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Autumnal fluxes of CH_4 and CO_2 from Mediterranean reed wetland based on eddy covariance and chamber methods

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ABSTRACT

Atmospheric methane (CH_4) and carbon dioxide (CO_2) concentration have been increasing during the last several centuries due to changes in agricultural practices and other anthropogenic activities. Both greenhouse gases (GHGs), have a significant impact on the Earth's radiative balance. GHG effluxes of CH_4 and CO_2 were measured in a warm Mediterranean wetland in south of Spain. The dominant vegetation cover at the site was by common reed (*Phragmites australis*) and the measurements were done during short measurement campaign in early autumn 2015. Gas-flux measurements were carried out applying two methods, the eddy covariance (EC) technique and the chamber method (CM). These two methods representing different ecosystem subsets, with EC representing the plant/ecosystem subset and CM representing the water/soil subset. In our measurement campaigns using CM, CH_4 emissions ranged from 7.2 to 17.7 mg CH_4-C m^{-2} d^{-1} and CO_2 emissions from 0.53 to 1.27 g CO_2-C m^{-2} d^{-1}. When using EC, the average fluxes of CH_4 and CO_2 were 31.4 mg CH_4-C m^{-2} d^{-1} and 1.32 g CO_2-C m^{-2} d^{-1}, respectively. Relationships between gas fluxes (CO_2 and CH_4) measured by the EC method were quite closely correlated with photosynthetically active solar radiation. Our results showed higher CO_2 carbon released from the water/soil ecosystem subset in comparison to plants subset. On the other hand, the estimated CH_4 carbon balance for the plant/ecosystem subset was about twice that of the water/soil ecosystem subset. Overall, we showed that EC and CM methods cover different areas making EC advantageous for integrated measurements over larger areas, while the CM approach is suitable for local and spatially well constrained flux measurements. Hence, EC and CM methods should be seen as complementary rather than fully comparable methods.

1. Introduction

The atmospheric CH_4 concentration has been increasing during the last several hundred years due to changes in agricultural practices and other anthropogenic activities (Dlugokencky et al., 1994; Ferretti et al., 2005). On the other hand, global increases in carbon dioxide (CO_2) are due to fossil fuel use (9.9 ± 0.5 GtC in 2016; Le Quéré et al., 2017), with land-use change providing another significant but smaller contribution (1.3 GtC yr^{-1}; Le Quéré et al., 2017). Both greenhouse gases (GHGs), CO_2 and CH_4, have a significant impact on the GHG balance (Archer, 2008) and account for over 60% and 20% of global warming, respectively (Stocker et al., 2013). Although over the last 20 years several studies concerning GHGs (mainly CO_2) have been realized from local to global scales (CarboEurope IP, Carbomont, Nitroeurope, etc.), there is still lack of detailed information in the determination of CO_2 and CH_4 fluxes in the land-atmosphere system at the local scale from different ecosystems.

Wetlands account for 80% of the natural atmospheric methane (CH_4) source (145–170 Tg CH_4 $year^{-1}$), and are also the second largest natural sink (−30 Tg CH_4 $year^{-1}$) after tropospheric CH_4 oxidation (Anderson et al., 2010; Wang et al., 2013). In wetlands, CH_4 is produced below the water table in anaerobic conditions, where fresh root litter and exudates from deep-rooting plants provide substrates for methanogens (Schütz et al., 1991; Chanton et al., 1995). The CH_4 is released to the atmosphere via diffusion through peat, via aerenchymatous vascular plants (Waddington et al. 1996, Vítková et al., 2017) and via ebullition (Martens and Val Klump, 1980). Previous studies have found that CH_4 emissions often show large spatial variability (Hendriks et al., 2010; Moore et al., 2011). Spatial patterns in CH_4 emissions are often attributed to differences in ground water level (Jungkunst and Fiedler,

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2007), peat temperature (Lai et al., 2014) and vegetation composition (Dias et al., 2010; Vítková et al., 2017). CO_2 released from sediments is produced by autotrophic and heterotrophic soil respiration (Kutsch et al., 2009). CO_2 is highly soluble in water and can accumulate near the sediment/water interface, which results in oversaturation and release to the atmosphere. It has been suggested that the transport of dissolved organic carbon (DOC) from terrestrial environments is an important source of carbon in aquatic environments (Rantakari and Kortelainen, 2005; Huttunen et al., 2002).

Accurate CH_4 and CO_2 flux measurements are crucial for estimating global carbon budgets but are largely constrained by methods that differ in their advantages, disadvantages and susceptibilities to measurement errors (Yu et al., 2013). The use of different complementary measurement techniques is essential for ensuring data quality. Comparison and synthesis of obtained data by different methods improve their interpretation and budget estimation. The chamber method (CM) is usually used to measure CH_4 and CO_2 due to the advantage of detecting low fluxes and the possibility of measuring individual ecosystem components, allowing also a high number of spatial replicates. Estimates of daily or even annual CH_4 and CO_2 fluxes are feasible using linear interpolations or regression models (Chen et al., 2011; Song et al., 2009). While manual chambers require manipulation by operators and are time-consuming, automated chambers can measure CH_4 and CO_2 fluxes at higher frequency without personal attention (Pavelka et al., 2004; Savage et al., 2014).

During past decades, the eddy covariance (EC) technique has measured mainly CO_2 and water vapour fluxes, adding CH_4 in the last decade (Hendriks et al., 2007). Contrary to the CM, the EC technique does not disturb the soil/air environment (Dugas, 1993; Kroon et al., 2007), and therefore does not alter the processes of gas exchange between the sources and the atmosphere. Most importantly, it provides continuous measurements that can be integrated over different temporal scales (daily, monthly, seasonally and yearly) as well as over large areas. However, the EC technique must fulfil several requirements for its application such as the existence of a horizontally homogeneous area with flat terrain and atmospheric steady-state conditions (Baldocchi, 2003; Foken and Napo, 2008).

Nowadays, some studies have tested the appropriateness of EC measurements of CH_4 (e.g. Kroon et al., 2007; Hendriks et al., 2007). Moreover, others studies have combined the CM with the EC technique for measuring CH_4 fluxes in wetland ecosystems such as heterogeneous peat meadows, rice paddy fields or northern peatlands (Poyda et al., 2017; Hendriks et al., 2010; Meijide et al., 2011; Sachs et al., 2010; Schrier-Uijl et al., 2010). The existing studies show disagreement in the results obtained with both techniques. The disagreement relates to ecosystem complexity and specific conditions that can limit the applicability of these methods (Myklebust et al., 2008). Using CM and EC techniques for measuring of CH_4 and CO_2 fluxes from complex wetlands ecosystems is advantageous in terms of ecosystems subsets (soil/water and plant/ecosystem). Both available methods can yield accurate measurements of gas fluxes at the ecosystem level. In this study, we measured CH_4 and CO_2 fluxes on a temporarily flooded Mediterranean wetland ecosystem using the CM and EC techniques at the beginning of the wet season. With this study, we aimed 1) to estimate the magnitude of CH_4 and CO_2 fluxes by both methods, 2) to determine the environmental factors influencing the spatial variability of CH_4 and CO_2 fluxes and 3) to assess the relative contribution of CH_4 and CO_2 effluxes from different ecosystem subsets (soil/water and plant/ecosystem).

2. Material and methods

2.1. Site description

Our study was carried out at the experimental wetland site "Padul" (37°0′42.26″N, 3°36′20.65″W). It is a warm Mediterranean wetland located in the Granada province, southern Spain (Fig. 1). The wetland

Fig. 1. The studied wetland site in south Mediterranean part of Spain near El Padul, a village in the Granada province.

of about 3.3 km^2 lies in the flat terrain (slope < 2%) of Padul valley at an elevation of 744 m. a. s. l. and is included in the Ramsar Convention for Wetlands (site number 1674, "*Convention on Wetlands of International Importance Especially as Waterflow Habitat*"). The "Padul" site is characterized by a mean annual temperature of 16 °C and a mean annual precipitation of 470 mm, and northwesterly winds prevail. There is a lake resulting from discontinued peat extraction activities that now provides a valuable bird habitat. Below the surface and drainage channel network, the wetland contains peat layers with Pleistocene sediments, which are > 100 m thick in the North-East (Ortiz et al., 2004).

The soil is mainly composed of sand and gravel intercalated with peat. Incubation experiments of anaerobic substrate samples taken from the eddy covariance tower fetch, reported CH_4 production ranging from 1% (at 5 °C) to 8% (at 25 °C) of the total gas production (CO_2 + CH_4) (Bockermann, 2013).

The wetland area has been altered over the past decades including drainage for small-scale agriculture, peat extraction, and eutrophication from surrounding human activities. A highly variable water table during the annual cycle is a result of strong seasonal discharge from spring snow melt in the mountains, human intervention (changes in hydrology), and the semi-arid warm climate including an extensive dry period in summer (July and August). A reed stand (*Phragmites australis* [Cav.], Trin. ex. Steud.) dominates vegetation cover. The common reed is a tall, helophytic, wind-pollinated grass with annual shoots up to 5 m above-ground level from an extensive system of rhizomes and stolons. The plant density is 290 ± 50 individuals m^2, estimated at the end of the growing season of 2013 by counting the number of individuals in 5 plots (0.25m^2) distributed randomly across the eddy covariance area of influence. On average (from 2013 to 2017) ground water level was below the surface from the end of June to the end of September, when the rain period starts. The lowest ground water level value below the surface during an annual cycle is −88 ± 11 cm and maximum ground water level is 34 ± 7 cm. The highly variable water table is the result of strong seasonal discharge from spring snow melt in the mountains and human intervention (hydric resources management).

Standing water during the measurements campaign can be characterized by a median oxygen (O_2) concentration of 2.85 mg l^{-1}, very near the average of 2.82 mg l^{-1}. Water conductivity was 665.4 μS and pH was 7.42 on average. The median redox potential of standing water was +72.5 mV related to Ag/AgCl reference electrode corrected to the normal H electrode.

2.2. Gas flux measurements

Fluxes of CH_4 and CO_2 at the plot and ecosystem scales were measured using two different techniques, eddy covariance (EC, Baldocchi et al., 2001) and the chamber method (CM, non-steady state flow-

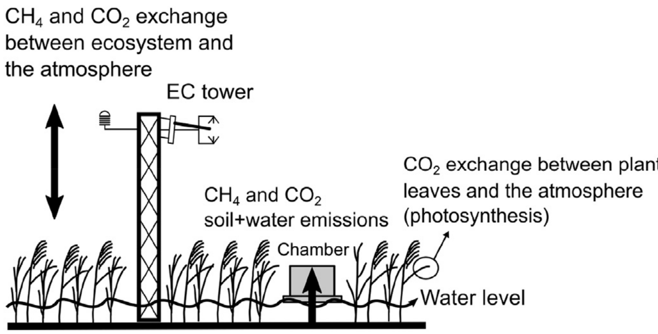

Fig. 2. Scheme of the conducted measurements at the different levels: (1) Ecosystem level (EC = eddy covariance measurements), (2) Soil and water table level (CM = chamber measurements) and (3) leaf level (net photosynthesis) at the "Padul" wetland (Spain).

through system; Matson and Harriss, 1995) during three consecutive days in Autumn (Fig. 2). An EC system was installed at a height of 6 m above wetland surface in June 2012. The EC system consists of a three-dimensional sonic anemometer (CSAT-3, Campbell Scientific, Logan, UT, USA), an open path CO_2 and H_2O infrared gas analyzer (Li-Cor 7500, Lincoln, NE, USA) and an open path CH_4 infrared gas analyzer (Li-Cor 7700, Lincoln, NE, USA). Gas concentrations were measured at 10 Hz. Data were logged with a datalogger (CR3000, Campbell Scientific, Logan, UT, USA).

Measurements of CH_4 and CO_2 fluxes from the flooded wetland soil were measured daily at five different sampling plots (real repetitions) by manual CM from early morning to sunset during the 20th, 21st, and 22nd of October. CM took 10 min per plot and each plot was measured four times on the 20th, seven times on the 21st and six times on the 22nd. Concentrations of both gases were measured "in situ" by an Ultraportable Greenhouse Gas analyzer (UGGA, LGR Inc., San Jose, CA, USA). The UGGA provides immediate values of CH_4 and CO_2 concentration corrected to actual water vapour concentrations. The self-made chamber was made of white PVC (cylinder-shape, 17.0 cm height and 19.8 cm in diameter) with a volume of 4.39 L. The chamber base has a border covered with neoprene to provide better sealing and stability when placed on the collar. The chamber was equipped with tubing (0.4 cm diameter and 10 cm long) to ensure pressure equilibrium between the inside and the outside (Acosta et al., 2013). At each measured position, a floating frame (20 cm × 20 cm, height 5 cm) of extruded polystyrene foam was placed. The floating frame had a hole (20 cm diameter) in the center to fit the chamber and one small hole in each corner of the frame in order to stabilize the floating frame on the water by fixing 1 m long plastic sticks into the soil. The chamber worked in closed mode e.g. directly connected by polyurethane tubing to the UGGA during analysis. Chamber closure time was 10 min (Heinemeyer and McNamara, 2011), yielding effective, accurate and quick CH_4 and CO_2 concentration data in order to calculate fluxes. Sampling plots were located close to the EC tower, where the water table was above soil surface. The water level was stable, on average 0.21 m above soil surface during the campaign. The sampling plots did not contain stems of common reed but a dense reed stand surrounded the plots.

The wooden platform (Fig. 1) was used during our experiment and there the Ultraportable Greenhouse Gas analyzer (UGGA) was located. Moreover, in order to avoid disturbance caused by installation of the chamber into the investigated collar, the investigated soil/water position where chosen within 2–3 m distance from the platform. In order to facilitate manipulation of the chamber and water/soil disturbances prior to CM monitoring, only one or two slow steps forward and back (depending of the measured position) were taken by the chamber operator causing a minimum impact. The remaining time during the CM monitoring the chamber operator sat on the platform. No distributions by walking where done during the 10 min period of the CM measurement.

2.3. Ancillary meteorological measurements

The eddy covariance tower is complemented with concurrent meteorological measurements that include continuous measurements of the following meteorological and soil parameters: Photosynthetic active solar radiation – PhAR (quantum sensors, Li-190, Lincoln, NE, USA), soil temperature (TCAV, Campbell Scientific, Logan, UT, USA; installed at 2 and 6 cm depth), ground water level (piezo-resistive level transmitter, series 26Y, Keller AG für Druckmesstechnik, Switzerland), and air temperature and relative humidity (thermohygrometer, HMP35-C, Campbell Scientific, Logan, UT, USA; installed at 5 m).

Conductivity, oxygen concentration, pH and redox potential were measured using following electrodes: WTW TetraCon325 (conductivity), WTW CellOx325 (oxygen), WTW SenTix41 (pH) and platinum electrodes as measuring and reference electrodes (Ag/AgCl) together for redox measurements. Electrodes were used with the multimeter Multi340i (WTW, Wissenschaftlich-Technische-Werkstätten, Germany).

2.4. Photosynthesis measurements

Parallel to the CH_4 and CO_2 flux measurements by EC and CM, daily courses of leaf photosynthesis (A, CO_2 assimilation rate) were measured using an InfraRed Gas Analyzer - IRGA (Li-6400, Li-Cor, NE, USA). Photosynthesis was measured in situ on the intact leaves of five different plant stems of reeds at their natural orientation and under natural light conditions at different time intervals from sunrise to sunset during two days. The air flow rate through the assimilation chamber was maintained at 500 $\mu mol\, s^{-1}$. External input air entered through a pipe at a height of 2 m above the soil surface. IRGA CO_2 and H_2O zeros and flow meters were calibrated each day before the beginning of the measurement. Sample and reference IRGA values were matched before each individual leaf measurement, and recorded once sample and reference CO_2 values had stabilized.

2.5. Flux calculation and data processing chamber data

Calculation of gas fluxes is based on the slope of the linear regression of gas concentration in the chamber headspace over a time period of about 10 min, taking into account the chamber volume (4.39 L) and surface area covered (307.095 cm^2). Calculations of gas fluxes also include corrections to the current air temperature and ambient air pressure by the physical law of ideal gas. Calculated fluxes were tested to follow a normal distribution using the Shapiro-Wilks test (Royston, 1995). As the distribution of the primary data differed significantly from normality ($p < 0.01$), differences among the fluxes of CH_4 and CO_2 measured within three consecutive days in October 2015 were tested using the nonparametric Kruskal-Wallis test (a distribution-free test for general alternatives) with possibility to multiple comparison between groups (Hollander et al., 2014). Moreover, a skewness test was applied in order to measure the asymmetry of the data probability distribution (Joanes and Gill, 1998). The relationship between CH_4 and CO_2 was also analyzed by correlation analyses (Spearman's nonparametric correlation coefficient). All statistical analyses were performed using R (www.r-project.org).

2.6. Eddy covariance data

The fetch is at least 200 m from the tower in every wind directions (Fig. 3). Half-hourly eddy covariance fluxes were calculated using the EddyPro 6.2.0 software (Li-Cor, Lincoln, Nebraska, USA), including corrections for density perturbations (Webb et al., 1980) and two coordinate rotations (Kowalski et al., 1997). Tests of stationarity and

Fig. 3. Fetch (patch of common reed delimited by a continuous white line) and crosswind-integrated footprint (dashed lines) of the experimental site following Kljun et al. (2004). The peak contribution and the distance from the tower contributing 50% to measured fluxes are delimited by continuous and dashed lines respectively, for daytime (black lines) and nighttime (dashed lines) periods.
Source Google Earth, image: Landsat, imagery date December 14, 2015.

turbulence development were applied, and only fluxes with high (differences < 30% for both tests) and intermediate (differences < 30% for one test) quality were selected for this study (Mauder and Foken, 2004). Additionally, averaging periods with low turbulence (friction velocity, u* < 0.13 m s^{-1}; (Papale et al., 2006)) were rejected. According to the flux crosswind-integrated footprint following Kljun et al. (2004), the peak contribution and the distance from where the footprint contributes 50% to measured fluxes during the studied period were inside the fetch.

For CO_2 fluxes, gaps were filled using the marginal distribution sampling technique, applied using the available on-line tool (https://www.bgc-jena.mpg.de/bgi/index.php/Services/REddyProcWeb) and based on the replacement of missing values using a time window of several adjacent days (see Reichstein et al., 2005). For CH_4 fluxes, we use a machine learning technique (R^2 = 0.49; RMSE = 0.04 μmol CH_4 m^{-2} s^{-1}), applied using Matlab (version R2017a). This method is a type of ensemble decision tree called "Bagging Regression Tree" that uses several decision trees instead of just one to improve the algorithm response; the bagging process is based on generating multiple versions of a predictor to construct a stronger aggregated predictor (Breiman, 1996, 2001). To avoid errors due to CH_4 storage during calm conditions, the data collected during weak turbulence were removed from further analysis by filtering out all half-hour flux values with friction velocities (u*) below 0.16 m s^{-1}. The CM fluxes were calculated correcting the measured concentrations of CH_4 and CO_2 to the current water vapour. The final fluxes were converted to a mass emission rate by using the ideal gas law. Stability of the atmosphere was checked based on Monin-Obukhov stability parameter (zeta = (z-d)/L). Footprints were estimated using the Kljun model (Kljun et al., 2004) calculated by the EddyPro® software (Li-Cor, Lincoln, Nebraska, USA).

3. Results

3.1. Environmental conditions

Environmental conditions during the measurement period were quite similar and stable. Only a decrease of the minimum air

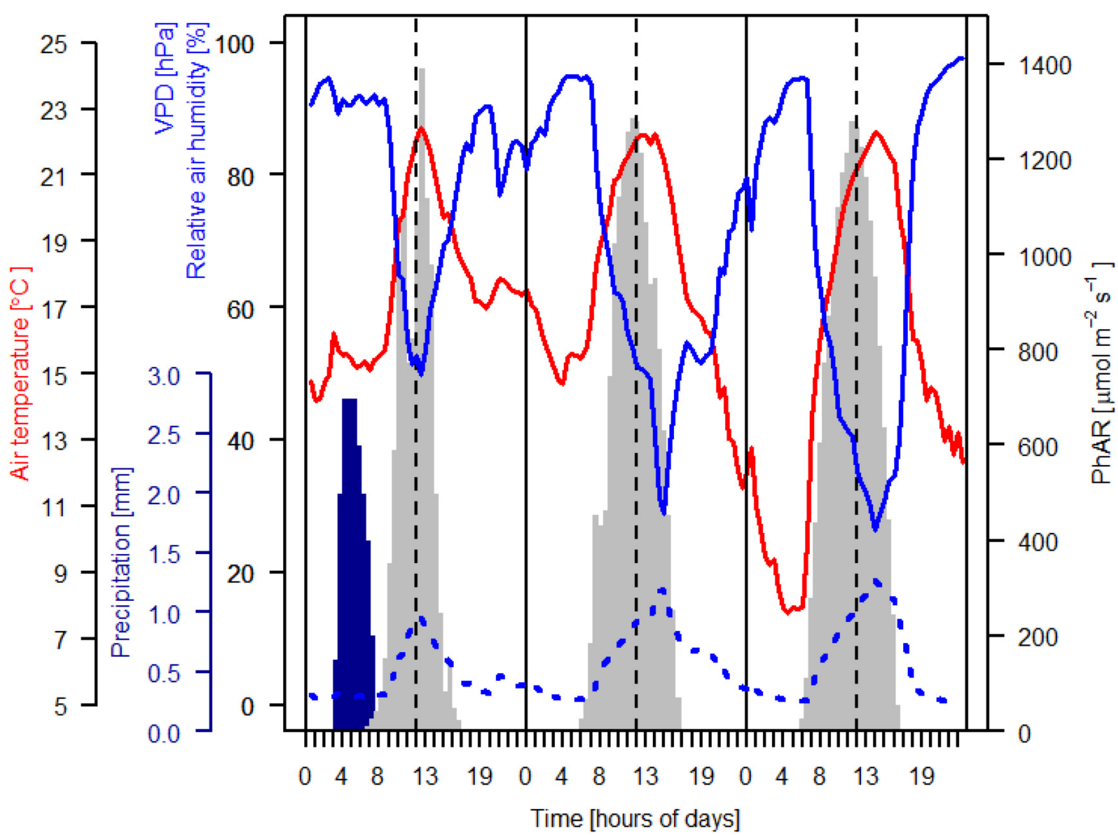

Fig. 4. Environmental conditions during the three days of the measurement campaign (20th-22nd October 2015) at the "Padul" wetland (Spain). Air temperature – solid red line, Relative air humidity – solid blue line, Vapour pressure deficit (VPD) – dashed blue line, Photosynthetic active solar radiation (PhAR) – grey bars, Precipitation – blue bars. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature was observed during the third day of measurements. A precipitation event was recorded during the night and morning time (from 3 to 7 am) of the first measurement day (21st October 2015) and the total amount of precipitation for this period was 17.7 mm. The water level increased slightly from 0.19 m to 0.21 m, on average above soil surface and remained stable during the next two measurement days. The minimum and maximum air temperatures were of 7.8 °C and 22.4 °C. The lowest air temperature was recorded in the morning of 22nd of October (7.8 °C). The average daily air temperatures during the three measurement days were 17.6 °C, 17.9 °C and 15.2 °C respectively (Fig. 4). Relative air humidity (RH) ranged from 26.3% to 97.6% and the water vapour pressure deficit (VPD) ranged from 18.7 hPa to 0.40 hPa. Due to cloudy weather conditions, the VPD was lower during the first day of measurements, reaching a maximum value of 13.1 hPa at midday. PhAR was lower during this day, showing a maximum value of 1390 μmol $m^{-2} s^{-1}$ at midday for short period (Fig. 4). The second and third days of measurements were characterized by sunny conditions almost without cloud. The highest VPD (minimum of RH) was recorded at 2–3 pm (22nd October), with a maximum PhAR value of 1279 μmol $m^{-2} s^{-1}$. The lowest VPD (maximum of RH) was recorded at 10 pm and 5–6 am of 21st and 22nd October, respectively. Daily sums of PhAR were 4.2, 6.3 and 6.6 MJ d^{-1}, respectively, for the three consecutive days of measurements (Fig. 4).

3.2. CH_4 and CO_2 fluxes measured by chambers

In our measurement campaign, CH_4 and CO_2 effluxes from the free water column above soil surface fluctuated slightly during the day. The CH_4 fluxes ranged from 7.2 to 17.7 mg CH_4-C m^{-2} d^{-1} (Fig. 5). The median (10.4 mg CH_4-C m^{-2} d^{-1}) position on the box and whisker plot (Fig. 5) was slightly asymmetric. Distributions of CH_4 fluxes were positively skewed (skewness = 0.603). Average fluxes of CH_4 (11.2 mg CH_4-C m^{-2} d^{-1}) were higher than the median. CO_2 fluxes ranged from 0.53 to 1.27 g CO_2-C m^{-2} d^{-1} with a median of 0.68 g CO_2-C m^{-2} d^{-1} and an average of 0.75 g CO_2-C m^{-2} d^{-1}. The position of the median was more symmetric in interquartile range than in the case of CH_4. However, the whole distribution was also positively skewed as in the case of CH_4 (skewness = 1.328). There was no statistically significant difference in fluxes of CH_4 and CO_2 among days ($p > 0.05$). The relationship between CH_4 and CO_2 was also analyzed by correlation analyses (Spearman's nonparametric correlation coefficient) with non-statistically significant results ($p > 0.05$). During the period of our field campaign, no trend or relations was found between CH_4 and CO_2 fluxes.

We analyzed expected relationships between CH_4 and CO_2 fluxes with measured environmental variables at the study site (air and soil/water temperatures and PhAR). There was a significant positive relationship between CH_4 fluxes and water temperature ($p < 0.05$) 0.241 (Spearman's nonparametric correlation coefficient). CO_2 fluxes showed a significant negative relationship with PhAR (−0.657, $p < 0.001$). In contrast, fluxes of CH_4 were not statistically significant correlated with PhAR.

3.3. Photosynthesis of *Phragmites australis* leaves

The photosynthetic activity of *Phragmites australis* was measured during the second and third day of the measurement campaign. Measured reed stems were 3.9 m height on average, with average basal stem diameter of 9.1 mm and about 23 stem nodes. The average stem had about 6 to 7 green leaves on the upper part of the stem, which were photosynthetically active even though the period of the measurement campaign was at the end of the growing season. The photosynthesis rate measured on these upper leaves showed high activity with positive fluxes (consumption) of CO_2 during light period of day. The maximum leaf photosynthetic rate was about 22.5 μmol CO_2 $m^{-2} s^{-1}$, with an average of 11.3 and 13.9 μmol CO_2 $m^{-2} s^{-1}$ for the 21st and 22nd October, respectively. These maximum values of photosynthesis relate to the first negative values (CO_2 assimilation) of net CO_2 ecosystem exchange (NEE) observed in the morning (9:30 am). The last net ecosystem uptake of CO_2 (negative value of NEE) was recorded at 4:00 pm

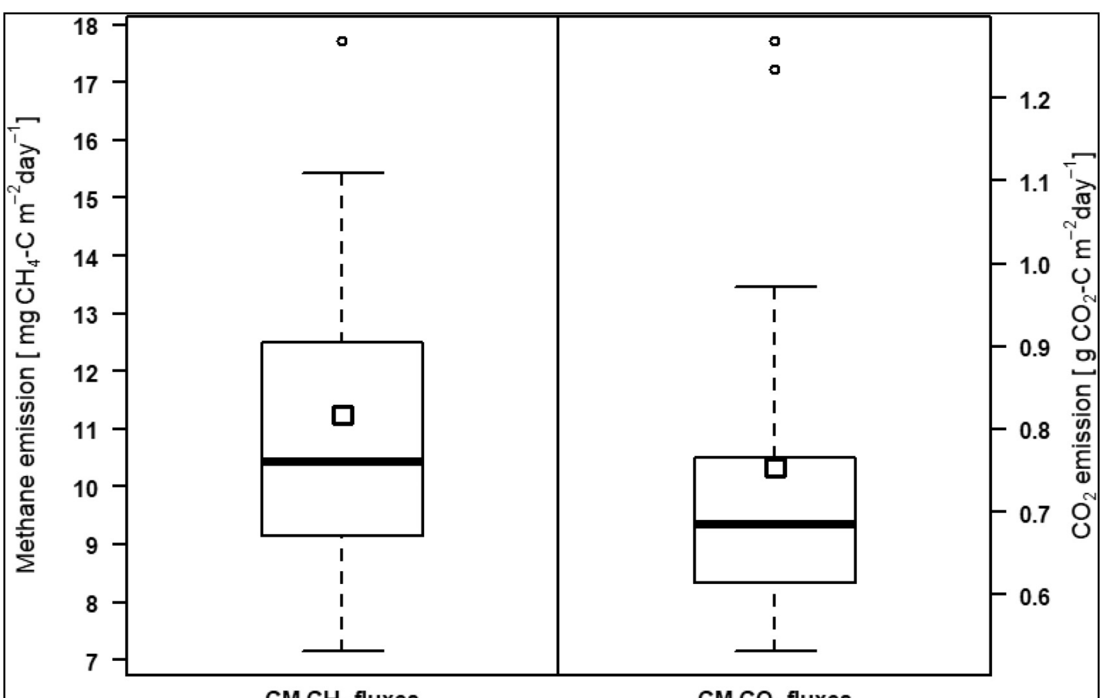

Fig. 5. Box and whisker plot of CH_4 and CO_2 fluxes measured by chambers (CM) from the open water column without emerged vegetation (n = 17 per each investigated gas species), during three consecutive days of the measurement campaign (20–22 October 2015) at the "Padul" wetland. Mean (small open box), second quartile (thick black lines), upper and lower quartile (boxes with 50% measured data) and error bars with upper and lower extremes are shown. Outliers are shown as individual circle points.

Table 1
Correlations (Spearman's nonparametric correlation coefficients) between fluxes of CH_4 and CO_2 measured by different methods (EC = eddy covariance, CM = chamber measurements) representing different ecosystem subsets. Significance of correlations were on 0.001 probability level, n.s = not significant at least 0.100 probability level.

Methods and ecosystem subsets	CH_4 fluxes		CO_2 fluxes	
	EC (ecosystem)	CM (water/soil)	EC (ecosystem)	CM (water/soil)
PhAR	0.559	n.s	−0.789	−0.657
Leaf photosynthesis	0.463	n.s	−0.577	−0.605

when leaf photosynthetic activity had decreased. A typical bell shape course of daily leaf photosynthesis was created from both measurements (21st and 22nd October) (Fig. 5). The average hourly bell shape course of photosynthesis was fitted to a fourth order polynomial functions (Adjusted R-squared = 0.873; F-statistic = 18.24, $p < 0.01$). Grey filled areas in Fig. 5 represent the amount of CO_2 fixed by photosynthesis of upper green leaves of *Phragmites australis*. These leaves fixed from 1.9 to 2.4 g CO_2-C m^{-2} during the central hours of the midday period (from 6 am to 4:30 pm). The amount of CO_2 fixed over the whole light period (about 10 h) was about 26.5 g CO_2 m^2, corresponding to 7.2 g C m^{-2}.

Measured leaf photosynthesis was separately correlated with gas fluxes measured by the EC and CM methods. We found a negative correlation −0.557 (Spearman's nonparametric correlation coefficient) ($p < 0.001$) between leaf photosynthesis and the CO_2 flux measured by the EC method (Table 1), thus indicating that an increase in net CO_2 uptake by plant leaves (positive values of photosynthesis) correlated with an increase in net ecosystem CO_2 uptake (negative EC values). Similar CO_2 flux results were found using the CM method (−0.605, $p < 0.001$). In the case of CH_4, we found statistically significant positive correlations between leaf photosynthesis and CH_4 fluxes for measurements conducted with the EC method (0.463, $p < 0.001$), meaning that increasing leaf CO_2 uptake coincided with increasing net ecosystem CH_4 emissions (positive EC values). However, the relationship with CH_4 fluxes measured by the CM was not significant.

3.4. Eddy covariance measurements

3.4.1. Estimation of eddy covariance footprint

The footprint of EC measurements was determined by prevailing winds and by the actual atmospheric situation of investigated site. The prevailing winds for the measured period were from two directions North west (NW) and South east (SE). Maximum wind speeds reached 3–6 m s^{-1} from the NW and 2–3 m s^{-1} from the SE. Sizes and shapes of footprints under different stability situation of the atmosphere were quite similar (Fig. 6). The largest area of estimated footprint calculated for neutral conditions (zeta in range of −0.06 to 0.06) was about 10.6 ha. Under stable (zeta ≥ 0.06) and unstable (zeta < −0.06) conditions, the estimated area of footprints were 8.9 ha and 9.9 ha, respectively. The ratio of occurrences of individual atmospheric conditions for stable, neutral and unstable conditions were 23%, 50% and 27%, respectively. During the measured period, the maximum length of source location (x-peak) was 94 m during daytime and 114 m during nighttime. During all atmospheric stability conditions, estimated footprints included homogenous stand of *Phragmites australis* in "Padul" wetland ecosystem (Fig. 7).

3.4.2. CH_4 and CO_2 fluxes measured by eddy covariance technique (EC)

Fluxes of CH_4 and CO_2 measured by EC at the scale were higher than water/soil fluxes of measured by the CM method (Fig. 8). The average and median fluxes (calculated from all available measurements) of CH_4 were 31.4 mg CH_4-C m^{-2} d^{-1} and 31.62 mg CH_4-C m^{-2} d^{-1}, respectively. Distributions of CH_4 fluxes were slightly negatively skewed (skewness = −0.816). The difference between average and median of CO_2 fluxes was higher than in CH_4 fluxes. Average and median of CO_2 flux were 1.32 g CO_2-C m^{-2} d^{-1} and 0.98 g CO_2-C m^{-2} d^{-1}, respectively. Distributions of fluxes were positively skewed (skewness = 1.877). Marked positive fluxes of CO_2 showed that the prevailing situation in the carbon balance of this ecosystem was carbon release, due to senescence of *Phragmites australis* during the end of the growing period and gas emission via sediment layer.

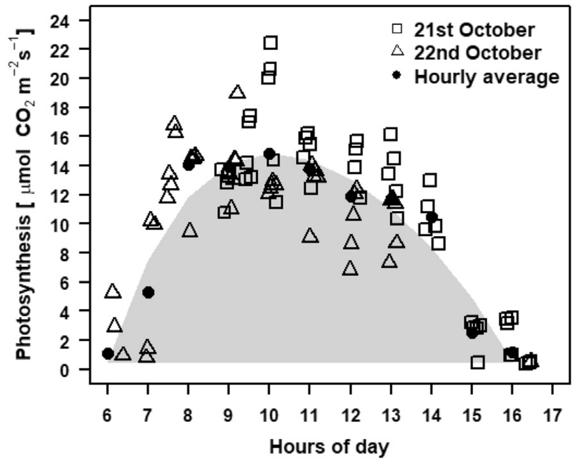

Fig. 6. Photosynthesis of *Phragmites australis* measured on the upper green leaves during two consecutive days at the "Padul" wetland. The grey area fits a fourth order polynomial function and represents the amount of CO_2 fixed by the plant leaves during daytime light period.

The gas fluxes (CO_2 and CH_4) measured by the EC method were quite closely correlated with PhAR (Table 1). While the CO_2 flux showed a strong negative correlation with PhAR (−0.789, $p < 0.001$), the CH_4 flux showed an opposite trend and was positively correlated with PhAR (0.559, $p < 0.001$).

3.5. CH_4 and CO_2 fluxes measured by EC and CM methods

To summarize our measurements we used a simple way to represent together gas fluxes measured by EC and CM. From all available measurements we calculate median fluxes and these medians were used for the carbon summary (balance) calculation presented in Fig. 9. The median fluxes from the soil/water table level were 10.4 mg CH_4-C m^{-2} d^{-1} and 0.68 g CO_2-C m^{-2} d^{-1} for the measured period. Thus, the total amount of carbon (C) released by the soil/water table was 0.69 g C m^{-2} d^{-1}. The median flux at the ecosystem level stand was 31.4 mg CH_4-C m^{-2} d^{-1} and 0.98 g CO_2-C m^{-2} d^{-1}, accounting for a total amount of C released by the stand of 1010.4 mg of C m^{-2} d^{-1}. We assumed that fluxes measured by EC integrated contributions from ecosystem components, i.e. plants and water/soil subsets. Thus, flux portions corresponding to plants (*Phragmites australis*) were calculated as the difference between ecosystem-scale fluxes measured by EC and water/soil fluxes measured by CM.

Based on the median flux balance, plants released 0.32 g C m^{-2} d^{-1}. The median flux balance individually for CH_4 and CO_2 forms of carbon is presented in Fig. 9. CH_4 was released mostly via plants (66.9%) versus water/soil (only 33.1%). The opposite situation was found for CO_2, which emerged from water/soil (about 69.4%) with less than one third released by plants. The median balance of CH_4 emission represented only 3.2% of overall CO_2 median flux balance (Fig. 9).

4. Discussion

Biogeochemical processes in wetlands are very dynamics including

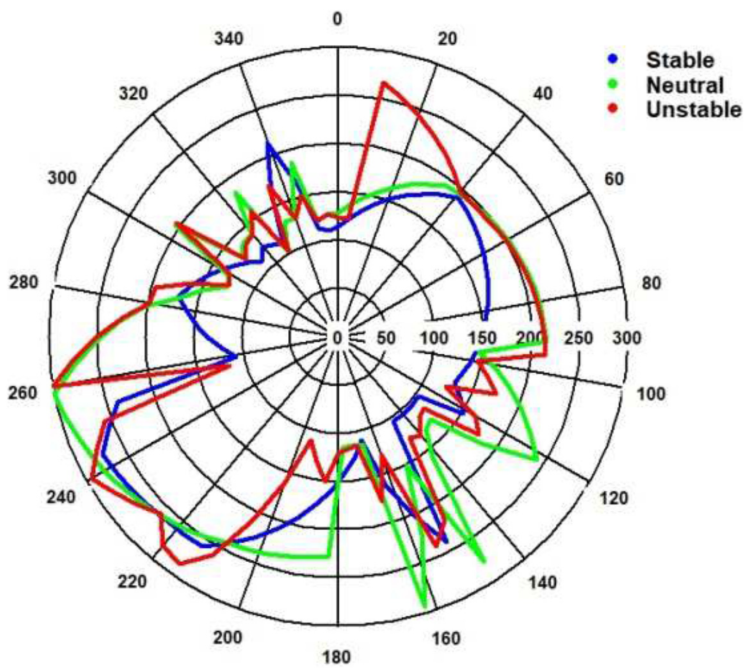

Fig. 7. Shape and size of 90% source of data footprints (20th–22nd October 2015) of eddy covariance measurements under different atmospheric conditions on the *Phragmites australis* stand of "Padul" wetland site. The EC tower is at the center (distance 0 m), and distances therefrom are in meters (m). Angular units are degrees (°).

fluxes of CH_4 and CO_2 between ecosystem and the atmosphere (Aurela et al., 2009; Bridgham et al., 2013; Acosta et al., 2017). Emissions of these gases take place in different complex ecosystem subsets, which may create difficulties for accurate estimates of CH_4 and CO_2 fluxes. The combination of CM and EC methods improve estimations of CH_4 and CO_2 fluxes at specific ecosystem subsets; and help to interpret obtained data (Schrier-Uijl et al., 2010; Yu et al., 2013). Whereas CM is able to represent the accurate fluxes on a plot-base (field) scale and therefore represent a practical and widely-used method for field survey (Matson and Harriss, 1995; Acosta et al., 2018), the EC method provides data for calculation of accurate fluxes from a large area that can consist of different landscape components (Göckede et al., 2004). Morin et al. (2017) in a study carried on a heterogeneous urban floodplain wetland, pointed out that gas fluxes observed by the two methods are similar in magnitude when brought to the same temporal and spatial scale. Our study carried on common reeds in a Mediterranean wetland "Padul" over three-days measurement campaign provided significant and interesting information concerning flux partitioning at different ecosystem subsets (Fig. 2) via the application of complementary methods, CM and EC. Fluxes measured by CM represent the water/soil ground and belowground components of the wetland ecosystem while fluxes measured by EC represent the whole ecosystem including reed stand aboveground, ground and belowground (water/soil) subset together. We consider that the combination of EC and CM methods improved the estimation of CO_2 and CH_4 fluxes in this complex wetland ecosystem and enabled estimation of the importance of plants as a simple difference between the fluxes measured by the EC and the CM methods.

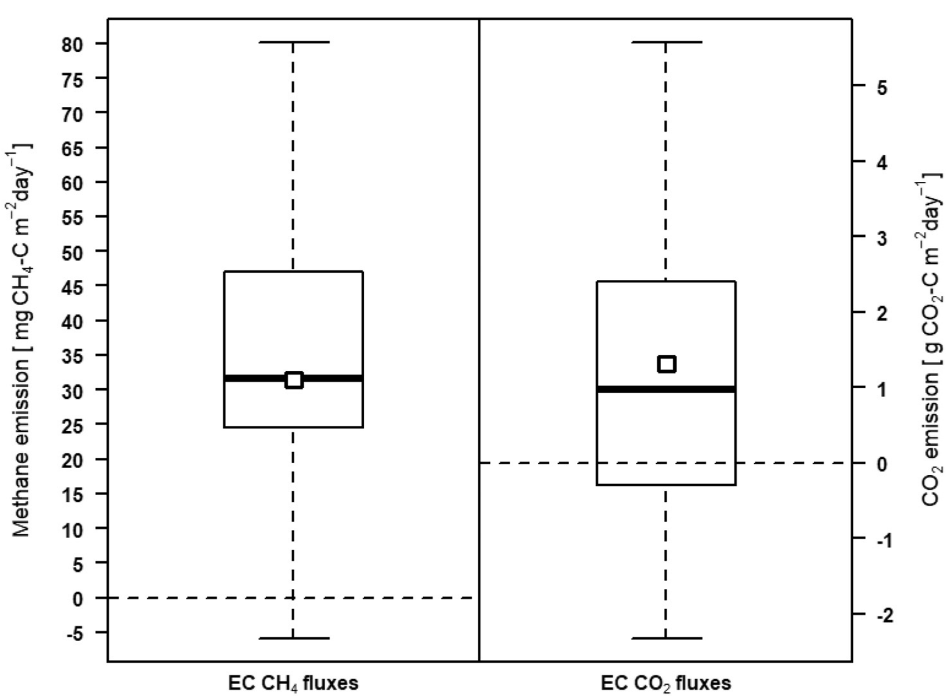

Fig. 8. Box and whisker plot of CH_4 and CO_2 fluxes of the highest quality (0) measured by eddy covariance (EC) above a reed stand (ecosystem scale) of the "Padul" wetland during three days of the measurement campaign (20–22 October 2015). Mean (small open box), the second quartile (thick black lines), upper and lower quartile (boxes with 50% measured data) and error bars with upper and lower extremes are shown.

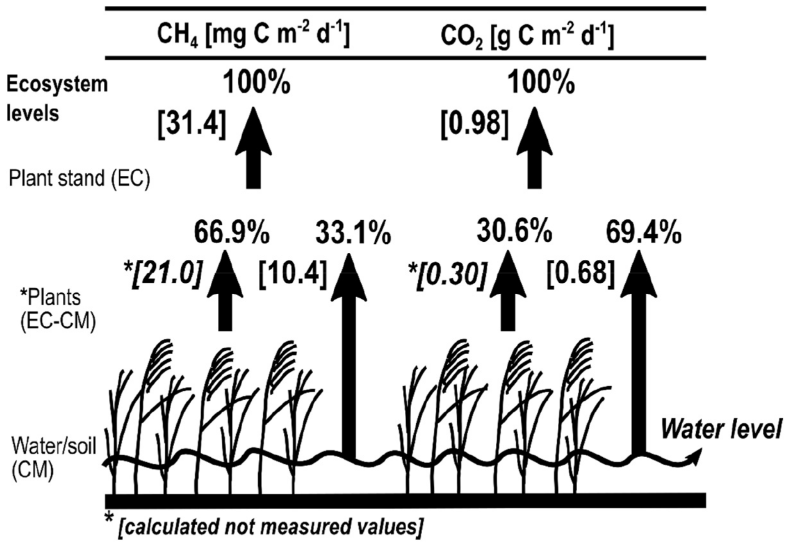

Fig. 9. Balance of carbon in forms of CH_4 and CO_2 based on medians fluxes calculated from the measurements of gas fluxes by different ecosystem components during a short campaign in *Phragmites australis* stand of the "Padul" wetland during autumn. Values in brackets are flux medians in mg CH_4-C m^{-2} d^{-1} and g CO_2-C m^{-2} d^{-1}. EC = eddy covariance technique, CM = chamber methods, *Plants (EC-CM) = calculated difference (not measured) between plant/ecosystem subset (EC) and Water/soil (CM) subset, median fluxes (EC-CM).

In general, our measured CH_4 and CO_2 fluxes based on CM were within the ranges reported in other studies (Guérin et al., 2007; Schrier-Uijl et al., 2010; Yu et al., 2013; Podgrajsek et al., 2014; Morin et al., 2017). On the other hand, in our study no trend or relations was found between CH_4 and CO_2 fluxes. We consider that the absence of expected relationship between CH_4 and CO_2 fluxes may be caused by decreased plant physiological activity due to plant senescence at beginning of autumn and not fully operative anaerobic decomposition of organic matter after the summer dry period in. Despite plant senescence the upper green leaves of some reeds were still photosynthetically active (Fig. 6). Photosynthetic activity also confirms indirectly significant negative correlation between CO_2 fluxes measured by EC method and PhAR (Table 1). Fluxes of CH_4 recorded by the EC method were positively correlated with PhAR. This correlation can be explained by the ventilation of internal plant spaces and flooded sediments if upper reed leaves are still photosynthetic active (Table 1).

Different CM studies of CO_2 and CH_4 emission reported contrasting results on the environmental controls of the gas emissions mainly affected by water level fluctuation (Bubier, 1995, Riutta et al., 2007, Pavelka et al., 2016, Dušek et al., 2009, 2018). Fluxes of CO_2 and CH_4 usually react differently to water level change. The CO_2 efflux rapidly decreases to near zero if the water level increases (Pavelka et al., 2016). On the other hand, fluxes of CH_4 usually increased when the water level increases markedly (Vítková et al., 2017). Among the parameters that control CH_4 emission is stand structure such as hummock stands created by sedges (Vítková et al., 2017). In our study, the water level was stable without significant fluctuation, following a short rainy event on the first day of the campaign.

We found no relationship between gas fluxes and water level, but significant relationship (correlation) between CH_4 fluxes and water temperature. Emissions of CH_4 are usually sensitive to temperature and temperature is an important factor mainly in cooler conditions where water/soil temperature control processes of methanogenesis (Mikkelä et al., 1995, van Winden et al., 2012). Kowalska et al. (2013) reported weak relationships for CH_4 emissions with water level and soil temperature in a study on CH_4 emission by EC in a temperate wetland during the warmest months of the summer.

Fluxes of CO_2 measured by EC fluctuated over wider range than fluxes from the water/soil measured by CM. The reason for this might be related to different ecosystem components measured by EC and CM methods, and to the diurnal dynamics of gas fluxes. The water/soil component is a subset the ecosystem scale, and hence variability of CO_2 fluxes is higher. We recorded negative fluxes of CO_2 measured by EC during daylight in the campaign measurements. This means that gross uptake of CO_2 from the atmosphere by the ecosystem (photosynthesis) is much higher than positive fluxes from the ecosystem (ecosystem respiration). Uptake of CO_2 by the ecosystem we can prove by direct measurement of photosynthesis on leaves of *Phragmites australis*. A high photosynthetic activity was found especially on upper leaves during daylight (Fig. 6).

We compiled a C balance based on median fluxes s calculated from all available measurements. Fig. 9 shows the water/soil component was an important source of C. Higher amount of C in form of CO_2 released from the water/soil relate to high respiratory activity of flooded soil which showed prevailing aerobic decomposition of organic matter (Ágoston-Szabó et al., 2006). Respiration of the water/soil includes respiration of living belowground plant parts including rhizomes and roots of *Phragmites australis* (Faußer et al., 2013).

Emissions of CH_4 measured by EC were higher than expected. An interesting fact is that CH_4 carbon emissions from plant/ecosystem level, calculated as the difference between EC and CM measurements, were about twice those of the water/soil ecosystem subset (66.9% via plants versus 33.1% from water/soil). In this context, there were important statistically significant correlations of EC CH_4 fluxes with leaf photosynthesis and PhAR, showing the enhancing of CH_4 fluxes by plants. The relationship between CM fluxes of CH_4 and leaf photosynthesis was not significantly correlated because aboveground parts of plants were excluded in this ecosystem level. The role of the *Phragmites australis* stand in CH_4 emissions from ecosystem at the end of the growing period is quite important. It is generally known that wetland plants can promote emissions of CH_4 from the wetland waterlogged soils (Laanbroek, 2010). A large part of the CH_4 emission in sedges and common reed dominated wetlands is transport via diffusion and pressurised gas flow achieved by temperature and/or humidity (Armstrong et al., 1991; Brix et al., 1992) in the aerenchymatic tissue. CH_4 bypasses e potential oxidation in the aerobic upper soil profile and is directly released from the soil to the atmosphere. Faußer et al. (2013) pointed out that *Phragmites australis* showed high capacity to ventilate actively to submerged tissues by the oxygen. Thus, vegetation can be a great emitter of CH_4 also in heterogeneous floodplain wetlands (Morin et al., 2017) as well as in wetlands constructed for wastewater treatment (Picek et al., 2007). This is consistent with our findings at Padul wetland where *Phragmites australis* contributed to CH_4 emissions from the wetland during flooded soil at early autumn period.

5. Conclusions

In wetland ecosystem populated by the common reed (*Phragmites* *australis*), a higher amount of estimated balance of CO_2 carbon released from the water/soil ecosystem subset was estimated in comparison to plants. However, the estimated plant contribution of the CH_4 flux was about two times higher than that of water/soil ecosystem subset. We assume this response was caused by transport of CH_4 via the aerenchymatic tissue in shoots and rhizomes of the *Phragmites australis* directly to the atmosphere. In our study, we also showed that vegetation can be a great CH_4emitter in floodplain wetlands, at Padul wetland where *Phragmites australis* contributed to CH_4 emissions from the wetland during flooded soil during early autumn.

Overall, our study showed that EC and CM methods cover different areas making EC advantageous for integrated measurements over larger areas, while the CM approach is suitable for local and spatially well constrained flux measurements. Hence, EC and CM methods should be seen as complementary rather than fully comparable methods. Moreover, we emphasise the importance of stratifying the whole ecosystem into different subset in order to partition ecosystem-scale fluxes. We also concluded that small-scale chamber measurements can be used to estimate fluxes of CO_2 and CH_4 at the ecosystem scale if fluxes are scaled appropriately.

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