra State University in the Khanty-Mansiisk Autonomous District of Western Siberia in 2010. Our own data and data kindly provided by our colleagues were used. Closed Plexiglas chambers of regular shape with a square section of 0.2 to 1 m in each side and a height of 0.09 to 0.6 m inserted into the soil (snow) to a depth (Δz) of 0.01 to 0.15 m were used during the measurements. In some cases, the volumetric concentrations of gases (CO_2, CO) in the chambers were directly recorded with portable gas analyzers AZ 7755 or PKG-4CO [6, 8]. For methane, gas samples were taken with plastic syringes (20 mL), which were sealed and transported to the laboratory, where the volumetric content of the gas was determined on a Kristall 5000.1 gas chromatograph with a flame-ionization detector [2].

The temperature was recorded with DS1921 and DS1923 programmable sensors; the atmospheric pressure was measured with RS8708P digital meteorological stations. The concentration (C) of a component in the gas phase was calculated from the measured volumetric content (T) of the component, its molecular
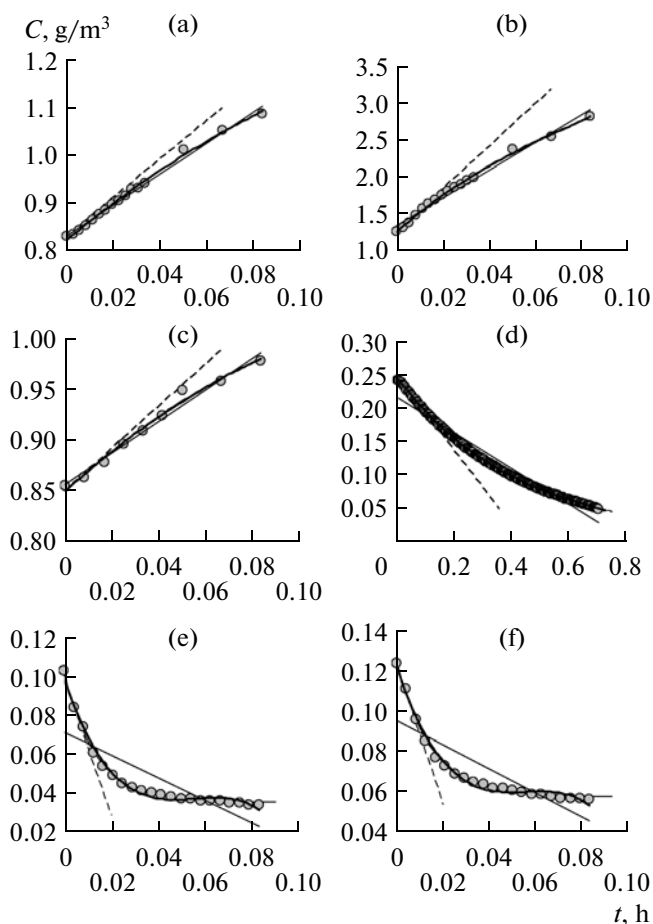
Fig. 1. Trends of gas concentrations in the closed chamber at the measurement of CO_2 and CO fluxes on automorphic objects: (A) CO_2 emission, urbanozem, Michurinskii Avenue, August 13, 2010; (B) CO_2 emission, urbanozem with a soil modifier (hydrogel), Krasnostudencheskii Passage, August 6, 2010; (C) CO_2 emission, urbanozem, Michurinskii Avenue, August 6, 2010; (D) CO absorption, urbanozem with a soil modifier (hydrogel), Michurinskii Avenue, August 6, 2010; (E) CO absorption, urbanozem, Michurinskii Avenue, August 19, 2010; (F) CO absorption, urbanozem with a soil modifier (hydrogel), Michurinskii Avenue, August 13, 2010; (straight solid line) linear model (5); (straight dashed line) tangent (12); (curved solid line) polynomial model; (circles) experimental data; (vertical bars) standard deviations.

weight (M), the absolute temperature (T), and the barometric pressure (P) using the following equation [8]:

$$C = \frac{M P X}{100 RT},\qquad(1)$$

where $[C]$ = g/cm³, $[X]$ = 5, $[P]$ = Pa, $[T]$ = K, and $R = 8.31$ J/(mole K) (universal gas constant).

The statistical processing of the results, the approximation of the trends in gas concentrations in the chamber, the mathematical calculations of gas fluxes, and the plotting of graphs were performed using Microsoft Excel 2003 and S-Plot 9 software.
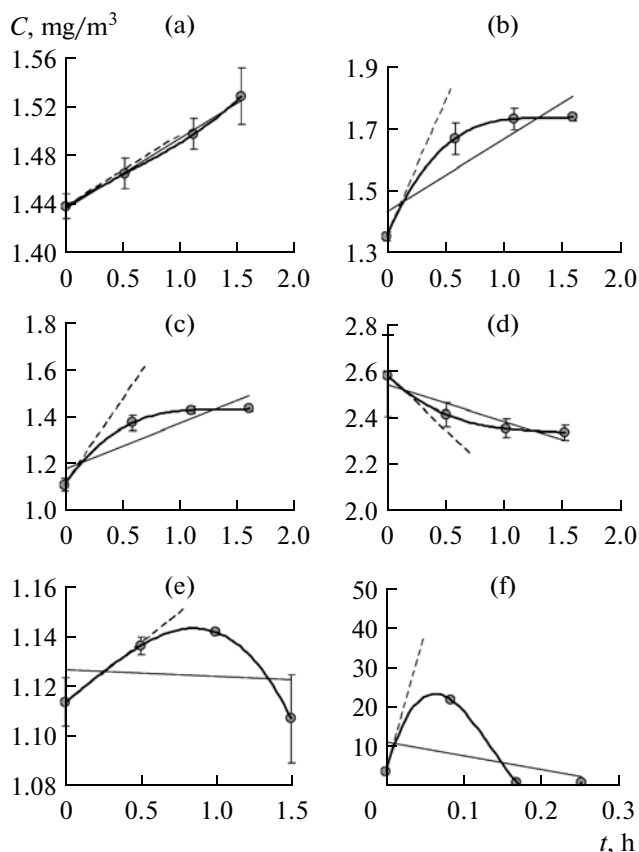

Fig. 2. Trends of gas concentrations in the closed chamber at the measurement of CH_4 fluxes on a hydromorphic object (oligotrophic bog, Khanty-Mansiisk Autonomous District): (A–C) March 15, 2010; (D, E) March 16, 2010; (F) May 12, 2010. Symbols see in Fig. 1.

RESULTS AND DISCUSSION

Examples of different trends in the dynamics of gas concentrations in the closed chamber obtained in the study of gas exchange between the soil and the atmosphere are given in Figs. 1 and 2. A peculiar feature is noteworthy. The trends are far from being always linear, and their linearity is not always due to the long accumulation (loss) of gaseous substances in the closed chamber, as is supposed in the theory of the method [7]. In some cases, an increase of gas concentration appears during short time periods (Figs. 2e, 2f), which is followed by a decrease to the initial level. Such a situation is especially typical for hydromorphic objects (bog ecosystems) and is probably related to the preferential convective flows [8]. During the snowy period, when the biological source of gases in the soil is suppressed, the emission fluxes decrease by one to two orders of magnitude, and the small inverse gas fluxes from the atmosphere with the corresponding decrease of concentrations in the closed chamber become evident (Fig. 2d). The nature of these processes is poorly understood, and their presence in the cold season apparently excludes the biological constit-

uent. The most probable abiotic processes include the physical and physicochemical constituents: diffusion from the chamber to the zone of lower concentration, absorption, and (for more soluble gases) absorption in the surface layers of soil or snow cover with dust particles. Purely chemical reactions, including enzymatic ones in the active layer of soil cover, apparently cannot be excluded. However, gas reactions with the participation of free radicals can also occur in the chamber under the impact of solar radiation, e.g., the photochemical oxidation of methane or gaseous nitrogen compounds [3]. Carbon dioxide and other soluble gases can be partially absorbed by the condensate and interact with water vapor within the chamber volume, the neglect of which can result in the underestimation of emission fluxes by 20% and more, according to the technical documentation of the LI-COR soil respiration system [4]. Photosynthesis, which is the main process of CO_2 uptake, apparently cannot be completely inhibited by using light-proof chambers, because the dark photosynthesis reactions theoretically can continue, although more slowly because of the inhibition of water photolysis. In addition, the use of a dark chamber cannot exclude the inverse process: the respiration of the aboveground phytomass, which cannot be separated from the emission of CO_2 from the soil. Therefore, in our opinion, the only way to measure the true soil respiration is to completely remove the aboveground parts of plants, including the epiphytic forms, from the plots on which the chambers are installed.

The generalization of all the above processes for the theoretical substantiation of the closed chamber method in a first approximation with the kinetics of gas absorption in physical, physicochemical, and chemical processes by the first-order reaction gives a relatively simple model for the dynamics of gas concentrations in the chamber

$$\frac{\partial C}{\partial t} = A - bC. \tag{2}$$

where C, g/m^3 is the gas concentration in the chamber; $A = Q/H + DC_0/(LH)$; $b = D/(LH) + k$; Q, g/m^2per hour is the measured flow; H, m is the effective height of the chamber above the soil surface (for the chambers of irregular shape or with the cross-section different from that of the base, it is calculated as the ratio of the chamber volume (V) above the soil surface to the surface area from which the gas is emitted (S)); D, m^2/h is the effective gas diffusion coefficient in the soil; L, m is the distance passed by the gas molecules diffusing from the chamber to the atmosphere; k, h^{-1} is the total (effective) kinetic constant of the first order for the corresponding processes of gas absorption in the chamber; and C_0, g/m^3, is the concentration of the gas in the atmosphere.

If the gas concentration in the chamber at the initial moment $t = 0$ is C_0, the solution of Eq. (2) is the exponential function

$$C(t) = y_0 + a\exp(-bt), \tag{3}$$

where $y_0 = A/b$, and $a = (C_0 - A/b)$.

It follows from Eq. (3) that after a certain characteristic time $\tau \sim 1/b$, the gas concentration in the chamber gradually ceases to vary and reaches a plateau at $C(t) = A/b$. In thermodynamic terms, this corresponds to a dynamic equilibrium, when the emission fluxes (sources) of gas are balanced by the corresponding fluxes and processes removing the gas from the chamber (sinks).

At the early dynamics stages, the trend of gas concentration changes in the chamber is almost linear, as follows from the Taylor expansion of function (3) at the zero point $t = 0$. The corresponding equation has the form

$$C(t) = C_0 + \left(\frac{Q}{H} - kC_0\right)t. \tag{4}$$

In the absence of gas absorption within the chamber ($k = 0$), Eq. (4) is reduced to

$$C(t) = C_0 + mt, \tag{5}$$

where $m = Q/H$ is the line slope. In the Russian literature, this equation was first obtained in an analogous way [7]. It underlined the so-called linear model for the calculation of gas fluxes in the closed chamber method. The approximation of experimental data by linear Eq. (5) apparently gives a simple equation for the calculation of the target gas flux (linear model according to [11])

$$Q = mH. \tag{6}$$

It can be seen that the flux is unambiguously determined from the linear trend slope (m) and the effective height of the regular chamber above the soil surface (H).

For the general (nonlinear) model, the flux is determined after the approximation of experimental data with Eq. (3) from the equations

$$C_0 = y_0 + a, \tag{7}$$

$$k = b - \frac{D}{LH}, \tag{8}$$

$$Q = (C_0 k - ab)H = ((y_0 + a)k - ab)H. \tag{9}$$

Additional information on the effective gas diffusion coefficient in the surface soil layer (D) and the distance of mass transfer to the atmosphere (L) is necessary in this case. The latter value is sometimes identified with the insertion depth of the chamber into the soil (Δz) [7], although we consider this statement disputable. On the way to the atmosphere, the gas molecules from the chamber should pass at least a double path Δz, first downward to the insertion depth and then backward to the soil−atmosphere interface. Thus, the minimum theoretical estimate is $L = 2\Delta z$. In reality, the mole-

cules move along complex trajectories depending on the initial location of the molecule (in the center or at the periphery of the chamber) and the corresponding concentration isolines, which form gradients in the soil both within the inserted area and beyond it, with consideration for the possible effect of fluxes from the deep soil around the chamber. Therefore, the geometrical determination of the L value is a difficult problem. The general solution for the diffusion outflow from the chamber can be found for a specific soil using a label (nonsorbable inert gas). In this case ($k = 0$), according to Eq. (8), the value of $b = D/(LH)$ unambiguously characterizes the kinetics of diffusional relaxation in the chamber.

In the absence of other than diffusion transfer of gas to the atmosphere in the chamber ($k = 0$), Eq. (9) is simplified, and the flux can be determined, regardless of the L value, directly from the nonlinear regression data as the product of a, b (exponential (3) parameters), and H (the chamber height)

$$Q = -abH. \qquad (10)$$

Thus, for the nonlinear monotonous trends obeying Eq. (3), there is a simple method for estimating the gas fluxes from Eq. (10) similar to linear model (6), with the only difference being that the processing of experimental data requires nonlinear approximation using special software like S-Plot 9. Note that the approximation of nonlinear exponential trends by linear Eq. (5), which is frequently used in the calculations of fluxes by the automated template method, will result in an underestimation. The correct estimate of emission from Eq. (10) will coincide with the calculation from the linear model only during the first short time periods, when the linear trend is close to the exponential tangent in the point $t = 0$. The analytical condition for the tangent is as follows: $C'(t) = (y_0 + a(-bt))'_t = -ab$; using the product of this value by the chamber height, the true flux can be estimated from the linear trend coinciding with Eq. (10): $Q = -abH = mH$. In all the other cases (longer time periods), the linear trend corresponds to a secant of the exponential rather than its tangent (Figs. 1d–1f, 2b–2d); the longer the exposure, the smaller the slope (m) and, hence, the resulting flux Q.

In some cases, the nonlinear trends have complex shapes and are not monotonous; they are characterized by points of extremum (maximum or minimum) concentrations (Figs. 2e, 2f). As was noted above, this can be related to convective gas emissions, when the flux is not constant during the exposure. Can such fluxes be estimated from the available experimental data and is there a universal method of calculating the fluxes for linear and nonlinear trends in the dynamics of concentrations in static chambers? In our opinion, the following simple approach (hereafter, the tangent method) can be used for this purpose. It involves the estimation of the maximum possible flux rate at the soil–atmosphere interface from the slope of the tan-

gent curve describing the trend of the gas concentration in the closed chamber at $t = 0$. In practice, it is sufficient to approximate the existing trend with a polynomial of the second order and higher and then to determine the equation of tangent at the zero point using the first derivative of the polynomial with time (the mathematical condition for the tangent at a given point). For the cubic polynomial

$$C(t) = C_0 + at^3 + at^2 + mt, \qquad (11)$$

where C_0 is the initial gas concentration in the chamber, g/m^3; and a, b, and m are parameters of the trend approximation, we have $C'(t) = m$ for $t = 0$; then, the tangent equation is as follows:

$$C(t) = C_0 + mt. \qquad (12)$$

Then, the equation for the calculation of flux $Q = mH$ coincides with Eq. (6).

By analogy, for polynomials of higher degrees (including spline approximation), the coefficient m at the first-degree term should be known, because all the other terms will be eliminated at the time differentiation and the substitution of $t = 0$.

The method is universal and suitable for trends of any complexity (nonlinearity), because an adequate approximation of data can be always reached depending on the number of terms in the polynomial. The potentialities of the standard package for the approximation of trends within the Microsoft Excel software, which include the set of polynomials of the second to the sixth degree, are quite sufficient for the implementation of the method.

In Figs. 1 and 2, the experimental data are approximated by three different methods: linear model (5), exponential model (3), and polynomial of the second or third degree with plotting a tangent according to Eq. (12). The approximation parameters and the values of gas flux Q calculated from eqs. (6) and (10) are given in Table 1. It can be seen that the flux estimates strongly differ depending on the model selected for the trend of gas concentrations. The value of approximation significance R^2 indicates that the traditional linear model (5) is frequently inadequate and almost always worse than the proposed polynomial model ($R^2 = 0.98$–0.999). Moreover, even for the values $R^2 = 0.98$–0.99 that are suitable for considering the trend linear (e.g., the trends in Figs. 1a–1c), the differences in the flux estimates can reach 1.3–2 times in favor of the physically based exponential model or the proposed method of polynomial tangent. In other words, even in this case, a significant underestimation cannot be excluded at the use of the traditional linear approach supposedly justified by high R^2 values. In all the other cases, where the trend is obviously nonlinear (Figs. 1d–1f, 2b–2f), an even more significant underestimation (by 5 to 10 (20) times) is observed. For the trends with extremums (Figs. 2e, 2f), the sign of the estimated trend can also change (Table 1). So, according to the linear model, the fluxes are negative (gas

Table 1. Approximation parameters for gas dynamics trends in closed chambers at the estimation of gas flux at the soil--atmosphere interface

Sample no.	Linear model (5)			Exponential model (3)				Polynomial tangent model (12)			
	m, g/m^3 per h	R^2	Q, mg/m^2 per h	a, g/m^3	b, h^{-1}	R^2	Q, mg/m^2 per h	C_0, g/m^3	m, g/m^3 per h	R^2	Q, mg/m^2 per h
	Automorphic objects										
1, A	3.31	0.991	298.1	−0.73	5.60	0.996	369.7	0.83	4.09	0.996	367.9
1, B	18.76	0.982	1688.8	−2.75	9.89	0.997	2446.8	1.25	28.71	0.997	2584.0
1, C	1.57	0.978	141.3	−0.29	7.32	0.987	188.7	0.85	2.08	0.978	187.2
1, D	−0.27	0.956	−24.4	0.24	2.39	0.999	−52.3	0.25	−0.37	0.999	−50.9
1, E	−0.58	0.657	−52.5	0.07	73.9	0.999	−451.7	0.10	−3.53	0.989	−317.4
1, F	−0.60	0.688	−54.1	0.07	68.6	0.996	−417.3	0.12	−3.42	0.989	−307.7
	Hydromorphic object										
2, A	0.06	0.993	0.01	—	—	—	—	1.44	0.06	0.994	0.01
2, B	0.24	0.776	0.02	−0.40	2.81	0.999	0.11	1.35	0.87	0.999	0.09
2, C	0.20	0.775	0.02	−0.33	2.81	0.999	0.09	1.12	0.72	0.999	0.07
2, D	−0.16	0.846	−0.02	0.25	2.12	0.999	−0.05	2.58	−0.48	0.999	−0.05
2, E	−0.003	0.012	−0.0003	—	—	—	—	1.11	0.05	0.999	0.005
2, F	−35.35	0.141	−3.54	—	—	—	—	3.89	695.8	0.999	69.6

The numbers of samples in Tables 1 and 2 correspond to those in Figs. 1 and 2.

absorption by the soil), while the method of polynomial tangent at the zero point, on the contrary, shows a positive flux (gas emission).

The above examples demonstrate the importance of the theoretical problem under consideration: the substantiation of a universal, physically based method for the estimation of gas fluxes at the soil–atmosphere interface from the dynamics of gas concentrations in the static chamber. This problem can be of greater current importance than the selection of versions for the implementation of the chamber method (facilities for gas detection; ventilation, mixing, and thermostating conditions; chamber insertion in the soil; etc.). The comparison of separate technological versions of the chamber method with one another and with other methods of determining gas fluxes (micrometeorological gradient methods, including the turbulent covariance method) most frequently shows differences by 20 to 100%, i.e., no more than by 2 times [1, 4, 5, 10]. However, according to our results, the variation of the estimates obtained by different theoretical approaches to the processing of experimental data and the calculation of fluxes can significantly exceed this range.

In conclusion, we analyze the physically based exponential model (3), which apparently provides the most objective estimates of gas fluxes at the soil–atmosphere interface. It can be seen (Table 1) that this model consistently gives high R^2 values (0.99 and higher) for the most of the studied trends. It also allows assessing the physical aspects of gas emission and absorption by simple calculations. Under the assumption that the minimum path length of molecules from the chamber to the atmosphere is $L = 2\Delta z$, the mini-

mum effective coefficient of gas diffusion (one of the mechanisms of gas loss from the chamber) can be estimated from the equation

$$D = 2\Delta z b H, \tag{13}$$

If the obtained value is higher than the diffusion coefficient for the studied gas in the atmosphere (under standard conditions, D_{st} is 0.049, 0.064, and 0.069 m^2/h for CO_2, CO, and CH_4, respectively [9]), another mechanism favoring the decrease of the gas concentration in the chamber should exist. Note that this is a relatively gross criterion for an upper estimate, because the diffusion occurs in the soil, where the effective diffusion coefficient is lower than in the atmosphere by at least 1.5−2 times because of porosity, pore sinuosity, and pore water.

Then, if the above additional mechanism is revealed by this method, we believe that it can be described by the first-order kinetics with a nonzero k, in accordance with the presuppositions to model (3). Note that the calculation of flux from Eq. (10) suggests the absence or zero rates of any mechanisms for such outflow. However, if the diffusivity test (13) reveals this mechanism, its rate (k) should be found. For this purpose, Eq. (8) should obviously be used, and the physically based value for the effective gas diffusion in the soil should be set as a function of aeration porosity (P), temperature, and pressure. In a first (linear) approximation, the modified Penman equation [8] can be used

$$D = 0.66 P D_{st}\left(\frac{T}{273}\right)^{1.75}\left(\frac{101.3}{D}\right), \tag{14}$$

Table 2. Estimation of gas fluxes by the physically based exponential model

Sample no	D_{ef}, m^2/h	D test	k, h^{-1}	D_{calc}, m^2/h	Q	Q_{max}
					mg/m per h	
1, A	0.010	+	0	–	369.7	–
1, B	0.018	+	0	–	2446.8	–
1, C	0.013	+	0	–	188.7	–
1, D	0.004	+	0	–	−52.3	–
1, E	0.133	–	48.8	0.045	−451.7	−451.7
1, F	0.123	–	37.1	0.057	−417.3	−417.3
2, B	0.084	–	1.53	0.038	0.111	0.318
2, C	0.084	–	1.53	0.038	0.092	0.262
2, D	0.064	+/−	0.21	0.057	−0.054	−0.054

D_{ef} is the estimate from Eq. (13); D test is the comparison of the estimate with the diffusivity in the atmosphere: (dash) test is failed; D_{calc} is the estimate from Eq. (14) for trends in Figs. 2b and 2c and from Eq. (16) for the other trends; Q is the initial flux estimate from Eq. (10); Q_{max} is the estimate from Eq. (9) for trends in Figs. 2b and 2C and from Eq. (17) for the other trends (gas absorption).

where D_{st} is the standard diffusion coefficient in the atmosphere (see above); the other terms are found in Eq. (1); $[D] =$ kPa. From the obtained estimates of D and k, the actual flux can be calculated from Eq. (9), which will apparently exceed the initial estimate from Eq. (10), because it also considers the latent mechanism of gas absorption (along with the diffusion outflow from the chamber).

Finally, for the trends of absorption (concentration loss), if $k > 0$ from the diffusivity test (13), we can set the constant flux Q equal to zero and attribute the gas loss from the chamber to diffusion and the biological, physicochemical, or chemical absorption (outflow) according to a first-order reaction. From the condition $Q = 0$ and with consideration for Eqs. (8) and (9), we obtain simple equations for calculating the values of k and D from the parameters of approximation of the experimental data by exponential model (3)

$$k = \frac{ab}{C_0}, \tag{15}$$

$$D = 2\Delta z(b - k)H. \tag{16}$$

In this case, the outflow (gas loss) corresponding to the absorption according to a first-order reaction will not be constant, as was a priori expected in the known theoretical works on the static chamber method [7, 11]. It will exponentially decrease with time according to the equation $Q = (D/(2\Delta z) - bH)C_0\exp(-bt)$, and its maximum estimate in the initial moment ($t = 0$) will apparently coincide with that calculated from Eq. (10) and have the form

$$Q_{max} = \left(\frac{D}{2\Delta z} - bH\right)C_0. \tag{17}$$

The results of calculations according to the above scheme are given in Table 2. It can be seen that for the emission of CO_2 (trends in Figs. 1a−1c), the hypothesis of diffusional outflow as a mechanism gradually balancing the emission, which was first proposed in

[7], is confirmed by the corresponding D test. The effective diffusion coefficients estimated from the experimental data are lower than those in the atmosphere by 3−5 times, which is typical for wet porous environments like the soil [8]. The same is true for the trend in Fig. 1d for the absorption of CO, where the value of D_{st} is lower than in the atmosphere by almost 15 times.

However, for the two other trends of CO absorption (Figs. 1e, 1f), where the gas fluxes were significantly larger, the hypothesis about the diffusion mechanism of outflow and absorption Q with a constant rate was found to be untenable. A similar situation was observed for the absorption of methane on the surface of an oligotrophic bog covered with snow in winter (Fig. 2d, trend), although the value of D_{ef} was largely close to that in the atmosphere, if the effect of low negative temperatures (decrease of diffusivity by 10−12% of the standard value) was not considered. In all of these cases, the kinetics of gas outflows was estimated according to the first-order reaction (Eq. (15)) at the null constant flux ($Q = 0$). The calculation of the corresponding maximum fluxes in the zero time moment from Eq. (17) expectedly gave the values coinciding with those obtained by the method of exponential tangent at the zero point, i.e., with the initial estimates from Eq. (10). The new estimation of diffusivity gave the D_{calc} values of 0.045–0.057 m^2/h, which were lower than in the atmosphere. At the same time, it should be kept in mind that such fluxes are not constant; they will exponentially decrease with time and result in an analogous decrease of gas concentration in the chamber according to model (3). Thus, the mechanism for the stabilization of concentrations is qualitatively different: this is a diffusional outflow and absorption by the soil, which decelerates with decreasing gas concentration, rather than diffusion balancing the flux with a constant rate (Q).

The two resting trends of methane emission also showed a negative D test, which indicated the pres-

ence of an additional mechanism for the stabilization of gas concentration in the chamber (along with the diffusional outflow). Its kinetic estimation at the typical diffusivity of methane $D = 0.038$ m^2/h in the snow cover with a high porosity of about 0.9 m^3/m^3 gave the constant $k = 1.53$ h^{-1}. The absorption of methane according to the first-order reaction, along with the diffusional outflow from the chamber, apparently should be balanced by the higher resulting emission of gas from the soil. Therefore, the new estimate $Q_{max} = 0.26-0.32$ mg/m^2 per hour exceeded the initial estimate obtained from Eq. (10) for $k = 0$ by almost 3 times. This example shows that the disregard of latent mechanisms for the absorption of gases on the background of their emission from the soil can significantly underestimate the emission flux and, hence, the function of the soil as a source of gases for the atmosphere.

CONCLUSIONS

(1) A significant dependence of the estimates of gas fluxes at the soil–atmosphere interface obtained by the static chamber method from the methods (models) used for the calculation of the fluxes from data on the dynamics of concentrations in the closed chamber was revealed. The differences vary from a few units to tens of times and can exceed the variation range of gas flux estimates upon the use of different technological versions of the closed chamber method or other methods applied to measure gas exchange between the soil and the atmosphere.

(2) The conventional assessment by the linear model can result in the underestimation of gas fluxes by $1.3-2$ times, even at the good agreement of the experimental data with the linear trends in the dynamics of gas concentrations in the chamber at $R^2 = 0.98-099$.

(3) A universal method for the calculation of gas fluxes from the tangent to the gas concentration dynamics approximated by a polynomial at the zero point was proposed as an alternative for the linear model. This method is suitable for both linear and nonlinear trends and can be easily automated using standard approximation functions of Microsoft Excel for the analysis of large bodies of experimental data.

(4) A generalized physically based model of gas dynamics in static (closed) chambers was proposed, as well as a simple analytical solution in the form of nonlinear exponential trends, which allows an objective estimation of the positive (emission) and negative (absorption) gas fluxes at the soil–atmosphere interface.

(5) The theoretical analysis of the trends in the dynamics of gas concentrations in a closed chamber shows that there may be various reasons (mechanisms) for their nonlinearity, among which the possible inconstancy of the measured gas flux claims special attention. The flux inconstancy can be due to its convective character (nonlinear trends in the form of concentration peaks) or to its decrease with time upon the absorption of gases in the chamber according to the first-order kinetics.

REFERENCES

1. K. I. Kobak, A. A. Yatsenko-Khmelevskii, and N. Yu. Kondrasheva, "Carbon dioxide budget in high- and low-productive communities," in *Problem of Atmospheric Carbon Dioxide* (Gidrometeoizdat, Leningrad, 1980), pp. 252–264.

2. E. A. Laktionova, V. V. savel'ev, M. A. Sergeeva, *Physical Chemistry and Biology of Peat: Determination of Greenhouse Gases (CO$_2$, CH$_4$, and N$_2$O) in Peat by Gas Chromatography: Manual on Gas Chromatography Analysis* (Center of Scientific-Technical Information, Tomsk, 2011) [in Russian].

3. T. A. Markova, N. F. Elanskii, I. B. Belikov, A. M. Grisenko, and V. V. Sevast'yanov, "Distribution of nitrogen dioxides in ambient atmospheric layer over continental regions of Russia," Pandia, 2009–2014. http://www.pandia.ru/text/77/465/16927.php

4. A. V. Mashika, "Comparison of two methods of measuring CO$_2$ efflux from the soil surface," in *Proceedings of the XV Komi Republic Conference of Young Scientists, Abstracts of Papers* (Syktyvkar, 2004), Vol. 2, pp. 176–178.

5. A. V. Mashika, "Carbon dioxide emission from the surface of podzolic soils," Eurasian Soil Sci. **39** (12), 1312–1317 (2006).

6. *Environmental Monitoring: Manual for BSci Students*, Ed. by I. S. Belyuchenko and A. V. Smagin (Kuban State Agricultural University, Krasnodar, 2012) [in Russian].

7. *Modern Physical and Chemical Methods of Soil Studies* (Moscow State University, Moscow, 1987) [in Russian].

8. A. V. Smagin, *Gas Phase of Soils* (Moscow State University, Moscow, 2005) [in Russian].

9. W. J. Massman, "A review of the molecular diffusivities of H$_2$O, CO$_2$, CH$_4$, CO, O$_3$, SO$_2$, NH$_3$, N$_2$O, NO, and NO$_2$ in air, O$_2$ and N$_2$ near STP," Atmos. Environ. **32** (6), 1111–1127 (1998).

10. 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).

11. R. T. Venterea, K. A. Spokas, and J. M. Baker, "Accuracy and precision analysis of chamber-based nitrous oxide gas flux estimates," Soil Sci. Soc. Am. J. **73** (4), 1087–1093 (2009).

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