Diffusive CH$_4$ fluxes from aquaculture ponds using floating chambers and thin boundary layer equations

Ping Yang$^{a,b,1}$, Jiafang Huang$^{a,b,1}$, Hong Yang$^{c,d,e,1}$, Josep Peñuelas$^{f,g}$, Kam W. Tang$^h$, Derrick Y.F. Lai$^i$*, Dongqi Wang$^j$, Qitao Xiao$^k$, Jordi Sardans$^{f,g,**}$, Yifei Zhang$^{a,b}$, Chuan Tong$^{a,b,**}$

$^a$Key Laboratory of Humid Subtropical Eco-geographical Process of Ministry of Education, Fujian Normal University, Fuzhou 350007, P.R. China
$^b$School of Geographical Sciences, Fujian Normal University, Fuzhou 350007, P.R. China
$^c$College of Environmental Science and Engineering, Fujian Normal University, Fuzhou 350007, P.R. China
$^d$Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China;
$^e$Department of Geography and Environmental Science, University of Reading, Reading RG6 6AB, U.K.
$^f$CSIC, Global Ecology Unit CREAF-CSIC-UAB, Bellaterra, Catalonia, Spain
$^g$CREAF, Cerdanyola del Vallès, Catalonia, Spain
$^h$Department of Biosciences, Swansea University, Swansea SA2 8PP, U.K.
$^i$Department of Geography and Resource Management, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China
$^j$School of Geographical Sciences, East China Normal University, Shanghai 200241, China
$^k$Key Laboratory of Watershed Geographic Sciences, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, 210008, China

*Correspondence to: Derrick Y.F. Lai
Email: dyflai@cuhk.edu.hk

*Correspondence to: Jordi Sardans
Email: j.sardans@creaf.uab.cat

**Correspondence to:** Chuan Tong

Email: tongch@fjnu.edu.cn

1Ping Yang, Jiafang Huang, and Hong Yang contributed equally to this work.
HIGHLIGHTS

- Aquaculture ponds emit CH$_4$
- Large variations in diffusive CH$_4$ fluxes are estimated by different thin boundary layer (TBL) models
- Methane fluxes measured by chambers and match those estimated by only some TBL models
ABSTRACT

Static floating chambers (FCs) are the conventional method to measure CH₄ fluxes across the water-air interface in ponds, while thin boundary layer (TBL) modelling is increasingly used to estimate CH₄ fluxes. In this study, both FCs measurements and TBL models of gas transfer velocity were used to determine CH₄ evasion from aquaculture ponds in southeastern China. The surface water CH₄ concentrations ranged from 0.4 to 9.1 µmol L⁻¹ with an average of 4.8±0.8 µmol L⁻¹. CH₄ flux was always positive, indicating the ponds as a persistent CH₄ source to air. Mean CH₄ flux based on different TBL models showed large variations, ranging between 19 and 316 µmol m⁻² h⁻¹. Compared against the direct measurement FCs, three TBL models developed for the open sea, flowing estuarine system and lentic ecosystem (TBLW92a, TBLRC01, and TBLCL98, respectively) overestimated CH₄ emission by 40-200%, while the wind tunnel-based TBL model (TBLLM86) underestimated CH₄ emission. Two TBL models developed for lakes (TBLW92b and TBLCW03) gave estimates similar to FCs.

Keywords: Methane fluxes; Thin boundary layer models; Floating chambers; Water-air interface; Shallow aquaculture pond; Subtropical estuary
1. Introduction

Methane (CH$_4$) emissions from inland and coastal aquatic systems are potentially significant sources of atmospheric CH$_4$ (Bastviken et al., 2011; Musenze et al., 2014; Yang et al., 2011). CH$_4$ release from open water can be via diffusion and/or ebullition (bubbling) (Bastviken et al., 2004). Diffusive fluxes across the water-air interface are usually determined by using static floating chambers (FCs) or thin boundary layer (TBL) models. The FCs approach determines CH$_4$ fluxes based on the change in CH$_4$ concentrations in the chamber headspace over time. The TBL approach calculates the CH$_4$ flux from piston velocity and gas concentration in the water (Natchimuthu et al., 2017; Zhao et al., 2019). Previous studies have used either one of the two approaches to quantify CH$_4$ fluxes from aquatic ecosystems (e.g., Musenze et al., 2014; Natchimuthu et al., 2016; Wang et al., 2017; Welti et al., 2017). However, detailed comparison of the two methods is rare (e.g., Duchemin et al., 1999; Matthews et al., 2003), particularly for small pond ecosystems.

Recent studies have shown that very small ponds (area <0.001 km$^2$) are hotspots for CH$_4$ emission (Holgerson, 2015; Holgerson and Raymond, 2016; Wik et al., 2016; Yuan et al., 2019). However, the scalability of these measurements are largely constrained by the lack of rigorous quantifications of the area, number, and spatial distribution of small ponds globally (Jonsson et al., 2008; Zhao et al., 2019) and the different flux measurement methods between studies. In particular, the lack of consensus on gas flux measurement methods remains a major source of uncertainty in greenhouse gas assessment. For instance, the $TBL_{LM86}$, $TBL_{Wan92a}$ and $TBL_{Wan92b}$,
The TBLRC01, TBLCL98, and TBLCW03 models, which were developed by Liss and Merlivatt (1986), Wanninkhof (1992), Raymond and Cole (2001), Cole and Caraco (1998), and Crusius and Wanninkhof (2003), respectively, are widely adopted wind-based models to estimate CH4 transfer velocities and fluxes. Among these TBL models, the TBLLM86, TBLWan92a, and TBLRC01 models were developed for wind tunnels, open sea, and flowing estuarine systems, respectively, while TBWan92b, TBLCL98 and TBLCW03 models were developed for the lentic ecosystem (e.g., lake). It is unclear to what extent these different models are transferable to other aquatic ecosystems (Musenze et al., 2014), and there is also a paucity of study comparing CH4 fluxes by the different approaches.

Aquaculture ponds are an important component of the global inland aquatic habitats (FAO, 2017), and the total surface area of freshwater and brackish aquaculture ponds is estimated to be around 110,000 km² (Verdegem and Bosma, 2009). Despite the importance of aquaculture ponds for CH4 emission (Hu et al., 2016; Wu et al., 2018; Yang et al., 2015, 2019a; Yuan et al., 2019), relevant CH4 flux data are disproportionately scarce, and the published results were predominantly determined by FCs rather than TBL modelling (Hu et al., 2016; Wu et al., 2018; Yang et al., 2015, 2019a). In this study, FCs and TBL models were used to compare CH4 fluxes in aquaculture ponds in southeastern China. The aims were: (1) to evaluate the performances of different wind-based TBL models for estimating CH4 fluxes; (2) to compare the diffusive CH4 emissions from aquaculture ponds derived from FCs measurements and TBL modelings; and (3) to assess which TBL model(s) can be used
to replace FCs for estimating CH$_4$ fluxes from ponds, with acceptable validity.

2. Materials and Methods

2.1. Study area

Our study sites are located at the central-western Shanyutan Wetlands in the Min River Estuary (MRE) in southeastern China (Figure S1, 26°00′36″–26°03′42″ N, 119°34′12″–119°40′40″ E). This area is characterized by a subtropical monsoon climate, with a multi-year annual average temperature and precipitation of 19.6 °C and 1,350 mm, respectively (Tong et al., 2010). The wetlands are dominated by a semidiurnal tide with a large tidal range (2.5-6 m) that follows a spring-neap-spring tidal cycle (Luo et al., 2014; Tong et al., 2010). The dominant vegetation are the native *Cyperus malaccensis* and *Phragmites australis*, and the invasive *Spartina alterniflora*. Over the past 10 years, much of area has been converted to aquacultural ponds (Yang et al., 2017a).

2.2. Aquaculture pond management

Small and shallow aquaculture earthen ponds (area of 0.8–2.5 ha and depth of 1.1–1.8 m) are a key feature in the MRE, covering a total area of around 234 ha in the Shanyutan Wetland (Yang et al., 2017b). Semi-intensive production is concentrated between June and November, which yields a single annual crop of shrimps. The ponds are filled with brackish water (average salinity of 2.0–8.5‰) from the MRE. The shrimps are fed twice daily (at 07:00 and 16:00 hr) with commercial aquatic feed pellets containing 42% protein. Three to five paddlewheel aerators operate four times
a day (07:00–09:00, 12:00–14:00, 18:00–20:00, and 00:00–03:00 hr) to provide oxygen. For this study, three ponds separated by <10 m (see Table S1 for basic characteristics) (Zhang et al., 2019) were selected for the measurements. Additional details about the shrimp pond system and management can be found in Yang et al. (2017b).

2.3. Determination of dissolved CH$_4$ concentration

Field campaigns were carried out at the three ponds between June and November 2017 following the main aquaculture operation. In each pond, water and gas samples were collected at three sites along a foot-bridge that extended ~10 m from the embankment to the pond center. Samples were collected two or three times each month in each pond for a total of 15 times. The total number of samples was 3 ponds $\times$ 3 sites $\times$ 15 times = 135. To measure the dissolved CH$_4$ concentrations, surface water (at a depth of ~20 cm) was collected by a homemade water sampler and transferred into 55-mL gas-tight glass serum bottles that had been flushed with pond water 2-3 times. A 0.2 mL aliquot of saturated HgCl$_2$ solution was added to each bottle to inhibit bacterial activity of water sample (Borges et al., 2018; Hu et al., 2018), and the bottle was immediately sealed with a butyl rubber stopper and an aluminum screw cap to exclude air bubbles. Sample bottles were transported back to the laboratory in an ice-packed cooler. Dissolved CH$_4$ concentrations were measured within 2 d of collection using the headspace equilibration method: Approximately 25 mL of water in each bottle was displaced by N$_2$ gas (>99.999% purity) to create headspace. The bottle was then shaken vigorously for 20 min and left at room
temperature for 30 min to attain equilibrium between the air and the water phases (Cotovicz et al., 2016). Afterward, approximately 10 mL of the headspace was extracted and injected into a gas chromatograph (GC-2010, Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) to determine the CH$_4$ concentration. Standard CH$_4$ gas (at 2, 8, 500, 1000, and 10,000 ppm) was used to calibrate the FID. Dissolved CH$_4$ concentration was calculated based on the volume of water, headspace air and gas solubility coefficient for the specific water temperature and salinity (Farías et al., 2017; Wanninkhof, 1992; Xiao et al., 2017).

2.4. Determination of diffusive CH$_4$ flux across the water-air interface

2.4.1. Measurement using floating chambers

This study used a modified chamber placed on a floating buoy (Figure S2). The opaque floating chamber was made from inverted plastic basin (polyethylene/plexiglas®) with a volume and area of 5.2 L and 0.1 m$^2$, respectively. The chamber was covered with aluminum tape to minimize internal heating by sunlight (Natchimuthu et al., 2016; Yang et al., 2019). A thin gauze (pore diameter 0.001 mm) covering the opening minimized the entry of bubbles into the chamber (Figure S2). A fan inside the chamber mixed the headspace air during the sampling. In order to quantify the potential contribution of CH$_4$ ebullition flux from the ponds, total CH$_4$ fluxes were also determined using floating chamber without gauze.

The chamber was deployed for a period of 45 min and headspace air samples being extracted at 15-min intervals (0, 15, 30, 45 min) using 60-mL syringes equipped
with three-way stopcocks. The gas samples were immediately transferred into pre-evacuated airtight gas sampling bags (Dalian Delin Gas Packing Co., Ltd., China), transported to the laboratory, and analyzed within 48 h using a gas chromatograph (GC-2010, Shimadzu, Kyoto, Japan) equipped with a FID, following the method of Tong et al. (2010). The detection limit for CH$_4$ was 0.3 ppm, and the relative standard deviations of the measurements were ≤ 2.0% in 24 h.

CH$_4$ emission flux ($F_{CH4}$, µmol m$^{-2}$ hr$^{-1}$) was calculated from the slope of the regression between headspace CH$_4$ concentration and time (Yang et al., 2019). Generally, if $r^2$ of the regression is > 0.90, the CH$_4$ emission is considered as diffusion only (Bastviken et al., 2010; Zhu et al., 2016). If $r^2$ is < 0.90, the emission is considered as a combination of ebullition and diffusion. The floating chambers with gauze (FCs-G) and without gauze (FCs-NG) showed distinctly linear ($r^2$>0.9) and nonlinear ($r^2$<0.9) increases in methane concentration, respectively; therefore, the contribution of ebullition could be calculated as the difference between the FCs-G and the FCs-NG measurements.

2.4.2. Estimation using thin boundary layer models

Saturation ($S$) of CH$_4$ in pond water was calculated as (Hu et al., 2018):

$$S = \frac{C_{\text{water}}}{C_{Ws}} = \frac{C_{\text{water}}}{(\alpha \times C_{\text{air}})} \times 100\%$$  \hspace{1cm} (Eq. 1)

where $C_{\text{water}}$ is dissolved CH$_4$ concentration in pond water; $C_{Ws}$ is the saturated CH$_4$ concentration (µmol L$^{-1}$); $C_{\text{air}}$ is the atmospheric CH$_4$ concentration (µmol mol$^{-1}$) at the sampling site; and $\alpha$ is the Bunsen coefficient (Wanninkhof, 1992).

Diffusive flux of CH$_4$ ($F$, µmol m$^{-2}$ hr$^{-1}$) across the water-air interface can be
described by a theoretical diffusion model (Musenze et al., 2014):

\[ F = k \times (C_{\text{water}} - C_{eq}) \]  
(Eq. 2)

where \( C_{\text{water}} \) (µmol L\(^{-1}\)) is the measured dissolved CH\(_4\) concentration in surface water, \( C_{eq} \) (µmol L\(^{-1}\)) is the dissolved CH\(_4\) concentration in equilibrium with the air above, and \( k \) is the gas transfer velocity (cm h\(^{-1}\)). The \( k \) value was parameterized as a function of wind speed and normalized for surface water temperature (\( T, ^\circ\text{C} \)) using a Schmidt number (\( Sc \)) derived from Eq. 3 (Wanninkhof, 1992):

\[ Sc = 2039.20 - 120.31T + 3.4209T^2 - 0.040437T^3 \]  
(Eq. 3)

This study evaluated the variations in CH\(_4\) fluxes estimated by eight widely used wind-based models developed for different environments, including wind tunnels, open sea, estuarine systems and lakes, as follows:

LM86 (Liss and Merlivatt 1986)

\[ F_{LM86} = 0.17U_{10} (Sc / 600)^{-2/3} (C_{\text{water}} - C_{eq}) \quad 0 < U_{10} \leq 3.6 \]  
(Eq. 4)

\[ F_{LM86} = (2.85U_{10} - 9.65)(Sc / 600)^{-1/2} (C_{\text{water}} - C_{eq}) \quad 3.6 < U_{10} \leq 13 \]  
(Eq. 5)

W92a (Wanninkhof, 1992)

\[ F_{W92a} = 0.31U_{10}^2 (Sc / 660)^{-1/2} (C_{\text{water}} - C_{eq}) \]  
(Eq. 6)

RC01 (Raymond and Cole, 2001)

\[ F_{RC01} = 1.91 \exp(0.35U_{10})(Sc / 600)^{-1/2} (C_{\text{water}} - C_{eq}) \]  
(Eq. 7)

CL98 (Cole & Caraco, 1998)
\[ F_{CLE} = \left[ 2.07 + (0.215 \times U_{10}^{-1.7}) \right] (\text{Sc} / 600)^{2/3} (C_{\text{water}} - C_{\text{eq}}) \]  
(Eq. 8)

W92b (Wanninkhof, 1992)

\[ F_{W92b} = 0.45U_{10}^{1.64}(\text{Sc} / 600)^{-1/2} (C_{\text{water}} - C_{\text{eq}}) \]  
(Eq. 9)

CW03 (Crusius & Wanninkhof, 2003)

\[ F_{CW03} = 0.72U_{10} (\text{Sc} / 600)^{2/3} (C_{\text{water}} - C_{\text{eq}}) \quad U_{10} < 3.7 \]  
(Eq. 10)

\[ F_{CW03} = (4.33U_{10} - 13.3)(\text{Sc} / 600)^{1/2} (C_{\text{water}} - C_{\text{eq}}) \quad U_{10} \geq 3.7 \]  
(Eq. 11)

In the above equations, \( U_{10} \) was determined according to the logarithmic wind profile relationship (Crusius and Wanninkhof, 2003):

\[ U_{10} = U_z \left[ 1 + \left( \frac{C_{d10}}{K} \ln \left( \frac{10}{z} \right) \right) \right] \]  
(Eq. 12)

where \( U_z \) is the wind speed (m s\(^{-1}\)) at height \( z \) above the water surface (2.5 m in this study), \( C_{d10} \) is the drag coefficient at 10 m above the water surface (0.0013 m s\(^{-1}\)), and \( K \) is the von Karman constant (0.41). Generally, the calculation of \( U_{10} \) is sensitive to the stability of the atmosphere. If the atmosphere over the aquatic systems is unstable, and the equation used to calculate \( U_{10} \) needs to be adjusted. The air-water temperature difference can be used to determine the atmospheric stability; if the air-water temperature difference is positive, the atmosphere is considered stable. During the study period, the air temperature was 0.1-3.8 °C higher than water temperature, indicating that the atmosphere over the ponds was largely in the stability regime. Therefore, no adjustment was needed for \( U_{10} \), and Eq. 12 was appropriate for calculating \( U_{10} \). Some recent studies have applied surface renewal models that take
into account both wind speed and buoyancy to determine the \( k \) values (e.g., Czikowsky et al., 2018; MacIntyre et al., 2010; MacIntyre et al., 2018).

2.5. Measurement of meteorological and environmental variables

Meteorological variables including air temperature \((A_T)\), air pressure \((A_P)\) and precipitation were recorded using an automatic meteorological station (Vantage Pro 2, China) installed at the MRE weather station in the China Wetland Ecosystem Research Network. The distance between the automatic meteorological station and sampling ponds is about 75 m. The precision for air temperature, atmospheric pressure, and precipitation were ± 0.2 °C, ± 1.5 hPa, and ± 0.4 mm min\(^{-1}\), respectively (Yang et al., 2020). Wind speed \((W_S)\) was measured at 1 Hz at a resolution of 0.4 m s\(^{-1}\).

Water temperature, electrical conductivity (EC), pH, dissolved oxygen (DO), total organic carbon (TOC) and total dissolved nitrogen (TDN) content of surface water (~20 cm below the water surface) were measured at each sampling site in all sampling campaigns. Water temperature and pH were measured by a portable pH/mV/Temperature meter (IQ150, IQ Scientific Instruments, USA), and EC and DO by an electrical conductivity meter (2265FS EC, Spectrum Technologies, USA) and a multiparameter water quality probe (550A YSI, USA), respectively. The relative standard deviations of EC, pH, and DO measurements were ≤1.0%, ≤1.0% and ≤2.0%, respectively.

Water samples for TOC and TDN analyses were collected using a 5-L plexiglass
water sampler, transferred to a 150-mL polyethylene bottle, and then transported to the laboratory in an ice-packed cooler. The water samples were filtered through a 0.45-μm cellulose acetate filter (Biotrans nylon membranes); the filtrates were then analysed by a TOC analyzer (TOC-VCPH/CPN, Shimadzu, Kyoto, Japan) for TOC and a flow injection analyzer (Skalar Analytical SAN++, The Netherlands) for NO$_3^-$-N. The detection limits for NO$_3^-$-N and TOC were 6 μg L$^{-1}$ and 4 μg L$^{-1}$, respectively. The relative standard deviations of NO$_3^-$-N and TOC measurements were $\leq 3.0\%$ and $\leq 1.0\%$, respectively.

2.6. Statistical analysis

Repeated-measures analysis of variance (RM-ANOVA) was conducted to test the differences in diffusive CH$_4$ flux between the different approaches over the study period. Pearson correlation analysis was used to examine the relationships between (1) dissolved CH$_4$ concentration or CH$_4$ fluxes and environmental variables, and (2) diffusive CH$_4$ fluxes measured using FCs and those estimated using the TBL models. The coefficient of variation (CV) for CH$_4$ fluxes on each sampling campaign was determined by dividing the standard deviation by the mean value. Statistical analyses were conducted using the software SPSS (v. 17.0, SPSS Inc., USA) and the significance level was set at $p < 0.05$. Data are presented as mean ± 1 standard error.

Generalized linear modelling was conducted to compare the variables that influenced CH$_4$ emission flux from the different methods (i.e. FCs + 8 TBL models). The “gls” function from the “nlme” R package (Pinheiro et al., 2018) with a saturated
model was conducted for all variables (dissolved CH₄, U₁₀, water temperature, dissolved oxygen, total dissolved carbon and dissolved nitrate). This model was run using the stepAIC function in R “MASS” package that follows the Akaike Information Criterion (AIC) (Venables and Ripley, 2002). It was used to identify the best model (lowest AIC value) in each case.

3. Results

3.1. Meteorological and environmental variables

The average air temperature (A_T) and air pressure (A_P) during the study were 28.7±0.4 °C (range: 18.6−35.6 °C) and 1010.0±0.5 hPa (range: 985−1025 hPa), respectively. Notably, the maximal A_T appeared in July and the minimal A_P happened in August, different from the other months. W_S ranged from 0.2 to 18.8 m s⁻¹, and it varied between seasons, with a peak in July (Figure S3a). Approximately 92% of W_S fell within the range of 0.2−4.0 m s⁻¹ (Figure S3b).

There were temporal variations in surface water characteristics during the study period. The mean water temperature ranged from 18.1 °C (November) to 34.4 °C (August) (Figure S4a), while the mean DO concentration varied between 9.4 mg L⁻¹ (August) and 19.9 mg L⁻¹ (November) (Figure S4). The mean TOC concentration varied between 9.9 mg L⁻¹ (July) and 57.3 mg L⁻¹ (November) (Figure S3), while NO₃⁻N concentrations ranged from 504 µg N L⁻¹ (June) to 10.7 µg N L⁻¹ (November) (Figure S4).

3.2. Model estimated k values and dissolved CH₄ concentrations
The mean $k$ value showed considerable variations between models: $k_{RC01} (6.5±0.8 \text{ cm h}^{-1}) > k_{W92a} (3.5±0.7 \text{ cm h}^{-1}) > k_{FCa} (3.2±0.4 \text{ cm h}^{-1}) > k_{CL98} (2.9±0.3 \text{ cm h}^{-1}) > k_{CW03} (2.5±0.5 \text{ cm h}^{-1}) > k_{W92b} (2.4±0.4 \text{ cm h}^{-1}) > k_{LM86} (0.6±0.1 \text{ cm h}^{-1})$ (Figure 1).

Dissolved CH$_4$ concentration varied considerably during the study period (0.1−31.1 µmol L$^{-1}$), with a large increase between June and August, followed by a small decrease toward November (Figure 2). The water was supersaturated in CH$_4$ in all ponds and on all sampling dates, with an overall mean of $4.8 ± 0.8 \text{ µmol L}^{-1}$ (162.0 ±18.4 ppmv), equivalent to 8700% saturation (range of $200 – 5.9×10^4$ % saturation).

### 3.4. CH$_4$ flux estimates by using TBL models and FCs method

There were considerable differences in the estimated diffusive CH$_4$ fluxes among the TBL models ($TBL_{RC01}$: 215.9 ±39.2 µmol m$^{-2}$ h$^{-1}$; $TBL_{CL98}$: 115.0 ±21.9 µmol m$^{-2}$ h$^{-1}$; $TBL_{W92a}$: 102.9 ±19.5 µmol m$^{-2}$ h$^{-1}$; $TBL_{W92b}$: 78.3 ±13.9 µmol m$^{-2}$ h$^{-1}$; $TBL_{CW03}$: 74.9 ±13.2 µmol m$^{-2}$ h$^{-1}$; and, $TBL_{LM86}$: 19.5 ±3.7 µmol m$^{-2}$ h$^{-1}$) (Table 1, Figure 3 and Figure S5). Although there were marked variations in the flux estimates among the various models, results from all models showed similar temporal patterns (Figure 3). The largest fluxes were generally recorded between August and October, while the lowest fluxes were consistently recorded in June and November (Figure 3).

Direct measurements using FCs with gauze (FCs-G) and without gauze (FCs-NG) methods were 75.0 ±12.5 (Figure 3) and 2231.3 ±681.3 µmol m$^{-2}$ h$^{-1}$ (Figure S6; Yang et al., unpublished data), showing significant difference between the
two methods (Independent Samples T-Test, $F = 118.190$, $p<0.001$). On average, ebullitive CH$_4$ flux accounted for 33%-99% of the total CH$_4$ emissions during the study period.

### 3.5. Environmental influences on dissolved CH$_4$ concentrations and fluxes

Pearson correlation analysis showed that dissolved CH$_4$ concentration was positively correlated with air temperature and TOC ($p<0.01$), and negatively with NO$_3^-$-N and EC ($p<0.01$) (Table 2). CH$_4$ flux was positively correlated with air temperature ($p<0.05$), TOC and dissolved CH$_4$ concentration ($p<0.01$), and negatively with NO$_3^-$-N ($p<0.01$) and EC ($p<0.05$) (Table 2 and Table S3). Environmental variables explained a larger proportion of variability in CH$_4$ flux derived from the TBL models ($R^2=0.46-0.54$) than those from direct FCs measurements ($R^2=0.35$) (Table S2).

### 4. Discussion

#### 4.1. CH$_4$ supersaturation and degassing from aquaculture ponds

There are very few studies on CH$_4$ in small ponds, particularly, those created for aquaculture purposes. In this study, the dissolved CH$_4$ concentration in surface water of the aquaculture ponds ranged from 0.1 to 31.1 µmol L$^{-1}$ during the study period, which was higher than that observed in many small ponds in Florida (~2.2 µmol L$^{-1}$; Barber et al., 1988), Colorado (~1.0 µmol L$^{-1}$; Bastviken et al., 2004), Wisconsin and Minnesota (0.3−2.3 µmol L$^{-1}$; Smith and Lewis, 1992) in the USA, in Sweden (~1.3 µmol L$^{-1}$; Natchimuthu et al., 2014), Canada (0.5−6.7 µmol L$^{-1}$; Pelletier et al., 2014),
and Siberia (~2.6 µmol L\(^{-1}\); Repo et al., 2007). In addition, CH\(_4\) concentration in our aquaculture ponds was generally larger than that in some nutrient-enriched rivers in China, i.e. Lixiahe River (0.2–0.8 µmol L\(^{-1}\); Wu et al., 2019), Beitang Drainage River and Dagu Drainage River (0.3–1.7 µmol L\(^{-1}\); Hu et al., 2018). Similar to other inland aquatic systems, such as lakes (e.g., Wen et al., 2016; Wik et al., 2016; Yan et al., 2018), reservoirs (e.g., Deemer et al., 2016; Musenze et al., 2014; Wang et al., 2017), rivers (e.g., Barbosa et al., 2016; Striegl et al., 2012), floodplains (Barbosa et al., 2020) and small ponds (e.g., Holgerson and Raymond, 2016; Wik et al., 2016), our aquaculture ponds were vastly supersaturated in CH\(_4\) relative to air (2.71–599.81 times the equilibrium concentration) (Figure 2b). The small temperate ponds in the Yale Myers Forest in Connecticut, the USA, have some of the highest concentrations of CH\(_4\) (21.0–58.9 µmol L\(^{-1}\), equivalent to 119–2907 times the equilibrium concentration) (Holgerson, 2015). The CH\(_4\) concentrations and supersaturation levels in our aquaculture ponds fall well within the range reported by Holgerson (2015), showing that aquaculture ponds in the subtropical estuaries are also hotspots for CH\(_4\) production and emission.

In inland aquatic ecosystems, the strong CH\(_4\) release is likely a result of large organic matter inputs from the catchment, algae and aquatic plants that sustain high methanogenesis rates (Finlay et al., 2009; Lundin et al., 2013; Venkiteswaram et al., 2013; Yan et al., 2018), as indicated by the significant relationship between dissolved CH\(_4\) and nutrient level (Huttunen et al., 2003; Kortelainen et al., 2001; Wen et al., 2016). The shrimp ponds in this study are semi-artificial ecosystems that are
maintained through a daily feed supply for the production of aquatic animals.

However, only a small portion of the feed input is converted into shrimp biomass, with the feed utilization efficiency of $\sim 4.0\text{--}27.4\%$ (Chen et al., 2016; Molnar et al., 2013; Yang et al., 2017b). Surface sediments in the aquaculture systems typically retain a large amount of organic matter from feces and residual feeds (Chen et al., 2016; Yang et al., 2017b) that can support high levels of CH$_4$ production and its subsequent release to atmosphere. Although organic matter content was not quantified in this study, our results confirmed the significantly correlation between dissolved CH$_4$ and TOC concentration ($p<0.01$; Table 2), which lends support to the notion that CH$_4$ supersaturation in the aquaculture ponds was related to the large input of organic matter.

### 4.2. Comparison of different TBL modelled CH$_4$ fluxes

Although previous studies have compared the performance of different TBL models in estimating diffusive CH$_4$ flux in inland waters (Amouroux et al., 2002; Li et al., 2015; Musenze et al., 2014; Xiao et al., 2017; Zappa et al., 2007), such comparison is scarce for shallow ponds, particularly aquaculture ponds. To the best of our knowledge, this study is the first attempt to compare the estimates of diffusive CH$_4$ flux using different TBL models over the whole aquaculture period in aquaculture ponds. Interestingly, although the patterns of temporal variations in diffusive CH$_4$ flux were largely consistent among the TBL models (Figure 3), there were clear differences in the magnitude of flux estimated from the different models (Table 1).
Notably, the mean flux estimated by the $TBL_{RC01}$ model (215.6 µmol m$^{-2}$ h$^{-1}$) was an order of magnitude greater than that derived from the $TBL_{LM86}$ model (19.4 µmol m$^{-2}$ h$^{-1}$, Figure 3). Moreover, CH$_4$ flux estimated by the $TBL_{RC01}$ model was 2 - 3 times larger than that by the $TBL_{W92a}$, $TBL_{CL98}$, $TBL_{W92b}$ and $TBL_{CW03}$ models (Table 1 and Figure S5). However, there was no significant difference between the $TBL_{W92a}$ and $TBL_{CL98}$ models ($p$>0.05; Table 1 and Figure S5) or between the $TBL_{W92b}$ and $TBL_{CW03}$ models ($p$>0.05; Table 1 and Figure S5). In other inland waters (river and reservoirs), Gao et al. (2014) and Musenze et al. (2014) also found that the estimated diffusive CH$_4$ fluxes derived from the $TBL_{RC01}$ model were substantially greater than those from other $TBL$ models.

The differences in the estimated CH$_4$ flux between different $TBL$ models were likely a result of different weighting of wind as a driver of gas transfer velocity (Musenze et al., 2014, Figure 1). Because these wind-based models were originally developed for specific environments under different conditions (Gao et al., 2014; Musenze et al., 2014), their suitability for other situations could be questioned (Bade, 2009; Musenze et al., 2014; Schilder et al., 2013). The $TBL_{CL98}$ and $TBL_{CW03}$ models were developed for lentic ecosystems under a range of wind speed, which most closely resemble aquaculture pond conditions. One may therefore argue that these two models would be most applicable to aquaculture ponds, although more in situ measurement will be needed to further increase the accuracy of the estimate.

4.3. Comparison of CH$_4$ fluxes derived from FCs measurement and TBL models

Previous studies have shown that CH$_4$ fluxes estimated by $TBL$ models tend to be
lower than those measured by FCs (Chuang et al., 2017; Duchemin et al., 1999; Li et al., 2015; Matthews et al., 2003). This study also compared CH₄ fluxes measured by 
FCs and those estimated by TBL models over the aquaculture season (Table 1 and Figure S5). Although there were significant correlations between TBL model estimates 
and FCs measurements ($p < 0.05$ in all cases), the agreement between the two 
methods varied considerably between models (Figure 4). The $TBL_{W92b}$ and $TBL_{CW03}$ 
modes gave the largest $r^2$ values (0.82 and 0.83, respectively) and good agreements 
with FCs measurements (slope = 0.92 and 0.89, respectively), whereas $TBL_{CL98}$ 
yielded mean estimates virtually identical to FCs measurements (slope = 1) but with 
larger variability around the mean ($r^2 = 0.53$) (Figures 4d-f). In contrast, $TBL_{LM86}$ 
vastly underestimated FCs fluxes whereas $TBL_{RC01}$ grossly overestimated FCs fluxes 
(Figures 4a,b). Approximately 80% of the diffusive CH₄ fluxes estimated by the 
models fell within the range measured by the FC method.

Balancing the consideration of overall agreement (regression slope) and estimate 
variability (regression $r^2$), the $TBL_{W92b}$ and $TBL_{CW03}$ models appeared to give the best 
approximations of FCs measurements. While previous studies showed that FCs were 
more appropriate for determining greenhouse gas fluxes in heterogeneous 
environments such as lakes and reservoirs (Cole et al., 2010; Duchemin et al., 1999; 
Murray et al., 2015; Vachon et al., 2010; Wu et al., 2018), our results suggest that 
$TBL_{W92b}$ and $TBL_{CW03}$ models are reliable alternatives for estimating CH₄ diffusive 
flux in shallow aquaculture ponds.

In addition to diffusive flux from the water column, bottom sediment could also
contribute to CH$_4$ emission via ebullition, especially in eutrophic, shallow aquaculture ponds. This is illustrated by the differences in the measured CH$_4$ flux using FCs with and without gauze in our aquaculture ponds (Figure S6). The CH$_4$ flux measured by FCs without gauze ($2231.3 \pm 681.3$ µmol m$^{-2}$ h$^{-1}$) were one to two orders of magnitude higher than that by FCs with gauze ($75.0 \pm 12.5$ µmol m$^{-2}$ h$^{-1}$) (Figure S6); from this ebullition was estimate to contribute 96.6% to the total CH$_4$ emissions. Overall, our results showed that ebullition was the primary path of CH$_4$ emission in aquaculture ponds, and that ebullitive flux vs. diffusive flux could be easily resolved with a simple design of FCs with a detachable gauze.

4.4. Implications of the comparison between different methods

The FCs method is the popular technique for measuring CH$_4$ emissions due to its ability to detect low fluxes and the simplicity of its operating principle (Bastviken et al., 2015; Lorke et al., 2015; Musenze et al., 2014; Podgrajsek et al., 2014). However, the FCs method requires time-consuming manual operation, which limits the frequency of measurements and can be difficult to deploy in remote areas (Acosta et al., 2017; Morin et al., 2017). Improvement of the global CH$_4$ budget would require high-resolution emission data covering large time and spatial scales, which obviously is difficult to achieve with the FCs method.

Large-scale estimates of aquatic CH$_4$ emissions using TBL models has been gaining popularity (Holgerson and Raymond, 2016; Martinez-Cruz et al., 2016; Musenze et al., 2014; Wang et al., 2017) due to their simplicity, practicality and low cost. There are, however, different TBL models to choose from, and the large
differences in the model performances (Figure 4) mean that selecting the appropriate model(s) would be critical, or otherwise large errors would occur when upscaling the results from small ponds to the regional/global scale. Our results suggest that $TBL_{W92b}$ and $TBL_{CW03}$ models could be used as effective and convenient alternatives to $FCs$ in shallow aquaculture ponds.

4.5. Limitation and future research

The $FCs$ method is a common method to measure CH$_4$ fluxes from aquatic ecosystems. However, $FCs$ may create microenvironments that affect the boundary layer conditions through, for instance, blockage of wind, change of atmospheric pressure at the measurement point, and change in the gas transfer rate through pressure build-up (Duchemin et al., 1999; Matthews et al., 2003; Musenze et al., 2014). For example, the turbulence resulted from the chamber walls can enhance the efficiency of gas exchange and increase gas fluxes during low wind conditions (Matthews et al., 2003; Xiao et al., 2016).

$TBL$ models rely on the gas transfer velocity coefficient ($k_x$), which itself is estimated from some empirical wind-based models. Effects of artificial aeration, which is commonly done in aquaculture ponds, on $k_x$ are unknown. More importantly, the $TBL$ models ignore the effect of buoyancy fluxes near the air-water interface on $k_x$. An alternative is the surface renewal model (SRM), which considers both wind speed and buoyancy (e.g., Czikowsky et al., 2018; MacIntyre et al., 2010; MacIntyre et al., 2018).

The use of eddy covariance (EC) technique is increasingly popular as it can
provide a better characterization of the variation in CH$_4$ fluxes through quasi-continuous measurements (Acosta et al., 2017; Morin et al., 2017; Xiao et al., 2014; Zhao et al., 2019). However, its application in small water bodies (e.g., ponds) is limited by footprint contamination (Zhao et al., 2019). Developing a practical and effective way to reduce the flux footprint and the contamination from gaseous sources outside the water body will allow broader application of EC method in the future.

Different methods have their own limitations; careful comparison and cross calibration would be needed to increase the overall accuracy of these methods and to improve the global CH$_4$ budget.

5. Conclusions

Despite the large CH$_4$ emission potential from small ponds, there are few studies comparing the different methods to estimate CH$_4$ fluxes across the water-air interface. In this study, FCs and TBL models were used to estimate CH$_4$ fluxes from aquaculture ponds. Our results indicate that dissolved CH$_4$ concentrations in the subtropical shallow aquaculture ponds were on average ~87 times oversaturated relative to the ambient air, and thus the ponds acted as strong atmospheric CH$_4$ sources. The high organic matter loading contributed to CH$_4$ supersaturation in the ponds. This study for the first time compared the CH$_4$ fluxes measured directly by floating chambers (FCs) and those estimated by thin boundary layer (TBL) models ($TBL_{LM86}$, $TBL_{W92a}$, $TBL_{RC01}$, $TBL_{CL98}$, $TBL_{W92b}$, and $TBL_{CW03}$). The model estimates of diffusive CH$_4$ fluxes were highly variable, and were overall 27 - 300% larger than those measured by FCs. The $TBL_{W92b}$ and $TBL_{CW03}$ models provided a robust and simple alternative to FCs in
estimating diffusive CH$_4$ fluxes. Our results suggest that the comparison of different
methods and selection of the most appropriate method(s) should be a high research
priority to improve the accuracy of greenhouse gas fluxes from aquaculture ponds and
other aquatic ecosystems.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or
personal relationships that could have appeared to influence the work reported in this
paper.

**Acknowledgments**

This research was financially supported by the National Science Foundation of China (grant
numbers 41801070 and 41671088), National Key Research & Development Plan "Strategic
International Scientific and Technological Innovation Cooperation" (2016YFE0202100), Council
of the Hong Kong Special Administrative Region, China (CUHK458913 and CUHK Direct Grant
SS15481), Spanish Government (grant CGL2016-79835), Catalan Government (grant SGR
2017-1005), European Research Council (Synergy grant ERC-SyG-2013-610028), Open Research
Fund Program of Jiangsu Key Laboratory of Atmospheric Environment Monitoring & Pollution
Control (grant KHK1806), Priority Academic Program Development of Jiangsu Higher Education
Institutions (PAPD), and Minjiang Scholar Programme. We thank Qianqian Guo, Guanghui Zhao,
and Ling Li of the School of Geographical Sciences, Fujian Normal University, for assistance in
the field.

**References**


Borges, A.V., Speeckaert, G., Champenois, W., Scranton, M.I., Gypens, N., 2018. Productivity and temperature as drivers of seasonal and spatial variations of dissolved methane in the Southern...
Bight of the North Sea. Ecosystems 21(4), 583-599. https://doi.org/10.1007/s10021-017-0171-7


northern lakes and ponds are critical components of methane release. Nat. Geosci. 9(2), 99.


Figure 1. Temporal variation in CH$_4$ transfer velocities from the aquaculture ponds during the aquaculture period in the Min River Estuary. Values represent the means of nine replicates samples, while the vertical lines indicate standard errors.
Figure 2. Temporal variation in (a) CH$_4$ concentration and (b) CH$_4$ saturation in the surface water (20 cm depth) of the aquaculture ponds in the Min River Estuary during the aquaculture period. Values represent the means of nine replicates samples, while the vertical lines indicate standard errors.
Figure 3. Temporal variation in CH$_4$ diffusive fluxes measured with the floating chamber method and the gas transfer velocity model methods during the aquaculture period from the aquaculture ponds in the Min River Estuary. Values represent the means of nine replicates samples, while the vertical lines indicate standard errors.
Figure 4. Comparison of CH₄ diffusive flux measured by using the FCs method and TBL models. Regression equation, linear correlation ($r^2$) and significance ($p$) are also shown. Parameter bounds on the regression coefficients are 95% confidence intervals.
Figure 5. Frequency distribution of CH$_4$ diffusive fluxes from (a) TBL$_{LM86}$, (b) TBL$_{W92a}$, (c) TBL$_{RC01}$, (d) TBL$_{CL98}$, (e) TBL$_{W92b}$, (f) TBL$_{CW03}$, and (g) FCs measurements at the aquaculture ponds in the Min River Estuary during the aquaculture period.
Table 1

Summary of the TBL and FCs methods applied to measure CH₄ diffusive fluxes from the aquaculture ponds in Min River Estuary during the aquaculture period.

<table>
<thead>
<tr>
<th></th>
<th>TBL methods</th>
<th>FCs method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TBL&lt;sub&gt;LM86&lt;/sub&gt;</td>
<td>TBL&lt;sub&gt;W92a&lt;/sub&gt;</td>
</tr>
<tr>
<td>Minimum (µmol m⁻² h⁻¹)</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Maximum (µmol m⁻² h⁻¹)</td>
<td>108.8</td>
<td>650.0</td>
</tr>
<tr>
<td>Average (µmol m⁻² h⁻¹)</td>
<td>19.4</td>
<td>103.1</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>23.1</td>
<td>130.6</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>1.18</td>
<td>1.27</td>
</tr>
</tbody>
</table>
Table 2

Pearson correlation coefficients for dissolved CH\textsubscript{4} concentration, CH\textsubscript{4} diffusive fluxes and environmental variables from the aquaculture ponds in Min River Estuary during the aquaculture period\textsuperscript{a}. Bold numbers denote correlation coefficients for significant relationships.

<table>
<thead>
<tr>
<th>Environmental variables</th>
<th>Dissolved CH\textsubscript{4} concentration</th>
<th>CH\textsubscript{4} diffusive fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorological parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air temperature</td>
<td>0.214\textsuperscript{*}</td>
<td>0.203\textsuperscript{*}</td>
</tr>
<tr>
<td>Wind speed (W\textsubscript{S})</td>
<td>NS</td>
<td>0.281\textsuperscript{*}</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Water parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water temperature</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Dissolved oxygen (DO)</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>TOC concentration</td>
<td>0.312\textsuperscript{**}</td>
<td>0.296\textsuperscript{**}</td>
</tr>
<tr>
<td>NO\textsubscript{3}-N concentration</td>
<td>-0.401\textsuperscript{**}</td>
<td>-0.392\textsuperscript{**}</td>
</tr>
<tr>
<td>Electrical conductivity (EC)</td>
<td>-0.361\textsuperscript{**}</td>
<td>-0.185\textsuperscript{*}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The symbols * and ** indicate significant correlations at the 0.05 and 0.01 levels, respectively. n = 135 for environmental variables and CH\textsubscript{4} diffusive fluxes from the aquaculture ponds. CH\textsubscript{4} diffusive fluxes were directly measured using floating chambers method.
Supporting Information

Title: Diffusive CH$_4$ fluxes from aquaculture ponds using floating chambers and thin boundary layer equations

Ping Yang$^{a,b,1}$, Jiafang Huang$^{a,b,1}$, Hong Yang$^{c,d,e,1}$, Josep Peñuelas$^{f,g}$, Kam W. Tang$^b$, Derrick Y.F. Lai$^i$, Dongqi Wang$^l$, Qitao Xiao$^k$, Jordi Sardans$^{f,g,**}$, Yifei Zhang$^{a,b}$, Chuan Tong$^{a,b,**}$

$^a$Key Laboratory of Humid Subtropical Eco-geographical Process of Ministry of Education, Fujian Normal University, Fuzhou 350007, P.R. China

$^b$School of Geographical Sciences, Fujian Normal University, Fuzhou 350007, P.R. China

$^c$College of Environmental Science and Engineering, Fujian Normal University, Fuzhou 350007, P.R. China

$^d$Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

$^e$Department of Geography and Environmental Science, University of Reading, Reading RG6 6AB, U.K.

$^f$CSIC, Global Ecology Unit CREAF-CSIC-UAB, Bellaterra, Catalonia, Spain

$^g$CREAF, Cerdanyola del Vallès, Catalonia, Spain

$^h$Department of Biosciences, Swansea University, Swansea SA2 8PP, U.K.

$^i$Department of Geography and Resource Management, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China

$^j$School of Geographical Sciences, East China Normal University, Shanghai 200241, China

$^k$Key Laboratory of Watershed Geographic Sciences, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, 210008, China

*Correspondence to: Derrick Y.F. Lai

Email: dyflai@cuhk.edu.hk

*Correspondence to: Jordi Sardans
Email: j.sardans@creaf.uab.cat

**Correspondence to:** Chuan Tong

Email: tongch@fjnu.edu.cn

1Ping Yang, Jiafang Huang, and Hong Yang contributed equally to this work.
Supporting Information Summary

No. of pages: 16    No. of figures: 4    No. of tables: 5

Page S5: Figure S1. Location of the study area and sampling sites at aquaculture ponds in Min River Estuary, Southeast China.

Page S6: Figure S2. Schematic diagram for the gas sampling device of CH\textsubscript{4} diffusive flux across the water-air interface. Numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 represents chambers body, Neoprene floats, thin gauze, mooring anchor, sampling tube, 60-mL plastic syringes equipped with three-way stopcocks, fixed rope, valve body, valve body, gas collecting hole, ribbon, and handle, respectively.

Page S7: Figure S3. (a) Temporal variation in the wind speed ($W_s$), and (b) frequency distribution of wind speed at the shrimp ponds in the Min River Estuary during the aquaculture period.

Page S8: Figure S4. Temporal variation in (a) water temperature, (b) dissolved oxygen, (c) TOC, and (b) N-NO\textsubscript{x-}\textsuperscript{-} in the surface water (20 cm depth) of the aquaculture ponds in the Min River Estuary during the aquaculture period. Error bars represent standard error ($n = 9$). Data are after Yang et al. [unpublished data] for reference and review only.

Page S9: Figure S5. Boxplots of CH\textsubscript{4} diffusive fluxes estimated using the TBL and FCs methods at the aquaculture ponds in Min River Estuary during the aquaculture period. The letters above the boxes represent the LSD (Least Significant Difference) test results, and different letters mean significant difference at 0.05 level. The centre line and square represent the median value and area-weighted average.

Page S10: Figure S6. Comparison of CH\textsubscript{4} fluxes measured using the FCs with gauze (FCs-G) and without gauze (FCs-NG) from the aquaculture ponds in the Min River Estuary during the aquaculture period. Data are after Yang et al. [unpublished data] for reference and review only. Values represent the means of nine replicates samples, while the vertical lines indicate standard errors.

Page S11: Table S1. Characteristics of the three aquaculture ponds in the Min River Estuary.
Page S12: Table S2. The best GLS model (lowest AIC values) with the CH₄ fluxes as functions of environmental values.

Page S15: Table S3. Pearson correlation coefficients for environmental variables, dissolved CH₄ concentration and CH₄ diffusive fluxes from the aquaculture ponds in Min River Estuary during the aquaculture period.
Figure S1. Location of the study area and sampling sites at aquaculture ponds in Min River Estuary, Southeast China.
Figure S2. Schematic diagram for the gas sampling device of CH$_4$ diffusive flux across the water-air interface. Numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 represents chambers body, Neoprene floats, thin gauze, mooring anchor, sampling tube, 60-mL plastic syringes equipped with three-way stopcocks, fixed rope, valve body, valve body, gas collecting hole, ribbon, and handle, respectively.
Figure S3. (a) Temporal variation in the wind speed ($W_S$), and (b) frequency distribution of wind speed at the shrimp ponds in the Min River Estuary during the aquaculture period.
Figure S4. Temporal variation in (a) water temperature, (b) dissolved oxygen, (c) TOC, and (b) NO$_3^-$-N in the surface water (20 cm depth) of the aquaculture ponds in the Min River Estuary during the aquaculture period. Error bars represent standard error ($n = 9$). Data are after Yang et al. [unpublished data] for reference and review only.
Figure S5. Boxplots of CH$_4$ diffusive fluxes estimated using the TBL and FCs methods at the aquaculture ponds in Min River Estuary during the aquaculture period. The letters above the boxes represent the LSD (Least Significant Difference) test results, and different letters mean significant difference at 0.05 level. The centre line and square represent the median value and area-weighted average.
Figure S6. Comparison of CH$_4$ fluxes measured using the $FC$s with gauze ($FC$s-G) and without gauze ($FC$s-NG) from the aquaculture ponds in the Min River Estuary during the aquaculture period. Data are after Yang et al. [unpublished data] for reference and review only. Values represent the means of nine replicates samples, while the vertical lines indicate standard errors.
Table S1 Characteristics of the three aquaculture ponds in the Min River Estuary. *

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pond-I</th>
<th>Pond-II</th>
<th>Pond-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrimp species</td>
<td><em>Litopenaeus vannamei</em></td>
<td><em>Litopenaeus vannamei</em></td>
<td><em>Litopenaeus vannamei</em></td>
</tr>
<tr>
<td>Water depth (m)</td>
<td>1.3 (0.3 – 1.7)</td>
<td>1.7 (0.5 – 2.1)</td>
<td>1.5 (0.3 – 1.8)</td>
</tr>
<tr>
<td>Water salinity (%)</td>
<td>3.6 (1.5 – 6.8)</td>
<td>2.2 (1.7 – 5.2)</td>
<td>2.8 (1.7 – 5.4)</td>
</tr>
<tr>
<td>Surface area (m²)</td>
<td>21426.94</td>
<td>18412.89</td>
<td>19112.71</td>
</tr>
<tr>
<td>Stocking density (PL m⁻²)*</td>
<td>150</td>
<td>120</td>
<td>119</td>
</tr>
<tr>
<td>Survival rate (%)*</td>
<td>45</td>
<td>62</td>
<td>59</td>
</tr>
<tr>
<td>Feed conversion rate*</td>
<td>3.5</td>
<td>2.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Based on Zhang et al. (2019).

* The data for the stocking density, survival rate, and yield were provided by the farmers;

* Feed conversion rate = dry weight of feeds added / wet weight of shrimps produced.
Table S2 The best GLS model (lowest AIC values) with the CH$_4$ fluxes as functions of environmental values.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Model</th>
<th>Model $R^2$ and $P$-value</th>
<th>Model independent factors statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$TBL_{LM86}$</td>
<td>gls(CH4flux ~ disCH4 + U10 + watertemp + NO3N, data=dades, method =&quot;REML&quot;)</td>
<td>$R^2=0.47$ $P&lt;0.0001$</td>
<td>Coefficients:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Intercept) -0.396</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disCH4 0.0300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>U10 0.0515</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>watertemp 0.0187</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO3N -0.786</td>
</tr>
<tr>
<td>$TBL_{W92a}$</td>
<td>gls(CH4flux ~ disCH4 + U10 + watertemp + NO3N, data=dades, method =&quot;REML&quot;)</td>
<td>$R^2=0.50$ $P&lt;0.0001$</td>
<td>Coefficients:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Intercept) -3.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disCH4 0.141</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>U10 0.614</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>watertemp 0.122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO3N -4.64</td>
</tr>
<tr>
<td>$TBL_{RC01}$</td>
<td>gls(CH4flux ~ disCH4 + U10 + watertemp + NO3N, data=dades, method =&quot;REML&quot;)</td>
<td>$R^2=0.54$ $P&lt;0.0001$</td>
<td>Coefficients:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Intercept) -3.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disCH4 0.331</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>U10 0.464</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>watertemp 0.178</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO3N -8.18</td>
</tr>
<tr>
<td>$TBL_{CL98}$</td>
<td>gls(CH4flux ~ disCH4 + NO3N, data=dades,</td>
<td>$R^2=0.53$</td>
<td>Coefficients:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S3 Pearson correlation coefficients for environmental variables, dissolved CH$_4$ concentration and CH$_4$ diffusive fluxes from the aquaculture ponds in Min River Estuary during the aquaculture period.

<table>
<thead>
<tr>
<th>Environmental variables</th>
<th>CH$_4$ diffusive fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$TBL_{LM86}$</td>
</tr>
<tr>
<td>$TBL_{W92b}$</td>
<td>gls(CH$_4$flux ~ disCH$_4$ + U10 + NO3N, data=dades, method =&quot;REML&quot;)</td>
</tr>
<tr>
<td></td>
<td>(Intercept)</td>
</tr>
<tr>
<td></td>
<td>disCH$_4$</td>
</tr>
<tr>
<td></td>
<td>U10</td>
</tr>
<tr>
<td></td>
<td>NO3N</td>
</tr>
<tr>
<td>$TBL_{CW03}$</td>
<td>gls(CH$_4$flux ~ disCH$_4$ + U10 + NO3N, data=dades, method =&quot;REML&quot;)</td>
</tr>
<tr>
<td></td>
<td>(Intercept)</td>
</tr>
<tr>
<td></td>
<td>disCH$_4$</td>
</tr>
<tr>
<td></td>
<td>U10</td>
</tr>
<tr>
<td></td>
<td>NO3N</td>
</tr>
<tr>
<td>FCs</td>
<td>gls(CH$_4$flux ~ disCH$_4$ + U10 + NO3N, data=dades, method =&quot;REML&quot;)</td>
</tr>
<tr>
<td></td>
<td>(Intercept)</td>
</tr>
<tr>
<td></td>
<td>disCH$_4$</td>
</tr>
<tr>
<td></td>
<td>U10</td>
</tr>
<tr>
<td></td>
<td>NO3N</td>
</tr>
<tr>
<td>Meteorological parameters</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Air temperature</td>
<td>NS</td>
</tr>
<tr>
<td>$U_{10}$</td>
<td>NS</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>NS</td>
</tr>
<tr>
<td>Water parameters</td>
<td></td>
</tr>
<tr>
<td>Water temperature</td>
<td>NS</td>
</tr>
<tr>
<td>Dissolved oxygen (DO)</td>
<td>NS</td>
</tr>
<tr>
<td>TOC concentration</td>
<td>0.301**</td>
</tr>
<tr>
<td>NO$_3^-$-N concentration</td>
<td>-0.439**</td>
</tr>
<tr>
<td>CH$_4$ concentration</td>
<td>0.619**</td>
</tr>
<tr>
<td>Gas transfer velocity ($k_x$)</td>
<td>NS</td>
</tr>
</tbody>
</table>

The symbols * and ** indicate significant correlations at the 0.05 and 0.01 levels, respectively. NS indicates non-significant.
References

https://doi.org/10.1007/s11356-018-3929-3