

Article

# Methane Emission from Mangrove Wetland Soils Is Marginal but Can Be Stimulated Significantly by Anthropogenic Activities

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**Abstract:** Mangrove wetland soils have been considered as important sources for atmospheric CH<sub>4</sub>, but the magnitude of CH<sub>4</sub> efflux in mangrove wetlands and its relative contribution to climate warming compared to CO<sub>2</sub> efflux remains controversial. In this study, we measured both CH<sub>4</sub> and CO<sub>2</sub> effluxes from mangrove soils during low or no tide periods at three tidal zones of two mangrove ecosystems in Southeastern China and collected CH<sub>4</sub> efflux data from literature for 24 sites of mangrove wetlands worldwide. The CH<sub>4</sub> efflux was highly variable among our field sites due to the heterogeneity of mangrove soil environments. On average, undisturbed mangrove sites have very low CH<sub>4</sub> efflux rates (ranging from 0.65 to 14.18 μmol m<sup>-2</sup> h<sup>-1</sup>; median 2.57 μmol m<sup>-2</sup> h<sup>-1</sup>), often less than 10% of the global warming potentials (GWP) caused by the soil CO<sub>2</sub> efflux from the same sites (ranging from 0.94 to 9.50 mmol m<sup>-2</sup> h<sup>-1</sup>; median 3.67 mmol m<sup>-2</sup> h<sup>-1</sup>), even after considering that CH<sub>4</sub> has 28 times more GWP over CO<sub>2</sub>. Plant species, study site, tidal position, sampling time, and soil characteristics all had no significant effect on mangrove soil CH<sub>4</sub> efflux. Combining our field measurement results and literature data, we demonstrated that the CH<sub>4</sub> efflux from undisturbed mangrove soils was marginal in comparison with the CO<sub>2</sub> efflux in most cases, but nutrient inputs from anthropogenic activities including nutrient run-off and aquaculture activities significantly increased CH<sub>4</sub> efflux from mangrove soils. Therefore, CH<sub>4</sub> efflux from mangrove wetlands is strongly influenced by anthropogenic activities, and future inventories of CH<sub>4</sub> efflux from mangrove wetlands on a regional or global scale should consider this phenomenon.

**Keywords:** greenhouse gas emission; soil respiration; coastal wetlands; anthropogenic effect

## 1. Introduction

Global wetlands are considered as important carbon sinks for sequestering high amounts of carbon dioxide (CO<sub>2</sub>) from the atmosphere and contain more than 30% of the world's organic carbon in the soils, despite accounting for only 5%–8% of the global terrestrial surface [1–3]. Mangrove wetlands could be key ecosystems in addressing climate regulation through their high productivity and effective carbon (C) sequestration rates [4–7]. The global carbon sequestration rate in mangrove wetlands is

on average  $174 \text{ g C m}^{-2} \text{ year}^{-1}$ , corresponding to about 10%–15% of global coastal ocean carbon storage [8]. Organic-rich soils dominate in mangrove carbon storage, accounting for 49%–98% of carbon stocks in mangrove wetlands [9,10]. However, the buried carbon may release back into the atmosphere as gaseous products such as  $\text{CO}_2$  and methane ( $\text{CH}_4$ ) [1]. Meanwhile, wetlands are also identified as major  $\text{CH}_4$  sources for the atmosphere, emitting 177 to 284 Tg  $\text{CH}_4 \text{ year}^{-1}$ , corresponding to approximately 40% of the total global  $\text{CH}_4$  emission [11].  $\text{CH}_4$  has a global warming potential 28 times greater than that of  $\text{CO}_2$  on a 100-year timescale and directly contributes to about 20% of recent climate warming, despite the fact its concentration is two orders of magnitude lower than that of  $\text{CO}_2$  [12]. Thus, proper quantification of  $\text{CH}_4$  efflux from mangrove wetlands is critical to evaluating its effect on climate warming mitigation. Additional knowledge of mangrove wetlands'  $\text{CH}_4$  emission will further provide guidance on mangrove wetlands restoration efforts to mitigate atmospheric  $\text{CO}_2$  increase.

$\text{CH}_4$  efflux from mangrove soils is generally identified to be low but highly variable [13–16]. The practice of mangrove carbon budget has shown that carbon burial, soil respiration, and soil  $\text{CH}_4$  emission are  $24 \text{ Tg C year}^{-1}$ ,  $36 \text{ Tg C year}^{-1}$ , and  $2 \text{ Tg C year}^{-1}$ , respectively [8], assuming a mangrove extent area of  $138,000 \text{ km}^2$  [17]. Low  $\text{CH}_4$  production and emission is mainly due to the presence of high sulfate in mangrove soil, which allows sulfate-reducing bacteria to outcompete  $\text{CH}_4$ -producing bacteria [18–20]. Additionally, mangrove ecosystems are inundated by periodic tides and receive nutrient input from anthropogenic activities, which provides an anaerobic environment and high availability of substrate for methanogenesis [21]. Recent studies reported a significant amount of  $\text{CH}_4$  efflux from mangrove wetland soils [21–23] and claimed that the contribution of  $\text{CH}_4$  efflux to climate warming was non-negligible in the estuarine mangrove wetlands, which could account for 9.3%–32.7% plant  $\text{CO}_2$  sequestration [24]. Thus, considerable uncertainty still exists regarding the magnitude of mangrove soil  $\text{CH}_4$  efflux and its contribution to climate warming, which requires further study.

The carbon stocks in mangrove wetlands of China play an essential role in global oceanic carbon cycling and differ among mangrove species in subtropical and tropical regions [25]. Large spatio-temporal variations in  $\text{CH}_4$  efflux have been observed in mangrove soils [18,23,26]. Previous studies indicated that  $\text{CH}_4$  efflux varied among different tidal positions, probably due to differences in soil temperature, salinity, and pH [27]. Temporal variation in  $\text{CH}_4$  efflux could be explained by soil temperature, the position of the water table, and the availability of suitable substrate [23,28,29]. Meanwhile, mangrove wetlands in China are facing greater pollution pressure due to chemical discharge from aquaculture activity and sea-wall construction [30]. However, there are few studies that investigate human perturbations such as nutrient loading from aquaculture ponds on mangrove soil  $\text{CH}_4$  efflux even though these activities can significantly change these factors [7,26].

In this study, we measured both soil  $\text{CH}_4$  and  $\text{CO}_2$  effluxes from mangrove wetland soils during low or no tide periods at three tidal zones of two mangrove ecosystems in Southeastern China and collected available  $\text{CH}_4$  efflux data from literature for global mangrove wetlands. The aims of this study were to identify the magnitude of  $\text{CH}_4$  efflux in mangrove wetlands with and without the influence of anthropogenic activities and to evaluate the relative contribution of  $\text{CH}_4$  efflux over  $\text{CO}_2$  efflux from mangrove wetland soils to climate warming.

## 2. Materials and Methods

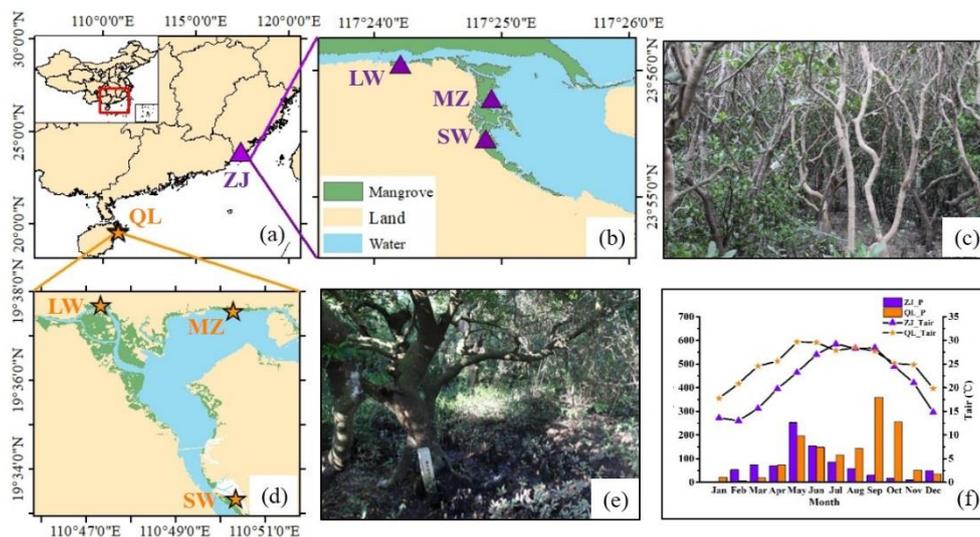
### 2.1. Study Site Description

The study was conducted in two mangrove wetlands in Southeastern China, including Zhangjiang Estuary Mangrove National Natural Reserve ( $23^\circ 55' 49'' \text{ N}$ ,  $117^\circ 24' 54'' \text{ E}$ , abbreviated as the ZJ (Zhangjiang Estuary) site) and Qinglan Harbour Mangrove Provincial Natural Reserve ( $19^\circ 37' 48'' \text{ N}$ ,  $110^\circ 46' 12'' \text{ E}$ , abbreviated as the QL (Qinglan Harbour) site) (Figure 1).

ZJ site is located in an estuary of the Zhangjiang River, Yunxiao County, Fujian Province, China, with a subtropical marine monsoon climate. The monthly mean air temperature ranged from  $13.5^\circ \text{ C}$

in January to 28.9 °C in August, and the annual mean air temperature was 21.2 °C. Annual mean rainfall was 1714.5 mm, most of which occurred during the wet season from April to September. Tides were semidiurnal, with an annual mean tidal-level variation of 2.32 m. The salinity of the seawater ranged from 12 to 26 ppt. The vegetation was dominated by *Kandelia obovata* Sheue, Liu & Yong (red mangrove), *Aegiceras corniculatum* (L.) Blanco (black mangrove), and *Avicennia marina* (Forssk.) Vierh. (grey mangrove), mixed with some other less common mangrove species such as *Bruguiera gymnorrhiza* (L.) Savigny (black mangrove) and *Acanthus ilicifolius* L. (holy mangrove) [31].

QL site, situated in Wenchang County, Hainan Province, China, experienced a tropical monsoon climate. Annual mean air temperature was 23.9 °C, and the lowest monthly mean temperature was 18.3 °C in January. The annual precipitation was 1974 mm, of which more than 82% occurred during the wet season from May to October. Tides were semi-diurnal, and the tidal-level ranged from 0.01 m to 2.38 m, with the largest tidal-level variation of 2.07 m in one tidal cycle. The dominant mangrove species at QL site, which had the largest number of mangrove species in China, were *Bruguiera sexangula* (Lour.) Poir. (upriver orange mangrove), *Sonneratia caseolaris* (L.) Engl. (mangrove apple), *Lumnitzera racemosa* Willd. (tonga mangrove), *Ceriops tagal* (Pers.) C.B.Rob. (spurred mangrove), and *Rhizophora apiculata* Blume (red mangrove) communities [32,33].



**Figure 1.** Map of sampling location and climatic conditions. (a) Geographical location of Zhangjiang Estuary (ZJ) and Qinglan Harbour (QL) mangrove wetlands. (b,c) Sampling sites and a typical scene from ZJ mangrove forest. (d,e) Sampling sites and a typical scene from QL mangrove forest. (f) Monthly precipitation (P, mm) and monthly air temperature (T, °C) from ZJ and QL mangrove wetlands. LW: landward zone, MZ: middle zone, and SW: seaward zone.

## 2.2. Measurements of Soil $CH_4$ and $CO_2$ Effluxes

Sampling campaigns were undertaken in July 2013 (represented wet season) and February 2014 (represented dry season) at ZJ site, and in August 2016 (represented wet season) and November 2017 (represented dry season) at QL site. For each sampling time, measurements were conducted in three tidal positions: landward zone (LW), middle zone (MZ), and seaward zone (SW), with the exception of SW at ZJ site during the dry season due to heavy rainfall making the site inaccessible. At each sampling position, four chambers were set up, and four replicated samples were collected on the same day at each site for a total of twelve samples. During low or no tide periods in the day time, we measured environmental variables and collected samples for laboratory analyses. The soil inundation and exposure duration were similar among three tidal positions and four replicates samples.

Gas effluxes from the soil were quantified through the standard static (closed) chamber technique [23]. Measurements were taken using PVC chambers (diameter 20 cm, length 15 cm, volume 4.50 L, and enclosing 0.025 m<sup>2</sup>). The open end of chamber was slightly inserted into the soil to a depth

of 2–3 cm to ensure minimal lateral gas leakage. A controllable valve above the chamber was left open for 30 min prior to sampling, which is adequate to remove impacts of root disturbance caused by the chamber insertion, and then the valve was closed during the whole measurements time. Deployment time was set at 2 h, with sampling at 0, 30, 60, 90, and 120 min intervals. Headspace gas was mixed carefully through the vent tube, and 8 ml gas samples were collected using a 50 mL gas-tight syringe equipped with a luer-lock valve (SGE Trajan Scientific and Medical Pty Ltd., Melbourne, Australia). Gas samples were then transferred into pre-evacuated gas sampling bags or vials for storage (Dalian Delin Gas Packing Inc., Dalian, Liaoning, China). The air temperature inside the chamber was measured simultaneously with the gas sampling.

All samples were transported to laboratory and analyzed within 24 h using an Agilent 7890A gas chromatograph (Agilent Technologies Inc., Wilmington, DE, USA) equipped with a flame ionization detector (FID) and a Poropak-Q column. 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 1200 mL s<sup>-1</sup>. Standard curves were gained by injecting a series volume of pure CH<sub>4</sub> (99.992%) and CO<sub>2</sub> (99.999%) in high purity N<sub>2</sub> (99.999%, HKO Co Ltd., Hong Kong, China). The CH<sub>4</sub> and CO<sub>2</sub> concentrations were quantified by calculating the peak areas of samples against standards of similar concentration ranges. During the gas measurement, standard gas (40 mL L<sup>-1</sup> CH<sub>4</sub> and 2000 mL L<sup>-1</sup> CO<sub>2</sub>) was analyzed every 10 samples to ensure data quality. Gas effluxes were calculated based on a linear least squares fit of the time series of gas concentrations. Data were accepted if the slope of the linear fit had a  $R^2 > 0.80$ .

### 2.3. Measurements of Environmental Factors

For each chamber measurement, soil cores (0–10 cm surface soil) were collected using a hand-held PVC tube after gas sampling. The soil samples were divided into two subsamples: fresh soil and air-dried soil. Soil moisture content was determined by oven-drying of 7 g fresh soil at 105 °C to a constant weight. Soil inorganic N (NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N) contents were extracted with 2 M KCl from fresh soil samples and then analyzed using a UV-2501PC UV-VIS spectrophotometer (Shimadzu Inc., Japan) [23]. While both NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N extraction methods require fresh soil samples, the samples from ZJ-SW during the wet season and ZJ-LW and ZJ-MZ during the dry season were dried before we could take any measurements. Air-dried soil was sieved through a 2 mm sieve. The pH and salinity were measured at a  $w$  (soil):  $v$  (water) of 1:5 and 1:2.5 soil slurry using an electrochemistry benchtop meter, Orion™ Versa Star Pro™ (Thermo Fisher Scientific Inc., Beverly, MA, USA). Soil total carbon content (TC), total nitrogen content (TN), and C:N ratio of air-dried soil were measured using the an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH Inc., Hanau, Germany). Analysis of soil characteristics all followed the standard methods described by Page et al. (1982), and data were expressed in term of 105 °C oven-dried weight.

### 2.4. Conversion to CO<sub>2</sub>—Equivalent Efflux

The global warming potential for CH<sub>4</sub> was converted to CO<sub>2</sub> equivalents using a multiplier of 28 for 100-year timescale [34] to compare their global warming effects.

### 2.5. Collecting CH<sub>4</sub> Efflux Data from Literature

A total of 24 studies of CH<sub>4</sub> efflux from mangrove soil were reviewed (Table S2). These studies were selected because the same static chamber method was used as our study, which made the results comparable. We divided the mangrove wetlands into undisturbed and anthropogenic sites according to the eutrophic status of the chosen study sites (Table S3). Undisturbed sites are defined as not affected by nutrient input from anthropogenic activities involving agricultural, domestic, aquaculture, or other run-off from treatment plants as indicated by the reference's study site descriptions. Anthropogenic sites are those known to be influenced by activities described above.

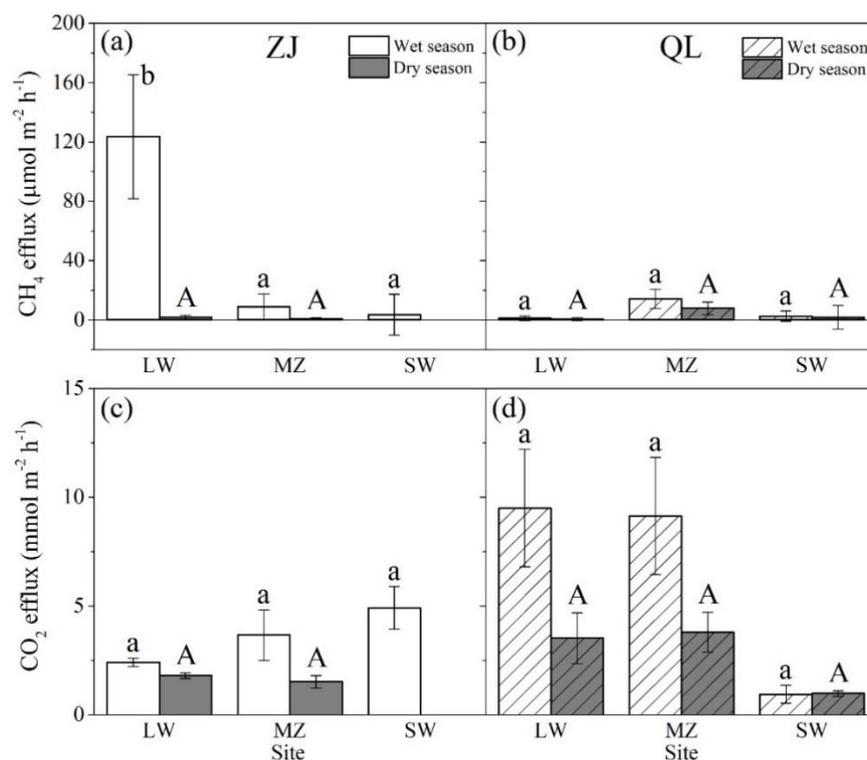
## 2.6. Statistical Analysis

Two-way analysis of variance (ANOVA) was used to determine significance of differences between means of soil characteristics and effluxes of CH<sub>4</sub> and CO<sub>2</sub> among tidal positions and sampling time. If the difference was significant at  $p < 0.05$ , a Post-hoc Turkey test was used to determine where the difference lay. All data were expressed as means  $\pm$  standard error (SE) with four replicates. Paired  $t$ -test was used to compare the differences in soil characteristics and effluxes of CH<sub>4</sub> and CO<sub>2</sub> among tropical and subtropical mangrove wetlands. Pearson correlation coefficient values ( $r$ ) were calculated to determine the relationship between soil characteristics and CH<sub>4</sub> and CO<sub>2</sub> effluxes. All analysis processes were performed using SPSS 21.0 for Windows (SPSS Inc., Chicago, IL, USA).

## 3. Results

### 3.1. Soil CH<sub>4</sub> and CO<sub>2</sub> Effluxes

CH<sub>4</sub> efflux was highly variable among the sampling sites, for most sampling sites; CH<sub>4</sub> efflux was small and almost negligible, ranging from  $0.65 \pm 0.91$  to  $14.18 \pm 6.35 \mu\text{mol m}^{-2} \text{h}^{-1}$ , while at the landward zone in Zhangjiang Estuary site (abbreviated as ZJLW) during the wet season, CH<sub>4</sub> efflux was about 10 times higher than the highest value found at other sites ( $123.59 \pm 41.79 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) (Figure 2a,b and Table S1). CO<sub>2</sub> efflux ranged from  $0.94 \pm 0.41$  to  $9.50 \pm 2.70 \text{mmol m}^{-2} \text{h}^{-1}$ , and the highest and lowest values were recorded at landward and seaward zones in Qinglan Harbour mangrove wetland during wet season (Figure 2c, Figure 2d and Table S1). No significant difference was found in soil CH<sub>4</sub> and CO<sub>2</sub> effluxes between ZJ and QL sites ( $p = 0.173$  and  $p = 0.111$ ).



**Figure 2.** CH<sub>4</sub> and CO<sub>2</sub> effluxes from ZJ and QL mangrove soils. (a,b) Comparison of the mean soil CH<sub>4</sub> efflux among three tidal positions during wet and dry seasons at ZJ and QL site. (c,d) Comparison of the mean soil CO<sub>2</sub> efflux among three tidal positions during wet and dry seasons at ZJ and QL site. Error bars represent the standard error (SE) of the means ( $n = 4$ ). Different letters indicate significant differences among tidal positions for each period (wet and dry seasons) according to analysis of variance (ANOVA) test (Turkey HSD test,  $p < 0.05$ ). Site abbreviations were the same as Figure 1.

At ZJ site, CH<sub>4</sub> efflux ranged from  $0.73 \pm 0.73$  to  $123.59 \pm 41.79$   $\mu\text{mol m}^{-2} \text{h}^{-1}$  (Figure 2a), and significant differences in CH<sub>4</sub> efflux among tidal positions and sampling time were found ( $p = 0.006$  and  $p = 0.002$ , respectively). The highest and lowest CH<sub>4</sub> values were recorded at landward zone during wet season and middle zone during dry season, respectively. Soil CH<sub>4</sub> efflux was higher in wet season than that in the dry season at all sites. The CO<sub>2</sub> efflux ranged from  $1.52 \pm 0.29$  to  $4.91 \pm 0.98$   $\text{mmol m}^{-2} \text{h}^{-1}$  and did not differ significantly with tidal positions and seasons ( $p = 0.160$  and  $p = 0.108$ ) (Figure 2c).

At QL site, the value of soil CH<sub>4</sub> efflux ranged from  $0.65 \pm 0.91$  to  $14.18 \pm 6.35$   $\mu\text{mol m}^{-2} \text{h}^{-1}$  and showed no significant differences among different tidal positions and sampling time ( $p > 0.05$ ) (Figure 2b). CH<sub>4</sub> efflux at the middle zone was the highest, followed by the CH<sub>4</sub> efflux at seaward zone. The CO<sub>2</sub> efflux ranged from  $0.94 \pm 0.41$  to  $9.50 \pm 2.70$   $\text{mmol m}^{-2} \text{h}^{-1}$  (Figure 2d) and changed with tidal position and sampling time significantly ( $p = 0.045$  and  $p = 0.042$ , respectively). The lowest value of CO<sub>2</sub> efflux was measured at seaward zone, and highest CO<sub>2</sub> efflux was observed during wet season rather than dry season.

### 3.2. Soil Characteristics

Soil characteristics measured during wet and dry season at ZJ and QL sites are shown in Table 1. There were significant differences in soil temperature, pH, TC content, TN content, and C:N ratio among subtropical (ZJ site) and tropical (QL site) mangrove wetlands ( $p < 0.05$ ). The mangrove soils had higher pH values (ranging from  $6.62 \pm 0.16$  to  $7.43 \pm 0.14$ ) at QL site than that at ZJ site (ranging from  $5.46 \pm 0.31$  to  $7.11 \pm 0.03$ ). Higher soil temperature, TC content, TN content, and C:N ratio were detected at QL site than at ZJ site ( $p < 0.05$ ). Salinity and soil moisture content were not significantly different between QL site and ZJ site and were not significantly influenced by tidal positions and sampling time ( $p > 0.05$ ).

At ZJ site, significantly higher soil temperatures were observed in the wet season rather than dry season ( $p = 0.015$ ). Tidal position had significant effect on pH, TN content, and C:N ratio ( $p < 0.05$ ). Lowest pH but highest TC content, TN content, and C:N ratio were observed in the middle zone ( $p < 0.05$ ).

At QL site, both soil temperature and C:N ratio were significantly different between wet and dry season. Higher soil temperature and a lower C:N ratio were observed in wet season ( $p < 0.05$ ). The pH value, NH<sub>4</sub><sup>+</sup>-N content, NO<sub>3</sub><sup>-</sup>-N content, TN content, TC content, and C:N ratio were significantly affected by tidal position ( $p < 0.05$ ). With an increase in tidal positions, salinity, pH value, and C:N ratio gradually increased, while the NH<sub>4</sub><sup>+</sup>-N content, NO<sub>3</sub><sup>-</sup>-N content, TN content, and TC content gradually decreased.

**Table 1.** Key characteristics for mangrove soils at various study sites measured during wet and dry seasons.

Mangrove Wetland	Season	Study Site	Species	T <sub>soil</sub>	Salinity (ppt)	pH	Soil Moisture Content	NH <sub>4</sub> <sup>+</sup> -N (ug g <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N (ug g <sup>-1</sup> )	TN (%)	TC (%)	C:N Ratio
ZJ	Wet season	LW	KO	27.19 ± 0.19c	2.07 ± 0.25a	5.46 ± 0.31a	0.85 ± 0.15a	9.50 ± 0.92	0.14 ± 0.04	0.15 ± 0.03a	1.82 ± 0.18a	12.50 ± 1.07b
		MZ	KO	27.74 ± 0.05c	5.70 ± 0.66ab	7.11 ± 0.03c	0.89 ± 0.23a	9.09 ± 0.88	0.15 ± 0.05	0.15 ± 0.01a	1.36 ± 0.01a	9.25 ± 0.35a
		SW	KO	27.42 ± 0.09c	7.70 ± 1.45ab	6.82 ± 0.03ab	1.04 ± 0.45a			0.17 ± 0.01a	1.96 ± 0.18a	11.44 ± 0.65ab
	Dry season	LW	KO	17.35 ± 0.19a	9.00 ± 1.27b	6.23 ± 0.10b	0.75 ± 0.07a			0.16 ± 0.02a	1.98 ± 0.16a	12.29 ± 0.47b
		MZ	KO	18.47 ± 0.09b	15.55 ± 2.56c	7.01 ± 0.14c	0.81 ± 0.50a			0.14 ± 0.01a	1.49 ± 0.09a	10.90 ± 0.31ab
		SW	KO									
QL	Wet season	LW	BS, HL	29.00D	12.09 ± 1.37A	6.81 ± 0.05AB	1.85 ± 0.25B	8.02 ± 0.90B	4.31 ± 0.45B	0.73 ± 0.10B	11.48 ± 2.00AB	15.44 ± 0.93A
		MZ	BS, RA	28.90D	17.84 ± 5.91AB	6.62 ± 0.16A	0.56 ± 0.12A	3.11 ± 0.55A	1.28 ± 0.13A	0.24 ± 0.05A	4.01 ± 0.66AB	17.03 ± 0.61A
		SW	Mixed	30.50E	25.91 ± 4.22B	6.85 ± 0.02AB	0.51 ± 0.01A	3.17 ± 0.13A	1.63 ± 0.05A	0.08 ± 0.01A	4.48 ± 0.12AB	57.81 ± 7.33B
	Dry season	LW	KO	25.18 ± 0.07B	11.12 ± 1.21A	7.30 ± 0.11BC	2.08 ± 0.39B	8.14 ± 1.10B	3.55 ± 0.35B	0.79 ± 0.11B	12.41 ± 2.58B	15.10 ± 0.89A
		MZ	KO	23.34 ± 0.03A	15.60 ± 0.67AB	6.76 ± 0.16A	0.60 ± 0.14A	2.26 ± 0.75A	1.42 ± 0.30A	0.19 ± 0.05A	3.52 ± 0.88A	19.47 ± 0.74B
		SW	KO	25.45 ± 0.01C	19.90 ± 0.30AB	7.43 ± 0.14C	0.44 ± 0.06A	2.26 ± 0.33A	1.31 ± 0.01A	0.07 ± 0.01A	4.75 ± 0.16AB	74.26 ± 7.84C

ZJ: Zhangjiang Estuary Mangrove National Natural Reserve; QL: Qinglan Harbour Mangrove Provincial Natural Reserve; LW: Landward zone; MZ: Middle zone; SW: Seaward zone; KO: *Kandelia obovata* Sheue, Liu & Yong (red mangrove) community; BS: *Bruguiera sexangula* (Lour.) Poir. (upriver orange mangrove) community; HL: *Heritiera littoralis* Aiton (looking-glass mangrove) community; RA: *Rhizophora apiculata* Blume (red mangrove) community; Mixed: Mixed species community. Mean and standard error (SE) of four replicates are shown ( $n = 4$ ). Different letters indicated significant differences among different sampling sites according to analysis of variance (ANOVA) test ( $p < 0.05$ ).

### 3.3. The Relationship between Gas Effluxes and Soil Characteristics

Among soil characteristics measured in current study, soil temperature and pH were correlated with CO<sub>2</sub> efflux. The soil temperature had positive effect on CO<sub>2</sub> efflux ( $p = 0.011$ ,  $r = 0.342$ ), while pH had negative effect on it ( $p < 0.001$ ,  $r = -0.506$ ). No significant relationship among CH<sub>4</sub> efflux and any soil characteristics was recorded in this study.

## 4. Discussions

### 4.1. Magnitude of CH<sub>4</sub> Efflux from Mangrove Wetland Soils

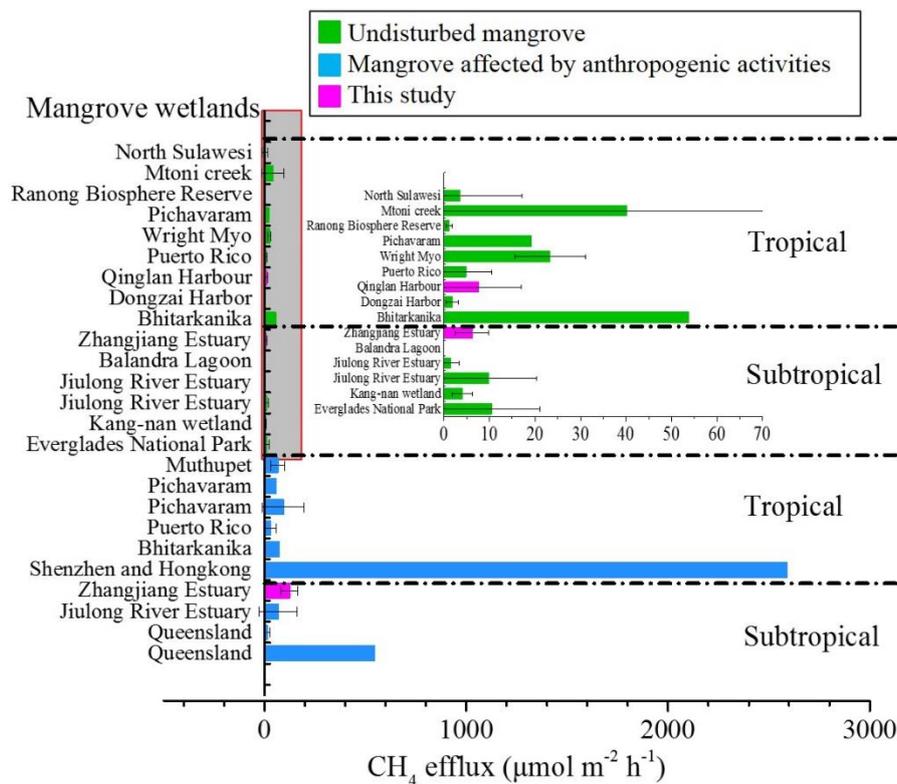
Combining our data and literature data, we found CH<sub>4</sub> efflux from undisturbed mangrove wetlands was negligible but can be stimulated significantly by anthropogenic activities (Figure 3). The results from our direct field measurements indicated that low CH<sub>4</sub> efflux was recorded in undisturbed mangrove soils of Southeastern China, ranging from  $0.65 \pm 0.91$  to  $14.18 \pm 6.35 \mu\text{mol m}^{-2} \text{h}^{-1}$ , which was consistent with the results found by others in nearby undisturbed mangrove areas [35–37]. The highest CH<sub>4</sub> efflux ( $123.59 \pm 41.79 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) was observed at landward zone in ZJ mangrove wetland, probably due to large and frequent discharge of freshwater as indicated by very low salinity at this site (as low as 2 ppt) (Table 1). This result was similar to the CH<sub>4</sub> efflux in the Jiulong River mangrove, which was also heavily influenced by human activities and positively correlated with NH<sub>4</sub><sup>+</sup>-N, organic carbon, and total Kjeldahl nitrogen [24]. Mangrove ecosystems are rich in carbon but nutrient-poor; in particular, they are limited by nitrogen and phosphorus [38]. Anthropogenic nutrient input improves microbial metabolic process, enhancing more emission of CH<sub>4</sub> efflux from soils into the atmosphere [39].

In addition, the CH<sub>4</sub> efflux data from literature for 24 sites of mangrove wetlands worldwide showed that mangroves affected by anthropogenic activities (ranging from 0.19 to  $5168.62 \mu\text{mol m}^{-2} \text{h}^{-1}$  with the median values of  $52.80 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) had emission rates 14 times higher than those from undisturbed mangroves (ranging from  $-6.05$  to  $79.00 \mu\text{mol m}^{-2} \text{h}^{-1}$  with the median of  $3.57 \mu\text{mol m}^{-2} \text{h}^{-1}$ ). These CH<sub>4</sub> efflux data revealed that the mangroves affected by anthropogenic activities made a greater contribution to climate warming rather than those undisturbed or not heavily disturbed mangrove forests. Anthropogenic activities cause significant increases in CH<sub>4</sub> emission, and if anthropogenic activities continue at the current pace without protective measures, these ecosystems could become potential major sources of CH<sub>4</sub> emission and decrease their ability to store carbon in the future [40]. The current study divided the mangrove wetlands into undisturbed and affected by anthropogenic activities based on whether the chosen study sites have involved agricultural, domestic, aquaculture, or other run-off from treatment plants in the references. Further research is needed to quantify the stimulation effect of nutrient input from anthropogenic activities on CH<sub>4</sub> emissions, combined with controlled experiments and microbial community analysis to model the extent of change.

### 4.2. Contribution of CH<sub>4</sub> Efflux from Mangrove Wetlands to Climate Warming

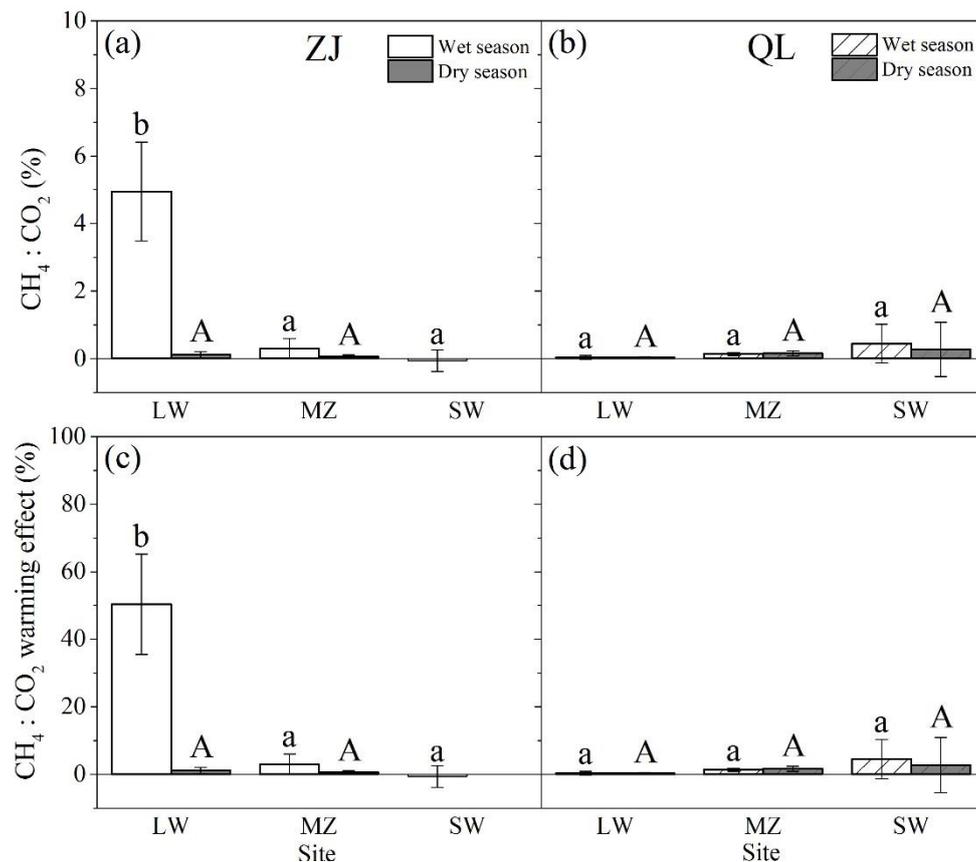
We calculated CH<sub>4</sub>:CO<sub>2</sub> efflux ratio and CH<sub>4</sub>:CO<sub>2</sub> warming effect ratio to evaluate the relative role of CH<sub>4</sub> efflux for warming potentials (Figure 4) among different tidal zones in two mangrove wetlands. The CH<sub>4</sub>:CO<sub>2</sub> efflux ratio ranged from  $-0.06\% \pm 0.32\%$  to  $0.45\% \pm 0.57\%$  in most sampling sites except for the disturbed ZJLW site ( $4.95\% \pm 1.46\%$ ). Considering CH<sub>4</sub> global warming potential in 100-year term, CH<sub>4</sub> accounted for  $-0.63\% \pm 3.21\%$  to  $4.54\% \pm 5.79\%$  of the warming effect, a relatively minor contributor to CO<sub>2</sub> equivalents, except at the ZJLW site, which was  $50.37\% \pm 14.85\%$ , making it a highly significant contributor. A higher CH<sub>4</sub>:CO<sub>2</sub> warming effect ratio had been reported in the Jiulong River mangrove (10.30% to 48.35%) [24] and Futian mangrove (18.36% to 255.96%) [21] in South China, which received significant amounts of anthropogenic nutrient inputs. This reveals that the magnitude and contribution of CH<sub>4</sub> efflux from undisturbed mangrove soils to climate warming

was marginal in comparison with CO<sub>2</sub> efflux, but could be a potential major contributor to warming effect under the influence of anthropogenic activities.



**Figure 3.** Comparison of CH<sub>4</sub> efflux from undisturbed mangrove wetlands and mangroves wetlands affected by anthropogenic activities. Detailed information on the literature sources of CH<sub>4</sub> efflux data is provided in Table S2. Nutrient concentrations and assignment of eutrophic status from mangrove wetlands are shown in Table S3.

In addition, the global median CH<sub>4</sub> efflux in mangrove wetlands (3.57 and 52.80 μmol m<sup>-2</sup> h<sup>-1</sup> for undisturbed mangroves and mangroves affected by anthropogenic activities, respectively) was negligible in contrast to other wetlands, such as freshwater wetlands (69.44 to 6944.44 μmol m<sup>-2</sup> h<sup>-1</sup>) (Chmura et al., 2003), peatlands (31.39 to 59.93 μmol m<sup>-2</sup> h<sup>-1</sup>) [41], and rice paddies (709.38 μmol m<sup>-2</sup> h<sup>-1</sup>) [42]. This indicates that mangrove wetlands were not significant contributors to global wetland CH<sub>4</sub> budget compared with other wetlands. Recent studies have also found that mangrove soils acted as a net carbon sink after subtracting the effects of CH<sub>4</sub> emission from carbon sequestration [43]. Overall, mangrove wetlands should be restored and protected to mitigate climate warming without great concern for warming effect caused by CH<sub>4</sub> emission.



**Figure 4.** CH<sub>4</sub>:CO<sub>2</sub> effluxes ratio and CH<sub>4</sub>:CO<sub>2</sub> warming effect ratio from ZJ and QL mangrove wetlands. (a–b) Comparison of CH<sub>4</sub>:CO<sub>2</sub> effluxes ratio among three tidal positions during wet and dry seasons at ZJ and QL sites. (c–d) Comparison of CH<sub>4</sub>:CO<sub>2</sub> warming effect ratio among three tidal positions during wet and dry seasons at ZJ and QL site. Site abbreviations were the same as Figure 1.

## 5. Conclusions

The current study suggests that undisturbed mangrove soils were minor contributors to climate warming, but the CH<sub>4</sub> efflux from mangrove wetlands was significantly increased by nutrient inputs from anthropogenic activities including nutrient run-off and aquaculture activities. This phenomenon should be considered in order to better quantify the emission of CH<sub>4</sub> from regional or global mangrove wetlands and to evaluate the potential roles of constructed or restored mangrove wetlands for mitigating climate warming.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/1999-4907/9/12/738/s1>, Table S1: CH<sub>4</sub> and CO<sub>2</sub> effluxes from ZJ and QL mangrove wetlands; Table S2: summary of CH<sub>4</sub> efflux data as reported by authors or calculated from literature in other mangrove wetlands; and Table S3: nutrient concentrations and assignment of eutrophic status.

**Author Contributions:** G.L. conceived and designed the experiment. X.Z., J.G., W.S. and J.F. conducted the experiment and collected data. X.Z. and G.L. analyzed the data and wrote the initial draft of the manuscript. All authors contributed to the editing and revising of the final version of the manuscript. The authors approved the final version for publication and agree to be held accountable for the content therein.

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