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Diel variation of CH_4 emission fluxes in a small artificial lake: Toward more accurate methods of observation

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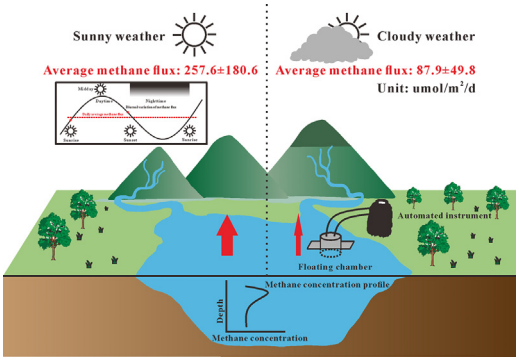
HIGHLIGHTS

- Hourly CH_4 fluxes from Lake Baihua have been measured using floating chamber method.
- CH_4 emission in the lake exhibited remarkably diel patterns.
- Solar radiation is likely a key driver to CH_4 in lakes and should be focused on.
- Floating chamber method is recommended for CH_4 flux observations in small lakes.
- Averaging results at sunrise and at sunset as daily values can reduce uncertainty.

GRAPHICAL ABSTRACT



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ABSTRACT

Lakes are significant sources in global methane (CH_4) budgets. However, estimations of the magnitude of global CH_4 emissions from lakes may be highly biased owing to the uncertainties in data originating from observation times, methods, and parameterizations of the gas transfer velocity (k). Here, we conducted continuous 48-hour measurements of CH_4 fluxes using the floating chamber method seasonally at Lake Baihua, a small reservoir in southwestern China, and compared the results with estimates derived from boundary layer models. Results showed that there was a weak dependency of k on wind speed, indicating that wind speed was not the major factor regulating gas exchange in such small lakes. It is thus concluded that the wind speed-dependent boundary layer model method is not suitable for CH_4 flux observations in small and medium-sized lake, and that the floating chamber method is recommended for use instead. The measured CH_4 fluxes displayed remarkably diurnal patterns, therefore the use of single observations to represent daily average values comes with unacceptably large uncertainties. A reasonable alternative is averaging observations made at sunrise and at sunset to represent daily values, which has a much smaller uncertainty (ranging from 0.8% to 13.6%). The coincident peaks of CH_4 and chlorophyll concentrations in the subsurface indicate that CH_4 originated mainly from aerobic methanogenesis. Solar radiation is likely one of the major factors regulating CH_4 production and emissions in the lake through enhancing CH_4 production, inhibiting CH_4 oxidation, and probably changing hydrodynamics conditions. Therefore, irradiation should be taken into consideration as a key factor in observing CH_4 fluxes in lakes. As sampling times are limited, observations during both sunny and cloudy weather should be proportionally included. This is the first time, to the best of our knowledge, that solar radiation has been proposed as a key driver of CH_4 emissions from lakes.

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1. Introduction

Lakes, especially small and medium-sized lakes, are important contributors to global methane (CH_4) budgets (Holgerson and Raymond, 2016). According to available data, lakes emit ~72 Tg of CH_4 per year globally (Barros et al., 2011), accounting for 32.7% of all natural methane emissions (Saunois et al., 2019). However, estimates of the magnitude of global CH_4 emissions from lakes are subject to large errors arising from uncertainties associated with methane cycling in the water column (Tang et al., 2016), parameterization of the gas transfer velocity (Eugster et al., 2003; Tang et al., 2016), estimates of the amount of CH_4 in the water, utilization of different monitoring methods (Duchemin et al., 1999; Matthews et al., 2003; Schubert et al., 2012; Erkkilä et al., 2018), and the particular timing of observations (Podgrajsek et al., 2014).

The traditional view holds that CH_4 is produced by methanogenic bacteria in anoxic environments, including lake bottom waters (Bastviken et al., 2004). However, numerous studies have found that dissolved CH_4 can be supersaturated in overlying oxic waters, a phenomenon known as the "methane paradox" (Damm et al., 2010; Grossart et al., 2011; Tang et al., 2016). Although the mechanisms responsible for this paradox are not yet known (DelSontro et al., 2018), Tang et al. (2016) indicated that this paradox is assumed to increase CH_4 emissions from lakes. Under conditions of CH_4 supersaturation in oxic waters, CH_4 needs to be transported over only short distances to reach the water-air interface. Moreover, water-side convection and internal waves, which often occur diurnally, could bring higher CH_4 concentrations to the air-water interface and accelerate gas transfer (Podgrajsek et al., 2014; Farrar et al., 2007; Tedford et al., 2014). However, these relatively complex scenarios for CH_4 emissions from lakes are not fully considered in widely-used boundary layer model methods (Wanninkhof, 1992; Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; MacIntyre et al., 2010; Podgrajsek et al., 2014; Erkkilä et al., 2018). Some recent studies focused on the diel cycling of CH_4 emission from lakes using various methods such as eddy covariance, floating chambers and boundary layer models (Podgrajsek et al., 2014; Erkkilä et al., 2018; Jansen et al., 2020), which may provide information about the controls over CH_4 production and emission (Bastviken et al., 2010; Martinez-Cruz, 2020). Temperature and wind speed are paid much attention on due to their influence on the short-term dynamics of CH_4 fluxes (Podgrajsek et al., 2014; Jansen et al., 2020). Solar radiation was thought to have limited influence on CH_4 production because of the large heat capacity of water (see Jansen et al., 2020). However, its role may be substantially underestimated. CH_4 supersaturation in surface oxic waters, known as "methane paradox", is related to light and photosynthesis (Grossart et al., 2011; Bižić et al., 2020). Similarly, recent studies have shown that diurnal variations of CH_4 emission from rice and wetlands are mainly controlled by gross ecosystem photosynthesis (Hatala et al., 2012) or gross primary photosynthesis (Mitra et al., 2020) through substrate availability. On the other hand, heat flux at the air-water interface is frequently used in explaining the diel cycles of gas exchanges (Podgrajsek et al., 2014).

The gas transfer velocity (k) is commonly estimated using wind speed models that are derived using empirical formulations from studies in oceans and lakes (Wanninkhof, 1992; Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; MacIntyre et al., 2010). The estimated k is then used to determine CH_4 fluxes using boundary layer models and concentration gradients between the surface water and air (Cole and Caraco, 1998). However, gas exchange across the air-water interface is mediated by numerous factors, including turbulence from wind shear, convection due to heat loss at the surface, rainfall, and breaking waves (Matthews et al., 2003; Eugster et al., 2003; Podgrajsek et al., 2014). In high wind speed areas such as oceans and large lakes, microscale wave breaking, convection in the water body, and wind shear all contribute to aquatic turbulence (Eugster et al., 2003). While in small and medium-sized stratified lakes with low wind speeds, other factors, including convection and internal waves, are considered key factors in regulating gas transfer (Crill et al., 1988; MacIntyre et al., 2009; Tedford et al., 2014; Podgrajsek et al., 2014). Thus, whether heavily wind speed-dependent boundary layer models are suitable for CH_4 flux calculations in small and medium-sized lakes is still debated.

Owing to significant differences in the results obtained using different sampling methods, estimations of global CH_4 emissions from lakes are still questionable. Studies have shown consistent differences in CH_4 flux measurements using boundary layer models and the floating chamber method, although both are widely used. Duchemin et al. (1999) compared the results of two methods used in lakes and reservoirs with different depths and flooded soil types and found that CH_4 fluxes obtained using a boundary layer model were ~ 4 times lower than those obtained using the floating chamber method. Similar results were also reported from two boreal lakes with different trophic statuses and water color, and the floating chamber method gave higher CH_4 fluxes (about 1.3 times) than those produced using the boundary layer model (Ojala et al., 2011). Moreover, the study in Lake Rotsee, Switzerland, during lake overturn (fall/winter) revealed that boundary layer model-based CH_4 fluxes were 5–30 times lower than those produced using the floating chamber (Schubert et al., 2012). Continuous 24-hour CH_4 measurements at Lake Kuivajärvi, Finland, also revealed that floating chamber-based CH_4 fluxes were, on average, 10.7 (daytime) and 3.1 (nighttime) times higher than those produced using the boundary layer model during stratified periods (Erkkilä et al., 2018).

Another factor leading to variability in CH_4 flux estimates is observation timing. A typical CH_4 flux measurement procedure involves observing the flux during daytime, with the assumption that the obtained data are valid for the entire day (24 h) (Podgrajsek et al., 2014). However, many studies have documented significant diurnal variation of CH_4 fluxes. Bastviken et al. (2004) reported substantial diurnal variations in CH_4 emissions, with 9–158% greater emissions during the day. Additional research by these authors also revealed considerable diurnal variability, with afternoon CH_4 fluxes approximately twice as high as fluxes near sunset and sunrise (Bastviken et al., 2010). Evidence from Lake Kuivajärvi found that CH_4 fluxes during the day were two times higher than those at night during stratified periods (Erkkilä et al., 2018). Moreover, research at Lake Tämnaren, Sweden, found that if methane flux was only observed at daytime hours between 12:00 and 20:00, the values would be ~40% lower than that obtained using mean or median values based on the entire data set from September 2010 to August 2012 (Podgrajsek et al., 2014). As one might expect, the result from a single observation can produce large errors when taken to represent a daily average value. An ideal scenario is that continuously running, automated chamber systems are deployed at all locations for the duration of observation, which is unrealistic for most scientists (Bansal et al., 2018).

Aiming to address the above-mentioned challenges in terms of producing representative observations of CH_4 emissions from lakes, much effort has been made to develop more accurate, comprehensive, and reproducible methods (Bastviken et al., 2010). Comparisons between eddy covariance, floating chambers, and boundary layer methods (Erkkilä et al., 2018; Podgrajsek et al., 2014), and from daily to multi-year timescales were made to identify more suitable approaches (Jansen et al., 2020). In this paper, we conducted continuous 48-hour observations of CH_4 emission fluxes at Lake Baihua, China, using the floating chamber method, and simultaneously measured CH_4 concentrations and other hydrochemical parameters in the lake water. The purpose of this study was to optimize and improve the observation methods for CH_4 emission flux measurements in small and medium-sized lakes.

2. Materials and methods

2.1. Site description

Lake Baihua (26°35′~26°42′N, 106°27′~106°34′E, Fig. 1) is a man-made reservoir, built in the 1960s. This deep lake lies in a mountainous

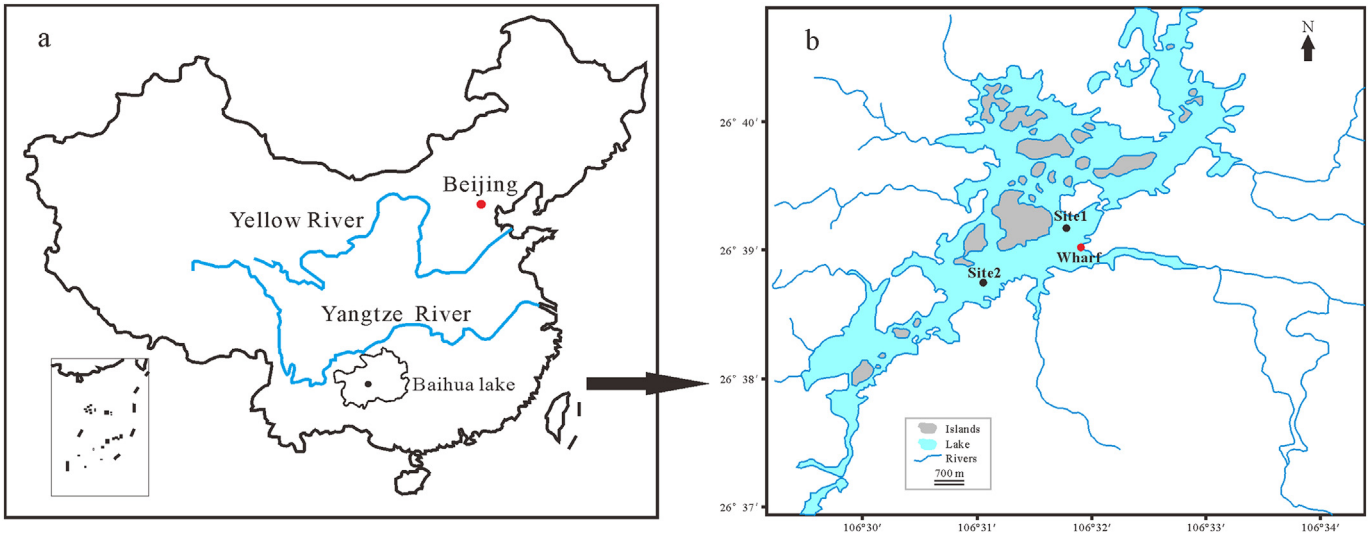

Fig. 1. Sampling sites in Lake Baihua.

area with primarily carbonate rocks (karst) in the Yungui Plateau, southwestern China. Lake Baihua has a subtropical, humid monsoon climate, with little annual temperature variation. Annual average temperature and precipitation are 14–15 °C, and 1095 mm, respectively. The lake has a surface area of 14.5 km^2, holds 190 million cubic meters of water, and has a mean depth of ~12 m, and a maximum depth of 45 m. Lake Baihua is eutrophic, with total nitrogen (TN) concentrations ranging from 0.73 mg/l to 2.85 mg/l, and total phosphorus (TP) concentrations ranging from 26.35 μg/l to 121.03 μg/l (Li et al., 2013). The abundance of phytoplankton varied seasonally in a large range from 244 × 10^4 cells/l in November to 959 × 10^4 cells/l in June of 1997 with an annual average of 519 × 10^4 cells/l (Zhang, 1999), increased to 969 × 10^4–193 × 10^6 cells/l in 2010 (Xia et al., 2012), and continued to rise to as high as 131 × 10^4–531 × 10^6 cells/l in 2013 (Chen et al., 2018) as a consequence of increasing input of nutrients from anthropogenic sources. The community is mainly comprised of green alga, cyanobacteria, and diatoms (Li et al., 2013; Chen et al., 2018).

2.2. Sampling and analysis

Seasonal sampling was performed in winter (January 23–27, 2019), spring (April 15–17 and 24–26, 2018) and summer (July 13–17, 2018). During each sampling, 48 h of continuous monitoring was firstly conducted at site 1 (Fig. 1), sequentially, 48 h of continuous monitoring was conducted at site 2 (Fig. 1). Surface water samples (upper 0.5 m) were collected at one-hour intervals. Water samples were also collected along depth profiles at 0:00, 6:00, 12:00 and 18:00 each day. The vertical intervals ranged from 1–3 m depending on the thermal structure in the profiles in different seasons in Lake Baihua.

Water temperature, dissolved oxygen (DO) and chlorophyll concentrations were measured *in situ* using a calibrated sonde (YSI 6920). During the sampling period, a KAMAX6036 handheld anemometer was fixed to the rail of the boat and was used to collect the wind speed at 1 m above the water surface. Solar radiation was automatically collected and recorded once per hour at the meteorological station located in the city of Guiyang (located ~10 km away from Lake Baihua). Triplicate water samples were collected for CH_4 concentration measurements and were packed in serum bottles (70 ml) with no air bubbles. A saturated $HgCl_2$ solution (0.2 ml) was added as a preservative, and the samples were stored in the refrigerator (4 °C) until analyzed. The dissolved CH_4 concentration was measured using the headspace equilibrium method (Kampbell et al., 1989). Highly purified N_2 (20 ml) was injected into the bottles and 20 ml of water was displaced. The bottles were then shaken for 30 min at 25 °C. After equilibration, the CH_4 concentration in the headspace was analyzed using a gas chromatograph (GC 6890) equipped with Flame Ionization Detector (FID).

2.3. Flux measurement experiment

Methane fluxes were measured *in situ* using a floating chamber connected to a Picarro G4301 Analyzer (Picarro Inc., Santa Clara, CA, USA). The boat used for sampling was anchored after arrival at the sites, and measurements did not commence until all visible disturbances caused by the boat had disappeared. The chamber was opened to the atmosphere, and after the air in the chamber was fully mixed with the atmosphere, hourly measurements began. The Picarro reads data at 1-second intervals, and each sampling event lasts 5 min. To minimize man-made disturbances, the chamber was allowed to drift freely on the water. The initial CH_4 concentration in the chamber was verified to be near the atmospheric concentration. The linear correlation coefficient of CH_4 concentration change in the chamber headspace against time was higher than 0.90 (Duchemin et al., 1999).

2.4. Floating chamber designs

The floating chamber was designed (Fig. S1) according to Matthews et al. (2003), Lorke et al. (2015) and Mannich et al. (2016). The steel chamber was cylindrical, 300 mm in diameter, and covered with a thick insulating layer and reflecting layer with headspace height of 300 mm and a skirt depth of 200 mm. It was supported by a wooden floating plate with sides measuring 1 m. A fan was used to keep the chamber well mixed. After the skirt was completely filled with water, we closed a valve to ensure balanced pressure inside and outside the chamber.

2.5. Calculations

(1) The flux of CH_4 is estimated by the boundary layer model as follows:

$$F_{CH4} = K(c_{water} - c_{air}) \quad (1)$$

where, F is the CH_4 flux, c_{water} is the CH_4 concentration in surface water, and c_{air} is the CH_4 concentration in the water equilibrated with the overlying atmosphere. The exchange coefficient K is calculated by:

$$K = K_{600}(Sc/600)^{-x} \quad (2)$$

where, K_{600} is the gas exchange coefficient ($cm \cdot h^{-1}$) of sulfur hexafluoride (SF_6), Sc is the Schmidt constant of CH_4 (see Eq. (3)), and

x is the coefficient related to wind speed. When the wind speed is less than 3 m/s, x is 0.66, when greater than 3 m/s, x is 0.5.

$$Sc_{CH4} = 1897.8 - 114.28\,t + 3.2902\,t^2 - 0.039061t^3 \quad (3)$$

where t is the temperature (in °C).

To calculate the gas exchange coefficient (K_{600}), we chose three models to test their suitability for monitoring CH_4 fluxes in small and medium-sized lakes. The simplest and the most often used model is the one proposed by Cole and Caraco (1998):

$$K_{600} = 2.07 + \left(0.215 \times U_{10}^{1.7}\right) \quad (4)$$

$$U_{10} = U_1\left[1 + (C_{d10})^{0.5}/k \cdot \ln(10/1)\right] \quad (5)$$

where U_{10} is the wind speed at 10 m height (in m/s), U_1 is the wind speed at 1 m height (in m/s), C_{d10} is the drag coefficient at a height of 10 m (1.3×10^{-3}), and k is the Von Karman constant (=0.4). Using the constants listed yields the relationship:

$$U_{10} = 1.22 \times U_1 \quad (6)$$

As the relationship between K_{600} *vs.* U_{10} is scattered ($r^2 = 0.61$), Crusius and Wanninkhof (2003) proposed two bilinear relationships based on wind speed, which show good correspondence between measured and predicted values ($r^2 = 0.94$)

for $U_{10} < 3.7$ m/s

$$K_{600} = 0.72\,U_{10}\ \text{cm h}^{-1} \quad (7)$$

and for $U_{10} \geq 3.7$ m/s

$$K_{600} = 4.33\,U_{10} - 13.3\ \text{cm h}^{-1} \quad (8)$$

MacIntyre et al. (2010) further considered the dominant physical processes modifying K_{600} in lakes and proposed two new models:

for a cooling lake

$$K_{600} = 2.04\,U_{10} + 2.0 \quad (9)$$

for a heating lake

$$K_{600} = 1.74\,U_{10} - 0.15 \quad (10)$$

where lakes were assumed to be cooling when air temperature was lower than the surface lake temperature but heating for all other cases.

(2) Methane flux is measured using the floating chamber method as follows:

$$F = \alpha \cdot b \cdot (V/A) \cdot (P/P_0) \cdot (T_0/T) \cdot 3600 \quad (11)$$

where F is CH_4 flux (mg/m^2/h); α is the transfer coefficient = molecular weight of gas/22.4 × [273/(273 + T)](pa pressure/101,325); b is slope of linear regression equation for CH_4 concentration; V is the chamber volume (including air chamber and air tube); A is the surface area of floating chamber; T_0 and P_0 are the absolute temperature (273.15 K [0 °C]) and pressure (101.325 KPa) of air, respectively; and P and T are the air pressure and absolute temperature of the sampling point, respectively.

(3) The gas exchange velocity (k) of methane was calculated from measured fluxes as:

$$k = F/(C_{water} - C_{air}) \quad (12)$$

where F is the measured CH_4 flux, C_{water} is CH_4 concentration in the surface water, and C_{air} is CH_4 concentration in the water equilibrated with the overlying atmosphere.

2.6. Statistical analyses

Statistical differences in CH_4 fluxes between day and night were analyzed using independent-samples *t*-tests. The statistical differences in CH_4 fluxes among different methods in the same season and sampling site, the statistical differences in collected parameters in different seasons and sampling sites were analyzed using one-way analysis of variance (ANOVA), and least significant difference (LSD) at the 0.05 significance level. All statistical analyses were performed using SPSS 19.0 statistical software.

3. Results

3.1. Water temperature, DO, Chl and methane concentrations in the water columns

The vertical variations of water temperature, DO/pH, chlorophyll, and CH_4 concentrations during the periods of observation at the two sampling sites in Lake Baihua are shown in Fig. 2 (for original data see Table S1). Water temperature profiles reflect thermal stratification in the water column during the warm season. In April, thermal stratification started to form at ~4 m depth (Fig. 2). In July, the thermocline (water layer where temperature gradient is >0.2 °C/m, Mao and Qiu, 1964) remained stable at 2–6 m, where temperature decreased from ~26 °C to approximately 22 °C (Fig. 2). In addition, at site 1, a second thermocline occurred between 12 and 15 m, where temperatures fell from 21.4 °C to ~20.3 °C (Fig. 2). In January, thermal stratification disappeared, with water temperature ranging from 8.5–9.0 °C (Fig. 2).

During the stratification period, DO concentrations in Lake Baihua decreased from 10 to 15 mg/l in the surface water to 1–5 mg/l in the deep water, and the maximum gradient of DO concentration change corresponded to the depth of the thermocline (Fig. 2). In January, when lake water was completely mixed, differences in chlorophyll concentrations between the surface and deep water were small, with somewhat higher values in the surface corresponding to the slightly higher pH. In April and July, when the lake was thermally stratified, vertical profiles of chlorophyll concentrations displayed peaks occurring at the subsurface at 2–6 m. On the other hand, chlorophyll concentrations showed some slight differences in the surface waters at different times of each day. The differences were the most remarkable at site 1 in April (Fig. 2). The peak chlorophyll concentrations were up to 35 μg/l at 0:00 and at 18:00, and lower than 20 μg/l at 06:00 and at 12:00. By comparison, chlorophyll often exhibited high concentrations at midnight 0:00, and chlorophyll concentrations in surface waters rose at 6:00 am.

Methane concentrations displayed similar vertical variations to those of chlorophyll. In January, CH_4 concentrations varied in the range of 50–75 nmol/l, with a trend of slightly increasing concentrations upward at site 1 (Fig. 2), and in the range of 50–120 nmol/l with a trend of slightly decreasing concentrations upward at site 2 (Fig. 2). Overall, the differences in CH_4 concentrations in the surface waters and deep waters were small. In April and July, CH_4 exhibited concentration peaks in the subsurface, which corresponded with peaks in chlorophyll concentration. In surface waters, CH_4 concentrations were significantly lower in January than in April and July. In deep waters, hypoxic or anoxic conditions occurred in the hypolimnion in summer so that CH_4 accumulated there and the concentration was as high as 3000 nmol/l.

3.2. Solar radiation and wind speed in Lake Baihua

Diel variations in solar radiation and wind speed for the entire sampling period are shown in Figs. 3–5. In January, the weather was cloudy during the sampling period, and average daytime solar radiation was 67.9 ± 59.1 w/m^2. In April, mean solar radiation at site 1 during the daytime of two days (April 15th and 16th) was 565.4 ± 342.3, and at site 2 during the daytime of two days (April 25th and 26th) was 116.0 ±

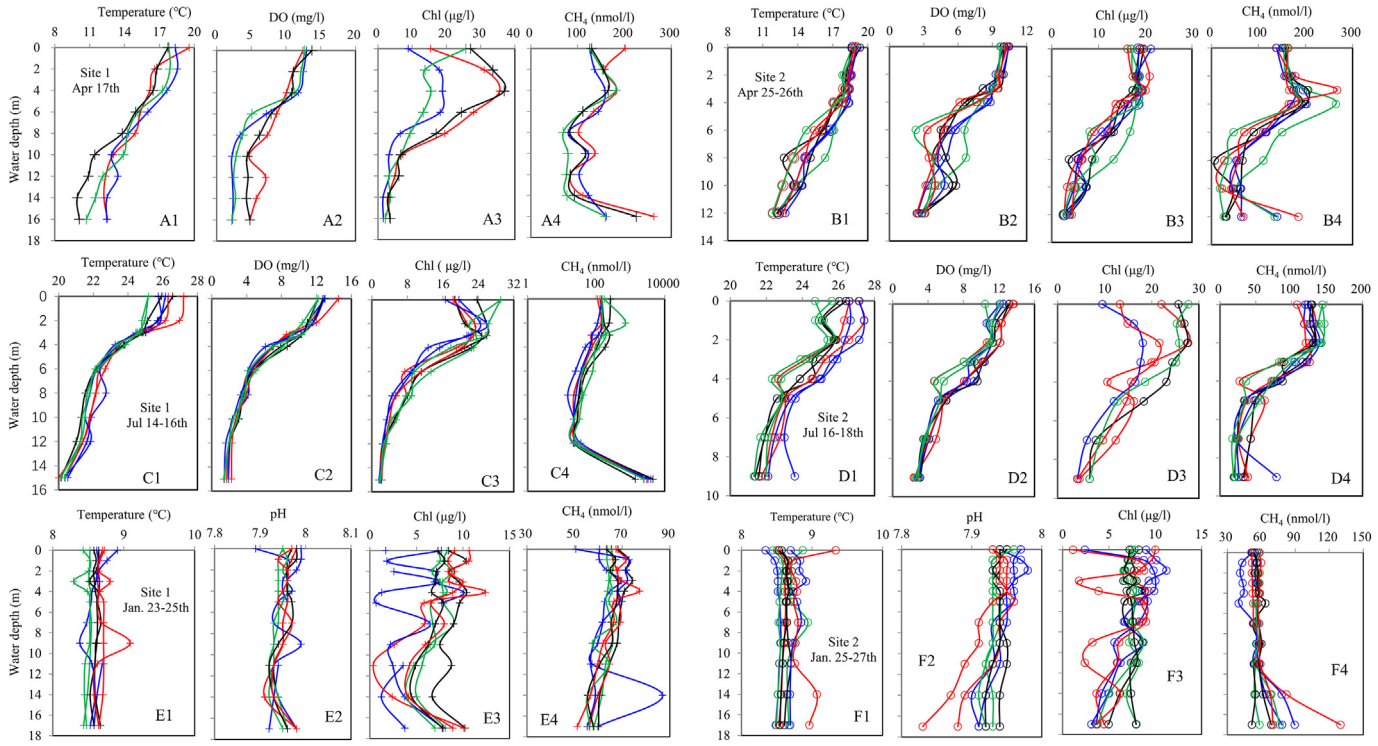

Fig. 2. Variations of the CH_4 concentrations and the hydrogeochemical parameters in the water columns of Lake Baihua. Crosses stand for the samples from site 1 and open circles from site 2. Black represents the measurements at 0:00 at night, green represents at 6:00 am, blue represents at 12:00 noon, and red represents at 18:00 pm. Note that the horizontal axis of panel C4 for the CH_4 concentrations at site 1 in July is logarithmic, and the horizontal axis of panels A2, B2 C2 and D2 are for DO, and of E2 and F2 are for pH.

98.5 w/m^2, corresponding to sunny and cloudy weather, respectively. In July, the weather was sunny during the sampling period, and mean daytime solar radiation was 419.9 ± 274.4 w/m^2. During the whole sampling period, wind speeds at Lake Baihua were always low. The average wind speeds in January, April, and July were 0.64 ± 0.34, 0.81 ± 0.48, and 0.86 ± 0.62 m/s, respectively. And the maximum wind speed values during these same months were 1.41, 2.74 and 2.60 m/s, respectively.

3.3. Variations of methane concentrations and other geochemical variables in surface waters

Methane concentrations in surface waters are shown in Figs. 3–5 (for original data see Table S2). In January, CH_4 concentrations were lower in comparison to those in April and July ($p < 0.05$), and varied between 55 and 75 nmol/l at site 1, and 50–60 nmol/l at site 2, with no obvious diurnal patterns (Fig. 3). Mean concentrations of CH_4 at sites 1 and 2 were 65.2 ± 4.5, and 54.4 ± 2.8 nmol/l, respectively, and these differences were statistically significant ($p < 0.05$). In April, CH_4 concentrations ranged from 120 to 205 nmol/l at site 1, and from 135 to 165 nmol/l at site 2 (Fig. 4). In July, CH_4 concentrations varied between 100 and 260 nmol/l at site 1, and between 110 and 148 nmol/l at site 2 (Fig. 5).

Overall, hourly CH_4 concentrations at the lake's surface varied greatly and irregularly with time (hour, day, and month) and weather. Methane concentrations during the daytime were not significantly different from those at night (Table 1), with an exception in July at site 1 where the mean concentration of CH_4 was 136.6 ± 28.3 nmol/l during the daytime and 161.5 ± 43.8 nmol/l at night ($p < 0.05$, Table 1). In January and April, the mean CH_4 concentrations during the daytime and at night at site 1 were 63.3 ± 5.6, and 66.9 ± 4.4 (January), and 138.0 ± 22.7, and 150.5 ± 23.2 nmol/l (April), respectively. There were no significant differences in the diurnal variation of CH_4 concentrations ($P > 0.05$). At site 2, CH_4 concentrations during daytime and at night were nearly equal, with no significant difference ($p > 0.05$). The hourly concentrations of CH_4 seem to exhibit a trend, with slight decreases between 6:00 and 12:00 in April (Fig. 4), and in July (Fig. 5). At site 1, the maximum CH_4 concentration occurred in the afternoon in April (Fig. 4) and occurred between 21:00 and 24:00 in July (Fig. 5).

Temperature in surface waters in the lake varied in the range of 8–10 °C in January (Fig. 3), 17–20 °C in April (Fig. 4), and 24–28 °C in July (Fig. 5). Temperature in surface waters was remarkably influenced by solar radiation. In January, low water temperature corresponded to the low solar radiation (Fig. 3). In April, temperature in surface waters at site 1 exhibited a diel pattern as the maximum of solar radiation approached 1000 W/m^2, while temperature at site 2 had no such diel pattern as the maximum of solar radiation was only ~350 W/m^2 (Fig. 4). In July, temperature displayed diel pattern at sites 1 and 2, as the weather was sunny and the maximum of solar radiation varied in 800–1000 W/m^2 (Fig. 5). DO and pH had similar fluctuation to temperature. Similarly, Chl concentrations displayed remarkably diel pattern as weather was sunny, while had no the diel pattern as weather was cloudy (Figs. 3–5). The diel pattern of Chl concentrations in the surface waters had higher values at night and lower values during daytime. It is due likely to the inhibition of light, just as the maxima of Chl concentrations occurred in the subsurface (Fig. 2), not in the surface.

3.4. Methane emission fluxes

Measured CH_4 emission fluxes using the floating chamber method exhibited great variability. Overall, CH_4 emission fluxes were higher, and displayed a clear diurnal variation pattern, with high values occurring during the daytime and low values occurring at night in sunny weather, while they were lower and displayed no such diurnal pattern in cloudy weather (Figs. 3–5, for original data see Table S2). In January, CH_4 emissions were lowest at sites 1 and 2 (Fig. 3), corresponding to the lowest solar radiation, as compared with results in April and July (Figs. 4 and 5). In April, the mean CH_4 flux at site 1 during the daytime was

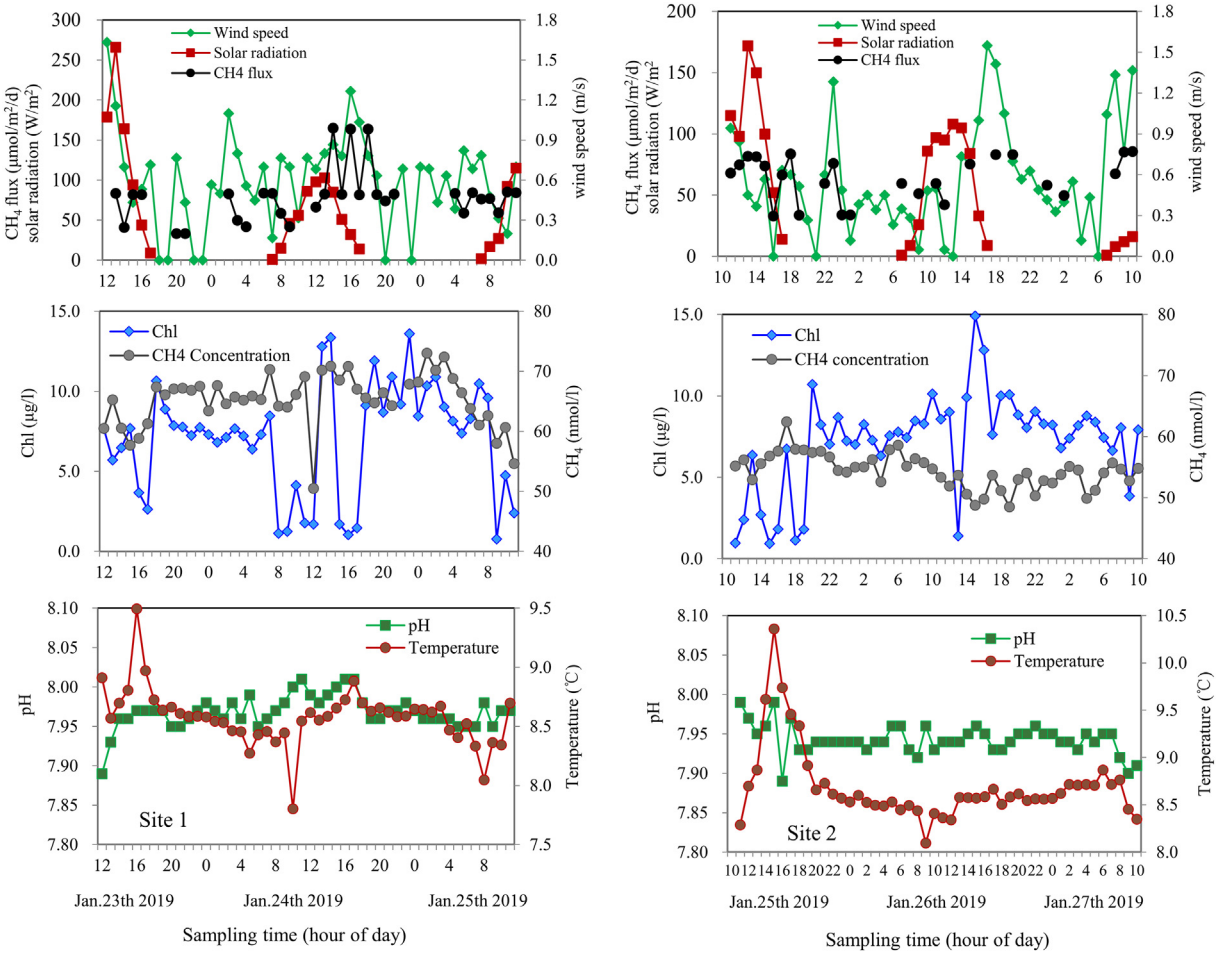

Fig. 3. Diurnal variations of CH_4 fluxes, solar radiation, wind speed, and geochemical parameters (CH_4 and Chl concentrations, pH and temperature) in surface waters in Lake Baihua in Jan. of 2019.

325.1 ± 204.9 μmol/m^2/d, which was significantly higher than the nighttime value of 123.0 ± 77.3 μmol/m^2/d ($p < 0.01$) (Table 1). At site 2, where solar radiation was low during the period of sampling, CH_4 emissions were generally low, and relatively high values occurred occasionally in the afternoon and at sunset (Fig. 4). In July, the mean CH_4 flux at site 2 during the daytime was 239.3 ± 127.8 μmol/m^2/d, which was 2.25 times higher than the values at night (106.5 ± 47.8 μmol/m^2/d) (Table 1). The high values occurred during the daytime and were in complete accord with solar radiation (Fig. 5), and the diurnal pattern was very clear ($p < 0.01$). At site 1, high emissions occurred between 21:00 and 24:00 of the first day of sampling (Fig. 5), which was concordant with high CH_4 concentrations and high temperatures. These high fluxes between 21:00 and 24:00 lead to a slightly higher nighttime average (362.6 ± 196.3 μmol/m^2/d) than the daytime average (352.4 ± 164.1 μmol/m^2/d) (Table 1).

In comparison, the measured CH_4 emission fluxes determined using the floating chamber method were significantly higher than the results obtained using the boundary layer models (Table1). The results calculated using different gas exchange coefficients differed greatly (Table 1). In Lake Baihua, the mean CH_4 flux calculated with K_{cw} was 18.2 ± 17.4 μmol/m^2/d, while the flux calculated with K_{cc} were 3 times higher than this. The mean CH_4 flux calculated with K_{mac} was the highest (83.8 ± 60.3 μmol/m^2/d). Overall, CH_4 fluxes measured using the floating chamber method were ~ 2 times higher than those estimated using K_{mac}, 3 times higher than with K_{cc}, and 10 times higher than with K_{cw} (Table 1).

4. Discussion

4.1. Solar radiation is a key factor in CH_4 emission fluxes

Solar radiation is likely a key driver of aerobic methanogenesis, and therefore a regulator of the long- and short-term variations of CH_4 flux. In general, lake characteristics, in particular lake depth and lake surface area, are believed to be the primary factors influencing CH_4 fluxes from lakes (Bastviken et al., 2004). Recently, several studies focused on the diel variations of CH_4 emissions from lakes to reveal the short-term dynamics of lake CH_4 (Podgrajsek et al., 2014; Erkkilä et al., 2018; Martinez-Cruz, 2020; Jansen et al., 2020). However, little remains known about the factors that drive diel variations of CH_4 emissions in lakes. Bastviken et al. (2010) found no strong relationships between CH_4 emissions and water temperature, surface CH_4 concentrations, pH, or alkalinity. The high variability of CH_4 emissions in Lake Baihu (Figs. 3–5) indicates that there are likely several factors or mechanisms regulating CH_4 production and emissions. Temperature, wind speed, and the surface CH_4 concentration are three factors that are most frequently regarded as the main drivers to CH_4 flux from lakes over different timescales (Jansen et al., 2020). In fact, various diel patterns appear in different lakes. Using the eddy covariance method, Podgrajsek et al. (2014) reported a marked diurnal pattern of CH_4 fluxes in a shallow lake, with the highest values recorded at night and in the early morning, and the lowest values recorded during the day. Some studies documented different patterns, with higher values recorded in the daytime, and lower values recorded at night (Bastviken et al., 2010), like the results reported herein (Figs. 4 and 5). Of the variables considered,

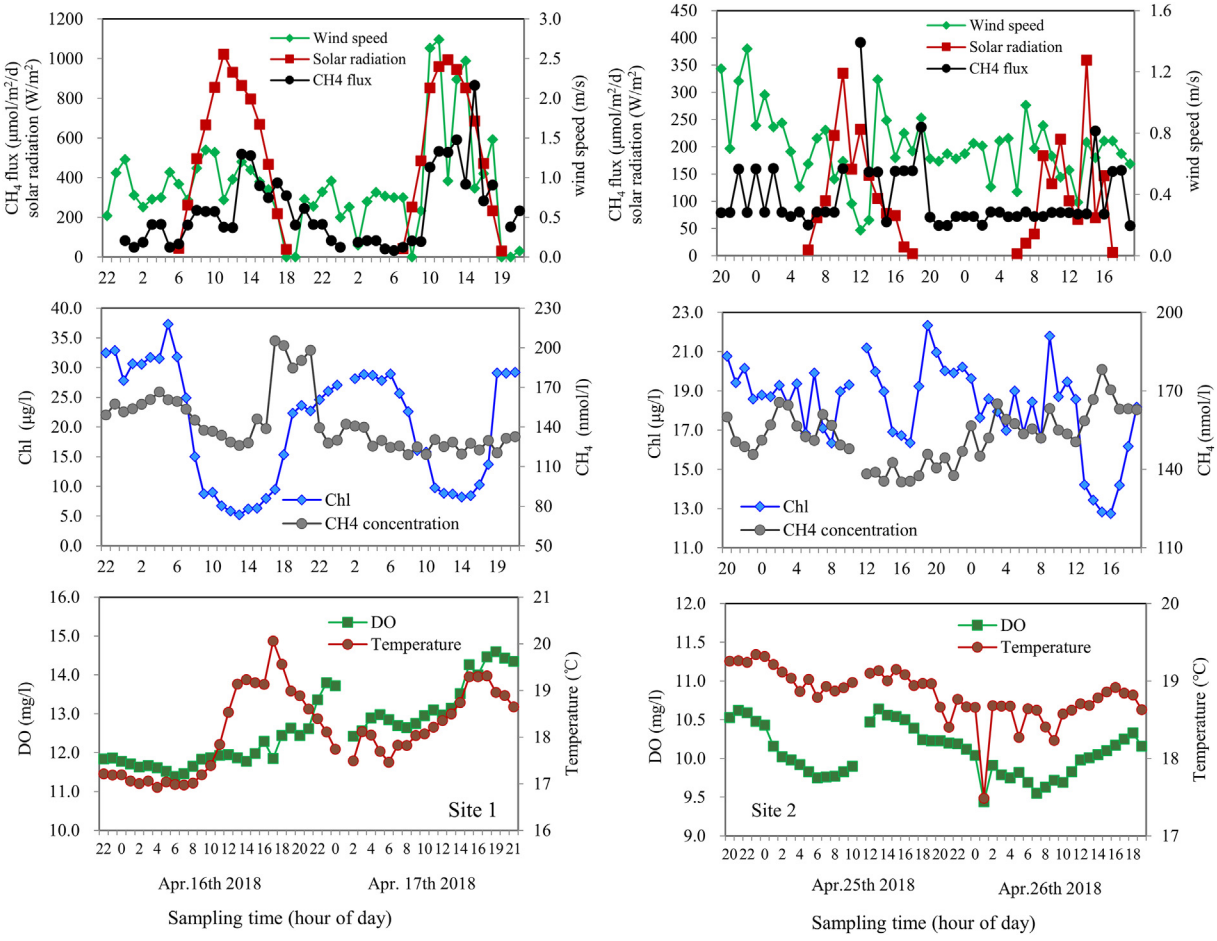

Fig. 4. Diurnal variations of CH_4 fluxes, solar radiation, wind speed, and geochemical parameters (CH_4 and Chl concentrations, DO and temperature) in surface waters in Lake Baihua in April of 2018.

water temperature was focused on due to the influence of temperature on enzyme activity and microbial community structure (Yvon-Durocher et al., 2014). Moreover, water temperature could change lake water convection, which could significantly influence CH_4 emissions (Podgrajsek et al., 2014). However, the results obtained in Lake Baihua show that the diel pattern of CH_4 fluxes seem to be more concordant with solar radiation during daytime than with water temperature (Figs. 4 and 5). Similar trends among CH_4 fluxes, CH_4 concentrations, and water temperature during the night (Figs. 4 and 5) indicate that temperature played a role as well. The mutual influences of several factors could cause the asynchrony of CH_4 emissions (Sturtevant et al., 2016), which could explain the high CH_4 fluxes occasionally occurring at night (Fig. 5) and on cloudy day (Fig. 4) that did not correspond to high solar radiation. In addition, CH_4 fluxes in sunny weather were always significantly higher than those in cloudy weather. Even in the same month, for example in April, the CH_4 fluxes were higher at site 1 when the weather was sunny and solar radiation was much higher, than that at site 2 when the weather was cloudy and solar radiation was lower while water temperature was approximately equal. It is speculated that solar radiation plays a more important role in driving CH_4 production and emissions in lakes than water temperature. This is in disagreement with the viewpoint that the diurnal cycle of insolation has a limited effect on CH_4 production because the heat capacity of the water buffers the temperature (see Jansen et al., 2020).

The peaks of CH_4 concentration in the subsurface corresponding to the peaks of chlorophyll (Fig. 2) indicates it is likely that CH_4 is produced chiefly from aerobic methanogenesis ("methane paradox"). Many studies have showed that CH_4 concentrations in the surface waters of lakes and oceans are positively correlated with DO and chlorophyll concentrations (Grossart et al., 2011; Tang et al., 2014; Bogard et al., 2014), and the same phenomena occurred in Lake Baihua ($r = 0.66$, $p < 0.001$). Although the mechanism for aerobic methanogenesis remains unknown (DelSontro et al., 2018), most studies assume that CH_4 production in oxic waters has a connection with algal growth during photosynthesis (Bogard et al., 2014; Bižić et al., 2020; Hartmann et al., 2020). The results of a recent light/dark incubation experiment suggested that cyanobacteria produce CH_4 at a substantial rate, and linked "methane production with light-driven primary productivity" (Bižić et al., 2020). In general, the primary factor regulating algal growth during photosynthesis is light (Krause and Weis, 1991), while the primary factor for organic decomposition during respiration is temperature (Yvon-Durocher et al., 2014). In Lake Baihua, Chl concentrations were the parameters that were most correlated (negatively) with CH_4 fluxes, and followed by wind speed (Table 2). Chl concentrations in the surface waters were foundationally controlled by solar radiation. Therefore, it is reasonable to assume that solar radiation plays a more important role in CH_4 production in oxic water than temperature. This is fully comparable with the results from wetlands. Mitra et al. (2020) found that it is substrate availability rather than environmental factors controlling the CH_4 emission from wetlands. A growing number of studies showed that primary production is the dominate factor to cause the diurnal variation of CH_4 emission fluxes from wetlands (Hatala et al., 2012; Song et al., 2015; Mitra et al., 2020). Another mechanism related to solar radiation's regulation of CH_4 concentrations is associated with CH_4 oxidation. It has been suggested that solar radiation in the epilimnion could inhibit CH_4 oxidation (Dumestre et al., 1999; Murase and Sugimoto, 2005; Tang et al., 2014). Lower CH_4 oxidation rates under solar radiation may result in increased CH_4 emissions.

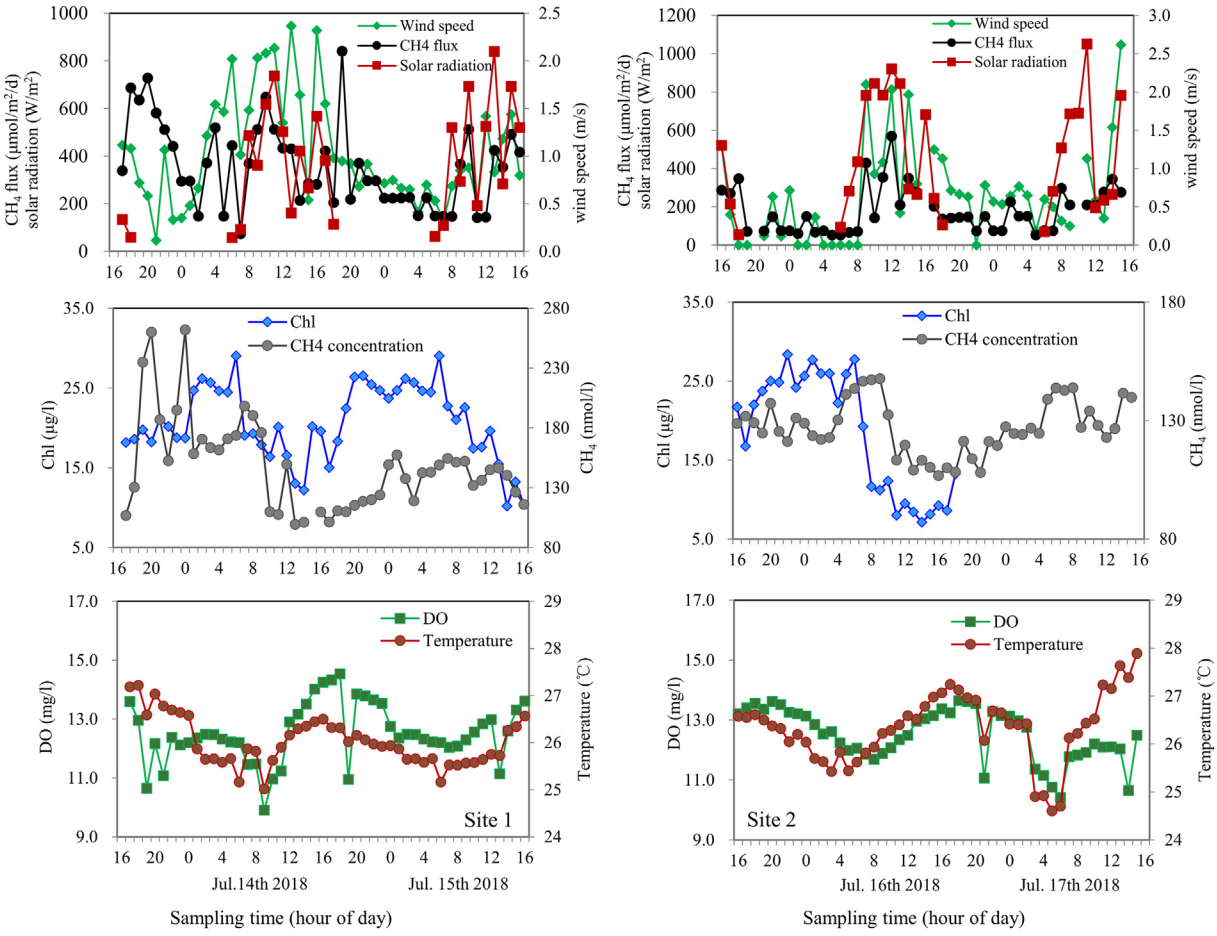

Fig. 5. Diurnal variations of CH_4 fluxes, solar radiation, wind speed, and geochemical parameters (CH_4 and Chl concentrations, DO and temperature) in surface waters in Lake Baihua in July of 2018.

As yet, little is known about the dynamics of CH_4 production and emission in surface oxic waters. Most diel observations of CH_4 in previous studies focused on shallow lakes (Bastviken et al., 2010; Podgrajsek et al., 2014; Jansen et al., 2020), where CH_4 produced in sediments can be conveyed to the surface and then emitted to the atmosphere. Therefore, turbulence induced by temperature and winds can drive CH_4 transport from sediments to surface waters. In a deeper Amazon lake (Lago Calado, 7 m), CH_4 emission fluxes during daytime were lower than at night (Crill et al., 1988). This diel pattern is opposite to the one reported in this paper. In general, at midday the depth of the warmed surface layer of lakes is highest, which results in lower CH_4 diffusive fluxes (Bastviken et al., 2010), while at night the temperature of warmed surface waters falls, leading to water convection and enhances CH_4 emissions (Crill et al., 1988; Podgrajsek et al., 2014). In the deep Lake

Table 1
Averages of CH_4 concentrations (nmol/l) in surface waters of Lake Baihua, the measured CH_4 fluxes (μmol/m²/d) using the floating chamber method, and the estimated CH_4 fluxes using the boundary layer model method during daytime and nighttime.

Month	Concentrations	Fluxes	Site 1				Site 2			
			Daytime	Nighttime	*p* value	Average flux	Daytime	Nighttime	*p* value	Average flux
January	CH_4 concentration		63.3 ± 5.6	66.9 ± 4.4	>0.05		54.5 ± 2.9	54.3 ± 2.7	>0.05	
	Measured CH_4 flux		83.1 ± 32.8	73.3 ± 33.8	>0.05	79 ± 33[a]	67.0 ± 15.7	59.5 ± 21.2	>0.05	64 ± 18[a]
		CW03	5.9 ± 3.1	4.3 ± 2.7	>0.05	5.0 ± 3.0[b]	4.4 ± 3.1	3.4 ± 2.2	>0.05	3.9 ± 2.7[b]
	Estimated Flux	CC98	21.1 ± 2.7	21.6 ± 1.1	>0.05	21.4 ± 2.0[c]	17.9 ± 1.8	17.3 ± 1.1	>0.05	17.6 ± 1.5[c]
		MAC10	35.5 ± 9.5	31.8 ± 7.6	>0.05	33.5 ± 8.7[d]	28.5 ± 8.8	25.5 ± 6.1	>0.05	26.9 ± 7.5[d]
April	CH_4 concentration		138.0 ± 22.7	150.5 ± 23.2	>0.05		152.1 ± 11.7	153.4 ± 8.2	>0.05	
	Measured CH_4 flux		325.1 ± 204.9	123.0 ± 77.3	<0.01	231 ± 187[a]	118.1 ± 73.8	94.1 ± 46.5	>0.05	106 ± 63[a]
		CW03	28.1 ± 17.9	14.7 ± 10.9	<0.01	23.2 ± 15.7[b]	19.6 ± 6.7	23.4 ± 7.1	>0.05	21.5 ± 7.1[b]
	Estimated Flux	CC98	75.6 ± 14.5	60.9 ± 24.3	<0.05	73.0 ± 14.7[c]	75.4 ± 6.4	77.8 ± 6.0	>0.05	76.6 ± 6.3[c]
		MAC10	85.0 ± 39.7	94.2 ± 50.1	>0.05	95.9 ± 41.6[c]	84.0 ± 49.9	134.8 ± 21.4	<0.01	108.9 ± 46.1[a]
July	CH_4 concentration		136.6 ± 28.3	161.5 ± 43.8	<0.05		129.5 ± 13.6	124.9 ± 7.2	>0.05	
	Measured CH_4 flux	CW03	352.4 ± 164.1	362.6 ± 196.3	>0.05	359 ± 179[a]	239.3 ± 127.8	106.5 ± 47.8	<0.01	177 ± 119[a]
		CC98	42.6 ± 19.7	29.0 ± 14.2	<0.01	36.2 ± 18.4[b]	28.5 ± 25.4	11.6 ± 9.4	<0.01	20.6 ± 21.2[b]
	Estimated Flux	MAC10	98.1 ± 21.6	103.0 ± 28.1	>0.05	100.4 ± 24.7[c]	88.9 ± 19.0	74.8 ± 3.6	<0.01	82.3 ± 15.7[c]
			135.3 ± 84.6	162.2 ± 55.8	>0.05	147.9 ± 73.1[d]	89.0 ± 51.6	98.3 ± 27.3	>0.05	93.4 ± 41.9[c]

The letters indicate significant differences of methane fluxes between different methods during the same season and sampling site. Values with the same letter are not significantly different.

Table 2
The parameters that were correlated with CH_4 fluxes and its correlation coefficient and significance.

Month	Sites	Parameters correlated with CH4 fluxes
January	Site 1	None
	Site 2	Wind speed ($r = 0.63$ p = 0.001)
April	Site 1	Chl concentration ($r = -0.72$ p<0.001)
	Site 2	None
July	Site 1	Temperature ($r = 0.38$ $p = 0.008$)
	Site 2	Wind speed ($r = 0.68$ p < 0.001)
		Chl concentration ($r = -0.63$ $p = 0.001$)

Stechlin, Germany, which has similar mean and maximum depths as Lake Baihua, CH_4 showed similar concentration peaks in the subsurface to Lake Baihua. Although there were lower CH_4 emissions between 0500 and 1100 h in Lake Stechlin, which seems to correspond to the decrease in CH_4 concentration between 6:00 and 12:00 in Lake Baihua, CH_4 fluxes increased to their maximum values between 1300 and 1500 h (Martinez-Cruz, 2020), which corresponds in time with when photosynthesis is the most intense.

Hydrodynamic condition is another important factor in regulating CH_4 emission from lakes. Bastviken et al. (2010) noticed that the differences in CH_4 fluxes between light and dark periods didn't correspond to CH_4 concentration and temperature changes, and linked it to hydrodynamic condition changes. In Lake Baihua, CH_4 concentrations in surface waters did not display a diel pattern, but CH_4 emission did (Figs. 4 and 5). It is worth studying whether solar radiation can enhance CH_4 emissions through changing hydrodynamic conditions. In fact, small changes in temperature gradients within the upper 2–3 m of water has happened with time of day (Fig. 2), which is enough to induce water-side convection and then influence CH_4 emissions (Vidal et al., 2013). This cannot be simply attributed to the effect of heat flux because the diurnal pattern of CH_4 emissions induced by the diurnal cycle of heat flux has higher values at night and lower values during the daytime (Podgrajsek et al., 2014), which is opposite to the pattern in Lake Baihua. Moreover, it is likely that solar radiation significantly influences temperature and wind speed in small mountain lakes, such as Lake Baihua, which could change water-side convection and internal waves and thus accelerate gas exchange (Table 2). Previous studies have shown that in lakes with surface areas >1 km^2, 66–90% of CH_4 emissions originate from aerobic CH_4 production (Donis et al., 2017; Günthel et al., 2019). Therefore, CH_4 produced from aerobic methanogenesis constitutes a large contribution to the global CH_4 budget. Solar radiation can regulate CH_4 production from aerobic methanogenesis by enhancing primary productivity, and can influence CH_4 emissions by inhibiting CH_4 oxidation, and probably also by changing hydrodynamic conditions. Therefore, solar radiation should be taken into consideration as a key factor in driving CH_4 fluxes from lakes. As sampling time is limited, observations during both sunny and cloudy weather should be proportionally included, considering the large differences in CH_4 emission fluxes between sunny and cloudy weather. This is the first time, to the best of our knowledge, that solar radiation has been proposed as a key driver of CH_4 emissions from lakes.

4.2. The floating chamber method is more suitable for CH_4 emission flux observations than boundary layer models

The dependency of the gas transfer velocity on wind speed in Lake Baihua was not as strong as was expected, indicating that wind speed was not the main factor regulating gas transfer velocity in the lake. The gas transfer velocity (k) obtained using the floating chamber method had a weak linear relationship with wind speed at 10 m (U_{10}) ($r^2 = 0.26$, $p < 0.01$ Fig. 6a) indicating low predictive power. Further, if those data whose U_{10} is >1.22 m/s (corresponding to $U_1 = 1$ m/s, the most common wind speed at Lake Baihua) are excluded, the gas transfer velocity is completely independent of wind speed ($r^2 = 0.038$, $p > 0.05$, Fig. 6b). This means that for most of the observations, CH_4 emissions from the lake are not controlled by wind speeds. However, gas transfer velocity in the three most commonly used models (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; MacIntyre et al., 2010) is parameterized uniquely by wind speed. Therefore, it is likely that the wind speed-dependent boundary layer models are not suitable for small- and medium-sized lakes, where wind speeds are often small. In fact, this is in agreement with recent findings suggesting that in low-wind speed areas, gas transfer across the air-water interface is influenced not only by surface meteorology but also by physical processes such as penetrative convection, internal waves, and bubbles (Jessup et al., 1997; Tedford et al., 2014; Heiskanen et al., 2014). Although wind speed contributes to all these processes, implicitly integrating other drivers into the wind speed–based model is problematic, for the regulation modes and intensities may differ significantly (MacIntyre et al., 2009; Read et al., 2012; Tedford et al., 2014; Heiskanen et al., 2014). Therefore, accuracy needs to be improved by including factors other than wind speed when estimating gas transfer velocities (Tedford et al., 2014; Heiskanen et al., 2014).

Use of boundary layer models coupled with wind speed is not appropriate for CH_4 flux measurements in small and medium-sized lakes where wind speed is not the key factor controlling gas exchange at the interface. In Lake Baihua, CH_4 fluxes calculated by the boundary layer model were 2–10 times lower than those measured using the

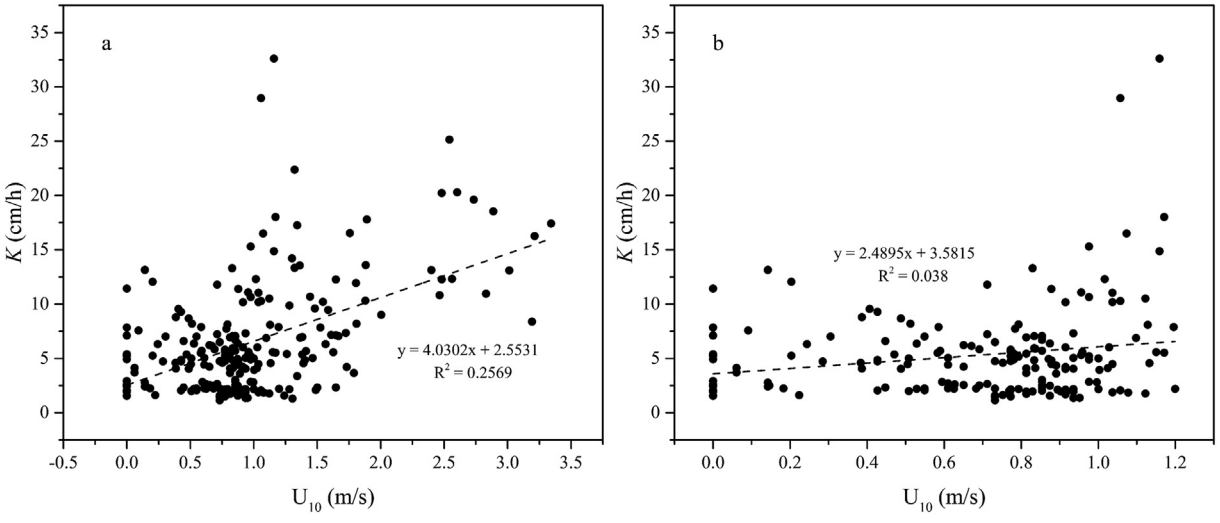

Fig. 6. Gas transfer velocity (k) are plotted *versus* wind speed at 10 m (U_{10}) in Lake Baihua (a for all samples, and b for the samples with U_{10} of less than 1.22 m/s).

floating chamber method (Table 1). This is consistent with previous studies, which showed that CH_4 fluxes estimated by boundary layer models generally were 1.3–30 times lower than those obtained using the floating chamber method (Duchemin et al., 1999; Ojala et al., 2011; Schubert et al., 2012; Erkkilä et al., 2018). The huge flux differences between the floating chamber and boundary layer models were previously believed to reflect chamber-induced turbulence, which may overestimate CH_4 fluxes (Kremer et al., 2003; Matthews et al., 2003). However, as described by Lorke et al. (2015), allowing the chamber to drift freely with the water masses, as done in this study, limits such disturbances. Notably, the chamber used in this study has 200 mm of skirt penetration into the water, which has been shown to be able to reduce chamber-induced turbulence (Matthews et al., 2003; Lorke et al., 2015). Thus, the difference between the two methods is due to the underestimation of fluxes by the boundary layer models. Previous studies have noted that if $u < 4.3$ (Schubert et al., 2012) or 5 m/s (MacIntyre et al., 2002), other factors rather than wind speed are dominant in air-water gas transfer (MacIntyre et al., 2002; Eugster et al., 2003). Like the findings of previous studies, the average wind speed at Lake Baihua was 0.77 m/s, and gas transfer velocity was not strongly correlated to wind speed (Fig. 6). Accordingly, the heavily wind speed-dependent boundary layer models likely led to erroneous results.

The relationship between CH_4 fluxes and CH_4 concentrations in surface waters or concentration difference across the boundary is also puzzling. It is unquestionable that CH_4 concentrations in surface waters or CH_4 concentration differences are important drivers of "diffusive" flux across the interface according to Eq. (1). Therefore, the CH_4 diffusive flux is assumed to be positively correlated to CH_4 concentrations or concentration differences. However, the measured CH_4 fluxes and CH_4 concentrations in surface waters were not correlated. Similar situations frequently appeared in previous studies (Bastviken et al., 2004; Bastviken et al., 2010; Jansen et al., 2020; Martinez-Cruz, 2020). This kind of phenomenon seems to contradict the theory of molecular diffusion (Eq. (1)). One explanation is that the measured flux contains "ebullition" emission. In fact, it is easy to identify the ebullition events, which usually lead to abrupt increases of CH_4 concentrations in the chamber headspace (Martinez-Cruz, 2020). In our experiment, those measurements that were not in conformity with linear regression ($R^2 < 0.9$) were excluded, thus the data did not contain ebullitive emissions. The CH_4 concentrations in surface waters are essentially controlled by a dynamic balance of several processes, including CH_4 production, CH_4 oxidation, CH_4 emission to the atmosphere, and CH_4 transport to the surface water from the deep waters/sediments. In view of CH_4 storage and residence time (Jansen et al., 2020), the irregular changes of CH_4 concentration (Figs. 3–5) is understandable. Some studies attempted to determine and further compare the rates of those processes and then to reveal the dynamics of CH_4 emission (West et al., 2015; Donis et al., 2017; Günthel et al., 2019). The study in Lake Hallwil, Switzerland, showed that although the CH_4 production rate in the surface mixed layer (110 ± 60 nmol/l/d) was much higher than in the thermocline (0.3 ± 3 nmol/l/d), CH_4 concentrations in the surface mixed layer (about 0.3–0.4 μmol/l) were lower than in the thermocline (0.4–0.75 μmol/l; Donis et al., 2017). Combined with the negligible surface CH_4 oxidation rate ($0.3–3.6 \pm 0.2$ nmol/l/d), the data fully demonstrated that the magnitude of surface CH_4 production was masked by the relatively rapid water-air exchange. The hysteretic pattern of fluxes and concentrations of CH_4 in the surface results from the combined influence of multiple processes, as shown in Figs. 3–5, and is common (Jansen et al., 2020). Sturtevant et al. (2016) used a combination of wavelet decomposition and information theory to address the cross-scale, asynchronous, and nonlinear response of CH_4 emission to the changes of different biological and environmental factors. This kind of phase lag and amplification may mask the true processes of gas exchange. Recently, several studies found that gas exchange at the air-water interface is more complex than previously thought (Cole et al., 2010; Schubert et al., 2012; Tedford et al., 2014; Podgrajsek et al., 2015; Rantakari et al., 2015; Erkkilä et al., 2018;). Further studies regarding gas exchange in relation to mass balance, considering physical, chemical, and biological processes at the air-water interface in much greater detail is necessary. The boundary layer model method needs to be improved in terms of both the gas transfer velocity model (Tang et al., 2016), and the mass balance model of CH_4 in the surface (Cole and Caraco, 1998). Before progress is made, we recommend using the floating chamber method to observe CH_4 emissions in small- and medium-sized lakes.

4.3. Optimal observation timing for methane emission

CH_4 emissions from lakes displays clear diurnal variations, thus requiring a distinctive sampling strategy. Considering the diel cycling of emission rates, Bastviken et al. (2010) recommend 24-h long measurements rather than short-term measurements. In Lake Baihua, the CH_4 fluxes tended to rise after sunrise, and to decrease after midday, with the maximum values appearing near midday and the minimum near midnight (Figs. 4 and 5). The highest daytime fluxes were 2.6–26 times higher than at night. Therefore, CH_4 fluxes obtained at a single time are subject to large errors when taken to represent the daily average value, which has been frequently mentioned in previous studies (Bastviken et al., 2010; Podgrajsek et al., 2014; Erkkilä et al., 2018).

It is hard to take 24-h or 48-h long measurements for many lakes. The simplest and most common method is to choose a narrow window in time during a day to capture average fluxes (Bansal et al., 2018). Therefore, we attempted to take a measurement at a specific time to represent the daily average value. Considering that the diurnal variations of CH_4 fluxes were likely controlled by solar radiation in Lake Baihua, we speculated that the mean flux observed at both sunrise and sunset could reflect the daily average value. The results showed that in sunny weather, the deviation between daily average flux and mean flux observed at sunrise and sunset is relatively large (range from 4.0–13.6%). In cloudy weather, the mean CH_4 fluxes obtained at sunrise and sunset were nearly equivalent to the daily average CH_4 flux (the deviation ranged from 0.8–3.3%; Table 3). Therefore, compared with a single observation, the average CH_4 flux observed at both sunrise and sunset could better represent the daily average value. In contrast, Bansal et al. (2018) found that midday samples captured average flux rates of CH_4 emission from wetlands and samples closer to sunrise or sunset better represented maximum or minimum. It should be noted that the conclusion drawn here might be generalizable only to small- and medium-sized lakes in middle and low latitudes, where sunshine

Table 3
Comparison of the daily average values and the mean methane fluxes obtained at both sunrise and sunset.

Month	Sites	Items	Values
January	Site 1	Mean flux obtained at sunrise and sunset	80.5 ± 3.8
		Daily average flux	79.0 ± 33.0
		Deviation	1.9%
	Site 2	Mean flux obtained at sunrise and sunset	64.5 ± 4.3
		Daily average flux	64.0 ± 18.1
		Deviation	0.8%
April	Site 1	Mean flux obtained at sunrise and sunset	213.4 ± 179.9
		Daily average flux	231.1 ± 187.3
		Deviation	7.7%
	Site 2	Mean flux obtained at sunrise and sunset	109.9 ± 53.0
		Daily average flux	106.4 ± 62.5
		Deviation	3.3%
July	Site 1	Mean flux obtained at sunrise and sunset	371.5 ± 246.4
		Daily average flux	357.1 ± 179.3
		Deviation	4.0%
	Site 2	Mean flux obtained at sunrise and sunset	153.2 ± 134.5
		Daily average flux	177.3 ± 118.6
		Deviation	13.6%

hours change little among seasons. In large lakes where wind speed is generally high, in high latitude lakes where sunshine hours vary greatly among seasons and under extreme weather conditions, such as heavy rain, the application of this conclusion requires further study when some factors other than solar radiation play dominant role in regulating CH_4 emission from lakes.

5. Conclusion

In Lake Baihua, there were CH_4 concentration peaks occurring in the subsurface corresponding to the peaks of chlorophyll concentration in the metalimnion during thermal stratification, indicating that aerobic methanogenesis contributed a large portion of CH_4 in the surface. The measured CH_4 emission fluxes using the floating chamber method showed marked diel patterns, with higher values during daytime and lower values at night on sunny days, while there were no clear diel patterns evident on cloudy days. Methane emission fluxes on sunny days were significantly higher than those on cloudy days. Solar radiation was assumed to be a primary factor driving CH_4 production and emissions, likely through enhancing primary productivity in relation to aerobic methanogenesis, inhibiting CH_4 oxidation, and probably changing hydrodynamics conditions. Thus, it is concluded that solar radiation should be taken in consideration as a key factor in observing CH_4 fluxes in lakes. As sampling time is limited, observations during both sunny and cloudy weather should be proportionally included.

The gas transfer velocity at the lake had weak dependency on wind speed, indicating that wind speed was not the main factor regulating CH_4 emission from the lake, which agrees with previous studies, revealing that in small wind speed areas, factors other than wind speed control gas exchange. Heavily wind speed-dependent boundary layer models strongly underestimated CH_4 fluxes, which were 2–10 times lower than measurements obtained using the floating chamber method. The boundary layer model methods are not suitable as is, and need to be modified for CH_4 flux measurements in small- and medium-sized lakes. We recommend using the floating chamber method instead for CH_4 emission flux observations before material progresses regarding gas exchanges models are made.

The marked diurnal variation of CH_4 emissions means that CH_4 flux observations are subject to large errors, as single measurements are commonly used to represent daily average values. We propose that averaging the observations obtained at both sunrise and sunset represents the daily average value, which has acceptable deviations between the measured flux and the daily average flux ranging from 0.8% to 13.6%. In sum, a comprehensive reconsideration, including inclusion of different weather conditions, employing suitable methods, and choosing appropriate sample timing would obtain data closer to the true fluxes of CH_4 from lakes, significantly improving observation accuracy.

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CRediT authorship contribution statement

This paper is authored by Di Tan, Qingguang Li, Shilu Wang, Kevin M. Yeager, Mingwei Guo, Kun liu, Yuchun Wang, all of whom are aware of its submission to *Science of The Total Environment*. S.W., Y. W and D.T. designed the study. D.T., M.G. and K.L. performed the experiments. D.T. and S.W. compiled the data and prepared the figures. D.T., S.W., Q.L. and K.M.Y. wrote the paper in consultation with other coauthors.

Declaration of competing interest

All authors declare that No conflict of interest exists.

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