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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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 north-eastern 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.
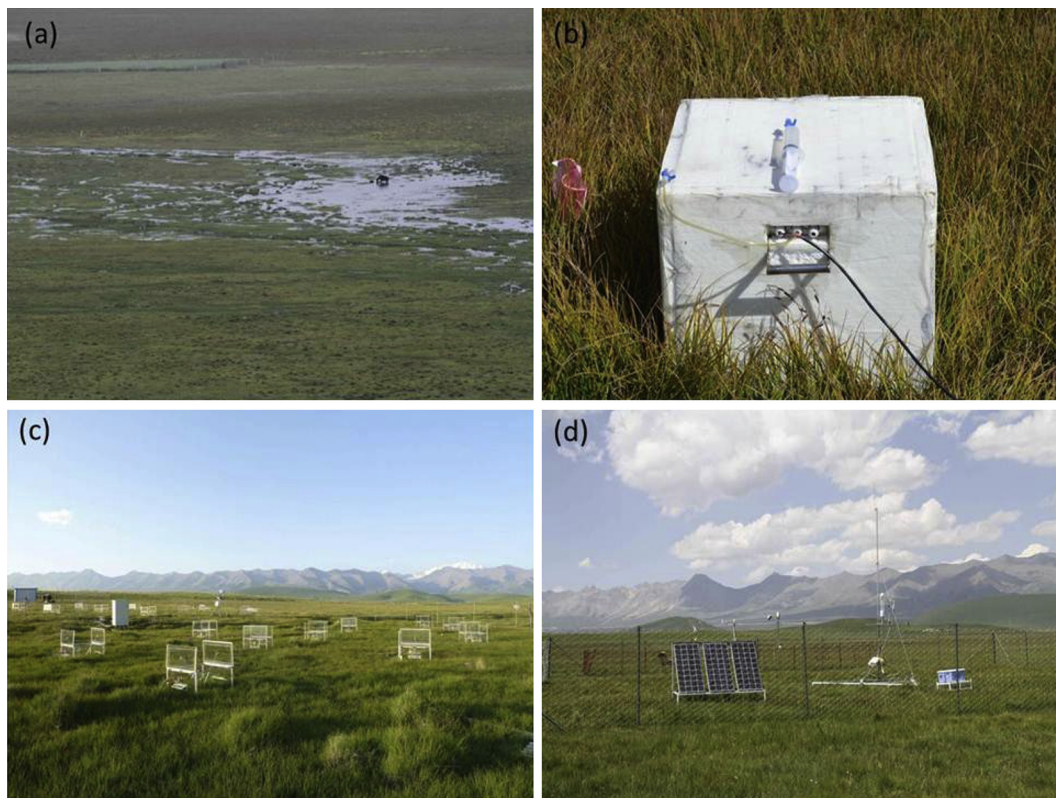
Fig. 1. Overview of the Tibetan Plateau wetland and the CH$_4$ flux measurement facilities for three methods. (a) Landscape of the studied wetland; (b) Manual static chamber (MSC); (c) Continuous automated chamber (CAC); (d) Eddy covariance (EC).

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.
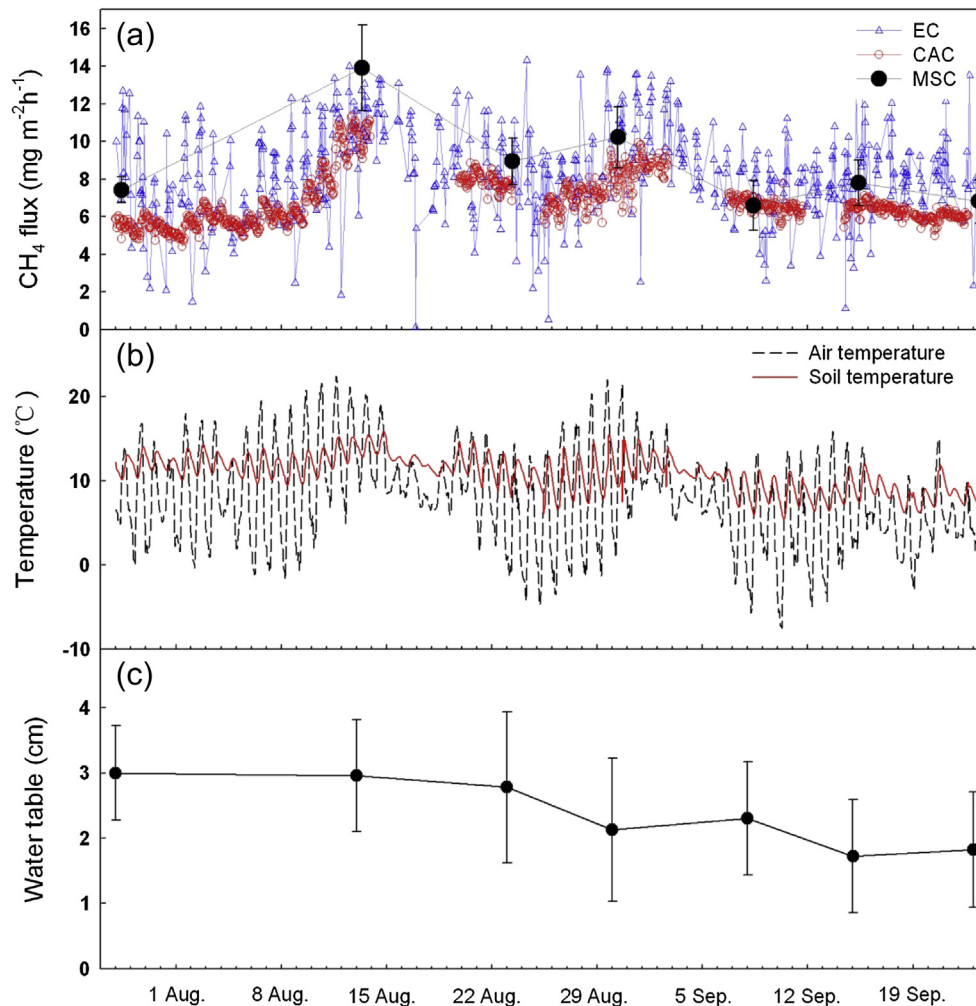
Fig. 2. CH_4 fluxes and meteorological conditions during the measurement period. (a) The hourly mean CH_4 fluxes as measured by manual static chamber (MSC), continuous automated chamber (CAC) and eddy covariance (EC) methods; (b) The hourly mean air temperature and soil temperature at a 5 cm depth measured 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
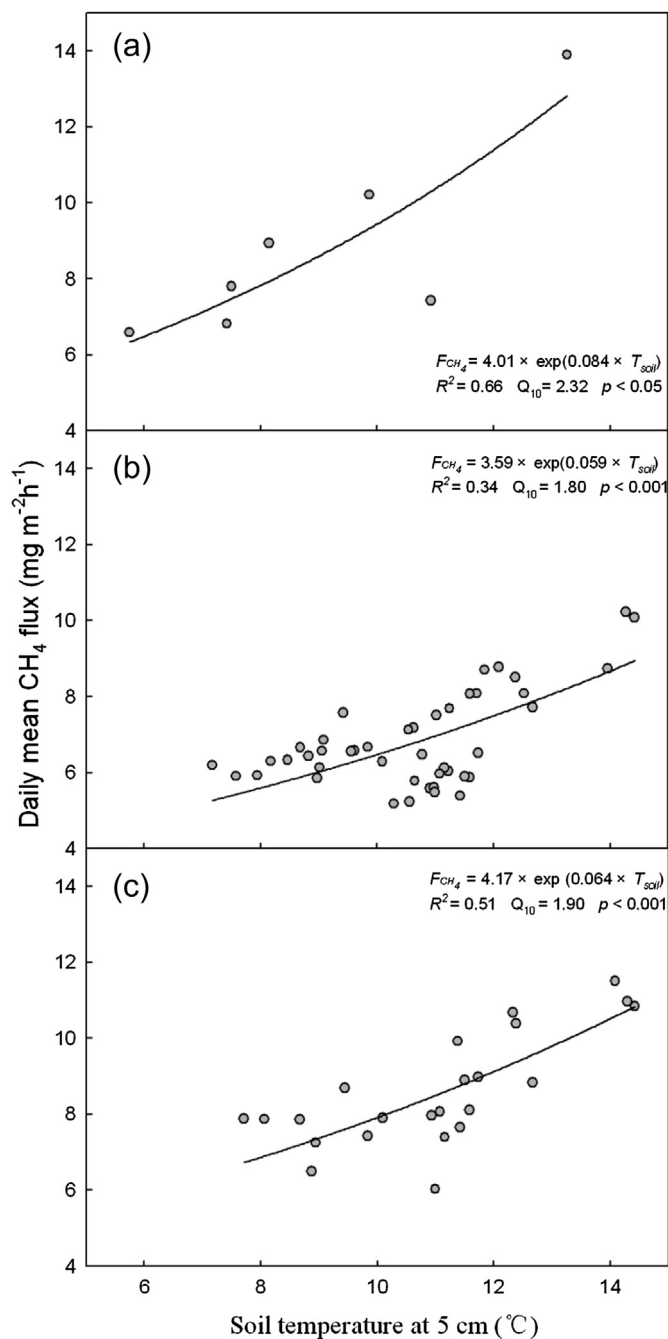
Fig. 3. The relationship between the daily mean CH_4 fluxes and daily mean soil temperatures at 5 cm depths. (a) Manual static chamber (MSC); (b) Continuous automated chamber (CAC); (c) Eddy covariance (EC).

In Fig. 3 (a): $F_{CH_4} = 4.01 \times \exp(0.084 \times T_{soil})$, $R^2 = 0.66$, $Q_{10} = 2.32$, $p < 0.05$

In Fig. 3 (b): $F_{CH_4} = 3.59 \times \exp(0.059 \times T_{soil})$, $R^2 = 0.34$, $Q_{10} = 1.80$, $p < 0.001$

In Fig. 3 (c): $F_{CH_4} = 4.17 \times \exp(0.064 \times T_{soil})$, $R^2 = 0.51$, $Q_{10} = 1.90$, $p < 0.001$

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
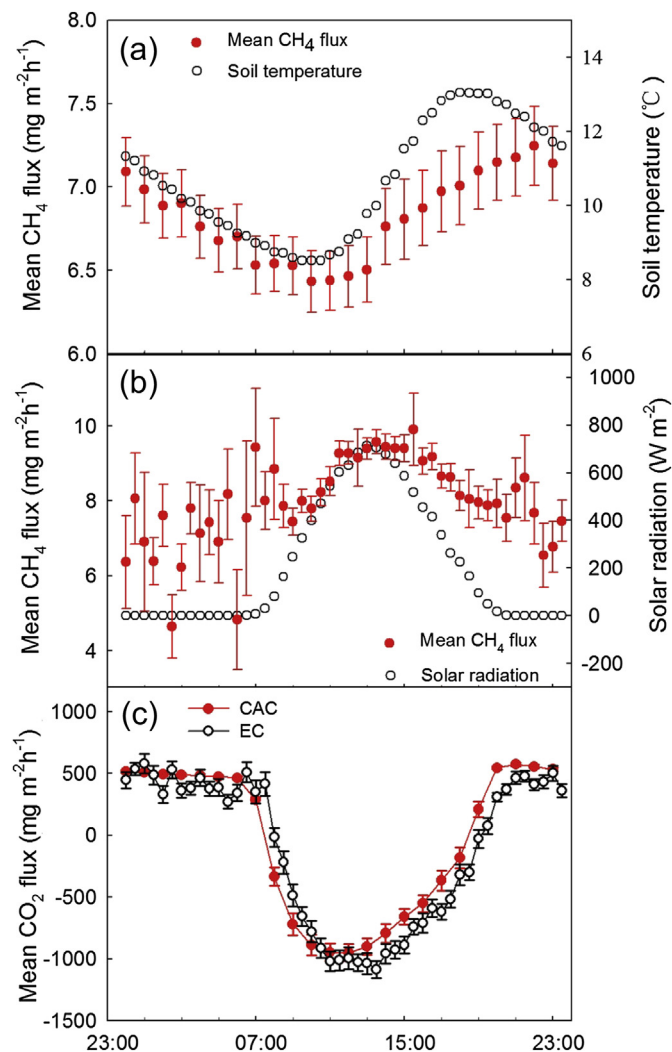
et al., 2009). In the current study, the variation in CH_4 fluxes was correlated with seasonal changes in the soil temperature at a 5 cm depth (Fig. 3). However, the soil temperature explained the seasonal CH_4 flux variations poorly, especially for the CAC methods (only 34%); this result is likely because 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.
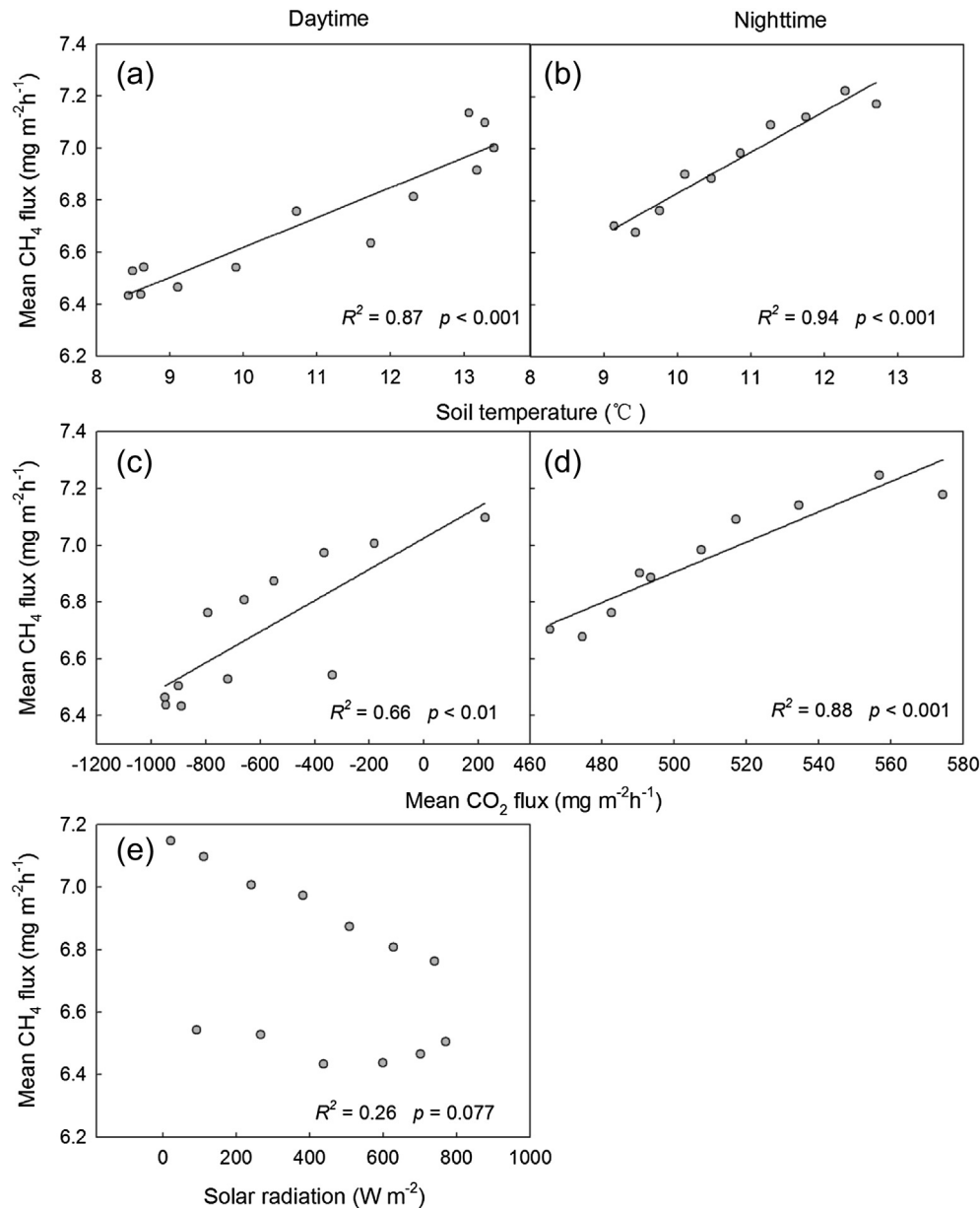
Fig. 5. The relationship between the mean CH₄ fluxes measured using the continuous automated chamber system and the soil temperature (a, b), mean CO_2 flux (c, d) and solar radiation (e) on a daily scale with measurements during the daytime (08:00–20:00) (a, c, e) and at nighttime (21:00–06:00) (b, d). The data were binned by time of day and then averaged for all days.

4.2. Diurnal CH₄ 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 CH₄ 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 CH₄ emission variations. In the present study, the CAC system enables this comparison.

Several factors have been shown to affect the diurnal CH₄ flux variation. First, the diurnal CH₄ 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 CH₄ 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 CH₄ 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 CH₄ 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 CH₄ 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 CH₄ emission late in the noon hour and an increase from night to day in EC method measurements. Other studies have also observed a
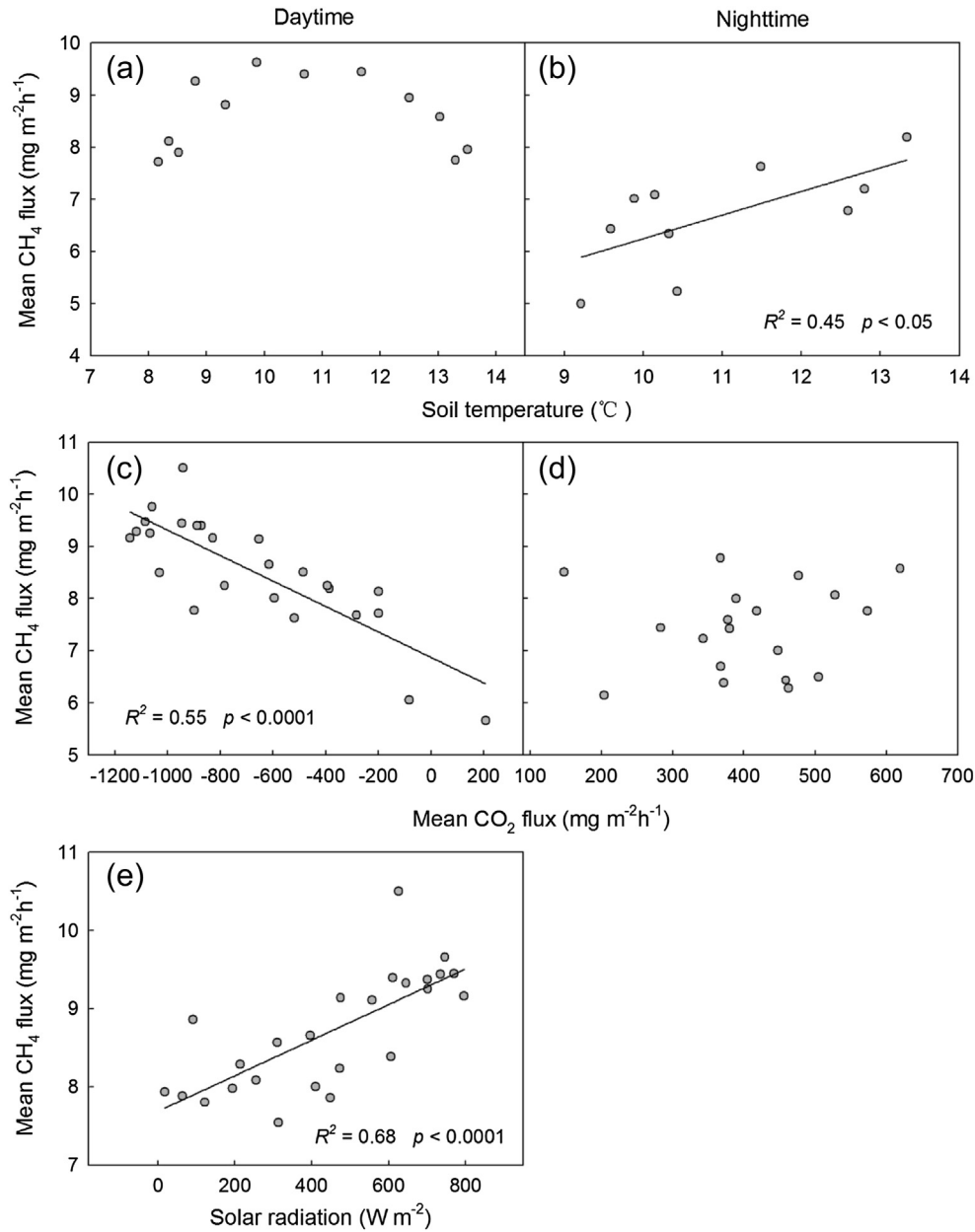
Fig. 6. The relationship between the mean CH_4 fluxes measured using the eddy covariance system and soil temperature (a, b), mean CO_2 flux (c, d) and solar radiation (e) on a daily scale with measurements during the daytime (08:00–20:00) (a, c, e) and at nighttime (21:00–06:00) (b, d). The data were 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.

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 land-cover 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

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

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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