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Biases in methane chamber measurements in peatlands*

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A b s t r a c t. The paper presents results of CH_4 emission measurements at peatland with the application of the dynamic chamber technique. The measurements were conducted in two types of chambers differing in shape, height, volume and technology used to assure their tightness. The study tested how the following factors: 1) forced chamber headspace mixing or its absence, 2) mistakes of the person conducting measurements, 3) improper application of linear technique for calculating CH_4 fluxes, and 4) simulated air sampling typical for static chambers, influence the significance of errors and the underestimation rate of CH_4 fluxes measured *in situ*. It was indicated that chamber headspace mixing allows estimating methane fluxes with a smaller error than in the case of measurements conducted without mixing, and CH_4 fluxes in such conditions can be 47 to 58% higher (depending on the chamber type) than in a chamber without fans. Using dynamic chambers and a fast analyzer to measure methane fluxes allows shortening the methane measurement process to a few minutes. On the other hand, using static chambers for methane flux measurements may lead to 70% underestimation of the calculated flux.

K e y w o r d s: chamber measurements, methane, flux calculation method, biases in chamber measurements

INTRODUCTION

Measurements of mass and energy fluxes are curried out in order to interpret and understand the ecosystem-atmosphere interactions (Eulenstein *et al.,* 2005; Olejnik *et al.,* 2001). The responsibility of the scientific community is to minimize the uncertainties of such assessments by minimizing the measurement errors and excluding the measurement artefacts in order to better understand the processes controlling the global climate.

Measurements of methane emissions at peatlands are conducted by means of micrometeorological techniques *eg* the eddy covariance method (Rinne *et al.,* 2007), the relaxed eddy accumulation method (Haapanala *et al.,* 2006), and also, most frequently, with the use of standard chamber techniques (Pihlatie *et al.*, 2013). However, while dynamic chamber systems are used commonly for CO_2 flux measurements (Juszczak *et al.,* 2012a,b), static chambers are applied for methane flux measurements (Pihlatie *et al.,* 2013). The difference between the systems is as follows: in the dynamic chamber system the concentrations of gases are measured in real time with a gas analyzer and the air circulates between the chamber and the analyzer in a closed system. In turn, no analyzer is used in static chambers and the air is sampled from the chamber with a syringe and then transferred into bottles and subsequently analyzed with a gas chromatograph (Christiansen *et al.,* 2011). In both closed chamber systems the concentration of the emitted gas inside the chamber increases and the gas exchange rate is estimated on the basis of its concentration changes in the chamber headspace (Kutzbach *et al.,* 2007). Fluxes of emitted gas may be calculated using linear methods (Conen and Smith, 2000) which assume a constant gradient of gas pressure between the source and the atmosphere and therefore a constant flux of this gas throughout the measurement. However, gas accumulation inside the chamber headspace affects the gas pressure gradient between the soil and the atmosphere, which significantly reduces the flux of the emitted gas (Conen and Smith, 2000; Davidson *et al.,* 2002; Livingston *et al.,* 2005;

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Kutzbach *et al.,* 2007). Therefore, an inappropriate application of linear methods in calculating fluxes of a particular gas may result in underestimating the values of these fluxes (Christiansen *et al.,* 2011; Kroon *et al.,* 2008; Kutzbach *et al.,* 2007; Livingston *et al.,* 2005) by as much as several dozen percent (Christiansen *et al.,* 2011; Pihlatie *et al.,* 2013). Hence, it is more and more frequently emphasized that non-linear methods should be used in calculating gas fluxes measured by chamber techniques which assume a curvilinear increase of gas concentration and enable the estimation of flux concentration in zero time, immediately after closing the chamber (Kutzbach *et al.,* 2007; Pihlatie *et al.,* 2013). However, using non-linear methods for that purpose does not necessarily increase flux estimation accuracy. The same studies which indicate the superiority of non-linear methods over linear ones point to the fact that fluxes of the emitted gas may be significantly overestimated, particularly when the fluxes are small (Forbrich *et al.,* 2010) or when high chambers are used for measurements (Pihlatie *et al.,* 2013). Hence, it may be concluded that an improper application of non-linear methods may also increase the estimation error of the gas exchange rate.

Much more significant errors in the estimation of greenhouse gas fluxes measured by the chamber technique may be caused by other factors such as mistakes of the person conducting the measurement (Christiansen *et al.,* 2011; Hutchinson and Livingston, 2001), an improperly sealed chamber (Hutchinson and Livingston, 2001), no system of pressure compensation between the chamber and the outer atmosphere (Hutchinson and Livingston, 2001), the method of air sampling (Christiansen *et al.,* 2011), or the lack of use of inner fans (Pumpanen *et al.,* 2004, Christiansen *et al.,* 2011); such fans, by chamber headspace mixing, make the air composition homogenous so that no inner gradients of pressure of a given gas are observed, which could limit the gas exchange. Earlier studies comparing the chamber flux with a given reference flux indicate that non-sufficient chamber headspace mixing or its absence may result in as much as 36% methane flux underestimation (Christiansen *et al.,* 2011; Pihlatie *et al.,* 2013). However, the underestimation rate of measured greenhouse gases varies and depends on the type of chamber and its equipment (Christiansen *et al.,* 2011; Pihlatie *et al.,* 2013; Pumpanen *et al.,* 2004). It is generally acknowledged that measurements carried out with static chambers result in much more significant errors and biases in gas exchange estimation than in the case of measurements conducted by means of dynamic chambers (Pumpanen *et al.,* 2004).

An additional difficulty in chamber measurements of methane fluxes at peatland is posed by rapid and short-term ebullition of methane into the atmosphere in the form of gas bubbles (Tokida *et al.,* 2007). These processes may be caused by a decrease in water hydrostatic pressure (Strack *et al.,* 2005), a decrease in atmospheric pressure (Tokida *et al.,* 2007), an increase in temperature (Beckmann *et al.,* 2004), or by mechanical disturbances caused by the presence of the person conducting measurements (Goodrich *et al.,* 2011). It is estimated that above 500 emissions of this type may occur in every square meter of peatland daily (Goodrich *et al.,* 2011), which may account for even 50-64% of total peat methane emission (Tokida *et al.,* 2007). These occurrences are frequently recorded at chamber measurements, influencing the increase of measurement biases and errors in methane flux estimation.

Therefore, the purpose of the study presented here was to analyse possible errors in methane flux estimation which may stem from the following factors:

– inappropriate analysis of methane concentration changes in the chamber and consequently inappropriate estimation of the increase of gas concentration rate at the time of measurement;
– no headspace mixing; and finally
– mistakes of the person conducting the measurement.

Methane fluxes were calculated by the linear method. The data used in the study came from methane concentration measurements conducted in two different types of dynamic chambers connected with a fast methane gas analyzer.

MATERIALS AND METHODS

The results of chamber measurements of methane fluxes described in the present study were conducted at the Rzecin peatland. The peatland (52°45' N 16°18' E, 54 m a.s.l.) has the area of 87 ha and is located in the south of the Notecka Primeval Forest in western Poland. In the eastern peatland there is a shallow lake which is overgrown with *Typha latifolia* L. and *Phragmites australis* (Cav.) Trin ex Stued. The peat substrate does not exceed 60-70 cm. This layer consists of a moss carpet floating on the water surface and a muddy sediment. The depth of the layer varies from 2 m around the rim to 11 m in the centre of the mire. According to the 2006 FAO soil classification, the peat substrate floating on the surface can be classified as Limnic Hemic Floatic Ombric Rheic Histosol (Epidystric). The methane measurement site is located in the middle of the mire near a 400 m long wooden footbridge leading to the eddy covariance tower where the CO_2, H_2O and CH_4 are measured (Chojnicki, 2013; Chojnicki *et al.,* 2007, 2010). The methane site is dominated by *Carex* spp., *Oxycoccus palustris* Pers. together with a dense cover of *Sphagnum teres* (Schmp.) Angstr. The LAI of vascular plants at this site does not exceed 1.8 m^2 m^{-2} (Juszczak *et al.,* 2012b).

Two types of closed chambers were used to measure methane fluxes:

– a round chamber in which the tightness was assured by a colar with a furrow containing water as the seal (Christiansen *et al.,* 2011) and
– a square chamber in which the tightness was assured by means of a neoprene gasket (Juszczak *et al.,* 2012b).

Both chambers were made of the same material *ie* white PVC. The round chamber is in the shape of a truncated cone 0.41 m in height. The surface area of the bottom base is 0.21 m^2,

T a b l e 1. Characteristics of the chambers used in the study

Type / shape of chamber	Dimensions of the chamber (m)	Basal area (A) (m^2)	Height (H) (m)	Volume (m^3)		H/A
				without collar	with collar	
Round	0.77 x 0.77	0.21	0.41	0.065	0.068	1.9
Square	0.50 (diameter)	0.56	0.50	0.304	0.309	0.9

and the volume 0.065 m^3 (Table 1, Fig. 1). The chamber was designed in the Leibniz-Centre for Agricultural Landscape Research Institute for Landscape, Müncheberg, Germany, as a static chamber for measurements of methane and nitrous oxide fluxes from peatlands. Originally it was equipped neither with fans nor with the pressure equilibration system. In turn, the square chamber is 0.5 m high, the base surface area is 0.56 m^2 and the volume is 0.304 m^3. The original chamber was designed in the Technical University of Munich (Drösler, 2005) and modified in the Department of Meteorology of Poznań University of Life Sciences. The chamber was designed in two versions, as a static chamber used for the measurement of CH_4 and N_2O fluxes (without fans and with the pressure compensation system) and as a dynamic chamber for the measurement of CO_2 fluxes (with fans and pressure compensation system, Drösler, 2005).

For the purpose of this study both chambers were equipped with fans for headspace mixing. One fan was installed in the round chamber and two in the square one (Fig. 1). In both cases the fans were fitted at ¾ height of the chamber. These were standard computer fans with electric power of 1.2 W and speed of 3 000 rpm. Laboratory tests indicated that the average air flow in both chambers was about 1 m s^{-1}, which corresponds to the average wind speed measured at the Rzecin peatland. Neither of the chambers used to measure methane fluxes was equipped with any pressure equilibration system.

The chambers were installed on soil PVC frames. The round collars were installed at the depth of about 10 cm, whereas the square collars at the depth of about 15-17 cm. The collars extended maximum 3-4 cm above the surface. The round collar was equipped with a 2 cm high furrow which was filled with water at the time of measurement. The square frame had a 2.5 cm high edge on which a neoprene gasket of the chamber was fitted. In order to assure tightness in the square chamber for measurement purposes the chamber was fixed to the collar with a rubber belt.

Both chambers were modified in a manner typical of dynamic chambers so as to enable measurements in real time with the use of a methane gas analyzer. A fast analyzer for CH_4 measurements produced by LOSGATOS Research, Mountain View, California, USA (LTD-100) was used for that purpose. The measurements were conducted at the frequency of 1 Hz. The gas analyzer was connected with the

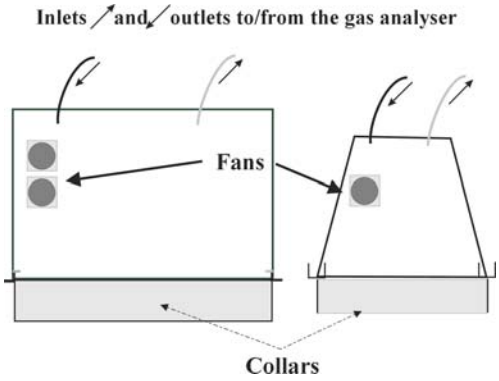

Fig. 1. Measurement chambers layout.

chamber in a closed system by two small teflon-coated pipes of 0.6 mm inner diameter. The speed of the air flux from the chambers to the analyzer and back was 0.35 l min^{-1} and it was maintained at a constant level. An inner pump of the gas analyzer was used. Peat temperature at the depth of 5 cm was monitored for the whole period of methane emission measurements. Thermistor T-107 made by Campbell Sci., North Logan, Utah, USA was used to measure temperature. The data were recorded on CR 1000 datalogger, also by Campbell Sci., North Logan, Utah, USA.

Given the different chamber sizes and differences in the tightness systems applied, the measurements were conducted at two measurement sites located 3 m from one another. The measurements in the round and square chambers were conducted on five and three collars, respectively, which should be treated as independent replicates necessary to reflect spatial variability in methane emission. Methane flux measurements were conducted between 10:00 a.m. and 4:00 p.m. Each time two full measurement series were carried out. On June 2, 2009, the first study was made which used only the round chamber. The chamber did not have a fan and was closed for a period of 30 min, which corresponds with the most frequently applied length of closing time in the case of static chambers, and simultaneously enables the observation of the saturation effect inside the chamber. On July 24, 2010, when the influence of fans on the measured fluxes was tested, two chambers were used – the round one and the square one, and a different measurement procedure was applied. Each time the measurements were conducted twice in the

same collar, with and without a fan. The chamber closure time was also shorter than 15 min. After the measurements in the round chamber were finished, the square chamber was used.

Methane fluxes were calculated on the basis of CH_4 concentration changes inside the chamber headspace during the measurement by means of the linear regression method, according to the formula:

$$F_{CH_4-C} = \frac{MPV\delta v f_1}{RTtA}, \quad (1)$$

F_{CH_4-C} – stands for CH_4 flux (μg CH_4-C m^{-2} h^{-1}), M for CH_4 molar mass (g mol^{-1}), P for atmospheric pressure (Pa), δv – represents the changes of CH_4 concentration in the chamber headspace (μmol mol^{-1}), V stands for the total chamber and collar volume (m^3), R – gas constant (m^3 Pa K^{-1} mol^{-1}), T – peat temperature (K) at the depth of 5 cm, t – duration of chamber closure (h), A – area of collar (m^2), f_1 – mass of C atoms in a CH_4 particle (0.75).

Methane fluxes were calculated for the entire measurement session regardless of the duration of a single measurement. The curve fitting errors were estimated on the basis of calculated normalized root mean square error (NRMSE). NRMSE is expressed in percentages and is calculated as the quotient of root mean square error (RMSE) and the range of CH_4 concentration changes during the chamber closure. Practically, it means that the lower the NRMSE, the bigger the conformity between the observed and calculated CH_4 concentration values (smaller residuals) and hence a smaller error in the CH_4 flux estimation. Following this rule, the time series of CH_4 concentration changes were shortened to a maximum of a few minutes after closing the chamber, when CH_4 fluxes were calculated, in order to minimise flux estimation errors.

The ANOVA test was used to estimate the significance of differences between the calculated NRMSE values for various calculation methods of CH_4 flux and to establish the significance of differences between the fluxes calculated on the basis of measurements with and without a fan. The software applied for that purpose was STATISTICA 9.1 by StatSoft Inc., Tulsa, Oklahoma, USA.

RESULTS

In the first experiment the chambers were closed for 30 min. From among the five measurements conducted in the first series, two indicated a rapid CH_4 emission known as ebullition (Fig. 2), which completely disturbed the measurement, changing dramatically, within 50 s, the initial value of methane concentration. In three subsequent measurements the above process was not observed and CH_4 concentration changes inside the chamber headspace occurred much more slowly, although in both cases a decrease in CH_4 emission rates with time was observed. These changes were reflected by a curvilinear diagram showing changes in CH_4 concentration in the chamber (Fig. 2). In one case this occurrence was connected with the saturation effect (curve CH4_2) and slow changes of CH_4 concentration gradients inside the chamber. A rapid decrease in emission rate after the 1300th second of the measurement may indicate that the chamber was not completely tight. In the case of curve CH4_1, the changes described can be caused only by the leakiness of the chamber, probably due to an insufficient amount of water in the collar furrow. This hypothesis may be confirmed initially by the same slope value of the curve, which for the first 120 s of the measurement does not differ significantly from the curves discussed (Fig. 2A). No disturbances occurred only in the case of curve CH4_3 and the increase in CH_4 concentration inside the chamber during the whole 30 min measurement is linear.

The application of linear methods to calculate CH_4 fluxes for 30 min measurement series is subject to a significant error. The NRMSE for CH_4 curves _1,2,4,5 varies from 7.7 to 19.8 % and only in the case of curve CH4_3 is the error below 1%. Flux values calculated on this basis are between 759 and 4427 μg CH_4-C m^{-2} h^{-1} (Table 2). The flux calculated for curve CH4_4, due to chamber leakiness, is completely erroneous and not taken into consideration in this analysis.

In order to estimate errors which may occur if CH_4 concentrations are measured by a static chamber, the simulation of taking six air samples was conducted after 300, 600, 900, 1 200, 1 500 and 1 750 s (Pihlatie *et al.,* 2013). Subsequently, the flux and the necessary statistics were calculated on the basis of known CH_4 concentrations. The results indicate even bigger biases as far as the values of estimated fluxes are concerned than in the example given above, where an entire series of one-second data was taken into consideration. Errors for curves CH4_1,2,4,5, expressed by NRMSE, fluctuate between 9.7 and 26.1%; the fluxes are in the range between 388 and 4481 μg CH_4-C m^{-2} h^{-1} and are significantly different from those calculated for one-second data ($p<0.001$). Only in the case of CH4_3 no differences in the value of the calculated flux was determined and the NRMSE was about 1%. In other cases the fluxes were much lower than those calculated for one-second data.

In order to minimise the error of estimating CH_4 fluxes determined by means of the linear regression method, it is necessary to shorten the length of measurement series for which the flux is calculated and consider only the time when the emission is being established or at least when it is the least disturbed by the measurement being conducted. Theoretically it is best to determine the methane rates in '0' time, just after the closure of the chamber. Non-linear methods of flux estimations provide such an opportunity. However, considering a high likelihood of initial disturbances connected with chamber installation (Christiansen *et al*., 2011), the applicability of non-linear methods seems to be questionable.

Therefore, CH_4 fluxes for 4 min data series were calculated by means of linear approximation. The calculations were conducted for curves CH4_1a, 2a, 3a (Fig. 2, Table 2). It appears that such an approach allows a decrease of the

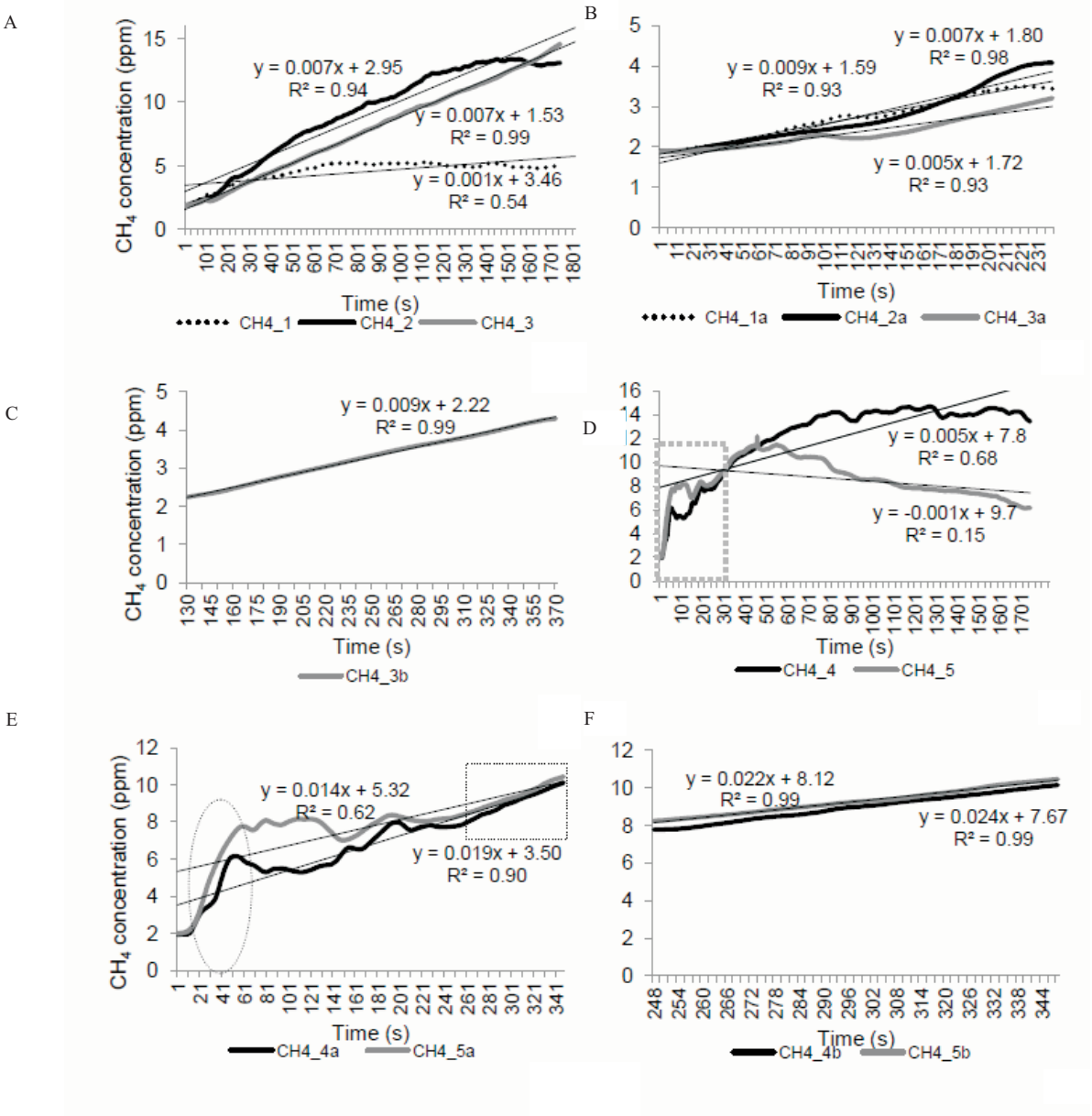

Fig. 2. Curves of CH_4 concentration changes for five consecutive measurements conducted in a round chamber with no headspace mixing. CH4_1…. CH4_5 designate successive measurements. a, b, c, d stand for shorter series of data taken out of 30 min series of one-second data (CH4_1…. CH4_5), for which the flux was calculated by means of the linear method; A – 30 min series of CH_4 concentration development for CH4_1...CH4_3 measurements, B – the same series of data (CH4_1...CH4_3), but time shortened to 4 min since closing the chamber, C – CH4_3 shortened to 4 min, but between 130 and 370 s of measurements since closing the chamber, D – 30 min series of CH_4 concentration development for CH4_4 and CH4_5 measurements, E – CH4_4 and CH4_5 shortened to 6 min, F – CH4_4 and CH4_5 shortened to 2 min but between 240 and 360 s of measurements since chamber closure. Note that the x and y axis have different scales. The thin solid lines correspond to the linear trends fitted to the curves showing the CH_4 concentration changes over time.

fitting error and flux estimation to 8%. Methane fluxes calculated in this way are very close in value and are within the range of 3226 to 5751 μg CH_4-C m^{-2} h^{-1}. In the case of CH4_3a, this procedure led to the increase of the error from 0.9 to 7.7%, due to disturbances which occur in the first two minutes of the measurement period. The flux for this curve (CH4_3b) was calculated separately, starting with the moment when these disturbances stopped influencing significantly the emission rates *ie* after 130 s of measurement (Fig. 2C, Table 2). The procedure led to decreasing the curve fitting error and, consequently, the error of CH_4 flux estimation, from the aforementioned 7.7 to 1.2%. The flux estimated in this way increased from 3226 to 5328 μg CH_4-C m^{-2} h^{-1}. And the fluctuation of flux value calculated by this method for curves CH4_1a, 2a, 3b decreased and was within the range of 4581 to 5328 μg CH_4-C m^{-2} h^{-1}.

T a b l e 2. Calculated values of the determination coefficient (R^2), rate of CH_4 concentration changes inside the chamber (Δv), CH_4 flux (F) and curve fitting errors (RMSE, NRMSE%) for five exemplary curves marked as CH4_1,2,3,4,5. Symbols *a, b, c* were introduced to distinguish between different parts of the same curves, for which CH_4 fluxes were calculated with the use of the linear method (explanation given in the text). The term '*static*' means that the above values were calculated on the basis of a simulated measurement in a static chamber, for six values of methane concentration measured at 300, 600, 900, 1 200, 1 500 and 1 750 s after chamber closure

Data	Time*	R^2	Δv (ppmv h^{-1})	F-CH_4 (μg C m^{-2} h^{-1})	RMSE	NRMSE
CH4_1	30 min	0.54	4.49	759.81	0.58	17.00
CH4_2		0.94	25.60	4 325.69	0.89	7.71
CH4_3		0.99	26.20	4 427.36	0.11	0.87
CH4_4		0.15	–	–	–	–
CH4_5		0.68	17.88	3 021.57	1.71	13.42
CH4_1a	4 min	0.99	27.11	4 581.22	0.06	3.73
CH4_2a		0.93	34.04	5 751.66	0.17	7.95
CH4_3a		0.93	19.09	3 226.09	0,10	7.70
CH4_3b		0.99	31.54	5 328.56	0.02	1.18
CH4_1_static	30 min	0.51	2.29	387.77	0.33	26.14
CH4_2_static		0.91	21.69	3 664.25	0.85	9.65
CH4_3_static		0.99	26.52	4 480.94	0.09	1.05
CH4_4_static		0.75			0.81	22.39
CH4_5_static		0.56	9.81	1 658.10	1.17	21.39
CH4_4a	6 min	0.62	50.17	8 477.05	1.09	12.87
CH4_5a		0.90	67.27	11 364.86	0.62	7.59
CH4_4b	2 min	0.99	80.98	13 681.13	0.05	2.18
CH4_5b		0.99	88.29	14 917.05	0.03	1.23
CH4_4c	30 s	0.98	497.59	84 068.86	0.20	4.13
CH4_5c		0.96	394.84	66 708.34	0.25	6.88

*Length of time series of CH_4 concentration used for flux calculation.

A completely different analytical issue arises in the case of curves CH4_4 and CH4_5. In both cases the initial rapid CH_4 emission and possible leakiness of the chamber were observed. Calculating fluxes by means of the linear method based on the whole 30 min series of one-second data is completely pointless for curve CH4_4 where, as a result of the improper tightness of the chamber, the headspace CH_4 concentration started to drop already after the eighth minute of the measurement procedure. The fitting error expressed as NRMSE for CH4_5 was above 13%, and the CH_4 flux reached the value of 3000 μg CH_4-C m^{-2} h^{-1} (Table 2, Fig. 2D). Using the procedure which simulates a static chamber only increased the curve fitting error and flux estimation up to as much as 21%, while the estimated CH_4 flux was almost half as small as in the above case. It is obvious that flux values calculated in this way are erroneous. The common feature of both curves is a very fast initial growth of CH_4 concentration, from about 2 to 6 ppm (CH4_4a) and to 8 ppm (CH4_5a) in time not exceeding 50 and 70 s, respectively. What is more, for the next 60-120 s both curves become nearly flat. After a rapid increase of the CH_4 concentration inside the chamber, the emission decreased and the plateau

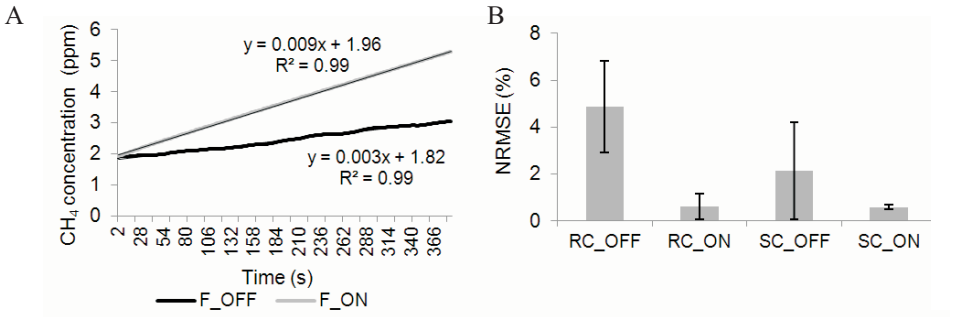

Fig. 3. Examples of CH_4 concentration development in the round chamber with the fan (A) on (F_ON) and off (F_OFF) and fitting errors relative to the changes in CH_4 (B) concentration expressed by NRMSE for measurements in the round chamber (RC) and the square chamber (SC) with the fan on (ON) and off (OFF). Error bars reflect standard deviation from error mean value.

phase should be connected with slow headspace mixing inside the chamber, which is probably forced exclusively by the air flow coming from the pipe turning back the air from the analyser. This air has a lower methane concentration than the air sucked into the analyser, which intensifies the observed occurrence. Only after about 240 s from the beginning of the measurement does a further steady increase of CH_4 concentration occur inside the chamber; it grows slower with time due to a saturation effect. Methane fluxes calculated for the first 6 min of the measurement (curves CH4_4a and CH4_5a, Table 2) are within the range of about 8470 to 11400 µg CH_4-C m^{-2} h^{-1}, and the fitting error varies from 7.6 to 12.9%. However, given the initial disturbances and a large fitting error for CH4_4a and CH4_5a (Fig. 2E), the methane flux was calculated for the data gathered between 240 and 360 s (Fig. 2F). The fitting error for CH4_4b and CH4_5b is significantly smaller ($p<0.001$) than in the case described above and is within the range of 1.2-2.2%, while the estimated fluxes have values 13 681 and 14 917 µg CH_4-C m^{-2} h^{-1}, respectively.

Momentary values of CH_4 emission during the initial rapid increase of CH_4 concentration inside the chamber headspace were in the range of 66 700-84 000 µg CH_4-C m^{-2} h^{-1}. Such excessive emission values, not reported in literature, may be connected exclusively with a momentary methane ebullition.

The application of fans in the round and square chambers led to a faster changes of CH_4 concentration inside the chamber than when the measurements were conducted in the same chambers with the fans turned off (Fig. 3A). It should be emphasized that the measurement with the fans on took place right after the measurement was conducted without forced headspace mixing and, consequently, the meteorological and hydrological conditions during successive measurements within one collar can be considered to have been the same. Thus, the observed higher increase of CH_4 concentration inside the chamber with fans in motion should be related only to forced headspace mixing. Fan application resulted in more stable CH_4 concentration development inside the chamber with time. Thereby, due to smaller CH_4 concentration fluctuations than in the measurement with the fans off, the curve fitting error was significantly ($p<0.001$) and several times smaller than in the case of measurements without headspace mixing (Fig. 3B). The NRMSE for curves determined for measurements conducted with the fan on (n=8) did not exceed 1%, and for measurements conducted in the square chamber it was smaller than for the round one, although differences in NRMSE were not statistically significant between the chambers. In other cases the curve fitting error was up to about 5% (±1.9) for the round chambers (n=5) and about 2% (±2%) for the square chambers (n=3). NRMSE values for the curves obtained for measurements without a fan and with a fan varied significantly from each other ($p<0.001$). It was also established that curve fitting errors for measurements conducted without forced headspace mixing in the round chambers were significantly bigger than in measurements in the square chambers ($p<0.001$).

The CH_4 fluxes calculated were bigger for measurements conducted in chambers with the fans switched on (Fig. 4). The mean CH_4 flux values for measurements without headspace mixing in the round chamber and the square chamber were 2 660 (±1 900) µg CH_4-C m^{-2} h^{-1} and 3 040 (±360) µg CH_4-C m^{-2} h^{-1}, respectively. The mean flux values for measurements with the fans switched on were 4 960 (±1 100) µg CH_4-C m^{-2} h^{-1} for the round chamber (n=5) and 7 180 (±1300) µg CH_4-C m^{-2} h^{-1} for the square chamber (n=3). The differences in the values of fluxes measured in both chambers were statistically significant ($p<0.001$).

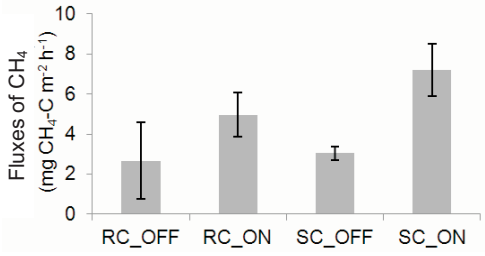

Fig. 4. Mean values of CH_4 fluxes measured in the round chamber (RC) and the square chamber (SC) with the fan off (OFF) and on (ON). Error bars reflect standard deviation from calculated mean CH_4 flux.

DISCUSSION

Two chambers with different shapes, surface area and slightly different heights were used for the testing, to show how they may impact the chamber measurements. The height to surface ratio in the round chamber was more than twice bigger than in the square chamber. CH_4 fluxes measured in the round chamber were smaller than those measured in the square chamber and this regularity did not depend on the use of fans. Obviously, the differences between the values of the measured fluxes can be connected with the fact that the measurements were conducted at two neighbouring sites rather than at the same one, and thus could be related to spatial variation in CH_4 emission. However, assuming that the mean expected CH_4 flux values should be the same, regarding the small distance (3 m) between the sites, then the cause of the observed flux differences should be identified in the chambers (installation procedure, use or lack of use of fans). Pihilatie *et al.* (2013), in a controlled study, indicated that the relation between CH_4 fluxes measured inside the chamber and reference fluxes did not depend on whether the chambers were equipped with fans or not, but that it was significantly correlated with the height, surface and volume of the chamber. It was also revealed that when the size of the chamber increased, the underestimation rate of CH_4 fluxes in the chamber decreased significantly. Assuming that the chamber size influences the underestimation rate of the measured fluxes, it can be hypothesized that CH_4 fluxes measured in the square chamber are closer to real fluxes. Obviously this hypothesis cannot be verified since there is no way of determining reference fluxes.

The influence of the use of fans on the values of CH_4 fluxes is very evident. Headspace mixing makes air inside the chamber homogenous, and therefore the gradients of CH_4 concentration inside the chamber are very small and hence the increase of CH_4 concentration resulting from occurring emission is distinctly rectilinear (Fig. 3). Consequently, the curve fitting error (NRMSE) is significantly smaller ($p<0.001$) than for the measurements in the chamber with the fan off. The observed slopes of the curve of CH_4 concentration increase inside the chamber are bigger than for the chamber without the fans on, which was also indicated by Pumpanen *et al.* (2004) and Christiansen *et al.* (2011). Fluxes of CH_4 measured in the chamber without fan were underestimated by 47% in the round chamber and by 58% in the square chamber relative to the measurements conducted with the fan on. Christiansen *et al.* (2011) estimated the differences between CH_4 fluxes measure non-mixed chambers under controlled conditions and the reference CH_4 flux to be 36%. Although the CH_4 fluxes underestimation rate in chambers without headspace mixing seems to be significantly higher than in the study by Christiansen *et al.* (2011), it should be remembered that these results are correct only in flux range of 90-2 300 $\mu g\ CH_4\ m^{-2}\ h^{-1}$ tested in the study. In our analyses the CH_4 fluxes measured *in situ* were 2-3 times higher than those analyzed in the above paper. Hence, although it is impossible to establish reference fluxes for comparison when conducting *in situ* measurements, it can be hypothesized that the CH_4 fluxes underestimation rate is significantly higher in the case of chamber measurements in which there was no headspace mixing and it considerably grows in parallel with the increase in absolute values of CH_4 fluxes. Inadequate tightness of chambers leads to uncontrolled leaks of gas through the gasket and consequently generates errors of unknown values (Hutchinson and Livingston, 2001), which is therefore difficult to correct. Leakiness was discovered during the first study when the round chamber was tested. Curves CH4_1 and CH4_5 give evidence that mistakes of the person conducting measurement, who did not assure proper tightness of the chambers, may influence the measurement by considerably underestimating the values of the measured fluxes. In the case of the round chamber, tightness was assured by water filling a round furrow of the collar. In the cases described above, probably as a result of improper levelling of the soil frames, or a crack of the collar and leak of water, the water level was too low and therefore the edge of the chamber was partly not filled with water and consequently not tight. Pihlatie *et al.* (2013) indicated also a significant decrease of fluxes in chambers without proper tightness. This error can be easily eliminated under the condition that the person conducting the measurement will assure proper tightness of the chamber. Moreover, measurements conducted with dynamic chambers with the use of an analyzer enable the correction of calculated fluxes by shortering the length of the analyzed measurement series until the leakiness has been observed. This procedure leads to obtaining fluxes whose values are comparable with those estimated in undisturbed conditions. It is disputable how long the measurement session should take in order to obtain CH_4 fluxes of relevant quality. In our peatland it seems that a few-minute measurement will be enough to estimate CH_4 fluxes properly with the use of linear methods. If initial disturbances occur in CH_4 concentration values, connected with the installation of the chamber, then the part of the curve with visible linear biases should be neglected when calculating the fluxes and they should be calculated only for the part of the curve which indicates the highest initial slope and the lowest normalized root mean square error (NRMSE). These guidelines are not applicable when a sudden increase of CH_4 concentration resulting from ebullition occurs in the chamber. Then the slope value should be calculated for the curve beyond the biased area, usually after the first 3-4 min of measurement.

Using the dynamic chamber and a fast gas analyzer to measure CH_4 fluxes provide a rare opportunity to record periodical rapid methane emissions coming from ebullition. The most frequent reason for such occurrences recorded at chamber measurements is the carelessness of the person conducting the measurement. The mechanical surface

disturbances *eg* when the chamber is laid rapidly, leads to pushing out the CH_4 stored in the peat (Goodrich *et al.,* 2011). These occurrences pose a big difficulty in measurements conducted in a static chamber and usually result in eliminating such measurements from calculation since the measurement does not meet quality standards and is treated as erroneous. In the cases analyzed for the purpose of the current study, such a situation was recorded twice at the beginning of the measurement, but it may happen at any moment and totally change the gradient of CH_4 concentration inside the chamber. Recorded fluctuations in CH_4 concentration from about 2 to 6-8 ppm (as in curves CH4_5 and CH4_4) may occur in a period of several seconds. The flux calculated for this part of the curve could be one order of magnitude bigger than that measured in undisturbed conditions; in our case it reached as much as 84 and 66 mg CH_4-C m^{-2} h^{-1}, curves CH4_5 and CH4_4, respectively. These pulsating and accidental emissions could significantly influence the overall balance of CH_4 emission from peatlands, as indicated by Tokida *et al.* (2007). Chamber measurements with a methane gas analyzer allow the recording of at least some emission occurrences of this type and, as indicated in the current paper, make possible a quantitative emission estimation.

Methane concentration measurements in real time with the use of a fast gas analyzer provide a rare opportunity to observe changing rates of methane concentration in the chamber during the measurement period. The results obtained clearly indicate a decrease with time in CH_4 emission rate, which should be explained by a slow decrease in the methane pressure gradient. This process should be connected with the saturation effect that is manifested in the curvilinear image of CH_4 concentration changes. The application of linear methods to calculate CH_4 fluxes on the basis of slope value of the line adjusted to 30 min data series leads to significant errors in flux estimations which are less than 26% to as much as 600% relative to fluxes calculated for the initial 4-6 min data series. Such a significant bias would indicate the superiority of curvilinear methods which better reflect the changing gas concentration in time (Kutzbach *et al.,* 2007). On the other hand, however, the initial disturbances typical for methane chamber measurements (Christiansen *et al.,* 2011; Davidson *et al.,* 2002) may exclude non-linear methods, mainly because it is impossible to determine the initial slope of the curve after closing the chamber, which is a pre-condition for the application of these methods. In our study the fluxes were not calculated by means of non-linear methods, but it attempts at indicating that a sufficiently short series of initial data which do not reveal any disturbances is sufficient to calculate CH_4 fluxes with a satisfactorily small error not exceeding 8% for measurements where no CH_4 ebullition occurred and 13% for measurements involving rapid outbursts of CH_4. In the latter case, in order to decrease the curve fitting error and obtain a higher CH_4 flux calculation precision, the fluxes were calculated for the first and steepest part of the curve beyond the initial disturbed period when the increase of CH_4 concentration in the chamber was linear (see above). The procedure allowed a decrease in the NRMSE to about 2%. A proper application of linear methods for CH_4 flux calculation results in minimizing the curve fitting error relative to the CH_4 concentration changes curve and thus minimizes the error in estimated CH_4 flux.

Static chambers are used the most frequently to measure methane fluxes emitted from peatland ecosystems; in such chambers syringes are normally used to take air samples for chromatographic analyses (Pihlatie *et al.,* 2013). This sampling technique leads to significant biases by changing methane gradients inside the chamber (Christiansen *et al.,* 2011) and consequently underestimating the calculated flux (Philatie *et al.,* 2013). Therefore, the first study involved a simulation in which six CH_4 samples were taken at particular time intervals (Pihlatie *et al.,* 2013) and methane fluxes were calculated on the bases of these samples by means of the linear method. Values of curve fitting errors were on average 15% (±11%), whereas for 30 min of 1 s data series they were 10% (±7%). Mean flux values calculated subsequently were about 590 μg CH_4-C m^{-2} h^{-1} lower than the average flux calculated for 30 min series of one-second data. Given that the first sample was taken 300 s after closing the chamber, it is hard to correctly establish the slope value immediately after closing the chamber; hence the application of non-linear methods to estimate CH_4 fluxes may be limited in such cases. Thereby it can be hypothesized that methane measurements conducted by means of static chambers significantly underestimate fluxes. Underestimation rate for CH_4 fluxes is between 20% (when CH_4 fluxes are calculated by the linear method for the whole 30 min data series) and about 70% (regarding CH_4 fluxes calculated on the basis of a few-minute initial data series beyond the disturbed area).

CONCLUSIONS

1. An improper application of linear methods to calculate methane fluxes may lead to significant errors. This error increases if a leak or ebullition occur during the measurement. Due to the observed saturation effect connected with the decrease of methane pressure gradients inside the chamber during the measurement period, the application of linear methods to calculate CH_4 fluxes is conclusive to underestimating the values of the calculated fluxes.

2. Shortening the CH_4 measurement period to a few minutes after closing the chamber allows a correct estimation of CH_4 fluxes by means of linear methods with a much smaller error than for the entire 30 min data series.

3. With the application of dynamic chambers and a fast analyzer to measure methane fluxes on peatlands the chamber closure time may be shortened to a few minutes.

4. The use of static chambers to measure methane fluxes may lead to underestimating methane flux values even by several times.

5. Equipping the chambers with fans mixing chamber headspace results in decreasing the fitting and flux estimation errors. However, since there is no possibility to compare measurements conducted *in situ* with reference fluxes, it is impossible to precisely determine the CH_4 fluxes underestimation rate for fluxes measured in a chamber without headspace mixing.

6. Mistakes of the person conducting the measurement can lead to leakiness of the chamber or to uncontrolled methane emissions caused by mechanical factors. Therefore, given that such mistakes can be easily eliminated, it is vital to assure adequate tightness of the chamber and to refrain from any rapid movements which could force methane emission by means of ebullition.

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