RESEARCH ARTICLE

Variations in Temperature Sensitivity ($Q_{10}$) of CH$_4$ Emission from a Subtropical Estuarine Marsh in Southeast China

Chun Wang$^{1,2}$, Derrick Y. F. Lai$^3$, Chuan Tong$^{1,4}$*, Weiqi Wang$^{1,4}$, Jiafang Huang$^{1,4}$, Chongsheng Zeng$^{1,4}$

$^1$ Key Laboratory of Humid Sub-tropical Eco-geographical Process of Ministry of Education, Fujian Normal University, Fuzhou, China, $^2$ School of Geographical Sciences, Fujian Normal University, Fuzhou, China, $^3$ Department of Geography and Resource Management, and Centre for Environmental Policy and Resource Management, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China, $^4$ Institute of Geography, Fujian Normal University, Fuzhou, China

* tongch@fjnu.edu.cn

Abstract

Understanding the functional relationship between greenhouse gas fluxes and environmental variables is crucial for predicting the impacts of wetlands on future climate change in response to various perturbations. We examined the relationships between methane (CH$_4$) emission and temperature in two marsh stands dominated by the $Phragmites$ australis and $Cyperus$ malaccensis, respectively, in a subtropical estuarine wetland in southeast China based on three years of measurement data (2007–2009). We found that the $Q_{10}$ coefficient of CH$_4$ emission to soil temperature ($Q_{s10}$) from the two marsh stands varied slightly over the three years ($P > 0.05$), with a mean value of 3.38 $\pm$ 0.46 and 3.89 $\pm$ 0.41 for the $P$. australis and $C$. malaccensis stands, respectively. On the other hand, the three-year mean $Q_{a10}$ values ($Q_{10}$ coefficients of CH$_4$ emission to air temperature) were 3.39 $\pm$ 0.59 and 4.68 $\pm$ 1.10 for the $P$. australis and $C$. malaccensis stands, respectively, with a significantly higher $Q_{a10}$ value for the $C$. malaccensis stand in 2008 ($P < 0.05$). The seasonal variations of $Q_{s10}$ ($Q_{a10}$ and $Q_{a10}$) differed among years, with generally higher values in the cold months than those in the warm months in 2007 and 2009. We found that the $Q_{s10}$ values of both stands were negatively correlated with soil conductivity, but did not obtain any conclusive results about the difference in $Q_{10}$ of CH$_4$ emission between the two tidal stages (before flooding and after ebbing). There were no significant differences in both $Q_{s10}$ and $Q_{a10}$ values of CH$_4$ emission between the $P$. australis stand and the $C$. malaccensis stands ($P > 0.05$). Our results show that the $Q_{10}$ values of CH$_4$ emission in this estuarine marsh are highly variable across space and time. Given that the overall CH$_4$ flux is governed by a suite of environmental factors, the $Q_{10}$ values derived from field measurements should only be considered as a semi-empirical parameter for simulating CH$_4$ emissions.
Introduction

Methane is a greenhouse gas that is 34 times more potent than carbon dioxide on a 100-year time scale and hence plays an important role in global climate change [1]. Natural wetlands in particular are the single largest global CH₄ source [2]. The global interannual variability of CH₄ emissions are primarily driven by fluctuations of CH₄ emissions from natural marshes, which on average emitted 177–284 Tg CH₄ yr⁻¹ during the period of 2000–2009 [1]. While numerous researchers have examined CH₄ dynamics in northern peatlands [3–7], relatively little has been done in the coastal and estuarine wetland ecosystems [8–10]. It is essential to develop a thorough understanding of the relationships between various environmental factors and CH₄ emissions from estuarine wetlands in order to accurately predict the impacts of natural and anthropogenic perturbations on CH₄ release, as well develop appropriate management strategies to minimize the potential adverse climatic impacts of wetlands.

The net CH₄ emission from wetland soil is a reflection of the balance between CH₄ production, oxidation and transport. Temperature is in general a major factor governing wetland CH₄ emission to the atmosphere [6, 11, 12], although some researchers have reported a weak correlation between CH₄ emission and temperature [13, 14]. The Q₁₀ coefficient has been commonly used to describe the temperature response of various microbial-mediated processes by standardizing temperature-related differences in reaction rates to proportional changes per 10°C rise in temperature. It is also considered to be one of the most important parameters used to assess the apparent temperature sensitivity of both soil respiration and ecosystem respiration [15–19]. However, few studies thus far have reported on the Q₁₀ of wetland CH₄ emission [6, 20, 21].

As soil respiration is widely regarded to be related exponentially to temperature, an exponential function is often used to determine the Q₁₀ of soil and ecosystem respirations. A number of studies have shown that Q₁₀ of soil respiration is not constant during the year, and that Q₁₀ tends to decrease with increasing temperature in both forest [22, 23] and grassland ecosystems [24]. Yet, it is not known whether Q₁₀ of CH₄ emission from wetland ecosystems will exhibit a similar pattern. In estuarine wetlands, tidal flow is a unique and important physical process that can influence various biogeochemical processes. While CH₄ emission from a tidal marsh was found to vary among different tidal stages [25], there is hitherto a lack of studies that compare Q₁₀ of CH₄ emission in tidal marshes among different tidal stages and different years. It is believed that a better understanding of Q₁₀ variations for both carbon dioxide and CH₄ fluxes could significantly improve our knowledge on the carbon balance of coastal estuarine wetland ecosystems [26].

In this study, we measured CH₄ fluxes continuously over a 3-year period from two stands dominated by Phragmites australis and Cyperus malaccensis, respectively, in a tidal marsh in southeast China to address the following objectives: (1) to examine the relationship between CH₄ emission and temperature in the two marsh stands; (2) to determine the seasonal and interannual variability of Q₁₀ of CH₄ emission from this tidal marsh; (3) to investigate the influence of two tidal stages (before flooding and after ebbing) on the Q₁₀ value of CH₄ emission; and (4) to elucidate on the influence of different vegetation on the Q₁₀ value of CH₄ emission.

Materials and Methods

The study was conducted in a tidal marsh at the Shanyutan wetland (26°00′36″–26°03′42″N, 119°34′12″–119°40′40″E, Fig 1) in the Min River estuary of Fujian Province in southeast China, with a total area 3120 ha (Fig 1). The climate of this subtropical region is warm and wet, with a mean annual temperature of 19.6°C and a mean annual precipitation of approximately 1,350 mm. Semi-diurnal tides are typical in the coastal area [27]. The soil surface is submerged
for about 7 h over a 24 h cycle. There is normally between 10 and 150 cm of water above the soil surface at high tide. At other times the soil surface is completely exposed to air.

The study site was located in the midwest section of the Shanyutan wetland, with C. *malaccensis* and *P. australis* (Cav.) Trin as the dominant plant species. We randomly selected two monoculture marsh stands dominated by *C. malaccensis* and *P. australis*, respectively, with almost identical environmental conditions for flux measurements. The characteristics of the two stands are shown in Table 1. Vegetation and soil properties were determined in 2007. In three replicate quadrats (50 x 50 cm) of both the *P. australis* and *C. malaccensis* stands, the above-

**Table 1.** Vegetation and soil properties of the two marsh stands dominated by *P. australis* and *C. malaccensis*, respectively.

|                      | *P. australis* | *C. malaccensis* |
|----------------------|---------------|------------------|
| Mean stem height (cm)| 149.9a        | 109.3b           |
| Mean plant density (individuals m⁻²) | 150a          | 912b             |
| Maximum above-ground live biomass (g m⁻²) | 1524.8 ± 78.9a | 1062.4 ± 129.6b |
| Annual mean below-ground biomass (0–60 cm) (g⁻²) | 2085.7 ± 663.0a | 3168.4 ± 486.4b |
| Soil organic carbon concentration (0–50 cm) (g kg⁻¹) | 19.30± 1.17a | 22.06±2.0a |
| Soil organic carbon stock (0–50 cm) (kg m⁻²) | 7.76a | 7.40a |

Different letters represent a significant difference between the two stands.
ground and belowground (0–60 cm depth) biomass were measured every two months, and every season, respectively. All biomass was oven-dried at 80°C to constant mass and weighed. Soil total organic carbon (TOC) content (0–50 cm depth) was measured via wet combustion of sediments in H₂SO₄/K₂Cr₂O₇ [27,28].

The closed, static chamber technique [29] was used to measure CH₄ emission from the two stands during two tidal stages in which the soil surface was exposed (i.e. before flooding, BF; after ebbing, AE). The maximum height of *C. malaccensis* was approximately 1.5 m, and the height of *P. australis* ranged from 1.6 to 1.8 m. The chambers consisted of three parts: a stainless steel bottom collar (50 cm length × 50 cm width × 30 cm height) and two individual PVC chambers (50 cm length × 50 cm width), with the lower and upper sections being 120 cm and 50 cm tall, respectively, for the *P. australis* stand, and 100 cm and 50 cm tall, respectively, for the *C. malaccensis* stand. The bottom collar was inserted permanently into the marsh sediment, with 2 cm left protruding above the sediment surface, while the PVC chambers were then placed on top of the collar during flux measurement. PVC chambers are commonly used in measuring wetland CH₄ fluxes since they are opaque and can reduce overheating of the chamber headspace over the deployment period. However, a recent study suggested that the use of opaque chambers could lead to underestimation of CH₄ fluxes from plants that transport gases actively through convection (e.g. *Phragmites* spp.) [30]. The top chamber was equipped with an electric fan to ensure a complete mixing of air inside the chamber headspace. Also, in the hot summer, the chamber top was covered by cotton quilts during flux measurements to keep the temperature inside within -0.8°C to 1.2°C of the ambient level. A wooden boardwalk was installed permanently throughout the three years of study to facilitate access to the measurement sites without causing significant disturbance during sampling.

Monthly CH₄ flux measurements were made from January 2007 to December 2009, with the exception of February in these three years (owing to the Chinese Lunar New Year). Three replicate chambers separated by about 5 m were deployed in each marsh stand for gas sampling. All samples were taken on the days between the spring and neap tides (i.e. the third or fourth day after the largest spring tide). On these dates, the sampling sites began to flood at 10:00 am (Beijing time) and the soil was exposed to air again after ebb tide at about 1:30 pm. Chambers were deployed at 9:00 am (one hour before the beginning of flooding), and at approximately 3:00 pm (1.5 h after the end of the ebb tide) to determine the CH₄ fluxes at two different tidal stages in a single day (before flooding, BF, and after ebbing, AE). To measure CH₄ fluxes, three gas samples inside the chamber headspace were collected at 30-min intervals by 100 ml polypropylene syringes equipped with a three-way stopcock.

On each sampling date, one set of environmental variables was measured for each plant stand. Soil temperature, pH and redox potential at a depth of 10 cm were measured using a Eh/pH/temperature meter (IQ Scientific Instruments, USA), while soil conductivity (mS cm⁻¹) was measured using an electrical conductivity meter (2265FS, Spectrum Technologies Inc., USA). Air temperature (1.5 m above ground) was measured by a pocket weather meter (Kestrel-3500, USA).

Methane concentrations in the gas samples were determined using a gas chromatograph (Shimadzu GC-2010, Japan) equipped with a FID detector within 48 h after sampling. The column and detector temperatures were set at 60°C and 130°C, respectively, with nitrogen as the carrier gas at a flow rate of 20 ml min⁻¹. The gas chromatograph was calibrated with gas standards containing 1.01, 7.99, and 50.5 μl CH₄ l⁻¹, respectively, on a monthly basis (i.e. every time when gas samples were analyzed). CH₄ emission into the atmosphere was estimated by linear regression of the change in headspace CH₄ gas concentrations with time [6]. The fluxes were rejected and removed from the analysis when the R² value of the linear regression was smaller than 0.90 [31].
We calculated the $Q_{10}$ value of CH$_4$ emission based on the exponential function that was commonly used to determine $Q_{10}$ of soil and ecosystem respiration [24] as well as CH$_4$ flux [6, 21], which was given as follows:

$$F = ae^{bt}$$  \hspace{1cm} (1)

where $F$ is CH$_4$ efflux (mg m$^{-2}$ h$^{-1}$), $t$ is the air temperature or soil temperature measured at 10 cm depth, and $a$ and $b$ are regression coefficients ($b$ is also called the temperature reaction coefficient).

The $Q_{10}$ value was then calculated as:

$$Q_{10} = e^{10b}$$  \hspace{1cm} (2)

where $Q_{s10}$ and $Q_{a10}$ are the $Q_{10}$ values based on soil and air temperatures, respectively.

The entire data set of each year was divided into two groups for analysis based on the timing of data collection, with one group in the warm months (warmer period between April to September) and the other in the cold months (colder period between January to March, and October to December). We determined the $Q_{10}$ values of CH$_4$ emission separately for these two groups of data. We also calculated the $Q_{10}$ values of CH$_4$ emission for the two different tidal stages.

All statistical analyses were performed using SPSS 16.0 software (SPSS Inc., Chicago, Illinois). The differences in vegetation, soil properties, and $Q_{10}$ between the two marsh sites dominated by *P. australis* and *C. malaccensis* were tested using the paired-sample T test. The relationships between $Q_{s10}$ values and other soil parameters were tested using the Pearson correlation analysis. We tested for any significance differences in $Q_{10}$ among different years and seasons from the two stands using one-way ANOVA with Tukey’s post-hoc test.

**Results**

**Relationship Between CH$_4$ Flux and Temperature**

Variations of soil and air temperature from the *P. australis* and *C. malaccensis* marshes during 2007 to 2009 are shown in Fig 2. In the three years of our study, annual mean CH$_4$ emissions from the *P. australis* stand ranged from 5.26 ± 0.67 to 6.41 ± 0.94 mg m$^{-2}$ h$^{-1}$, with minimum and maximum fluxes of 0.10 and 61.40 mg m$^{-2}$ h$^{-1}$, respectively. For the *C. malaccensis* stand, annual mean CH$_4$ emissions ranged from 0.84 ± 0.12 to 2.97 ± 0.65 mg m$^{-2}$ h$^{-1}$, with minimum and maximum fluxes of 0.01 and 27 mg m$^{-2}$ h$^{-1}$, respectively. The temporal variation of CH$_4$ fluxes from the *P. australis* stand and the *C. malaccensis* stand had been reported previously [27]. CH$_4$ emission from the *P. australis* stand was significantly higher than that of the *C. malaccensis* stand ($P < 0.05$, Fig 3). The relationship of CH$_4$ emissions with both soil temperatures at a depth of 10 cm and air temperature could be described significantly by the exponential function ($P < 0.01$, Fig 3). Except in 2009, the percentage variance in CH$_4$ emission explained by air or soil temperature was greater for the *C. malaccensis* stand compared to the *P. australis* counterpart (Fig 3).

**Inter-annual Variations in $Q_{10}$ Values**

The $Q_{s10}$ values of CH$_4$ emission from the two marsh stands showed little inter-annual variations in the three study years ($P > 0.05$, Fig 4). Annual mean $Q_{s10}$ values of CH$_4$ emission from *P. australis* stand were 3.41 ± 0.29, 4.07 ± 1.33 and 2.67 ± 0.45 in 2007, 2008 and 2009, respectively, while those from *C. malaccensis* stand were 3.96 ± 0.53, 4.26 ± 0.73 and 3.45 ± 1.04, respectively. In general, the $Q_{s10}$ values from the *P. australis* stand was lower than that of the *C.
Fig 2. Monthly mean soil temperature (°C) at 10 cm depth or air temperature (°C) in the two marsh stands from 2007 to 2009. Data of soil (air) temperature was missing in April 2007 due to instrument failure.

doi:10.1371/journal.pone.0125227.g002
malaccensis stand ($P > 0.05$). On the other hand, for $Q_{210}$ of CH$_4$ emissions, the values from C. malaccensis stand were significantly higher in 2008 compared to the other two years ($P < 0.05$), while that from P. australis stand were not distinct different ($P > 0.05$). In 2007–2009, annual mean $Q_{210}$ of CH$_4$ emission from P. australis stand was $3.06 \pm 0.04$, $4.78 \pm 1.58$ and $2.35 \pm 0.27$, respectively, while that from the C. malaccensis stand was $3.02 \pm 0.24$, $8.26 \pm 2.09$ and $2.76 \pm 0.69$, respectively. The annual mean CH$_4$ fluxes from the two stands were also highest in 2008, with values of $6.41 \pm 0.94$ and $2.97 \pm 0.65$ mg m$^{-2}$ h$^{-1}$ for the P. australis and C. malaccensis stands, respectively. The variations in $Q_{210}$ and $Q_{210}$ of the two stands among these three years were consistent with CH$_4$ emission, except for the $Q_{210}$ of the P. australis stand (Figs 4 and 5).

Seasonal Variations in $Q_{10}$ Values

For the two marsh stands, both $Q_{210}$ and $Q_{210}$ generally exhibited a distinct difference between the warm and cold months except in 2009 (Fig 6). In 2007, both $Q_{210}$ and $Q_{210}$ of CH$_4$ emission from the two marsh stands were considerably lower in the warm months compared to those in
the cold months ($P < 0.05$, Fig 6), particularly for the $Q_{a10}$ of CH$_4$ emission from the *P. australis* stand ($P < 0.05$, Fig 6). In 2009, both $Q_{s10}$ and $Q_{a10}$ from the *C. malaccensis* stand were also slightly lower in the warm months ($P > 0.05$), but the seasonal difference was less discernible for the *P. australis* stand ($P > 0.05$, Fig 6). In contrast, the $Q_{s10}$ values of CH$_4$ emission from the two stands in 2008 were significantly higher in the warm months than in the cold months ($P < 0.05$).

**Difference in $Q_{10}$ Values Between Two Tidal Stages**

Fig 7 shows the mean $Q_{s10}$ and $Q_{a10}$ of CH$_4$ emission from the two marsh stands in two tidal stages (before flooding and after ebbing) over three years. In 2007, we found significantly lower $Q_{s10}$ and $Q_{a10}$ of CH$_4$ emission from the *P. australis* stand before flooding (BF) compared to those after ebbing (AE) ($P < 0.05$), while for the *C. malaccensis* stand, the difference was not statistically significant between the two tidal stages ($P > 0.05$). In 2008, the $Q_{s10}$ and $Q_{a10}$ values of both stands were higher during BF and AE, respectively, yet the difference was only statistically significant for the $Q_{a10}$ value in the *C. malaccensis* stand ($P < 0.05$). In 2009, no significant difference in both $Q_{s10}$ and $Q_{a10}$ values were observed between the two tidal stages in the two stands ($P > 0.05$), although we observed considerably higher mean values during AE compared to BF in the *C. malaccensis* stand.
Fig 6. $Q_{s10}$ and $Q_{a10}$ of CH$_4$ emissions from the two marsh stands in the warm months and cold months from 2007 to 2009. Values are represented by means of triplicates ± 1 standard error. Significant differences in $Q_{s10}$ or $Q_{a10}$ ($P < 0.05$) between the two periods are indicated by different letters.

doi:10.1371/journal.pone.0125227.g006
Relationships between \(Q_{s10}\) values and other soil parameters

The \(Q_{s10}\) values were not significantly different among the three years of study in both marsh stands \((P > 0.05)\). Therefore, the \(Q_{s10}\) values in the three different years trial could be treated as replicates of the stands. Correlation analysis shows that the \(Q_{s10}\) of both stands were negatively correlated with soil conductivity, but positively correlated with soil redox potential (Table 2). The \(Q_{s10}\) of CH\(_4\) emission from the \(P. australis\) stand was positively correlated with soil pH, while an opposite relationship was observed in the \(C. malaccensis\) stand (Table 2).

Discussion

Relationship Between CH\(_4\) Flux and Temperature

In our study, the annual mean CH\(_4\) emission ranged from 5.26 ± 0.67 to 6.41 ± 0.94 mg m\(^{-2}\) h\(^{-1}\) for the \(P. australis\) stand, and 0.84 ± 0.12 to 2.97 ± 0.65 mg m\(^{-2}\) h\(^{-1}\) for the \(C. malaccensis\) stand, which was consistent with previous findings of a lower CH\(_4\) emission associated with a higher salinity condition [32]. This was likely a result of the high availability of electron acceptors (e.g. sulfate, nitrate) in seawater that completely eliminated methanogens and shifted the dominant anaerobic pathways of organic carbon mineralization [33,34]. Moreover, we found that CH\(_4\) emission rate in our tidal wetland study site was lower than that in a tidal freshwater marsh from the Daoqingzhou wetland upstream of the Minjiang estuary, China, but within the range reported in the estuarine wetlands in the Yangtze River in China and Sundarban in India [35,36] (Table 3). The exponential model expressed the relationships between CH\(_4\) emission and temperature fairly well (Fig 3), which was consistent with findings in a boreal forest wetland in Saskatchewan Canada [37] and a high \(P. australis\) marsh of the Wuliangsu Lake, Inner Mongolia, northern China [38]. Temperature governs soil biogeochemical processes directly by altering microbial metabolism which is largely driven by enzymatic kinetics, or indirectly by controlling substrate availability [39–41]. Numerous studies [37, 42–44] have demonstrated a positive relationship between CH\(_4\) emission and temperature as a result of the increased C availability at higher temperatures. Meanwhile, the influence of temperature on CH\(_4\) emission is very complex as the overall CH\(_4\) emission from wetland soils to the atmosphere is a net result of CH\(_4\) production, oxidation, and transport, which could be independently controlled by temperature or other factors such as precipitation, soil carbon input amount and quality, soil texture, etc. [40,41].

Inter-annual Variations in \(Q_{10}\) Values

Understanding the response of soil biogeochemical processes to a warmer world is critical for predicting short-term and long-term changes in the cycling of soil carbon and nitrogen. Field
measurements of both the magnitude and temperature sensitivity of CH$_4$ emission are important for understanding methane dynamics in wetlands. We observed the highest $Q_{10}$ values of CH$_4$ emission from the tidal marsh stands dominated by *P. australis* and *C. malaccensis* in 2008, with the $Q_{10}$ values of 4.07 ± 1.33 for the *P. australis* stand and 4.26 ± 0.73 for the *C. malaccensis* stand, and the $Q_{s10}$ values of 4.78 ± 1.58 for the *P. australis* stand and 8.26 ± 2.09 for the *C. malaccensis* stand, respectively (Figs 4 and 5). The higher temperature sensitivity of CH$_4$ emission from both stands in 2008 was likely the result of a higher soil temperature in 2008 than the other two years (Fig 4), which could speed up the dissolution and diffusion of substrates [41,42]. At the same time, the annual mean CH$_4$ fluxes from the two stands were found to be highest in 2008. Interannual variability of $Q_{10}$ was not significant among the three years in both stands ($P > 0.05$), except for $Q_{s10}$ in the *C. malaccensis* stand with significantly higher value in 2008. The high temporal and spatial heterogeneity of soil metabolism might have partly masked some possible differences in mean $Q_{s10}$ values of the two stands among years [40]. Updegraff et al. [45] found a large variation in $Q_{10}$ of CH$_4$ production potential among the soils of northern wetlands, ranging from $Q_{10}$ values of 1.98 in sedge meadow to 16.2–28.0 in various peat soils to a depth of 1 m, which implied a strong temperature-substrate interaction influencing methanogenic metabolism. In a review of the potential rate of CH$_4$ production, Segers [46] reported a high variability of $Q_{10}$ for methanogenesis in wetland soils, with an overall mean of 4.1 ± 0.4 and a range of 2–28 and 1.5–6.4 for minerotrophic and oligotrophic peat soils, respectively. A very wide range of $Q_{10}$ of CH$_4$ production between 1 and 35 has been observed in some acid mire soils [47]. Valentine et al. [48] found that the higher $Q_{10}$ coefficients (1.7 to 4.7) observed for methanogenesis in peat slurries were related to the lower lignin to nitrogen ratios.

### Seasonal Variations in $Q_{10}$ Values

We found that the $Q_{10}$ values (both of the $Q_{s10}$ and $Q_{a10}$ values) of CH$_4$ emission for the *P. australis* stand and the *C. malaccensis* stand were higher in the cold months than those in the warm months during 2007 and 2009, which was consistent with the findings of previous studies [16,22–24,49], with the exception of $Q_{10}$ values from the *P. australis* stand. The $Q_{10}$ value reflects the apparent temperature sensitivity of the underlying microbial processes involved in CH$_4$ production. Temperature has been found to govern microbial populations more strongly at lower temperatures [16, 49]. Temperature affects both production and turnover of extracellular enzymes in soils [50], and thus possibly indirectly alters the $Q_{10}$ values of CH$_4$ emission. The $Q_{10}$ value of *Methanosarcina barkeri*, which was able to metabolize both acetate and H$_2$–CO$_2$ in the production of CH$_4$, was found to range from 1.3 to 4 [51], while methanogenic
bacteria in rice paddy soils had a $Q_{10}$ value of up to 12 [52]. The large variation of CH$_4$ production could be due to the anomalous temperature behavior of the methanogens themselves as well as the interactions between several distinct microbial processes [46]. Dunfield et al. [53] reported a higher $Q_{10}$ value for CH$_4$ production (3.3–16) compared to that of CH$_4$ oxidation (1.4–2.1) in some northern peat soils which suggested that the $Q_{10}$ of the overall CH$_4$ emission may be further affected by the different temperature responses of methanogens and methanotrophs due to different enzymatic processes. Several studies also have indicated that the temperature sensitivity of extracellular enzymes varied seasonally [54,55]. In this study, the seasonal pattern of $Q_{10}$ values (both $Q_{10}$ and $Q_{a10}$) of CH$_4$ emission for the two stands in 2008 was opposite to that observed in 2007 and 2009 (Fig 6). Unfortunately, we cannot provide a credible explanation for this variability because we did not have any information regarding the influence of different temperature ranges on methanogen populations to provide further insights regarding the causes for the seasonal variations in $Q_{10}$ values of CH$_4$ emission during the three years.

Difference in $Q_{10}$ Values Between Two Tidal Stages

We did not obtain any conclusive results whether there was a consistent difference in the $Q_{10}$ of CH$_4$ emission between the two tidal stages (BF and AE) (Fig 7). A considerable temporal variation in CH$_4$ emission was found, with a higher flux during BF in some months but a greater emission during AE in some other months. In a 4-year study, Chang and Yang [8] also showed that the monthly CH$_4$ emissions were sometimes higher during BF, whereas in other months, they were higher during AE. This inherently high temporal variability of CH$_4$ emission during BF and AE would further add to the difficulty of examining the influence of tidal stages on the temperature sensitivity of CH$_4$ emission in the two marsh stands. Salinity is an important stressor factor in coastal marshes through its effects primarily on ionic strength and the microbial pathway of soil carbon mineralization [33]. Neubauer [34] found that the $Q_{10}$ of CH$_4$ emission were comparatively lower in the added salt plots ($Q_{10} = 1.6–2.5$) than that in the added fresh plots ($Q_{10} = 3.2–3.5$) at Brookgreen Gardens tidal freshwater marsh, USA. In our study, the $Q_{10}$ values of both stands were negatively correlated with soil conductivity, although statistically not significant ($P > 0.05$) (Table 2). The annual mean soil conductivity was 3.58–4.29 mS cm$^{-1}$, with no significant difference between BF and AE ($P > 0.05$). Soil pH is another major variable that could govern the ionization of organic molecules, as well as the activity and function of enzymes [56]. Min et al. [56] found that the C-acquiring β-glucosidase (βGase) activity was higher in more alkaline conditions regardless of soil temperature, but the temperature sensitivity of βGase was higher at pH 4.5. In our study, we found lower soil pH values in the two stands during AE than at BF, although the range of annual mean was small (6.44–6.78) and some of the differences were not significant statistically. Soil redox potential could also profoundly affect CH$_4$ production and emission from wetland soils as methanogens are anaerobic microorganisms, but we found no significant correlation between soil redox potential and the $Q_{10}$ of CH$_4$ emission in both stands during BF and AE ($P > 0.05$). Overall, our results suggest that the temporal and spatial variations of soil properties may exert little influence on the $Q_{10}$ of CH$_4$ emission over the short term between the two tidal stages.

Difference in $Q_{10}$ Values Between Two Marsh Stands

It is known that some wetland plants capable of convective transport substantially influence CH$_4$ emission by providing a pathway for gases through aerenchyma [57]. Simultaneously, aerenchyma tissues of wetland plants could transport oxygen to the anaerobic root zone [30]. In our study, we found the CH$_4$ fluxes from the $P$. australis stand were higher than those from the
C. malaccensis stand, which could be attributed to a better developed aerenchyma system in P. australis. However, it is hard to extrapolate this effect of wetland vegetation to temperature sensitivity ($Q_{10}$ values) of CH$_4$ emission owing to the complicated biogeochemical processes. It is possible that CH$_4$ emission induced by convective transport in wetland plants is susceptible to changes in the local micro-environment (e.g. air temperature and relative humidity) [58]. Alternatively, wetland plants physiological functions (such as transpiration, photosynthesis and respiration) may also contribute to the CH$_4$ metabolic processes [30]. Song et al. [6] found significant difference in $Q_{10}$ values of CH$_4$ emission between the Carex lasiocarpa and Calamagrostis angustifolia marshes of the Sanjing Plain, northeastern China (2.50 vs. 1.90). In our study, we also found lower mean $Q_{10}$ values ($Q_{s10}$ and $Q_{a10}$) of CH$_4$ emission for the P. australis stand when compared with the C. malaccensis stand, albeit the difference was not significant.

No significant differences in the annual $Q_{10}$ values ($Q_{s10}$ and $Q_{a10}$) of CH$_4$ emission were found among the three study years for both stands ($P > 0.05$), with the exception of $Q_{a10}$ for the C. malaccensis stand ($P < 0.05$) (Figs 4 and 5). Meanwhile, the $Q_{s10}$ values of CH$_4$ emission determined in our tidal wetlands were found to be higher than those in the freshwater marshes in the Sanjiang Plain of northeast China (2.67–4.26 vs. 2.49), which suggests a stronger positive climatic feedback to warming in the subtropical brackish marshes compared to the freshwater counterparts in the temperate region. On the other hand, the $Q_{s10}$ values in the peat bogs of Moorhouse Nature Reserve in North Pennines, UK as well as the paddy fields in Hangzhou and Taoyuan of China were higher than those in our estuarine marshes (5.2–5.93, Table 4), which might be related to differences in root exudation, methanotrophic communities, etc. that deserve further investigation.

### Conclusions

In summary, we found that CH$_4$ emission from the two tidal marsh stands in the Min River estuary increased exponentially with both soil and air temperatures. Both $Q_{s10}$ and $Q_{a10}$ exhibited a strong seasonal pattern, yet the variations were not consistent among different years. We also observed differences in $Q_{10}$ of CH$_4$ emission between the two tidal stages, with the pattern being quite variable from one year to the other. Meanwhile, we found a lower $Q_{10}$ values ($Q_{s10}$ and $Q_{a10}$) of CH$_4$ emission for the P. australis stand compared with the C. malaccensis stand, although the difference was not statistically significant.

Although measurements in the field has the advantage of being more realistic than laboratory assays, our results suggest that the $Q_{10}$ values of CH$_4$ emission derived from field data should generally be regarded as a semi-empirical fitting parameter for simple models only as the fluxes determined reflect a combination of a number of processes (e.g. substrate production, methane production, oxidation and transmission). $Q_{10}$ is actually only an indicator of the apparent temperature sensitivity, with the actual fluxes in the field being affected by a suite of factors like temperature, root biomass quantity and activity, moisture conditions, and perhaps other unknown variables. In view of the large variability of the temperature response of CH$_4$ emissions

### Table 4. Summary of $Q_{s10}$ values of methane emissions from different types of wetlands reported in previous studies.

| Sites                                      | Wetland types                   | $Q_{s10}$ values | References |
|--------------------------------------------|---------------------------------|------------------|------------|
| Wuliangsu, Inner Mongolia, China           | Lake wetlands                   | 3.17–5.07        | [59]       |
| Sanjiang Plain, Northeast China            | Freshwater marshes             | 2.49             | [60]       |
| Hangzhou, Zhejiang and Taoyuan, Hunan, China | Rice fields                     | 5.93             | [61]       |
| Moorhouse Nature Reserve, North Pennines, UK | Peat bogs                      | 5.2              | [62]       |
| The Shanyutan wetland, Minjiang Estuary, China | Tidal brackish water marshes   | 2.67–4.26        | This study |

doi:10.1371/journal.pone.0125227.t004

Temperature Sensitivity of CH$_4$ Emission from an Estuarine Marsh

PLOS ONE | DOI:10.1371/journal.pone.0125227 May 28, 2015 15 / 18
over space and time, a longer-term monitoring with more frequent measurements might be necessary to obtain a better understanding of the variations of $Q_{10}$ values. Given the paucity of data on $Q_{10}$ of CH$_4$ emission from the subtropical region, our findings provided some useful data on the temperature sensitivity to better predict the response of CH$_4$ emission to future climate change.

**Acknowledgments**

This work was financially supported by the National Science Foundation of China (Grant No: 40671174 and 41071148), the Program for Innovative Research Team in Fujian Normal University (IRTL1205), Research Grants Council of the Hong Kong Special Administrative Region, China (CUHK458913), and The Chinese University of Hong Kong (SS12434). We thank Cong-Ping Yan, Lu-Ying Lin, Bo Lei, An E, Ji Lia, Chun Yao, Ze-Qiong Liu, Zhi-Qiang Hu for their field assistance. We would also like to thank the anonymous reviewers for their valuable comments that have substantially improved our manuscript.

**Author Contributions**

Conceived and designed the experiments: CW CT CZ. Performed the experiments: WW JH. Analyzed the data: CW DYFL. Wrote the paper: CW CT DYFL.

**References**

1. IPCC. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Stocker TF, Qin D, Plattner GK, Tignor M, Allen SK, Boschung J, et al., editors. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2013.

2. Denman KL, Brasseur G, Chidthaisong A, Ciais P, Cox PM, Dickinson RE, et al. Couplings between changes in the climate system and biogeochemistry. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, et al., editors. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom: Cambridge University Press; 2007. p. 499–587.

3. Lai DYF, Roulet NT, Moore TR. The spatial and temporal relationships between CO$_2$ and CH$_4$ exchange in a temperate ombrotrophic bog. Atmos Environ 2014; 89: 249–259.

4. Moore TR, De Young A, Bubier J, Humphreys E, Lefleur P, Roulet N. A multi-year record of methane flux at the Mer Bleue bog, southern Canada. Ecosystems 2011; 14: 646–657.

5. Olefeldt D, Turetsky MR, Crill PM, McGuire AD. Environmental and physical controls on northern terrestrial methane emissions across permafrost zones. Global Change Biol 2013; 19: 589–603. doi: 10.1111/gcb.12071 PMID: 23504795

6. Song CC, Xu XF, Tian HQ, Wang YY. Ecosystem-atmosphere exchange of CH$_4$ and N$_2$O and ecosystem respiration in wetlands in the Sanjiang Plain, Northeastern China. Global Change Biol 2009; 15: 692–705.

7. Treat CC, Bubier JL, Varner RK, Crill PM. Time scale dependence of environmental and plant-mediated controls on CH$_4$ flux in a temperate fen. J Geophys Res 2007; doi: 10.1029/2006JG000210

8. Chang TC, Yang SS. Methane emission from wetland in Taiwan. Atmos Environ 2003; 37: 4551–4558.

9. Magenheimer JF, Moore TR, Chmura GL, Daoust RJ. Methane and carbon dioxide flux from a macrotidal salt marsh, Bay of Fundy, New Brunswick. Estuaries 1996; 19: 139–145. PMID: 8900046

10. van der Nat FJWA, Middelburg JJ. Methane emission from tidal freshwater marsh. Biogeochemistry 2000; 49: 103–121.

11. Harris RC, Sebacher DI, Day FP. Methane flux in the Great Dismal Swamp. Nature 1982; 297: 673–674.

12. Sansone FJ, Martens CS. Methane production from acetate and associated methane fluxes from anoxic coastal sediments. Science 1981; 211: 707–709. PMID: 17776653

13. Crill PM, Bartlett KB, Hattriss RC, Gorham E, Verry ES, Sebacher DI, et al. Methane flux from Minnesota peatlands. Global Biogeochem Cycles 1988; 2: 371–384.
14. Moore TR, Knowles R. Methane emissions from fen, bog, and swamp peatland in Quebec. Biogeochemistry 1990; 11: 45–61.
15. Chen H, Tian HQ. Does a general temperature-dependent Q10 of soil respiration exist at biome and global scale. J Integr Plant Biol 2005; 47: 1288–1302
16. Janssens IA, Pilegaard K. Large seasonal changes in Q10 of soil respiration in a beech forest. Global Change Biol 2003; 9: 911–918.
17. Mahecha MD, Reichstein M, Carvalhais N, Lasslop G, Lange H, Seneviratne SI, et al. Global convergence in the temperature sensitivity of respiration at ecosystem level. Science 2010; 329: 838–840. doi: 10.1126/science.1189587 PMID: 20603495
18. Raich JW, Schlesinger WH. The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. Tellus B 1992; 44: 81–90.
19. Zheng ZM, Yu GR, Fu YL, Wang YS, Sun XM, Wang YH. Temperature sensitivity of soil respiration is affected by prevailing climatic conditions and soil organic carbon content: A trans-China based case study. Soil Biol Biochem 2009; 41: 1531–1540.
20. Dise NB, Gomarm E, Verry ES. Environmental factors controlling methane emission from peatlands in northern Minnesota. J Geophys Res 1993; 98: 10583–10594.
21. Macdonald KJ, Fowler D, Hargreaves KK, Skiba U, Leith D, Murray MB. Methane emission from a Northern wetland: response to temperature, water table and Atmos. Environ 1998; 32: 3219–3227.
22. Chen BY, Liu SR, Ge JP, Chu JX. Annual and seasonal variations of Q10 soil respiration in the sub-alpine forest of Eastern Qinghai-Tibet Plateau, China. Soil Biol Biochem 2010; 42: 1735–1742.
23. Drewitt GB, Black TA, Nesis Z, Humphreys ER, Jork EM, Swanson R, et al. Measuring forest floor CO2 fluxes in Douglas-fir forest. Agr Forest Meteorol 2002; 110: 299–317.
24. Luo Y, Wan S, Hui D, Linda L, Wallace L. Acclimatization of soil respiration to warming in a tall grass prairie. Nature 2001; 413: 622–625. PMID: 11675783
25. Tong C, Wang QW, Zeng CS, Marns R. Methane (CH4) emission from a tidal marsh in the Min River estuary, southeast China. J. Environ. Sci. Health A 2010; 45: 506–516. doi: 10.1080/10934520903542261 PMID: 2090897
26. Wang CK, Yang JY, Zhang QZ. Soil respiration in six temperate forests in China. Global Change Biol 2006; 12: 2103–2114.
27. Tong C, Wang QW, Huang JF, Gauci V, Zhang LH, Zeng CS. Invasive alien plants increase CH4 emissions from a subtropical tidal estuarine wetland. Biogeochemistry 2012; 111: 677–693.
28. Bai JH, Hua OY, Wei D, Zhu YM, Zhang XL, Wang QG. Spatial distribution characteristics of organic matter and total nitrogen of marsh soils in river marginal wetlands. Geoderma 2005; 124: 181–186.
29. Tong C, Wang C, Huang JF, Wang WQ, Yan E, Liao J, et al. Ecosystem respiration does not differ before and after tidal inundation in brackish marshes of the Min River estuary, southeast China. Wetlands 2014; 34: 225–233.
30. Guenther A, Jurasinski G, Huth V, Glatzel S. Opaque closed chambers underestimate methane fluxes of Phragmites australis (Cav.) Trin. ex Steud. Environmental Monitoring and Assessment 2014; 186:2151–8. doi: 10.1007/s10661-013-3524-5 PMID: 24213640
31. Hirota M, Tang YH, Hu QW, Hirata S, Tomomichi K, Mo HW, et al. Methane emissions from different vegetation zones in a Qinghai-Tibetan Plateau wetland. Soil Biol Biochem 2004; 36: 737–748.
32. Sun Z, Jiang H, Wang L, Mou X, Sun W. Seasonal and spatial variations of methane emissions from coastal marshes in the northern Yellow River estuary, China. Plant and Soil 2013; 369: 317–33.
33. Chambers LG, Osborne TZ, Reddy KR. Effect of salinity-altering pulsing events on soil organic carbon loss along an intertidal wetland gradient: a laboratory experiment. Biogeochemistry 2013; 115: 363–383.
34. Neubauer SC. Ecosystem responses of a tidal freshwater marsh experiencing saltwater intrusion and altered hydrology. Estuaries and Coasts 2013; 36:491–507.
35. Ma A, Lu J, Wang T. Effects of elevation and vegetation on methane emissions from a freshwater estuarine wetland. Journal of Coastal Research 2012; 28:1319–29.
36. Biswas H, Mukhopadhyay SK, Sen S, Jana TK. Spatial and temporal patterns of methane dynamics in the tropical mangrove dominated estuary, NE coast of Bay of Bengal, India. Journal of Marine Systems 2007; 68:55–64.
37. Rask H, Schoenau J, Anderson D. Factors influencing methane flux from a boreal forest wetland in Saskatchewan Canada. Soil Biol Biochem 2002; 34: 435–443.
38. Duan XH, Wang XK, Chen L, Mu YJ, Yang ZY. Methane emission from aquatic vegetation zones of Wulingsu Lake, Inner Mongolia. Environmental Sci 2007; 3: 455–459.
39. Davidson EA, Janssens IA. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 2006; 440:165–173. PMID: 16525463
40. Conant RT, Ryan MG, Agren GI, Birge HE, Davidson EA, Eliasson PE. Temperature and soil organic matter decomposition rates—synthesis of current knowledge and a way forward. Global Change Biology 2011; 17:3392–3404.
41. Schipper LA, Hobbs JK, Rutledge S, Arcus VL. Thermodynamic theory explains the temperature optima of soil microbial processes and high Q10 values at low temperatures. Global Change Biology 2014; 20: 3578–3586. doi: 10.1111/gcb.12596 PMID: 24706438
42. Inglett KS, Inglett PW, Reddy KR, Osborne TZ. Temperature sensitivity of greenhouse gas production in wetland soils of different vegetation. Biogeochemistry 2012; 108: 77–90.
43. Roulet NT, Ash R, Moore TR. Low boreal wetlands as a source of atmospheric methane. J Geophys Res 1992; 97: 3739–3749.
44. Verville JH, Hobble SE, Chapin FS, Hooper DU. Response of tundra CH4 and CO2 flux to manipulation of temperature and vegetation. Biogeochemistry 1998; 41: 215–235.
45. Segers R. Methane production and methane consumption: a review of processes underlying wetland methane fluxes. Biogeochemistry 1998; 41: 23–51.
46. Bergman I, Svenson BH, Nilsson M. Regulation of methane production in a Swedish acid mire by pH, temperature and substrate. Soil Biol Biochem 1998; 30: 729–747.
47. Valentine DW, Holland EA, Schime DS. Ecosystem and physiological control over methane production in northern wetlands. J Geophys Res 1994; 99: 1563–1571.
48. Andrews JA, Matamala R, Westover KM, Schlesinger WH. Temperature effects on the diversity of soil heterotrophs and the δ13C of soil-respired CO2. Soil Biol Biochem 1993; 25: 321–326.
49. Koch O, Tscherko D, Kandeler E. Temperature sensitivity of microbial respiration, nitrogen mineralization, and potential soil enzyme activities in organic alpine soils. Global Biogeochemical Cycles 2007; 21: GB4017.
50. Miller RL. Carbon gas fluxes in re-established wetlands on organic soils differ relative to plant community and hydrology. Wetlands 2011; 31:1055–66.
51. Arkebauer TJ, Chanton JP, Verma SB, Kim J. Field measurements of internal pressurization in Phragmites australis (Poaceae) and implications for regulation of methane emissions in a midlatitude prairie wetland. American Journal of Botany 2001; 88:653–8. PMID: 11302851
52. Duan XN, Wang XK, Chen L, Mu YJ, Ouyang ZY. Methane emission from aquatic vegetation zones of Wuliangsu Lake, Inner Mongolia. Environmental Science 2007; 28:455–459.
53. Song CC, Zhang LH, Wang YY, Zhao ZC. Annual dynamics of CO2, CH4, N2O emissions from freshwater marshes and affected by nitrogen fertilization. Environmental Science 2006; 27:2369–2375.
54. Van Winden JF, Reichart GJ, McNamara NP, Benthien A, Damsté JSS. Temperature-induced increase in methane release from peat bogs: A mesocosm experiment. Plos One 2012; 7:1–5.