# A comparison of methane emission measurements using eddy covariance and manual and automated chamber-based techniques in Tibetan Plateau alpine wetland

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## ARTICLE INFO

## ABSTRACT

Comparing of different $CH_4$ flux measurement techniques allows for the independent evaluation of the performance and reliability of those techniques. We compared three approaches, the traditional discrete Manual Static Chamber (MSC), Continuous Automated Chamber (CAC) and Eddy Covariance (EC) methods of measuring the $CH_4$ fluxes in an alpine wetland. We found a good agreement among the three methods in the seasonal $CH_4$ flux patterns, but the diurnal patterns from both the CAC and EC methods differed. While the diurnal $CH_4$ flux variation from the CAC method was positively correlated with the soil temperature, the diurnal variation from the EC method was closely correlated with the solar radiation and net $CO_2$ fluxes during the daytime but was correlated with the soil temperature at nighttime. The MSC method showed 25.3% and 7.6% greater $CH_4$ fluxes than the CAC and EC methods when measured between 09:00 h and 12:00 h, respectively.

## 1. Introduction

Methane ($CH_4$) has a global warming potential of 25 in a 100-year time horizon and 72 in a 20-year time horizon (IPCC, 2007). Accurate $CH_4$ flux measurements are crucial to global carbon budgets but are largely constrained by methods that differ in their advantages, disadvantages and susceptibilities to measurement errors. The main $CH_4$ flux measurement techniques are the chamber method and the micrometeorological eddy covariance method. No standard or reference exists to test the accuracies of these methods, and large uncertainties characterize all types of measurements (Lund et al., 1999). Using several independent measurement methods is essential to help identify errors in the measurements and to develop confidence in the $CH_4$ flux measurements.

Traditionally, the manual static chamber methods have been widely applied due to their low costs (Song et al., 2009; Tuittila et al., 2000). During sampling, air samples are collected with a syringe and then analyzed using gas chromatography. The $CH_4$ fluxes are then calculated by measuring the rates of change in the $CH_4$ concentrations inside the chamber. The static chamber measurements cannot be sampled frequently due to the high labor intensity and time consumption of the manual operators. Static chambers usually provide periodic measurements, which are often used to estimate the daily and even annual $CH_4$ fluxes using linear interpolations or regression models (Chen et al., 2011; Song et al., 2009). However, large errors may result from the estimation because the $CH_4$ fluxes are not always predictable and vary temporally (Dinsmore et al., 2009; Long et al., 2010). Therefore, a more frequent sampling method is required to accurately capture the temporal $CH_4$ flux variation.

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The continuous automated chamber method can measure $CH_4$ fluxes at a much higher frequency without personal attention (e.g. once per hour). However, the automated chamber systems are more expensive than the static chamber systems and need complicated maintenance and greater infrastructure. Chamber methods (including the static and automated chambers) are often criticized because of poor spatial representation and the so-called chamber effects (Mosier, 1990). The $CH_4$ fluxes are measured with chamber methods covering small patches of soil. The chambers may cause soil disturbance, modify the temperature and moisture in the soil and air under the chamber, alter the $CH_4$ diffusion gradient within the soil profile, turbulent fluctuations and air flow. Although most chamber effects have been eliminated in recent set-ups, the problem of neglecting the influence of wind remains (Denmead, 2008).

To avoid chamber-related problems, alternative techniques, such as the micrometeorological eddy covariance method, have been applied for continuous $CH_4$ flux measurements (Hendriks et al., 2007; Kroon et al., 2010; Long et al., 2010; Rinne et al., 2007; Schrier-Uijl et al., 2010; Zona et al., 2009). The eddy covariance method measures net vertical turbulent $CH_4$ fluxes between the atmosphere and surface (vegetation and soil); these fluxes represent the integrated net fluxes from the landscape upwind from the measurement point. The eddy covariance method has advantages over the chamber method because the eddy covariance method does not disturb the soil surface microenvironment (Dugas, 1993), and most importantly, it integrates over larger areas and thereby can sample the spatial heterogeneity. Another advantage is that the technique is capable of measuring $CH_4$ fluxes continuously over long time periods. However, the eddy covariance method also has a wide array of limitations, such as it is most applicable over horizontally homogeneous area, in flat terrain and in atmospheric steady-state conditions. It has been suggested that the measured total fluxes can be underestimated during nighttime low turbulence conditions due to the large $CH_4$ concentration buildup in the nocturnal boundary layer (Long et al., 2010).

Even though a wide variety of techniques have been developed, a remaining issue is the difficulty of determining which is more accurate when they disagree. The uncertainties related to both the chamber and eddy covariance flux measurements motivate a comparison of these independent methods. Until recently, many studies have been published where the $CO_2$ fluxes measured using different methods were compared in forest (Janssens et al., 2000, 2001; Liang et al., 2003; Liang et al., 2004; Norman et al., 1997; Savage and Davidson, 2003; Wang et al., 2009), grassland (Myklebust et al., 2008; Schrier-Uijl et al., 2010), and wetland systems (Burrows et al., 2005). However, only a few studies have compared the chamber methods with the eddy covariance method for measuring $CH_4$ fluxes in heterogeneous peat meadows, rice paddy fields and northern peatland (Hendriks et al., 2010; Meijide et al., 2011; Sachs et al., 2010; Schrier-Uijl et al., 2010).

Our current study presents the $CH_4$ emissions measured on a Tibetan Plateau alpine wetland using the manual static chamber, continuous automated chamber and eddy covariance methods. Wetlands are the largest natural source of atmospheric $CH_4$, accounting for 20–39% of the total annual emissions worldwide (Denman et al., 2007; Mitsch and Gosselink, 2007). Wetlands on the Tibetan Plateau are predicted to have lowered water tables due to the permafrost degradation caused by rapid climate warming (Cheng and Wu, 2007), and these changes in the soil hydrological conditions may affect the release of the soil carbon stock as greenhouses gases, such as $CH_4$, further inducing climate change. In this paper, we compare the three approaches to measuring the $CH_4$ emission in a Tibetan Plateau alpine wetland. The objectives of this paper are (1) to compare the performances of the three $CH_4$ flux measurement techniques during the 2011 growing season; and (2) to determine the factors driving $CH_4$ flux variations on diurnal and seasonal scales in the alpine wetland.

## 2. Methods

### 2.1. Site description

The methane emission was measured at the Luanhaizi wetland on the northeastern Tibetan Plateau in China (37°35′ N, 101°20′ E) (Fig. 1a). The average altitude is 3200 m, and the local climate is characterized by strong solar radiation with long, cold winters and short, cool summers. The mean annual air temperature was $-1.5 \pm 10.9$ °C in 2011. The highest daily mean temperature was $14.6 \pm 3.7$ °C in August, while the lowest was $-23.4 \pm 8.6$ °C in January. The annual mean precipitation was 501 mm, and 90% of the precipitation was concentrated in the growing season from May to September. The air pressure was low, approximately 70 kPa, due to the area's high altitude.

The wetland is underlain by high-altitude permafrost. The topsoil (0–20 cm) is nearly full of roots, so we only measured the soil C and N contents, which are 12.25% for C and 0.98% for N, respectively, at depths of 20–100 cm. The wetland is characterized by a unique microtopography, with many hummocks scattered. The water depth was approximately 2.7 cm above the flat field, and dry hummocks (with irregular shapes) were approximately 25 cm high over the standing water level from June to October in 2010 and 2011 at the study site. The wetland plant community is dominated by *Carex pamirensis* Clarke with 63.4% coverage in the flat field. In 2011, the average height of this species is 15.8 cm, and the average biomass is 135.8 g m$^{-2}$. Several other species are also present in the flat field, including *Carex alrofusca* Schkuhr, *Hippuris vulgaris* L., *Triglochin palustre* L. and *Heleocharis* spp. The dry hummocks are mainly dominated by *Cremanthodium pleurocaule*. A wide range of moss species are scattered in the wetland.

### 2.2. Measurement techniques

#### 2.2.1. Manual Static Chamber (MSC) system

Stainless steel chambers (40 cm × 40 cm × 40 cm) were used to collect the $CH_4$ (Fig. 1b). To prevent heating inside the chamber caused by solar radiation, the chambers were covered with polystyrene foam. A small fan was installed in the chamber to homogenize the inside air. When sampling, the chamber was inserted into a water-filled groove on a 6 cm high frame inserted into the soil to prevent leakage. The 60 ml gas samples were extracted with plastic syringes every 10 min over a 30 min total period. The $CH_4$ concentrations were analyzed using gas chromatography (Agilent 7890A, Agilent Technologies, Santa Clara, CA, USA) within 24 h. The $CH_4$ was separated with a 2 m stainless steel column packed with 13XMS (60/80 mesh) and was directly measured using a flame ionization detector. The fluxes were determined from the slope of the concentrations in four samples taken at 0, 10, 20 and 30 min after the chamber closure and were corrected for atmospheric pressure and the chamber air temperature. The sample sets were rejected unless they yielded a linear regression $R^2$ value greater than 0.9. The $CH_4$ was sampled approximately once per week between the hours of 09:00 h and 12:00 h. The air temperature inside the chambers was measured using a thermometer (JM222, Jin Ming, Tianjin, China) during the chamber closure. The atmospheric pressure was measured once per half hour at a nearby meteorological station.

We established five plots in the flat field dominated by *C. pamirensis* within the eddy covariance fetch along the installed wood boardwalk. One chamber was placed on each plot when sampling. The distance between two adjacent plots was approximately 5 m.

#### 2.2.2. Continuous automated chamber (CAC) system

We deployed a multichannel automated chamber system to measure the $CH_4$ fluxes over entire seasons (Fig. 1c). This system has been previously described in detail (Liang et al., 2003, 2004), but a brief summary follows. This system measures the $CH_4$ flux in a flow-through and non-steady-state manner and comprises 20 automated chambers, a 24-channel gas sampler, an IRGA (Li-Cor 840, Li-Cor, Lincoln, NE, USA), a datalogger (CR1000, Campbell Scientific, Utah, USA) and a $CO_2/CH_4/H_2O$ gas analyzer (Picarro G1301, Picarro, Santa Clara, CA, USA). The automated chambers (90 cm × 90 cm × 50 cm) are made of clear PVC glued to a steel pipe frame. The bottom of each chamber is 5 times larger than that of the static chamber to minimize the small-scale spatial variability. Between measurements, the chamber lids are opened to allow precipitation to reach the enclosed soil surface to keep the soil conditions as natural as possible. When a chamber is closed, the chamber air is pumped continuously from the side wall of chamber to the IRGA and $CO_2/CH_4/H_2O$ gas analyzer. Meanwhile, the air is returned from the IRGA and $CO_2/CH_4/H_2O$ gas analyzer to the chamber through a manifold. The flow rate through the system is 0.7 L min$^{-1}$. Each chamber is equipped with two fans to mix the air and three small vents to equilibrate the pressure between the outside and inside of the chamber during measurements. Over the course of an hour, the 20 chambers are closed in sequence by the CR1000 installed in the 24-channel gas sampler. We set the sampling period for each chamber to 180 s to finish a cycle of measurements within 1 h.
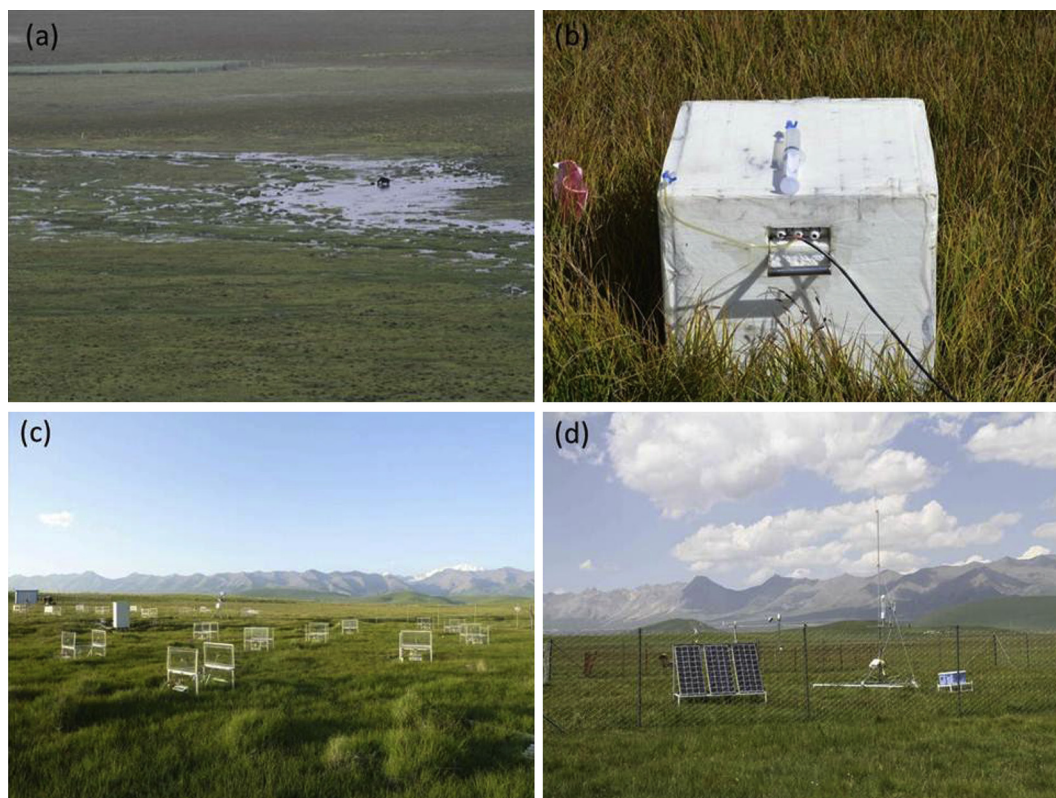
**Fig. 1.** Overview of the Tibetan Plateau wetland and the $CH_4$ flux measurement facilities for three methods. (a) Landscape of the studied wetland; (b) Manual static chamber (MSC); (c) Continuous automated chamber (CAC); (d) Eddy covariance (EC).

The CR1000 records the $CH_4$ concentration every 10 s. The $CH_4$ fluxes are calculated from the increase in the $CH_4$ concentration over time within the chamber. Five chambers were placed on the *C. pamirensis*-dominated flat field near static chambers and were used for measuring $CH_4$ fluxes.

### 2.2.3. Eddy covariance (EC) measurement

An eddy covariance measurement system was installed at a height of 2 m above the wetland surface, which is approximately 200 m away from the static and automated chamber systems (Fig. 1d). The system consists of a three-dimensional sonic anemometer (Gill R3, Gill Instruments Ltd., Hampshire, England), a Li-Cor 7500 open path infrared gas analyzer (Li-Cor, Lincoln, NE, USA) for measuring the $CO_2$ concentration and a Li-Cor 7700 open path infrared gas analyzer (Li-Cor, Lincoln, NE, USA) for measuring the $CH_4$ concentration. Data are logged with a datalogger (CR5000, Campbell Scientific, Utah, USA).

The $CO_2$ and $CH_4$ concentrations were measured at rates of 10 Hz. The fluxes were calculated as half-hour covariance using block averaging. Bad data due to rain and instrument malfunction were removed. The data were filtered for spikes and linearly detrended. The collected data were adjusted using the WPL (Webb, Pearman and Leuning) density adjustment (Webb et al., 1980). Double coordinate rotations were performed before the scalar flux calculations. 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$^{-1}$. After screening the $CH_4$ flux data, the remaining data coverage was 46%, which were further analyzed. We calculated the daily average for days with greater than 33% data coverage, which lead to 1, 14 and 8 daily $CH_4$ fluxes in July, August and September, respectively.

### 2.3. Environmental measurements

In each of the five MSC plots, the water table height was manually measured in wells made from 3 cm PVC pipe, and the soil temperature was manually measured at 5 cm depths during gas sampling. Meanwhile, the air temperature inside the automated chamber and the soil temperature at 5 cm depths were continuously measured by a type T thermocouple during the chamber measurements. The air temperature was also measured using a type T thermocouple mounted 2.0 m above the surface. A tripping bucket gauge measured the precipitation rates. The net radiation was measured using a net radiometer at the meteorological station near the automated chamber system. All data from the CAC and EC measurements were recorded every 30 min with a CR1000 and CR5000 datalogger (Campbell Scientific, Utah, USA), respectively.

### 2.4. Data analysis

The temperature model: $F_{CH_4} = a \times \exp (b \times T_{soil})$ was used to examine the relationship between the temperature and $CH_4$ fluxes, where $F_{CH_4}$ is the $CH_4$ flux, $T_{soil}$ is the soil temperature at a 5 cm depth, $a$ is the fitted $F_{CH_4}$ at a 0 °C soil temperature, and $b$ is the sensitivity of $F_{CH_4}$ to temperature. The $Q_{10}$ value, which represents the temperature response of $F_{CH_4}$, was calculated as: $Q_{10} = \exp (10 \times b)$.

## 3. Results

### 3.1. Seasonal $CH_4$ flux variations

The MSC, CAC and EC methods agreed well in the seasonal $CH_4$ flux patterns throughout most of the sampling period (Fig. 2a). The hourly average $CH_4$ fluxes measured between 09:00 h and 12:00 h ranged from 6.59 to 13.90 mg m$^{-2}$ h$^{-1}$ using the MSC method. The daily average $CH_4$ fluxes ranged from 5.19 to 10.23 mg m$^{-2}$ h$^{-1}$ using the CAC method and from 6.03 to 11.5 mg m$^{-2}$ h$^{-1}$ in the EC system, with higher values in the middle of August and early September and lower values in late July and September. The data filtering as well as some technical problems created some data gaps in the CAC and EC method data. The $CH_4$ fluxes followed general trends with air and soil temperature (Fig. 2b). The water table remained slightly above the soil surface, and changed by only 1.2 cm during the measured period (Fig. 2c).

Seasonal variations in the daily average $CH_4$ fluxes were closely correlated with associated changes in the daily average soil temperature at 5 cm over the measurement period (Fig. 3). The nonlinear regression showed that the daily average soil temperature explained 66%, 34% and 51% of the daily average $CH_4$ flux variations obtained from the MSC, CAC and EC methods, respectively. The fitted $Q_{10}$ value was 2.32, 1.80 and 1.90 in the MSC, CAC and EC methods, respectively.
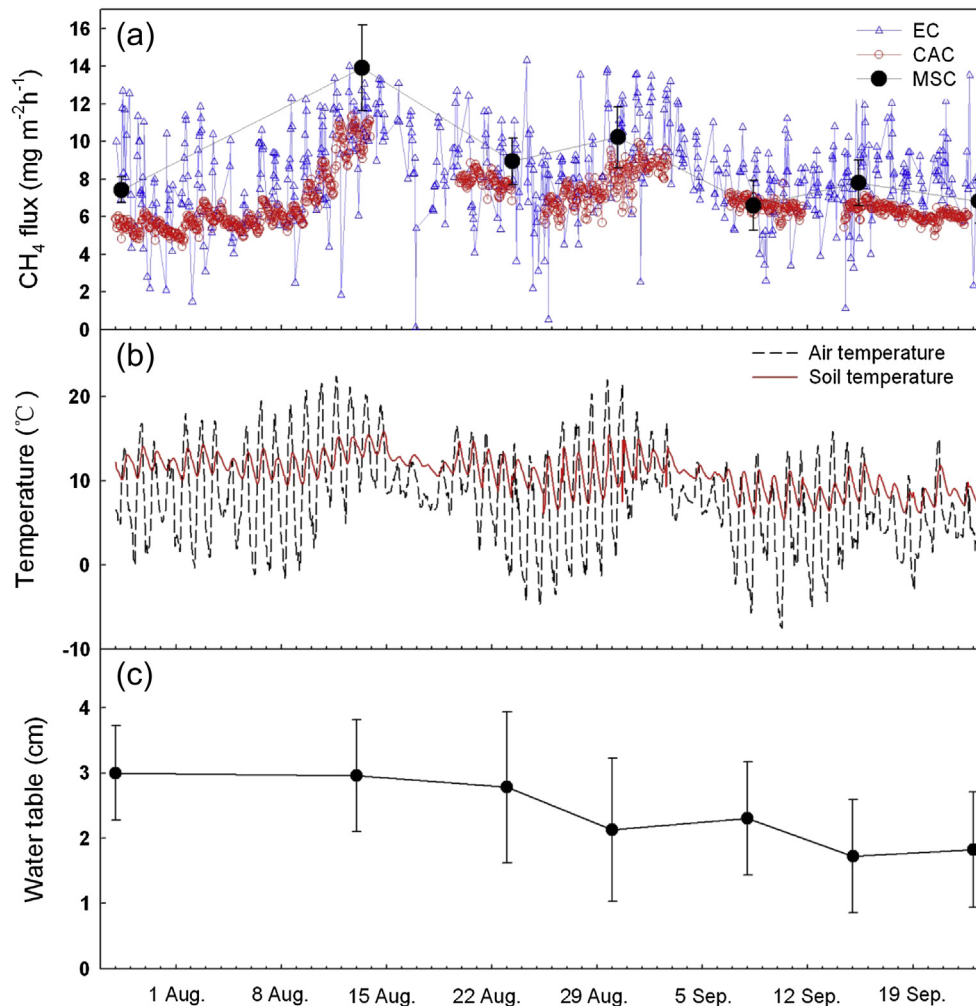
**Fig. 2.** $CH_4$ fluxes and meteorological conditions during the measurement period. (a) The hourly mean $CH_4$ fluxes as measured by manual static chamber (MSC), continuous automated chamber (CAC) and eddy covariance (EC) methods; (b) The hourly mean air temperature and soil temperature at a 5 cm depth measured at a meteorological station and using a CAC system, respectively; (c) The water depth measured during MSC gas sampling. The error bars represent ± SE.

### 3.2. Diurnal variation in $CH_4$ fluxes

The results obtained using the CAC method showed peak $CH_4$ fluxes occurring at night (22:00–24:00), and the lowest $CH_4$ fluxes appeared in the late morning (10:00–12:00) (Fig. 4a). The daily cycle of $CH_4$ flux was more evident as measured by the EC method than the CAC method, with peak $CH_4$ fluxes observed in the afternoon (approximately 13:30) and lowest $CH_4$ fluxes in the early morning (07:00) (Fig. 4b). The daily cycle of net $CO_2$ fluxes showed a very similar pattern in the two methods (Fig. 4c). We selected the data with solar radiation less than 1 W m$^{-2}$ for nighttime and solar radiation greater than 20 W m$^{-2}$ for daytime. The diurnal $CH_4$ flux pattern measured from the CAC method coincided with the soil temperature variation and was positively correlated with the soil temperature during the daytime and nighttime (Figs. 4a and 5a, b) but was negatively correlated with the $CO_2$ sequestration (Fig. 5c) and had no correlation with the solar radiation during the daytime (Fig. 5e). The diurnal $CH_4$ flux pattern measured by the EC method agreed well with the solar radiation (Fig. 4b) and net $CO_2$ fluxes (Fig. 4c) and showed positive correlations with the two variables (Fig. 6c, e) in the daytime measurements but was only significantly correlated with the soil temperature in the nighttime measurements (Fig. 6b).

### 3.3. Comparison of the MSC, CAC and EC methods

Because the $CH_4$ flux static chamber measurement was conducted between 09:00 and 12:00, the $CH_4$ fluxes obtained using the three methods were compared during approximately the same time period across the sampling dates. No significant difference was found in the comparisons (Table 1) (two-sample t-test for MSC vs. CAC; one-sample t-test for MSC vs. EC and CAC vs. EC). For the 4 days when the three measurements overlapped, the average $CH_4$ fluxes were 9.63 ± 3.22 mg m$^{-2}$ h$^{-1}$, 7.67 ± 1.42 mg m$^{-2}$ h$^{-1}$ and 8.51 ± 1.72 mg m$^{-2}$ h$^{-1}$ for MSC, CAC and EC methods, respectively. The results from the three methods were closely correlated with each other (Fig. 7) ($R^2 = 0.85$ for MSC and CAC, $R^2 = 0.65$ for CAC and EC, $R^2 = 0.63$ for MSC and EC).

## 4. Discussion

### 4.1. Seasonal $CH_4$ flux variations: a consistent pattern from the three methods

The eddy covariance technique has been used to continuously quantify the landscape-scale temporal $CH_4$ variability (Kroon et al., 2010; Rinne et al., 2007), whereas chamber methods are widely
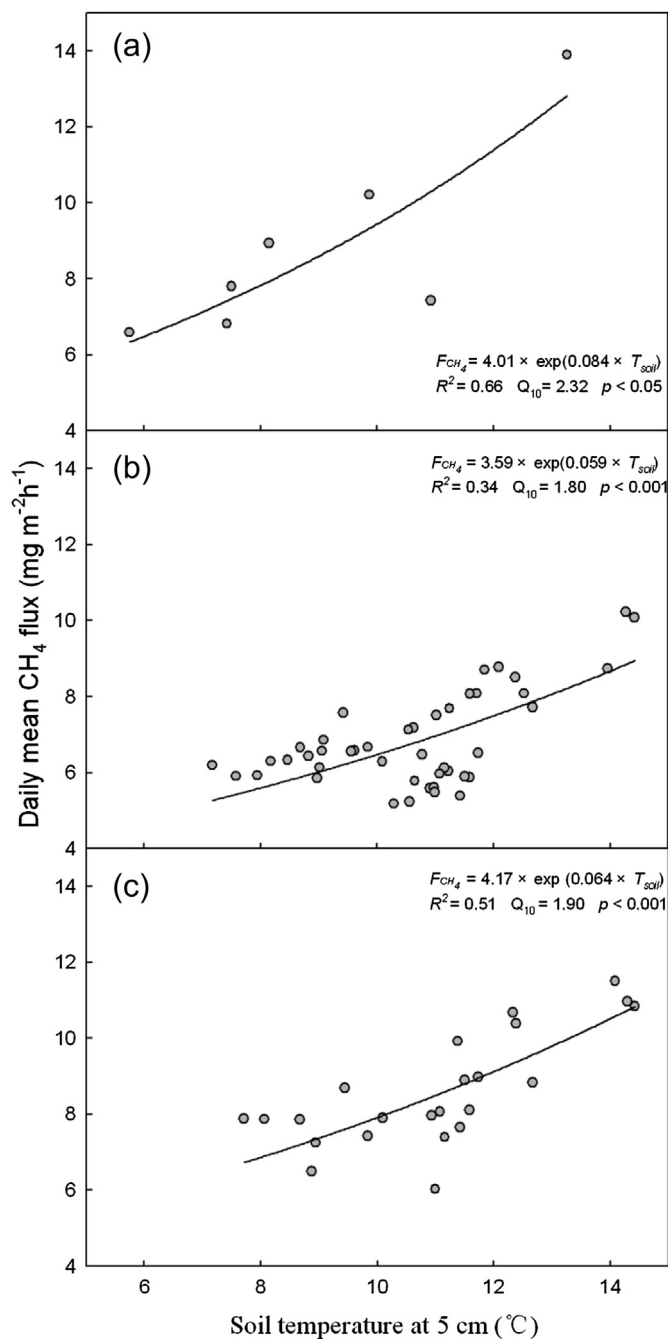
**Fig. 3.** The relationship between the daily mean $CH_4$ fluxes and daily mean soil temperatures at 5 cm depths. (a) Manual static chamber (MSC); (b) Continuous automated chamber (CAC); (c) Eddy covariance (EC).



**Fig. 4.** The mean daily $CH_4$ flux variations measured using the continuous automated chamber (CAC) method and the soil temperature at a 5 cm depth (a), $CH_4$ fluxes measured using the eddy covariance (EC) method and solar radiation (b) and $CO_2$ fluxes (c). The data were binned by time of day and then averaged for all days during the measurement period. The error bars represent ± SE.

used for small-scale measurements. In the Siberian arctic tundra, a comparison of the closed chamber and EC showed that no clear seasonal trend was visible on the ecosystem scale, whereas wet low-center polygons showed a clear seasonal variation on the microsite scale (Sachs et al., 2010). In our study, however, although we only measured the $CH_4$ fluxes on the flat field using two chamber methods, comparing the chamber-based data and EC data revealed similar patterns in terms of the seasonal $CH_4$ flux variations throughout most of the sampling period, with two peak values in middle August and early September, respectively (Fig. 2a).

Methane fluxes generally followed the seasonal air or soil temperature pattern (Herbst et al., 2011; Song et al., 2009; Zona
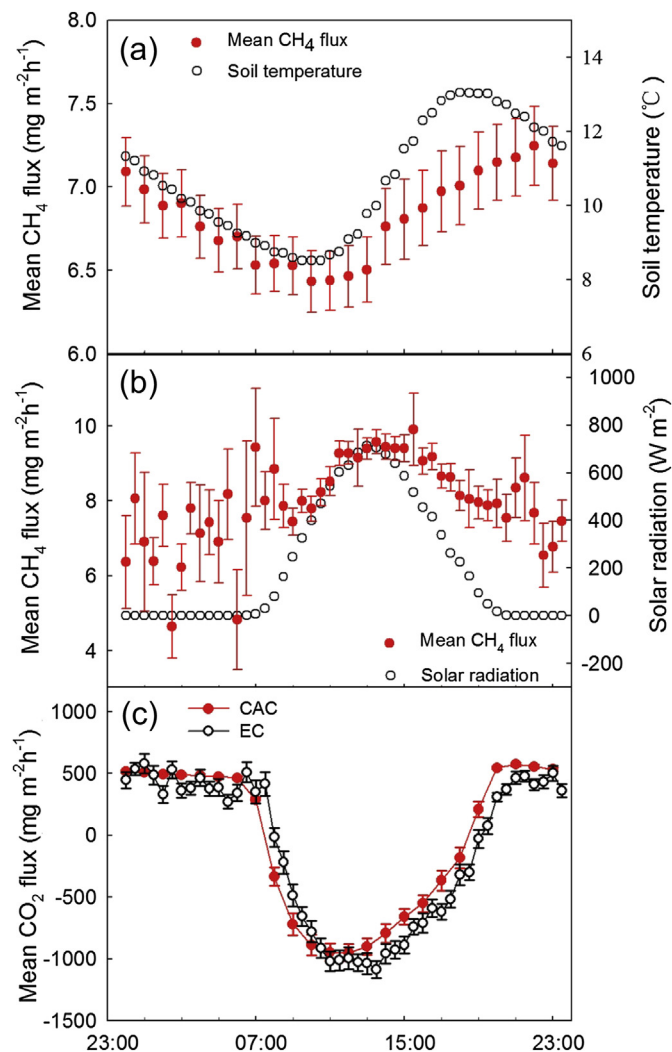
et al., 2009). In the current study, the variation in $CH_4$ fluxes was correlated with seasonal changes in the soil temperature at a 5 cm depth (Fig. 3). However, the soil temperature explained the seasonal $CH_4$ flux variations poorly, especially for the CAC methods (only 34%); this result is likely because the $CH_4$ flux changes were not synchronous with the soil temperature changes in the days from July 28 to August 8 (Fig. 2a, b). That is, the temperatures were relatively higher in this period, but the $CH_4$ fluxes did not increase with the temperature; thus, other factors such as plant phenology may have confounded the effects of temperature on the $CH_4$ fluxes during these days.

Anaerobic conditions, as determined by the water table, are necessary for $CH_4$ production in wetland ecosystems. However, no relationship on the seasonal scale was found between the water table and $CH_4$ emission at our site (Fig. 2a, c). This result is likely because the seasonal water table fluctuation at our site was very small (only 1.2 cm) during the measurement period and because the water table remained above the soil surface; thus, the water table changes did not alter the oxic and anoxic soil column ratio.
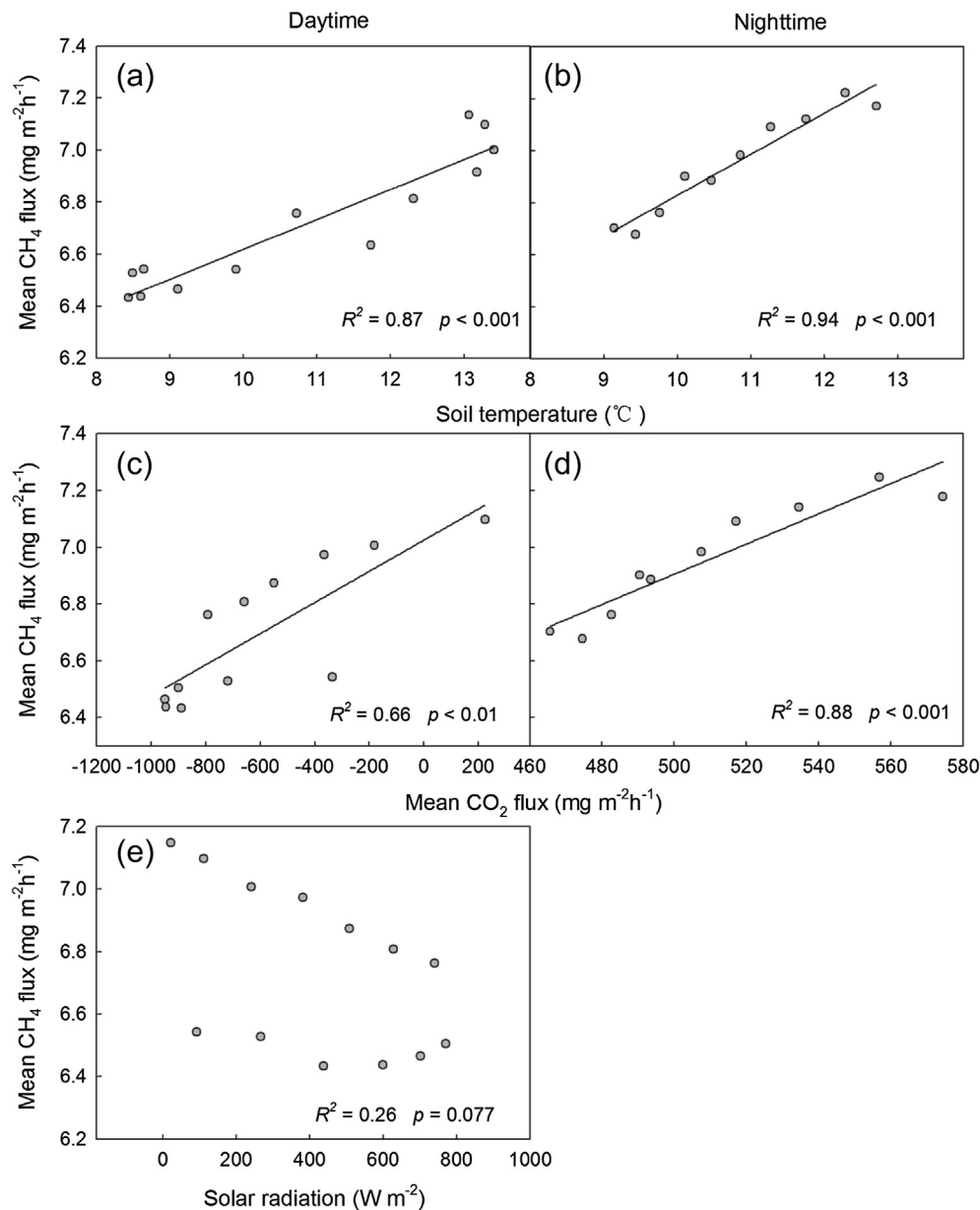
**Fig. 5.** The relationship between the mean $CH_4$ fluxes measured using the continuous automated chamber system and the soil temperature (a, b), mean $CO_2$ flux (c, d) and solar radiation (e) on a daily scale with measurements during the daytime (08:00—20:00) (a, c, e) and at nighttime (21:00—06:00) (b, d). The data were binned by time of day and then averaged for all days.

## 4.2. Diurnal $CH_4$ flux variations: different patterns from the CAC and EC methods

Due to the labor involved and time limitations, it is difficult to determine the diurnal $CH_4$ emission patterns with high frequency (e.g., per hour) using manual chamber based methods in the field, so very few studies have able to compare between chamber-based and EC measurements of the diurnal $CH_4$ emission variations. In the present study, the CAC system enables this comparison.

Several factors have been shown to affect the diurnal $CH_4$ flux variation. First, the diurnal $CH_4$ cycles that were related to the soil temperature were found to be caused by changes in molecular diffusion (Hendriks et al., 2007; Schutz et al., 1989). Second, the $CH_4$ diurnal cycles related to the light intensity resulted from either stomatal opening (Knapp and Yavitt, 1992; Morrissey et al., 1993; Wang and Han, 2005) or convective flow (Kim and Verma, 1998;

Kim et al., 1998; Whiting and Chanton, 1996). The convective flow of $CH_4$ through plants results from pressure gradients generated in different plant parts; these gradients are associated with air—leaf temperature and humidity differences that are ultimately driven by diurnal variation in solar radiation (Brix et al., 1992; Dacey, 1981).

We observed a diurnal cycle in the $CH_4$ fluxes during our measured time period, but the diurnal patterns obtained from the two methods were very different (Fig. 4a, b). The highest and lowest emissions occurred in the evening and late morning, respectively, when measured using the CAC method. In previous studies, the diurnal $CH_4$ flux cycles were also observed using the chamber-based method (Ding et al., 2004; Duan et al., 2005; Mikkelä et al., 1995; Wang and Han, 2005). In contrast, in the current study, the diurnal pattern was characterized by a peak $CH_4$ emission late in the noon hour and an increase from night to day in EC method measurements. Other studies have also observed a
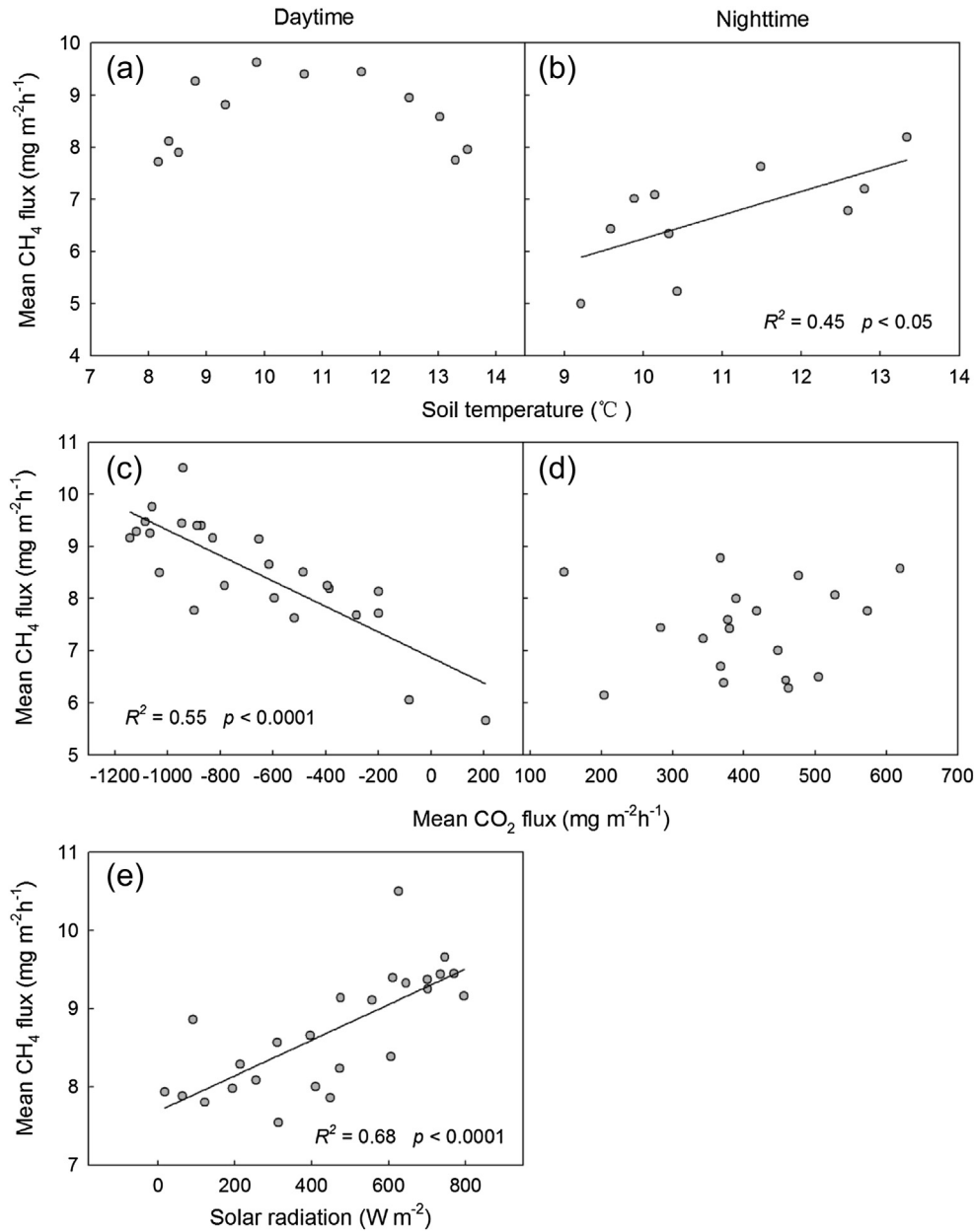
**Fig. 6.** The relationship between the mean $CH_4$ fluxes measured using the eddy covariance system and soil temperature (a, b), mean $CO_2$ flux (c, d) and solar radiation (e) on a daily scale with measurements during the daytime (08:00–20:00) (a, c, e) and at nighttime (21:00–06:00) (b, d). The data were binned by time of day and then averaged for all days.

**Table 1**
Comparison of mean $CH_4$ fluxes for manual static chamber (MSC), continuous automated chamber (CAC) and eddy covariance (EC) measurements conducted during 9:00–12:00 on the days when the MSC measurement was conducted. NA = data not available. Means ± SD are shown.

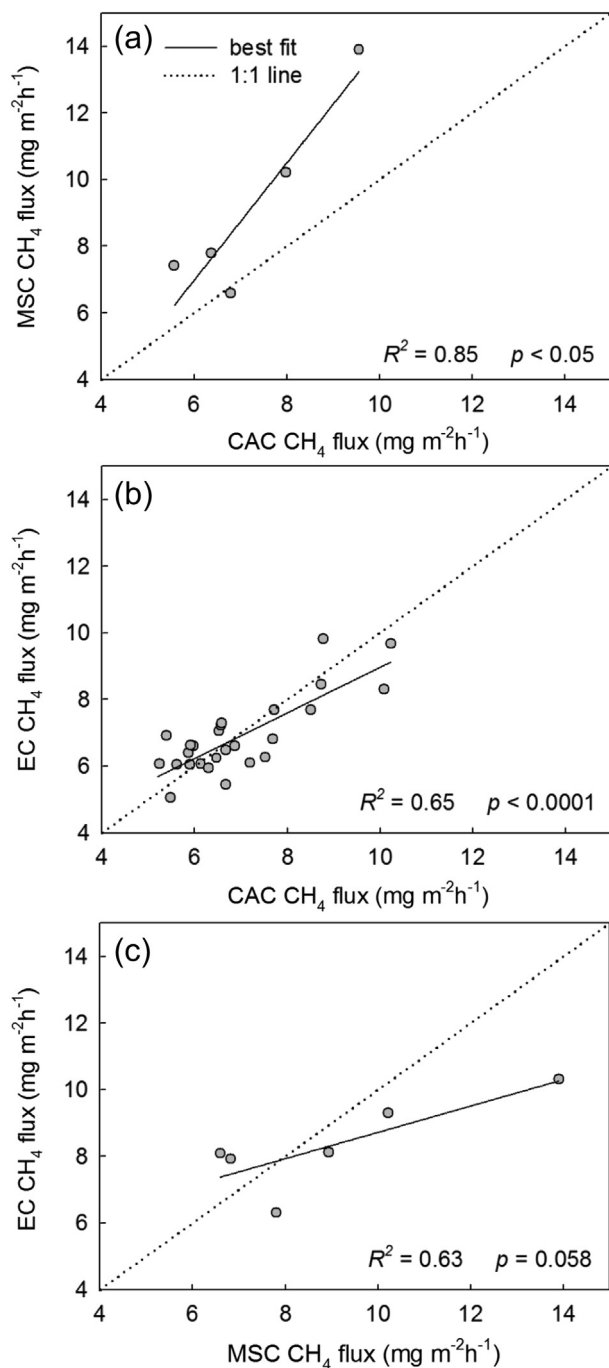| Sample date | MSC (mg m$^{-2}$ h$^{-1}$) | CAC (mg m$^{-2}$ h$^{-1}$) | EC (mg m$^{-2}$ h$^{-1}$) | MSC vs CAC | MSC vs EC | CAC vs EC |
|---|---|---|---|---|---|---|
| | | | | p | p | p |
| 28 July | 7.42 ± 1.56 | 5.57 ± 1.55 | NA | 0.12 | NA | NA |
| 13 Aug | 13.90 ± 3.26 | 9.55 ± 1.21 | 10.32 | 0.14 | 0.19 | 0.30 |
| 23 Aug | 8.94 ± 2.76 | NA | 8.13 | NA | 0.55 | NA |
| 30 Aug | 10.22 ± 3.64 | 7.97 ± 0.85 | 9.30 | 0.25 | 0.60 | 0.053 |
| 8 Sep | 6.59 ± 2.97 | 6.79 ± 1.30 | 8.09 | 0.90 | 0.32 | 0.14 |
| 15 Sep | 7.80 ± 2.69 | 6.37 ± 0.94 | 6.31 | 0.35 | 0.28 | 0.91 |
| 23 Sep | 6.82 ± 2.57 | NA | 7.92 | NA | 0.39 | NA |
| **Mean** | 8.81 ± 2.57 | 7.25 ± 1.55 | 8.34 ± 1.36 | | | |

**Fig. 7.** The relationships between the CH$_4$ fluxes measured using the three methods.

similar diurnal CH$_4$ emission cycle in wetlands during the growing season using the EC method, with higher CH$_4$ emission during the daytime (Kim et al., 2009; Long et al., 2010; Suyker et al., 1996). At other measurement sites, however, no diurnal CH$_4$ emission cycle was found during any period of the year (Rinne et al., 2007; Sachs et al., 2008).

In our study, the CH$_4$ diurnal cycle from the CAC method measurements was a strong function of soil temperature as has been observed in other studies (Kroon et al., 2010; Schutz et al., 1989), indicating the molecular diffusion pathway (Fig. 5a, b). In addition, the CH$_4$ emission measured by the EC system was positively correlated with the variation in the solar radiation but not the soil temperature during the daytime (Fig. 6a, e); the variation is

consistent with the stomatal opening (Knapp and Yavitt, 1992; Morrissey et al., 1993; Wang and Han, 2005) or convective flow (Kim and Verma, 1998; Kim et al., 1998; Whiting and Chanton, 1996) pathway as found in other studies. The significant correlation between the CH$_4$ emission and net CO$_2$ fluxes supported this conclusion (Fig. 6c). However, at night, the CH$_4$ emission was only correlated with the soil temperature (Fig. 6b), indicating a likely switchover from the stomatal opening or convective flow pathway in the daytime to the molecular diffusion pathway. It is interesting that the chamber and EC methods measured the diurnal CH$_4$ emission cycles with different pathways. The convective flow of CH$_4$ through plants results from pressure gradients in different parts of the plant due to temperature and humidity differences between the plant aerenchyma and atmosphere (Brix et al., 1992). It is generally believed that the uncertainties in the results from chamber-based methods are primarily due to chamber effects, which include temperature and moisture changes in the air and soil and the elimination or alteration of the ambient turbulent pressure fluctuations within the chamber (Mosier, 1990; Rayment and Jarvis, 1997). These micro-environmental changes inside the chamber most likely inhibit the role of plant-mediated transport on the diurnal CH$_4$ emission pattern; therefore, molecular diffusion seems to be the primary pathway of the CH$_4$ emission. Actually, the diurnal CH$_4$ emission variations measured using the EC method were most likely correlated with the soil temperature, as observed on the seasonal scale. However, the plant-mediated convective flow or stomatal opening may weaken the effect of soil temperature as in the chamber method. The soil temperature-dependent CH$_4$ emission can be considered as a "background emission".

### 4.3. Comparison of the three methods

A problem with comparing different methods is the difficulty of determining which is more accurate, because all methods have uncertainties, which may cause biases in the measurement results. Our comparison of the two chamber-based measurements of the CH$_4$ emission for five days showed that the MSC measured average CH$_4$ fluxes that were 25.3% greater than CAC (Table 1). This result most likely occurred because when the sample air was sucked from the chamber, the corresponding negative pressure of approximately 66 Pa (60 ml × 70 kPa × 1000/(40 cm × 40 cm × 40 cm + 60 ml) = 66 Pa) inside the chamber may have had the effect of pumping gas near the soil surface and cause an overestimation of the CH$_4$ emission using the MSC method (Fang and Moncrieff, 1998; Liang et al., 2004).

Several studies have compared the up-scaled CH$_4$ fluxes with the EC method measurements (Hendriks et al., 2010; Riutta et al., 2007; Sachs et al., 2010; Schrier-Uijl et al., 2010; Zhang et al., 2012). Most of these studies show that the up-scaled CH$_4$ fluxes agree well with the EC method observations in monthly, seasonal and annual totals (Riutta et al., 2007; Sachs et al., 2010; Schrier-Uijl et al., 2010; Zhang et al., 2012), although the chamber method made discrete measurements and regression equations were used to upscale temporally. All of these studies emphasized the importance of spatial heterogeneity for up-scaling the CH$_4$ fluxes. Sachs et al. (2010) reported that closed chamber measurements within the EC footprint could be scaled by an area-weighting approach of landcover classes to match the total ecosystem-scale emission despite the different controls and CH$_4$ dynamics on the two scales. Schrier-Uijl et al. (2010) stratified the landscape into landscape elements before up-scaling the fluxes measured using chambers to the landscape scale. They found that the EC and chamber-based estimates agreed well when the main elements (field, ditch edge and ditch) were considered, with a 13.0% CH$_4$ flux difference, but both methods differed by 55.1% when only field emissions were

considered. In our study, the MSC and EC CH$_4$ flux estimates measured between 09:00 and 12:00 agreed well for six days with only a 7.6% difference (Table 1), although the MSC measured the CH$_4$ emission at flat field and the EC was applied at a significantly large scale that averaged the small-scale spatial differences (including the flat field and hummocks). The difference in the CH$_4$ fluxes measured using the two methods was much smaller than that reported by Meijide et al. (2011), who found that the CH$_4$ fluxes measured with chambers were 26% higher than those observed with the EC in a rice paddy field. Our results indicate that the CH$_4$ fluxes between 09:00 and 12:00 can be measured using the MSC method at the ecosystem scale without considering the hummock microsites in our study site during the growing season.

Despite the discrepancies in the CH$_4$ fluxes measured using the three methods between 09:00 and 12:00, the values are strongly correlated with each other (Fig. 7), indicating that the different systems can be calibrated to each other.

## 5. Conclusions

Three independent methods for measuring CH$_4$ fluxes were tested at different temporal scales in an alpine wetland on the Tibetan Plateau. The three methods showed good agreement in the seasonal patterns measured throughout most of the sampling period, but the diurnal patterns measured from the CAC and EC methods were different, possibly due to different pathways of CH$_4$ transport to the atmosphere. The micro-environmental changes inside the chamber most likely inhibit the role of plant-mediated transport during measurement. Comparing the three methods on 3-h scales reveals that the MSC yielded the highest mean CH$_4$ flux value followed by the EC method and the CAC. However, the three methods were highly correlated with each other; therefore, the three methods may be cross-calibrated.

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