Response of gaseous carbon emissions to low-level salinity increase in tidal marsh ecosystem of the Min River estuary, southeastern China

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ABSTRACT

Although estuarine tidal marshes are important contributors to the emission of greenhouse gases into the atmosphere, the relationship between carbon dioxide (CO2), methane (CH4) emission, and environmental factors, with respect to estuarine marshes, has not been clarified thoroughly. This study investigated the crucial factors controlling the emission of CO2 and CH4 from a freshwater marsh and a brackish marsh located in a subtropical estuary in southeastern China, as well as their magnitude. The duration of the study period was November 2013 to October 2014. Relevant to both the field and incubation experiments, the CO2 and CH4 emissions from the two marshes showed pronounced seasonal variations. The CO2 and CH4 emissions from both marshes demonstrated significant positive correlations with the air/soil temperature (p < 0.01), but negative correlations with the soil electrical conductivity and the pore water/tide water Cl− and SO42− (p < 0.01). The results indicate no significant difference in the CO2 emissions between the freshwater and brackish marshes in the subtropical estuary, whereas there was a difference in the CH4 emissions between the two sites (p < 0.01). Although future sea-level rise and saltwater intrusion could reduce the CH4 emissions from the estuarine freshwater marshes, these factors had little effect on the CO2 emissions with respect to an increase in salinity of less than 5‰. The findings of this study could have important implications for estimating the global warming contributions of estuarine marshes along differing salinity gradients.

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Introduction

Carbon dioxide (CO2) and methane (CH4) are significant active greenhouse gases (GHGs) that contribute to the warming of the surface of the Earth. Therefore, it is essential to measure the GHG emissions from the major ecosystems to estimate their effect on global warming [IPCC, 2013]. The coastal and estuarine marsh ecosystems have relatively high net primary
productivity and have been recognized as important contributors to GHG emissions (Magenheimer et al., 1996; Middelburg et al., 2002; Tong et al., 2014). Considerable efforts have been made to quantify the CO₂ and CH₄ emissions from tidal freshwater and brackish marshes, as well as salt marshes (Van der Nat and Middelburg, 2000; Avery et al., 2003; Hirota et al., 2007; Bastviken et al., 2011), including those in wetlands along salinity gradients in estuarine areas (DeLaune et al., 1983; Smith et al., 1983; Bartlett et al., 1987; Nyman and DeLaune, 1991; Poffenbarger et al., 2011; Weston et al., 2014; Wilson et al., 2015). In general, wetlands are important ecosystems for carbon storage because of the high productivity and low decomposition rates. The decomposition rates (gaseous efflux) are of more concern in subtropical estuarine areas, where large quantities of gaseous carbon (CO₂ and CH₄) are produced and emitted into the atmosphere. These large emissions are ascribed to the warmer conditions and much longer growing seasons in such environments (Turetsky et al., 2014). However, in China, few studies have measured simultaneously the emissions of CO₂ and CH₄ from freshwater and brackish marshes, especially from those situated in subtropical estuaries. To predict the future atmospheric CO₂ and CH₄ concentrations, accurate estimations of such emissions from subtropical estuarine ecosystems are required. Furthermore, most previous studies have focused on the plant communities of Phragmites australis and Spartina alterniflora, whereas scant attention has been paid to Cyperus malaccensis, a native species that is widely distributed throughout the southeastern coastal region of China.

Salinity is an important driving force of ecosystem processes in estuarine areas, especially of CO₂ and CH₄ production and emission. It is generally acknowledged that coastal salt marshes have high concentrations of sulfate (SO₄²⁻). The presence of SO₄²⁻ in marsh soils is conducive to sulfate-reducing bacteria (SRB) that outcompete methanogens for energy sources, consequently inhibiting methane production (Bartlett et al., 1987; Middelburg et al., 2002). Considerable efforts have been made to investigate the relationship between CO₂ and CH₄ emissions and the salinity in different coastal marsh ecosystems. In Chesapeake Bay, Virginia (USA), the annual atmospheric CH₄ emission was indicated as 5.6 g/(m²·year) at the most saline site, 22.4 g/(m²·year) at an intermediate saline site, and 18.2 g/(m²·year) at the least saline site (Bartlett et al., 1987; Poffenbarger et al. 2011) have concluded that CH₄ emission from freshwater tidal wetlands (salinity range 0‰–0.5‰) was greater than that from mesohaline marshes (salinity range 5‰–18‰), although the difference was non-significant. Smith et al. (1983) found that the CO₂ emissions were highest (618 g/(m²·year)) from a freshwater marsh, lowest (180 g/(m²·year)) in a brackish marsh, and that a salt marsh demonstrated intermediate CO₂ emission (418 g/(m²·year)). In addition, Nyman and DeLaune (1991) found that the CO₂ emissions from brackish and salt marshes were lower than those from freshwater marshes. Wilson et al. (2015) found no significant differences in the CH₄ emissions across the sites despite the salinity differences; however, the net CO₂ emission was highest at the freshwater site, followed by the brackish and salt marsh sites. Consequently, gaseous carbon emissions from estuarine marsh ecosystems are likely to be affected by the soil salinity. However, the relationship between salinity and gaseous carbon emissions remains unclear, especially in subtropical estuarine marshes. This subject is particularly important in the context of sea-level rise and saltwater intrusion.

The Min River estuary has a long macrotidal course, with the extent of the saltwater intrusion upstream affecting the compositional character of the marshes. Despite the large variation in marsh types, research on GHG emissions from freshwater and tidal marshes is lacking. Therefore, the current study was undertaken to compare the spatiotemporal variations in CO₂ and CH₄ emissions from a freshwater C. malaccensis marsh and a brackish C. malaccensis marsh in the Min River estuary, southeastern China. The primary objectives of this study were (1) to establish whether there were significant differences in CO₂ and CH₄ emissions from tidal marshes within a relatively narrow salinity range, and (2) to quantify the relationship between CO₂ and CH₄ emissions, salinity, and other environmental factors in subtropical estuarine marshes.

1. Materials and methods

1.1. Site description

This study was conducted in the Min River estuary area, southeastern China. The climate of the area is defined as warm and wet, with an annual mean temperature of 19.85°C and precipitation of 1905 mm. The main vegetation types include the native species C. malaccensis and P. australis, and the invasive species S. alterniflora (Tong et al., 2012). To study the effect of low-level salinity increase on greenhouse gas emissions in tidal wetlands, two marshes, approximately 28 km apart, were selected as the freshwater and brackish marshes (Fig. 1). The brackish site (26°01′46″N, 119°37′31″E), located at the mouth of the Min River estuary, is affected by tidal saltwater intrusion, with a monthly average salinity of 3.79‰ ± 1.35‰. The entire freshwater site (25°57′21″N, 119°24′25″E) has freshwater throughout the year, with an average salinity of 0.20‰ ± 0.02‰. The maximum height of C. malaccensis in the two marshes is approximately 1.3 m.

At each marsh site, on a line parallel with the coastline or riverline, four sampling plots (four replicates) were established at intervals of 3 m in the selected freshwater and brackish marshes. The sites exhibited uniform characteristics relevant to vegetation, soil, and hydrology. At both sites, the tides were semidiurnal over a 24-hr cycle. At the brackish marsh site, the average total duration of the two submerged periods of tidal flooding and ebbing during the day and night was approximately 7 hr. The duration of both the exposed-before tidal inundation and the exposed-after tidal inundation periods was 8.5 hr, respectively. Normally, there was between 20 and 150 cm of tidal water above the soil surface at high tide (Tong et al., 2014). However, at low tide, the soil surfaces of both marshes were completely exposed. The physical and chemical properties of the soil, from 0-15 cm deep in the two sampled marshes, are shown in Table 1.

1.2. Gas sampling

The enclosed opaque static chamber technique (Magenheimer et al., 1996; Hirota et al., 2004; Tong et al., 2012; Datta et al., 2013) was used to measure simultaneously the CO₂ and CH₄
emissions from the two marshes. In this study, the sampling chambers comprised two parts, namely, a stainless steel bottom collar (35 cm × 35 cm × 30 cm) and a polyvinyl chloride (PVC) top chamber (35 cm × 35 cm × 140 cm). The collar was permanently inserted into the sediment, with 2 cm protruding above the soil surface. The top chambers were equipped with electric fans to ensure full mixing of the internal air. Cotton quilts were used in the top chambers to limit air temperature rises in the chambers, especially during the summer. Furthermore, to minimize the disturbance of the measurement sites during sampling, a wooden access boardwalk was constructed adjacent to each sampling plot.

In order to investigate the emission characteristics of CO$_2$ and CH$_4$ in the freshwater and brackish marshes after the soil surface had been completely exposed during the day, we conducted measurements from 8:00 to 10:00 on one low or neap tide day (Chauhan et al., 2015; Wilson et al., 2015) in each month from November 2013 to October 2014. Four replicate chambers were applied for the gas sampling. The gas samples were collected with 100 mL polypropylene syringes, equipped with three-way stopcocks, and then stored in 100 mL gas bags (Dalian Delin gas Packing Co., Ltd., China). In total, four gas samples were collected at 10-min intervals.

1.3. Pore water sampling and analyses

Before October 2013, a series of pore water collection tubes (5 cm inner diameter) with sampling depths of 5, 15, and 25 cm were installed near each chamber, with 5 cm of the tubes protruding above the soil surface. The top of each tube was sealed tightly with a cover. Two days before the gas sampling dates, we emptied all the pore water from each pore-water collection tube. At the time of gas sampling, the pore water was sampled by using 100 mL gas-tight glass syringes, connected to a rubber hose. The collected pore water was transferred immediately to different containers (Ding et al., 2003). The pore water samples were transported to the laboratory within 6 hr and were stored at 4°C for a week for subsequent analyses. The pore water samples were first filtered through 0.22 μm cellulose membrane filters (Millipore, USA), and were used subsequently to determine the sulfate (SO$_4^{2−}$), chloride (Cl$^−$), ammonium (NH$_4^+$-N), and nitrate (NO$_3^−$-N) concentrations. In addition, after each gas sampling, tidewater was collected close to the sites. The SO$_4^{2−}$ and Cl$^−$ concentrations of the pore water/tidewater were measured by using an ion chromatograph (Dionex 2100, USA). The NH$_4^+$-N and NO$_3^−$-N concentrations were analyzed using flow injection analysis (Skalar Analytical SAN++, Lachat, Netherland).

1.4. Estimation of CO$_2$ and CH$_4$ emissions

The CO$_2$ and CH$_4$ concentrations were determined within 48 hr of sampling by using a gas chromatograph (GC-2010, Shimadzu, Kyoto, Japan), equipped with a methane reformer and a flame ionization detector (FID). The column and detector temperatures were set at 45°C and 280°C, respectively, with nitrogen at a flow rate of 20 mL/min as the carrier gas, and air and H$_2$ for the FID at flow rates of 400 and 47 mL/min, respectively. The CO$_2$ and CH$_4$ emissions to the atmosphere were estimated from the linear slope of the concentration change over time. The rates of increase for the CO$_2$ and CH$_4$ concentrations in the chamber were determined by linear regression, and the data were rejected if the $R^2$ values were $\leq 0.90$ (Hirota et al., 2004).
1.5. Environmental variables measurements

On each sampling date, the soil temperature, pH, and electrical conductivity (EC) in each chamber were measured. The soil temperature and pH were measured by using an IQ150 instrument (IQ Scientific Instruments, USA), and the EC was measured by using a 2265FS FieldScout Direct Soil EC Meter (Spectrum Technologies Inc., USA). The soil bulk density was determined by the core method (Huang et al., 2013), and the soil particle size was determined by using a Malvern Mastersizer-2000 laser particle-size analyzer (Malvern Instruments, UK). The soil moisture content was measured by using the oven-drying method. After extraction with 2 mol/L KCl, the soil NH$_4^+$-N and NO$_3^-$-N concentrations were analyzed using flow injection analysis (Skalar Analytical SAN++, Lachat, Netherland).

1.6. Incubation experiments

The incubation soil cores (four replicates) were sampled in situ at depths of 0–5, 5–10, and 10–15 cm in January, April, July, and October 2014 (representing winter, spring, summer, and autumn, respectively.) The samples were placed in a PVC chamber (diameter 5 cm, height 12 cm) with intact structures, which was sealed with a rubber stopper to prevent exposure to the air. The CH$_4$ and CO$_2$ production rates from the soil were determined by using the anoxic incubation method, in which the chambers were filled with N$_2$ gas for 8–10 min to replace all the oxygen (Wassmann et al., 1998). The chambers were filled with tidewater up to 1 cm above the soil surface, and were incubated at 17.45°C, 27.45°C, 21.36°C, and 11.01°C, respectively (the temperatures during the four sampling dates), in a dark shaking incubator. An air sample of 3 mL was withdrawn from the headspace through the rubber stopper, using a 5 mL polypropylene syringe equipped with a three-way stopcock. The CO$_2$ and CH$_4$ concentrations were analyzed as mentioned previously. All the incubations consisted of two stages (four days per stage), in which N$_2$ was injected into the CH$_4$ and CO$_2$ incubation chambers to flush the chambers (approximately 8–10 min) at the end of each stage.

1.7. Statistical analysis

The results are presented as the mean with standard error. We tested the significance of the observed differences in the CO$_2$ and CH$_4$ emissions between the two marshes each month, using analysis of variance (ANOVA). In this analysis, the multiple measurements in a given marsh represent the variables repeated over time. Correlation analyses were performed to examine the relationships between the emissions and single environmental variables.

2. Results

2.1. Monthly and seasonal variations in carbon dioxide and methane emissions

The CO$_2$ emissions from the two marshes were similar in magnitude, but showed significant monthly variations, with an average of 1456.60 ± 593.31 mg/(m$^2$·hr) at the freshwater
marsh and $1435.23 \pm 689.71 \text{ mg/(m}^2\text{·hr)}$ at the brackish marsh (Fig. 2). The CH$_4$ emissions were significantly lower in magnitude at the brackish marsh ($p < 0.01$), but were the highest ($15.92 \pm 2.80 \text{ mg/(m}^2\text{·hr)}$) in August 2014 and the lowest ($0.15 \pm 0.03 \text{ mg/(m}^2\text{·hr)}$) in February 2014. The average CH$_4$ emission from the freshwater marsh was $14.75 \pm 6.94 \text{ mg/(m}^2\text{·hr)}$, reaching a maximum of $51.76 \pm 5.59 \text{ mg/(m}^2\text{·hr)}$ in August 2014, and a minimum of $1.42 \pm 0.53 \text{ mg/(m}^2\text{·hr)}$ in April 2014. The CO$_2$ and CH$_4$ emissions showed distinct seasonal patterns at both marshes, with higher emissions occurring during the warm seasons (Fig. 2). The CO$_2$ emission from the freshwater marsh was significantly higher in summer than it was in the other seasons ($p < 0.05$), whereas it was significantly higher in spring than in autumn and winter ($p < 0.05$). The CH$_4$ emissions from both marshes were significantly higher in summer than in winter and spring ($p < 0.05$).

2.2. Seasonal and vertical variations in carbon dioxide and methane production rates

The two marshes showed a similar seasonal trend in CO$_2$ and CH$_4$ production rates over all the seasons (Fig. 3). The CO$_2$ production rates at both marshes in summer were significantly higher than they were in the other seasons ($p < 0.05$), and were significantly higher in spring than in autumn and winter ($p < 0.05$). The statistical analysis showed no significant differences in the CO$_2$ production rates between the two marshes ($p > 0.05$). Furthermore, in both marshes, the rates of CO$_2$ production generally declined with increasing soil depth.

The CH$_4$ production rates at both the freshwater and the brackish marshes were significantly higher in summer and lowest in winter. The CH$_4$ production rate at the freshwater marsh was significantly higher in summer than in the other
seasons ($p < 0.05$), whereas at the brackish marsh, the CH$_4$ production rate was significantly higher in summer than in autumn and winter ($p < 0.05$). The CH$_4$ production rates throughout the year were significantly higher in the freshwater marsh than in the brackish marsh ($p < 0.01$); however, at both marshes, these rates did not differ significantly with soil depth during autumn and winter.

2.3. Environmental variables

No significant differences were indicated in the air temperature, soil temperature, or pH between the freshwater and brackish marshes ($p > 0.05$) (Fig. 4). The soil EC in the brackish marsh was significantly higher than that of the freshwater marsh ($p < 0.01$). The soil EC remained low and unchanged in the freshwater marsh, but varied significantly in the brackish marsh. The temporal variation in soil moisture and bulk density showed no regular patterns, although they tended to be inversely related (Fig. 4).

The SO$_4^{2-}$ concentration of the pore water in the brackish marsh was significantly higher than that of the freshwater marsh ($p < 0.01$) (Fig. 5). The Cl$^-$ concentrations of the pore water of both sites varied significantly between the sampling months, but varied little with depth, and were significantly higher at the brackish than at the freshwater site ($p < 0.01$). The Cl$^-$ concentration differed significantly between the seasons at the freshwater marsh ($p < 0.01$). The NH$_4^+$-N concentrations in the pore water were significantly higher at the brackish marsh ($p < 0.01$). Moreover, both sites showed significant differences in NH$_4^+$-N concentrations between the bottom two sampling depths. The NO$_3^-$-N concentrations of the pore water at a depth of 0–10 cm were lower than those at depths of 10–20 and 20–30 cm, especially at the freshwater site ($p < 0.05$).

2.4. Relationship between carbon dioxide, methane emissions and environmental factors

The CO$_2$ and CH$_4$ emissions from both marshes were significantly positively correlated with the air temperature and the soil temperature ($p < 0.01$), while they were significantly negatively correlated with the soil EC, pore water Cl$^-$ and SO$_4^{2-}$, tidewater SO$_4^{2-}$, and NO$_3^-$-N ($p < 0.01$) (Table 2). At the freshwater marsh, the CO$_2$ and CH$_4$ emissions were negatively correlated with the soil pH ($p < 0.05$) and positively correlated with NH$_4^+$-N ($p < 0.05$). At the brackish marsh, the CO$_2$ and CH$_4$ emissions were significantly negatively correlated with the soil moisture ($p < 0.01$) and positively correlated with the bulk density ($p < 0.05$).

3. Discussion

3.1. Gaseous carbon emissions and influencing factors in tidal marsh

3.1.1. CH$_4$ emission

In the present study, it was found that the CH$_4$ emissions in the freshwater marsh showed obvious monthly and seasonal variations, and they were significantly higher than those from the brackish marsh ($p < 0.01$) (Fig. 2). These findings are consistent with a previous study (Poffenbarger et al., 2011). The positive relationships between the CH$_4$ emissions and the air/soil temperature ($p < 0.01$) at the two marshes (Table 2) indicate that temperature is one of the most important factors in CH$_4$ emissions. Whalen (2005) has confirmed that temperature variation could affect water availability and stimulate substrate and microbial activity. Chin et al. (1999) revealed
that the structure and function of the archaeal community in anoxic soil changed with time and temperature, and that the CH$_4$ production capacity of methanogens was promoted by a succession of dominant methanogen communities. These changes were attributed to an alteration of the carbon and electron flow in the methanogenic degradation pathway of organic matter that was caused by the temperature shift (Chin and Conrad, 1995). Moreover, Zogg et al. (1997) reasoned that dominant microbial communities at higher temperatures had the ability to metabolize substrates that were not used by the members of the microbial community at lower temperatures. Furthermore, Gauci et al. (2004) demonstrated that low temperatures favored the reduction of sulfate, whereas high temperatures favored methanogenesis, such

<table>
<thead>
<tr>
<th>Environment</th>
<th>Parameters</th>
<th>Freshwater marsh</th>
<th>Brackish marsh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Air temperature (°C)</td>
<td>0.760*</td>
<td>0.943*</td>
</tr>
<tr>
<td></td>
<td>Soil temperature (°C)</td>
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<td>0.769*</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>-0.356*</td>
<td>-0.425**</td>
</tr>
<tr>
<td></td>
<td>EC (mS/cm)</td>
<td>-0.506*</td>
<td>-0.489**</td>
</tr>
<tr>
<td></td>
<td>Bulk density (g/cm$^3$)</td>
<td>0.186</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>Soil moisture (%)</td>
<td>-0.223</td>
<td>-0.164</td>
</tr>
<tr>
<td>Pore water</td>
<td>Cl$^-$ (mg/L)</td>
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<td>-0.395**</td>
</tr>
<tr>
<td></td>
<td>SO$_4^{2-}$ (mg/L)</td>
<td>-0.471**</td>
<td>-0.409**</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$-N (mg/L)</td>
<td>0.537*</td>
<td>0.325</td>
</tr>
<tr>
<td></td>
<td>NO$_3^-$-N (mg/L)</td>
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<td>-0.239</td>
</tr>
<tr>
<td>Tide water</td>
<td>Cl$^-$ (mg/L)</td>
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<td>-0.380*</td>
</tr>
<tr>
<td></td>
<td>SO$_4^{2-}$ (mg/L)</td>
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<td>-0.609*</td>
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<td>EC (mS/cm)</td>
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<td>NH$_4^+$-N (mg/L)</td>
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<tr>
<td></td>
<td>NO$_3^-$-N (mg/L)</td>
<td>-0.570**</td>
<td>-0.678**</td>
</tr>
</tbody>
</table>

The symbols * and ** indicate significant correlations at the 0.05 and 0.01 levels, respectively, (n = 48).
that the competition between the SRB and the methanogens for substrates was affected by the temperature.

In the present study, the soil EC, Cl\(^{-}\), and SO\(_4\)\(^{2-}\) concentrations of the pore water and tidewater showed a negative correlation with the CH\(_4\) emissions from both sites (\(p < 0.01\)) (Table 2), indicating that salinity inhibited the CH\(_4\) production in and emission from estuarine marshes. In general, salinity affects the CH\(_4\) emission mainly through two main biogeochemical driving forces in the estuarine marsh soil. These forces are a sulfate-reduction effect caused by abundant SO\(_4\)\(^{2-}\) and an ionic effect caused by the increased ionic (Cl\(^{-}\) and SO\(_4\)\(^{2-}\)) strength in the seawater (Chambers et al., 2013). In coastal estuarine marshes, high SO\(_4\)\(^{2-}\) concentrations can encourage SRB to outcompete methanogens for energy sources because of their greater affinity for acetate, H\(_2\), and other substrates, which ultimately inhibit CH\(_4\) production (Purdy et al., 2003). Theoretically, high ionic strength could induce osmotic stress in microorganisms, interfering with cellular functions and reproduction, or even cause cell lysis and the divergence of microbial community composition along salinity gradients (Chambers et al., 2013). Furthermore, Neubauer et al. (2005) reported that the greater availability of the electron acceptors SO\(_4\)\(^{2-}\), Cl\(^{-}\), and Fe\(^{3+}\) in salt and brackish marsh soil limited CH\(_4\) production, compared with freshwater wetlands, by causing methanogens to be surpassed in competition for common substrates. Generally, the SO\(_4\)\(^{2-}\) and Cl\(^{-}\) in the estuarine marsh mainly derive from seawater, and should be in a consistent ratio with each other. However, in the present study, it was found that the SO\(_4\)\(^{2-}\) peaked in January 2014, while the Cl\(^{-}\) peaked in September 2013 at the freshwater site (Fig. 5). The reason is probably that the higher temperature and substrate input in summer led to increased reduction of sulfate, resulting in the substantial consumption of the available SO\(_4\)\(^{2-}\). When the temperature is low in winter and sulfate reduction is suppressed because of temperature limitations, the SO\(_4\)\(^{2-}\) storage is maximized.

The CH\(_4\) emissions showed a significant negative correlation with pH (\(p < 0.05\)) at the freshwater marsh (Table 2), indicating that pH is a crucial factor influencing CH\(_4\) emission from this marsh. The majority of soil microbes is adapted to survive in a neutral or weak alkaline environment and is sensitive to changes in the soil pH (Wang et al., 1993). The optimum pH for methanogens is 6.8–7.2 in wetland soil (Wang et al., 1993). However, in the present study, the pH range in the freshwater marsh was 4.5–7.8, which could inhibit the activity of the methanogens. In the present study, the fluctuations of pH could be the result of saltwater and freshwater intersection in the estuary zone. The negative relationship between the CH\(_4\) emission and the tidal water NO\(_3\)-N concentration at the two marshes (\(p < 0.01\)) (Table 2) indicates that NO\(_3\)-N could inhibit the activity of methanogens because of toxic effects (Ettwig et al., 2010). A greater supply of NO\(_3\)-N could relieve the N limitation on cell growth and could subsequently increase the activity of the methanotrophic community (Bodelier and Laanbroek, 2004). The CH\(_4\) emission from the freshwater marsh shows a significant positive correlation with the pore water NH\(_4\)-N (\(p < 0.01\)) (Table 2), which indicates that increases in NH\(_4\) could limit or inhibit the activity of the methanotrophic community by competing with methane monooxygenase (Crill et al., 1994).

Furthermore, the CH\(_4\) production rates at both marshes showed obvious seasonal variations (Fig. 3), which were significantly higher in summer and lowest in winter (Fig. 3). The seasonal trends of the CH\(_4\) emissions in the field and the production rates in the incubation experiment were not entirely consistent. For example, the CH\(_4\) emissions were higher in autumn than in spring in the field, but the production rates were quite the opposite at the brackish marsh (Figs. 2 and 3), although no statistically significant differences were found (\(p > 0.05\)). In a wetland ecosystem, the CH\(_4\) emission is the net result of CH\(_4\) production, oxidation, and transport (Bodelier and Laanbroek, 2004). High CH\(_4\) production rates do not necessarily result in high CH\(_4\) emissions, as these could be influenced by multiple factors, such as CH\(_4\) oxidation. This aspect is discussed in a study by Mitra et al. (2012), who additionally found that the temporal pattern of CH\(_4\) emission deviated from the temporal pattern of CH\(_4\) production. The CH\(_4\) emissions were higher in autumn than in spring in the field in the present study, which could be related to a lower CH\(_4\) oxidation rate in autumn, although the CH\(_4\) production rate was low. Moreover, vegetation affects CH\(_4\) emission by promoting transportation from the roots through the shoots, thereby bypassing the oxic soil layer and reducing aerobic oxidation (Ding et al., 2004). In the field, the prevailing vascular plant (C. malaccensis) was in the mature stage during autumn, potentially promoting higher CH\(_4\) emissions.

3.1.2. CO\(_2\) emission

Our results showed that the monthly variations in the CO\(_2\) emissions were similar, with no significant difference in the CO\(_2\) emissions being found between the freshwater and the brackish marshes (\(p > 0.05\)). Our findings are inconsistent with those of previous studies (Nyman and DeLaune, 1991). In addition, in the present study, the CO\(_2\) emissions showed a significantly positive correlation with the air and soil temperatures at the two marshes (\(p < 0.01\)) (Table 2). Temperature is a primary factor regulating soil carbon mineralization (Hou et al., 2013) in respect of controlling the decomposition of the root exudates (Svensson, 1984) and adjusting enzyme activity (Koch et al., 2007), which, ultimately, affect the production and emission of CO\(_2\).

The soil EC and the pore and tidewater Cl\(^{-}\) and SO\(_4\)\(^{2-}\) show a negative correlation with the CO\(_2\) emissions (\(p < 0.03\)) (Table 2), indicating that salinity is a main factor in the variability of the CO\(_2\) emission from the estuarine marshes. Nyman and DeLaune (1991) investigated CO\(_2\) emissions at various levels of salinity and found that the CO\(_2\) emissions from freshwater marsh soil were the highest, those from salt marsh soil were intermediate, and those from brackish marsh soil were the lowest. The estuarine tidal marshes were significantly affected by a periodic tide that contained abundant SO\(_4\)\(^{2-}\) and Cl\(^{-}\). The availability of these terminal electron acceptors could affect organic matter mineralization and GHG emissions (Craft et al., 2009). The production and emission of CO\(_2\) are the main pathways for the gaseous output of wetland soil carbon; therefore, the soil organic carbon decomposition and mineralization processes affect CO\(_2\) emissions. Our finding of a negative linear correlation between the CO\(_2\) production and salinity is consistent with that of Weston et al. (2006), who found that the organic matter mineralization decreased by 62% in freshwater sediment. In addition, the soil bacteria communities differed along the salinity gradient. Ikenaga et al. (2010) showed a definite shift in
the bacterioplankton metabolic capabilities along a salinity gradient. These authors concluded that the shift in substrate utilization from carbohydrates to amino acids was caused either by physiological adaptation or nitrogen limitation of bacterial communities with the increasing salinity. Additionally, high salinity was reported to cause amino acid uptake and protein synthesis (Norbeck and Blomberg, 1998) and respiration (Chowdhury et al., 2011). Although in the present study a negative correlation was found between the CO2 emissions and salinity (p < 0.01) (Table 2), there was no significant difference in the CO2 emissions between the two marshes (Fig. 4). The reason is probably the slight difference in salinity between the freshwater and brackish marshes and, consequently, the limited influence of salinity. If the difference in salinity were more pronounced (i.e., as between freshwater and polyhaline environments), a more pronounced difference in CO2 emission would probably be observed.

The CO2 emissions showed a significantly negative correlation with pH (p < 0.01) in the freshwater marsh (Table 2), indicating that pH was an important influencing factor in CO2 emission from this marsh. In the present study, the pH range at the freshwater marsh was 4.5–7.8. Acidic soil could inhibit organic matter decomposition, which, in turn, suppresses soil carbon mineralization (Anderson and Joergensen, 1997). Additionally, the dissolution equilibrium of CO2 in the soil solution as a function of pH is another important factor in CO2 emissions. At lower pH, such as that of the freshwater site, the partial pressure of CO2 (pCO2) increases dramatically, potentially leading to more CO2 fluxing from the solution to the atmosphere (Cai and Wang, 1998). Furthermore, the CO2 emissions from the freshwater marsh showed a significant positive correlation with the pore water NH4-N (p < 0.01) (Table 2), which indicates that the emission of CO2 was related to the nutrient regime of the marsh. Higher NH4-N content could increase biomass, promote the decomposition of soil organic matter, stimulate microbial activity and respiration, and facilitate the conversion of carbon in wetlands (Zhu et al., 2014). The significant positive relationship between the CO2 emissions and bulk density (p < 0.01) and the negative relationship with soil moisture (p < 0.01) in the brackish marsh (Table 2) indicate that the hydrological conditions could be important influencing factors in the emission of CO2. Waterlogged conditions and flooding in coastal marshes usually provide an anoxic environment for microbes, which limits soil microbial respiration and, in turn, affects organic carbon mineralization (Hou et al., 2013). The tides in the Min River estuary are considered typical semidiurnal tides. This implies that the soil surface is generally submerged for approximately 8 hr over a one-day cycle, leading to high soil moisture, forming an anaerobic soil environment and reducing CO2 emissions. Furthermore, in the present study, the presence of opposite variation tendencies between the soil bulk density and moisture (Fig. 4) indicates that the fluctuations of soil bulk density are mainly affected by the soil moisture (p < 0.01). The soil moisture and soil bulk density are mainly affected by precipitation and the tides, which fluctuate with the different seasons. The negative relationship between the CO2 emission and the NO3-N concentration in the pore water (p < 0.05) and tidewater (p < 0.01) in the two marshes (Table 2) indicates that the increase of NO3-N could inhibit the counts and activities of fungi, bacteria, and enzyme in the soil, potentially inhibiting the CO2 emissions (Compton et al., 2004).

### 3.2. Comparison of gaseous carbon emissions from various estuarine marshes

A review of the literature has indicated that, in general, the regular patterns of CH4 and CO2 emissions along salinity gradients are highest for the freshwater (salinity range <0.5‰) and oligohaline marshes (salinity range 0.5‰–5‰). However, these patterns are significantly lower in polyhaline conditions (salinity range 18‰–35‰), but show fluctuations in mesohaline conditions (salinity range 5‰–18‰) (Table 3). Our analysis confirmed and extended the relationship between the gaseous carbon emissions and salinity at different salinity gradients, particularly at the low salinity range (0‰–5‰), and suggested that it was generally applicable to estuarine tidal marshes.

Our study indicated higher CO2 and CH4 emissions from the Min River estuary in subtropical China in comparison with the published data relevant to temperate and tropical zones (Table 4). For instance, in the present study, the CH4 emissions

<table>
<thead>
<tr>
<th>Location</th>
<th>Salinity (%)</th>
<th>CO2 emission</th>
<th>CH4 emission</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Savannah River, USA</td>
<td>&lt;0.2‰; 0.4–2.1‰; 1.9–6.8‰</td>
<td>① &gt; ② &gt; ③</td>
<td>① &gt; ③ &gt; ②</td>
<td>Krauss and Whitbeck (2012)</td>
</tr>
<tr>
<td>Waccamaw River, USA</td>
<td>① = ②; ② = ③</td>
<td>① &gt; ② &gt; ③</td>
<td>③ &gt; ② &gt; ①</td>
<td>Neubauer et al. (2013)</td>
</tr>
<tr>
<td>Delaware River, USA</td>
<td>0.06‰; 4.95‰</td>
<td>① = ② &gt; ③</td>
<td>③ &gt; ② &gt; ①</td>
<td>Weston et al. (2011)</td>
</tr>
<tr>
<td>Mississippi River, USA</td>
<td>Fresh; brackish; saline</td>
<td>① &gt; ② &gt; ③</td>
<td>ND</td>
<td>Nyman and DeLaune (1991)</td>
</tr>
<tr>
<td>Barataria basin, USA</td>
<td>Fresh; brackish; saline</td>
<td>① &gt; ② &gt; ③</td>
<td>ND</td>
<td>Smith et al. (1983)</td>
</tr>
<tr>
<td>Dovey estuary, England</td>
<td>1.3‰; 2.6‰; 6.6‰; 17.3‰</td>
<td>① &gt; ② &gt; ③</td>
<td>③ &gt; ② &gt; ①</td>
<td>Dausse et al. (2012)</td>
</tr>
<tr>
<td>Delaware River, USA</td>
<td>0.5‰–5.5‰; 5–18‰</td>
<td>① = ② &gt; ③</td>
<td>③ &gt; ① &gt; ②</td>
<td>Weston et al. (2014)</td>
</tr>
<tr>
<td>York River, USA</td>
<td>0–7(2.6‰); 1.5–11.5(5.5‰); 8–12(8.8‰)</td>
<td>ND</td>
<td>③ &gt; ② &gt; ①</td>
<td>Bartlett et al. (1987)</td>
</tr>
<tr>
<td>Barataria basin, USA</td>
<td>0.36‰; 1.81‰; 18.1‰</td>
<td>ND</td>
<td>① &gt; ② &gt; ③</td>
<td>DeLaune et al. (1983)</td>
</tr>
<tr>
<td>Mobile Bay estuary, USA</td>
<td>2.3‰; 4.7‰; 20.7‰</td>
<td>① = ② &gt; ③</td>
<td>③ = ② &gt; ①</td>
<td>Wilson et al. (2015)</td>
</tr>
<tr>
<td>Waccamaw River, USA</td>
<td>0.5‰; 10.2‰</td>
<td>① &gt; ③ &gt; ②</td>
<td>③ &gt; ② &gt; ①</td>
<td>Neubauer (2013)</td>
</tr>
<tr>
<td>Bay of Fundy, Canada</td>
<td>31.6‰; 33.7‰; 35.1‰</td>
<td>① &gt; ② &gt; ③</td>
<td>③ &gt; ② &gt; ①</td>
<td>Magenheimer et al. (1996)</td>
</tr>
<tr>
<td>Coastline of Tamil Nadu, India</td>
<td>&lt;15‰; 15–25‰; &gt;33‰</td>
<td>ND</td>
<td>③ &gt; ② &gt; ①</td>
<td>Purvaja and Ramesh (2001)</td>
</tr>
<tr>
<td>Pearl River estuary, China</td>
<td>0.2‰; 1.4‰; 12.5‰; 22.3‰</td>
<td>ND</td>
<td>③ &gt; ② &gt; ①</td>
<td>Guo et al. (2009)</td>
</tr>
<tr>
<td>Min River estuary, China</td>
<td>0.2‰; 3.79‰</td>
<td>① &lt; ③ &gt; ②</td>
<td>③ &gt; ② &gt; ①</td>
<td>This study</td>
</tr>
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ND: No Data. “① = ②” indicates that there is no significant difference between ① and ②.
<table>
<thead>
<tr>
<th>Location</th>
<th>Climate zone</th>
<th>Habitat</th>
<th>Vegetation</th>
<th>CO₂ emissions (mg/(m²·hr))</th>
<th>CH₄ emissions (mg/(m²·hr))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min River estuary, China</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Cyperus malaccensis</td>
<td>199.78–3710.79</td>
<td>1.42–51.76</td>
<td>This study</td>
</tr>
<tr>
<td>Savannah River, USA</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Taxodium distichum; Nyssa aquatica</td>
<td>179.1 (average)</td>
<td>0.13 (average)</td>
<td>Krauss and Whitbeck (2012)</td>
</tr>
<tr>
<td>Jiulongjiang estuary, China</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Kandelia candel</td>
<td>31.2–73.5</td>
<td>ND</td>
<td>Alongi et al. (2005)</td>
</tr>
<tr>
<td>York River, USA</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Spartina cynosuroides</td>
<td>ND</td>
<td>2.08 (average)</td>
<td>Bartlett et al. (1987)</td>
</tr>
<tr>
<td>Mississippi River, USA</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Paniceum hemitomon</td>
<td>34.70 (average)</td>
<td>ND</td>
<td>Nyman and Delaune (1991)</td>
</tr>
<tr>
<td>Banatrina basin, USA</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Spartina alterniflora</td>
<td>70.55 (average)</td>
<td>ND</td>
<td>Smith et al. (1983)</td>
</tr>
<tr>
<td>Mobile Bay estuary, USA</td>
<td>Subtropical</td>
<td>Freshwater</td>
<td>Cladium jamaicense</td>
<td>240.17 (average)</td>
<td>1.2 (average)</td>
<td>Wilson et al. (2015)</td>
</tr>
<tr>
<td>Yellow River estuary, China</td>
<td>Temperate</td>
<td>Freshwater</td>
<td>Suazaeda salsa</td>
<td>ND</td>
<td>−0.39–0.50</td>
<td>Sun et al. (2013)</td>
</tr>
<tr>
<td>White Oak River estuary, USA</td>
<td>Temperate</td>
<td>Freshwater</td>
<td>Ceratophyllum; Najas</td>
<td>ND</td>
<td>0.8–4.73</td>
<td>Kelley et al. (1995)</td>
</tr>
<tr>
<td>Scheldt estuary, Belgium</td>
<td>Temperate</td>
<td>Freshwater</td>
<td>Scirpus lacustris; Phragmites australis</td>
<td>ND</td>
<td>0.51–8.58</td>
<td>Van der Nat and Middelburg (2000)</td>
</tr>
<tr>
<td>Delaware River, USA</td>
<td>Temperate</td>
<td>Freshwater</td>
<td>Peltandra virginica; Pontederia cordata</td>
<td>2.17 (average)</td>
<td>0.86 (average)</td>
<td>Weston et al. (2011)</td>
</tr>
<tr>
<td>Pulicat Lake, India</td>
<td>Tropical</td>
<td>Freshwater</td>
<td>Halophila ovalis; Enteromorpha; Chaetomorpha</td>
<td>ND</td>
<td>2.1–4.63</td>
<td>Shalini et al. (2006)</td>
</tr>
<tr>
<td>Min River estuary, China</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Cyperus malaccensis</td>
<td>246.68–4199.95</td>
<td>0.15–15.92</td>
<td>This study</td>
</tr>
<tr>
<td>Savannah River, USA</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Taxodium distichum; Nyssa aquatica</td>
<td>162.3 (average)</td>
<td>0.21 (average)</td>
<td>Krauss and Whitbeck (2012)</td>
</tr>
<tr>
<td>Brisbane River, Australia</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Avicennia marina; Aegiceras corniculatum</td>
<td>ND</td>
<td>0.003–17.37</td>
<td>Allen et al. (2011)</td>
</tr>
<tr>
<td>Mobile Bay estuary, USA</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Cladium jamaicense</td>
<td>117.75 (average)</td>
<td>0.6 (average)</td>
<td>Wilson et al. (2015)</td>
</tr>
<tr>
<td>York River, USA</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Spartina alterniflora</td>
<td>ND</td>
<td>2.55 (average)</td>
<td>Bartlett et al. (1987)</td>
</tr>
<tr>
<td>Mississippi River, USA</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Spartina patens</td>
<td>13.01 (average)</td>
<td>ND</td>
<td>Nyman and Delaune (1991)</td>
</tr>
<tr>
<td>Banatrina basin, USA</td>
<td>Subtropical</td>
<td>Brackish</td>
<td>Spartina alterniflora</td>
<td>20.55 (average)</td>
<td>ND</td>
<td>Smith et al. (1983)</td>
</tr>
<tr>
<td>Yellow River estuary, China</td>
<td>Temperate</td>
<td>Brackish</td>
<td>Phragmites australis; Tamartix chinensis</td>
<td>ND</td>
<td>−0.39–0.50</td>
<td>Sun et al. (2013)</td>
</tr>
<tr>
<td>Mai Po mangrove swamp, Hong Kong</td>
<td>Tropical</td>
<td>Brackish</td>
<td>Kandelia obovata</td>
<td>10.6–1374.1</td>
<td>ND</td>
<td>Chen et al. (2012)</td>
</tr>
</tbody>
</table>

ND: No Data.
were higher than those at the Scheldt estuary near Antwerp (0.51–8.58 mg/(m²·hr)) (Van der Nat and Middelburg, 2000) and at the Yellow River estuary coastal marshes in Shandong Province, China (0.392–0.495 mg/(m²·hr)) (Sun et al., 2013). In addition, in this study, the CO₂ emissions were higher than those from the Delaware River marshes in the USA (2.17 mg/(m²·hr)) (Weston et al., 2011). However, analyses of the CO₂ and CH₄ emissions from estuarine tidal marshes in different climate zones have revealed that these emissions did not show significant differences or regular patterns relevant to the different climate zones. These results suggest that the GHG emissions are affected additionally by vegetation types, community structure, biomass (above- and belowground), organic carbon content, and the tidal phases in the natural wetlands. However, temperature remains a crucial factor. In this study, we showed that the GHG emission data for the C. malaccensis estuarine marsh could clarify various unknown factors and could enrich the international GHG emissions database.

4. Conclusions

This study recorded relatively high gaseous carbon emissions from the Min River estuarine tidal marshes compared with those of most other estuarine freshwater and brackish marshes worldwide. The two marshes examined in this study are positive emitters of CH₄ and CO₂, with the magnitudes of the emissions from each marsh showing a similar seasonal pattern. Furthermore, our results showed that the CO₂ emissions from the two marshes were similar in magnitude and monthly variation. Salinity was not a significant controlling factor for CO₂ emissions from these marshes, which have a relatively narrow salinity range. The CH₄ emissions from the brackish marsh were significantly lower than those from the freshwater marsh. This finding indicates that intrusion of comparatively low-salinity saltwater in the future could reduce the emission of CH₄ from the estuarine freshwater marshes. However, there would be little effect on the CO₂ emissions, ultimately leading to a significant change in the C-cycling dynamics. Future studies on estuarine tidal marshes should consider the balance of the gaseous carbon, saltwater intrusion timescales (short or long), and the salinity in order to accurately estimate the global warming potential of these marshes. In addition, detailed investigation should be conducted on the factors that control the gaseous carbon emissions at differing salinity levels, especially microbial activity and C-mineralization rates.

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REFERENCES


