Wetlands (2016) 36 (Suppl 1):S113–S123
DOI 10.1007/s13157-014-0587-1

ORIGINAL RESEARCH

Anthropogenic Effects on Fluxes of Ecosystem Respiration and Methane in the Yellow River Estuary, China

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Received: 30 March 2014 / Accepted: 1 October 2014 / Published online: 7 March 2015

Abstract To evaluate the influence of human activities on ecosystem respiration (CO_2) and CH_4 fluxes and determine the seasonal and spatial variations, we measured CO_2 and CH_4 fluxes at four sampling sites (west side of the seawall, WSS; oilfield, OF; *Spartina alterniflora* coastal marsh, SCM; aquaculture pond, ACP) in the Yellow River estuary from June to December in 2013. Both CO_2 and CH_4 fluxes showed seasonal and spatial variations in the Yellow River estuary. The average CO_2 fluxes from WSS, OF, SCM and ACP were 125.36, 111.03, 241.97 and −39.49 mg CO_2 m^{-2} h^{-1}, while CH_4 fluxes were −0.0110, −0.0165, 0.2012 and 0.0034 mg CH_4 m^{-2} h^{-1}, respectively. Spatial variations of CO_2 and CH_4 fluxes were mainly affected by vegetation and soil moisture. There were significant relationships between both CO_2 fluxes in WSS and SCM and CH_4 flux in SCM with temperature. CO_2 and CH_4 fluxes were mainly affected by the interactions of thermal conditions and other abiotic factors in OF and ACP. Human activities have great effect on greenhouse gas emission, especially in the area where exotic-species *S. alterniflora* invaded. The construction of seawall blocked sea water transporting into the study area leading to low soil moisture which accelerated CO_2 emission. Aquaculture ponds act as an emission of CH_4 and consumption of CO_2.

Keywords Carbon dioxide · Methane · Plant invasion · Yellow River estuary

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Introduction

Carbon dioxide (CO_2) and methane (CH_4) are important greenhouse gases (GHG). The concentrations of CO_2 and CH_4 in atmosphere increased from 280 ppm and 715 ppb in pre-industrial times to 379 ppm and 1,774 ppb in 2005, respectively (IPCC 2007). The levels of CO_2 and CH_4 have a significant impact on global warming. Therefore, there is a need for quantifying the potential of an individual ecosystem as a source or sink for atmospheric CO_2 and CH_4 (Purvaja and Ramesh 2001).

Coastal marsh ecosystem is characterized by high temporal and spatial variations including topographic feature, environmental factors, and astronomic tidal fluctuation, and is very sensitive to global climate changes and human activities (Sun et al. 2013). Considerable efforts have been invested in the past two decades to quantify the CO_2 and CH_4 fluxes in different coastal wetlands (Purvaja and Ramesh 2001; Allen et al. 2007; Cheng et al. 2007; Tong et al. 2012; Sun et al. 2013; Poffenbarger et al. 2011). However, most of the research focused on the emission of GHG from natural wetlands; data of GHG emission from anthropogenic coastal wetland is insufficient. As the development of economy, human activities, such as land-use changes and introduction of invasive alien plants, have more and more impact on coastal wetlands. The phenomenon of transformation of natural coastal wetlands into a harbor, seawall, industrial complex or urban district is very common, this transformation will change the geomorphology of the coastal line and the physical processes of the coastal system permanently, which can result more negative influence on the coastal environment and ecosystem (Bi et al. 2012). Changes in land use have a profound impact on GHG flux. Inubushi et al. (2003) suggested that converting a secondary forest peatland to paddy field increased the annual emissions of CO_2 and CH_4 to the atmosphere, while transforming the secondary forest to upland decreased the emissions.

Human-induced invasion by exotic-species also have a profound impact on the GHG flux. Invasion by exotic plant species has been considered to be one of the most serious problems for natural ecosystems (Walker and Smith 1997). *Spartina alterniflora* was introduced to China in 1979, to protect the coastal banks and stabilize the sediment along the eastern coast in Fujian province, Southeast China . Currently, *S. alterniflora* distributs widely along the east coast of China (Wang et al. 2006a) due to its faster growth rate compared to the native species (Qin and Zhong 1992; Wang et al. 2006b). The coverage of *S. alterniflora* was approximately 260 ha in six counties by 1985 and increased to more than 112,000 ha by 2,000 (An et al. 2007). Therefore, information on emission of GHG from ecosystem invaded by *S. alterniflora* is urgently needed, however, studies in this field were mainly conducted at the estuary in the southern part of China (Tong et al. 2012; Cheng et al. 2007; Cheng et al. 2010; Zhang et al. 2010), but information for the estuary in the northern part of China is largely unknown as yet. Thus, it is very important to evaluate how the invasion by exotic-species affects GHG emission in wetlands at estuary area in Northern China.

The Yellow River is well known as a sediment-laden river. Approximately 1.05×10^7 tons of sediment is carried to the estuary and deposited in the delta each year (Cui et al. 2009) resulting in vast area of floodplain and special wetland landscape (Xu et al. 2002; Wang et al. 2004). Typical reclaimed land patterns in the Yellow River estuary included harbor, seawall, salt pans, oilfield, aquaculture ponds and industrial complex. A recent study showed that the area of natural wetlands decreased by 44.5 % in four decades (1976–2008) in the Yellow River estuary, while constructed wetland increased by 1.997×10^4 hm^2 in the same period due to rapid development of coastal aquaculture and salt industry (Chen et al. 2011). Wang et al. (2013) pointed that the exploitation of tidal flats resources and construction of artificial ponds related to holothurian culture in the Yellow River delta had become an emerging industry. And the field occupied by holothurian culture covered an area of 1.5×10^4 ha in the Yellow River delta. *S. alterniflora* was transplanted into Yellow River estuary for three times in 1985, 1987, and 1990. The coverage of *S. alterniflora* has now reached up to 614.59 hm^2 (Zhu et al. 2012). Human activities have more and more impact in Yellow River estuary. Therefore, evaluating the influence of human activities on the emission of GHG is a big necessary in this area.

In this paper, we quantitatively evaluated the variations in the levels of CH_4 and CO_2 in a typical coastal marsh which was significantly influenced by human activities. The objectives of this study were to: (i) measure the emissions of CO_2 and CH_4 from exotic *S. alterniflora*; (ii) determine the relationship between GHG emission and environmental factors; and (iii) estimate the difference of the seasonal change in CO_2 and CH_4 emissions under different human activities.

Materials and Methods

Site Description

This study was conducted in the Yellow River estuary in Dongying City, Shandong Province, China. The Yellow River estuary has a typical continental monsoon climate with distinct seasons; summer is warm and rainy, and winter is cold. The annual average temperature is 12.1 °C and the frost-free period is 196 d. The average temperatures for spring, summer, autumn and winter are 10.7, 27.3, 13.1, and −5.2 °C, respectively. The mean tidal range of the irregular semidiurnal tide is 0.73 to 1.77 m in the intertidal zone of the Yellow River estuary. Soils in the study area are dominated by intrazonal tide and salt soil. The dissoluble salt content in surface layer (0 to 20 cm) of salt soil is very high (>8 g/kg), and its grain composition is dominated by sand and silt (50–80 %). The average annual evaporation and precipitation are 1962 and 551.6 mm, respectively, with about 70 % of the precipitation occurs in June to August. The main types of vegetation are *Sueada salsa*, *Phragmites australis*, *Triarrhena sacchariflora*, *Myriophyllum spicatum*, *Tamarix chinensis*, and *Limoninum sinense*.

Due to its rich oil and gas resources, Wuhaozhuang region, part of the Yellow River estuary, is significantly affected by human activities. Seawalls were constructed in this region to improve oil production and other economic activities (e.g. aquaculture). *S. alterniflora* was introduced to Wuhaozhuang in 1990 to protect the seawall from damage. Additionally, Wuhaozhuang is one of important aquaculture farms in Yellow River estuary. We selected four sampling sites in this region, which represented the four typical human-influenced areas in this region, including (a) the west side of the seawall (WSS) (east side of the seawall is the Bohai Sea) (38°01′8.79″N, 118°58′6.84″E); (b) oil field (OF, there are lots of oil wells on the ground) (38°01′8.73″N, 118°57′44.63″E); (c) *S. alterniflora* coastal marsh (SCM) (38°00′24.8″N, 118°58′23.2″E); and (d) aquaculture pond (ACP) (38°00′26.16″N, 118°58′23.0″E) (Fig. 1).

Experimental Design

Fluxes of CO_2 and CH_4 from WSS, OF, and SCM were measured using static, manual stainless steel chamber and gas chromatography techniques. A stainless steel base with a water groove on the top was inserted into the ground for 20 cm depth in May 2013. A chamber was placed into the groove during measurement; meanwhile water was injected into the

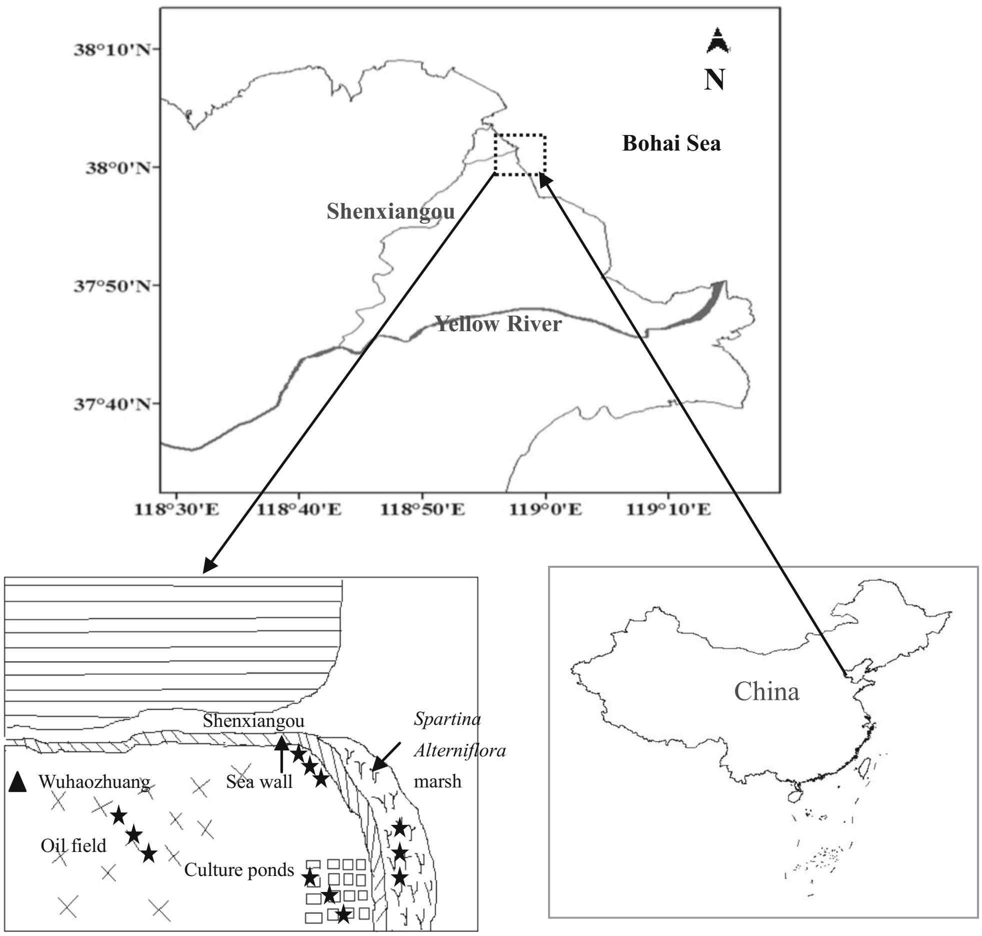

Fig. 1 Sketch of the study area and experimental plots (black star) in the Yellow River estuary

groove to build an open-bottom square box. The outside of the chamber was covered with an insulating layer (2 cm thick) to reduce the impact of direct radiative heating during sampling, which can cause very little difference in temperature between the inside and the outside of the chamber (Teiter and Mander 2005; Søvik and Kløve 2007; Jiang et al. 2010; Tong et al. 2010; Sun et al. 2013, 2014). Air inside the chamber was circulated with battery-driven fans installed inside the chamber to make sure that the gas sample was uniform in the chamber. CH_4 and CO_2 emissions from ACP were measured using floating chambers and gas chromatography techniques. The floating chambers were made of opaque PVC. A flotation gear was installed to make sure that the chamber can float on water. Insulating layer and fans also placed for floating chambers.

Measurements were made in June, August, October, and December of 2013 at the four sites. Each measurement campaign consisted of 12 chambers set up at four positions (three chambers per site). Gas samples were collected at 7:00, 9:30, 12:00, 14:30; and 17:00 h on each sampling date, which have been shown to be the optimum measurement period by Sun et al. (2013, 2014). The gas samples were withdrawn from the headspace of the chamber in a 20-min interval (totally 60 min for each measurement) using a 50 ml syringe equipped with a three-way stopcock. Samples were injected into pre-evacuated packs and taken to the laboratory for determination within 36 h.

The gas samples were determined with gas chromatography (Agilent 7890A, Agilent Co., Santa Clara, CA, USA) equipped with FID. The CH_4 was separated from the other gases with a 2 m stainless-steel column, with an inner diameter of 2-mm 13XMS column (60/80 mesh). The CO_2 was separated with a 2 m stainless-steel column with an inner diameter of 2 mm Porapak Q (60/80 mesh). The FID operated at 200 °C using high-pure nitrogen as a carrier gas, at a flow rate of 30 ml/min. The column temperatures were maintained at 55 °C for all separations. The greenhouse gas concentrations were quantified by comparing the peak areas of samples against standards. During the gas measurement, standards were analyzed every eight samples of determination to ensure the data quality, the relative standard deviation (RSD) for each sample should below 6 %. The gas flux was calculated using the following equation (Song et al. 2008):

$$J = \frac{dc}{dt} \times \frac{M}{V_0} \times \frac{P}{P_0} \times \frac{T}{T_0} \times H$$

where J is the gas flux (mg m^{-2} h^{-1}), dc/dt is the slope of the gas concentration curve variation, along with time, M is the mole mass of each gas, P is the atmospheric pressure at the sampling site, T is the absolute temperature during sampling, V_0, T_0 and P_0 are respectively, the gas mole volume, air absolute temperate and atmospheric pressure under standard conditions, H is the height of chamber above the water surface. The rates of CH_4 and CO_2 emissions were calculated by fitting the changes in the determined concentrations of CH_4 and CO_2 over a 60-min period to a linear model. The regression concentration coefficients from linear regressions were rejected when R^2 was less than 0.9. Positive values indicate net flux to the atmosphere (efflux), and negative values indicate consumption of atmosphere gases by the soil (influx).

Environmental data were measured at each site during sampling. Air temperature inside the chamber was measured with a thermometer inserted into the chamber. Soil temperature at 5, 10, 15, 20, and 25 cm depth was measured with five ground thermometers inserted into the corresponding depth. On each sampling date, three soil samples per layer (0 to 10, 10 to 20, and 20 to 30 cm) were collected at each site to determine soil water content. Water temperature was also measured with the thermometer during gas sampling. In August 2013, the aboveground biomass in WSS, OF and SCM was estimated. Three quadrants (50×50 cm for OF and SCM, 5×5 m for WSS) were selected for biomass measurement at each of the three sites. Biomass was oven-dried (80 °C) to a constant weight.

Statistical Analysis

Statistical analyses were conducted using SPSS 16.0 and Origin 7.5. The results were presented as a mean of replicates, with standard error (SE). Significant differences in GHG emissions and environmental factors between different sites were determined by one-way analysis of variance [ANOVA, followed by Tukey's Honest Significant Difference (HSD) test]. Correlation analysis was conducted to examine the relationship between fluxes and the measured environmental variables. In all tests, differences were considered significant when $p<0.05$.

Results

Plant Growth

Vegetation in WSS is predominated by *Tamarix chinensis* (>60 %), while that in OF and SCM are *Suaeda salsa* (>99 %) and *S. alterniflora* (>99 %), respectively. The coverage and maximum aboveground biomass of *T. chinensis*, *S. salsa*, and *S. alterniflora* are 10, 70, 95 %, and 200.11± 15.82 (mean ± SE) g m^{-2}, 376.862±31.50 g m^{-2}, 1281.92± 176.93 g m^{-2}, respectively. The aboveground biomass of *S. alterniflora* was greater than these of *T. chinensis* and *S. salsa*.

Variation in CO_2 Fluxes

CO_2 flux includes respiration from living aboveground and belowground plant parts as well as aerobic and anaerobic microbial activities in the soil column. This CO_2 flux can be called ecosystem respiration and is associated with the overall carbon flow of the ecosystem (Nykänen et al. 1998). CO_2 fluxes from the four sites ranged from −181.23 to 878.03 mg CO_2 m^{-2} h^{-1} over the entire sampling period (Fig. 2). Average CO_2 fluxes in WSS, OF, SCM and ACP from June to December were 125.36, 111.03, 241.97 and −39.49 mg CO_2 m^{-2} h^{-1}, respectively. All sites except ACP (negative value) released CO_2 during the entire experimental period. The CO_2 flux rates from WSS, OF, and SCM showed the similar seasonal pattern, initial increase followed by a subsequent fall. The greatest CO_2 flux rates from WSS (334.69 mg CO_2 m^{-2} h^{-1}), OF (264.32 mg CO_2 m^{-2} h^{-1}), and SCM (583.07 mg CO_2 m^{-2} h^{-1}) were observed in August while the smallest CO_2 flux rates (27.08, 13.41, and 37.22 mg CO_2 m^{-2} h^{-1}, respectively) were observed in December. A significantly greater CO_2 flux was observed from SCM than WSS (p=0.028), OF (p=0.016), and ACP (p=0.000). The CO_2 flux from ACP varied significantly from June to December, and smaller than that from WSS (p=0.002), OF (p=0.006) and SCM (p=0.000). The greatest consumption was observed from ACP in August (−71.14 mg CO_2 m^{-2} h^{-1}).

Variation in CH_4 Fluxes

CH_4 fluxes from the four sites ranged from −0.2390 to 0.5252 mg CH_4 m^{-2} h^{-1} (Fig. 3). Average CH_4 fluxes in WSS, OF, SCM, and ACP from June to December were −0.0110, −0.0165, 0.2012, and 0.0034 mg CH_4 m^{-2} h^{-1}, respectively. The flux rate of CH_4 from SCM was significantly greater than that from WSS (p=0.000), OF (p=0.000), and ACP (p=0.000). During the entire experimental period, SCM was a net source of CH_4, while both net emission and net consumption of CH_4 occurred at other sites. The greatest CH_4 flux rate from SCM (0.4107 mg CH_4 m^{-2} h^{-1}) was observed in August, while it was observed in October from OF (0.0157 mg CH_4 m^{-2} h^{-1}) and ACP (0.0165 mg CH_4 m^{-2} h^{-1}). The CH_4 flux from WSS varied significantly from month to month during the measurement period, with the greatest consumption being observed in October (−0.0258 mg CH_4 m^{-2} h^{-1}).

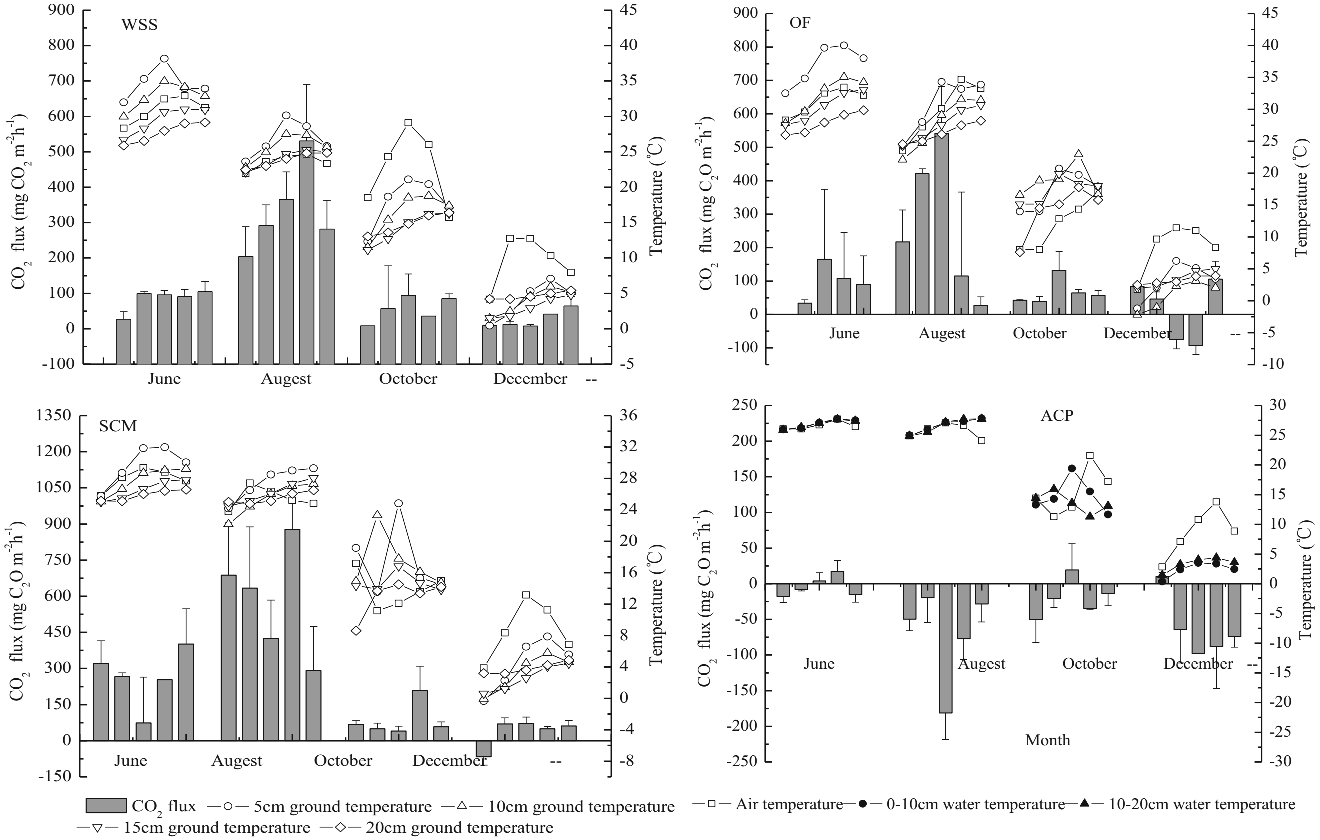

Fig. 2 Carbon dioxide (CO2) fluxes from WSS (west side of the seawall), OF (Oil field), SCM (*Spartina alterniflora* coastal marsh) and ACP (aquaculture pond) in different months in the Yellow River estuary

Environmental Factors

There was no significant difference in the air temperature among the four sites ($p>0.05$), and so did in soil temperature among different layers (5, 10, 15 and 20 cm depth) at WSS, OF, and SCM ($p>0.05$) (Table 1). Spearman correlation analysis indicated that most of the relationships between CO_2 (or CH_4) fluxes and air temperature (or soil temperature) from OF and ACP were not significant ($p>0.05$) (Table 2). CO_2 fluxes from SCM and WSS showed significantly positive relationships with air or soil temperature ($p<0.05$). And there was no significant relationship between CH_4 flux and air/soil temperature ($p>0.05$) at the sampling sites except SCM. In addition, CH_4 flux significantly correlated with soil water content (positive, $p<0.05$), but not for the CO_2 flux.

Discussions

Seasonal Variation of CO_2 and CH_4 Fluxes

CO_2 and CH_4 emissions varied markedly among different seasons at the four sites (Figs. 2 and 3). Similar variations have been reported in previous studies (Allen et al. 2007; Song et al. 2008; Cheng et al. 2010; Sun et al. 2013). Chen et al. (2010) reported a seasonal variation in CO_2 flux in a subtropical mangrove swamp in Hong Kong showed that seasonal variations and the flux in warm seasons was greater than in cold seasons. We also found that CO_2 flux in warm seasons (June and August) was significantly greater than that in the cold seasons (October and December) in WSS, OF, and SCM. The significant relationship between CO_2 flux and air temperature and soil temperature was consistent with those reported by Cheng et al. (2010) who found that CH_4 emissions from *S. alterniflora* and *S. mariqueter* soils positively correlated with soil temperature. Similarly, Whalen (2005) observed that seasonal patterns of trace gas emissions were governed by seasonal variability in temperatures affecting water availability, production of substrate precursors, and microbial activity. No significant relationship were found between CO_2 flux and air or soil temperature from OF, maybe due in part to the complex interactions of temperature and other biotic/abiotic factors, such as water content.

CH_4 flux was not related to temperature significantly expect SCM. Sun et al. (2013) suggested that, in coastal marsh of the Yellow River estuary, seasonal variations in CH_4 emission was not affected by seasonal variability in temperatures. In our study, the greatest CH_4 emission rate from OF (0.0157 mg CH_4 m^{-2} h^{-1}) and WSS (−0.0258 mg CH_4 m^{-2} h^{-1}) were both

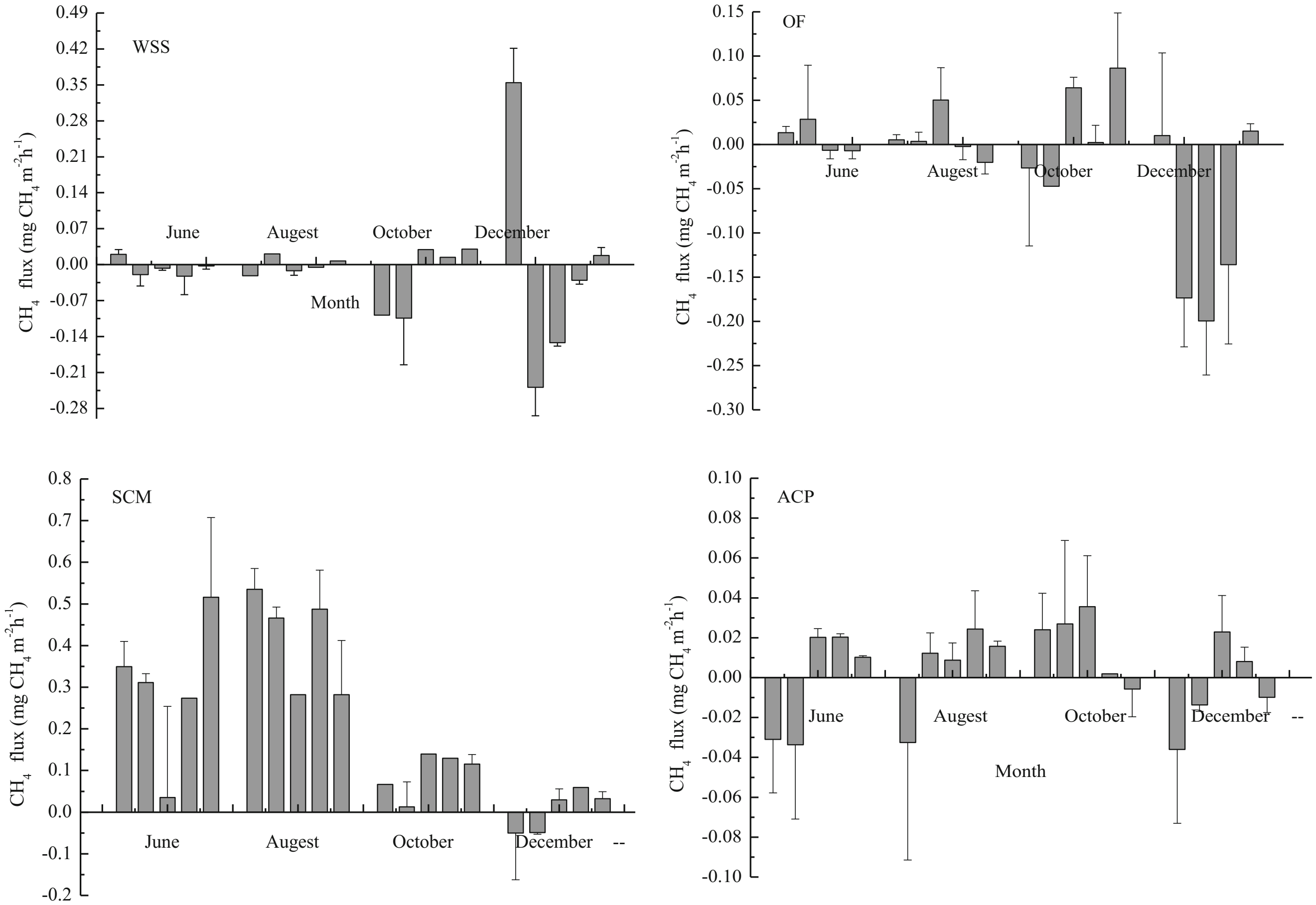

Fig. 3 Methane (CH4) fluxes from WSS (west side of the seawall), OF (Oil field), SCM (*Spartina alterniflora* coastal marsh) and ACP (aquaculture pond) in different months in the Yellow River estuary

observed in October. This result indicated that the influence of temperature on CH_4 emission was masked by other biotic/abiotic factors, such as vegetation or soil moisture. Factors affecting CH_4 emission are diverse and controlled by the interplay of CH_4 production, oxidation, and transport processes (Ding et al. 2004). Kutzbach et al. (2004) reported that the

Table 1 Air, ground and water temperatures, and soil water contents of the four study sites in the Yellow River estuary

Environmental parameters	WSS	OF	SCM	ACP
Air temperature (°C)	21.72±4.45 [a]	20.92±11.31 [a]	18.99±9.23 [a]	19.12±8.61 [a]
5 cm ground temperature (°C)	20.84±6.78 [a]	22.37±7.46 [a]	19.75±5.77 [a]	–
10 cm ground temperature (°C)	19.68±6.24 [a]	19.86±6.91 [a]	18.43±5.53 [a]	–
15 cm ground temperature (°C)	17.72±5.82 [a]	19.69±6.10 [a]	17.51±5.69 [a]	–
20 cm ground temperature (°C)	17.74±5.13 [a]	17.87±5.76 [a]	17.00±5.34 [a]	–
Water content (%)				
0–10 cm	9.99±1.99 [a]	18.14±0.33 [b]	23.07±0.73 [c]	–
10–20 cm	10.64±1.70 [a]	17.64±0.92 [b]	26.94±2.12 [c]	–
20–30 cm	11.26±1.01 [a]	21.61±0.82 [b]	28.91±1.21 [c]	–
0–10 cm water temperature (°C)	–	–	–	17.70±5.82
10–20 cm water temperature (°C)	–	–	–	17.62±5.67

WSS, West side of the seawall; *OF*, oil field; *SCM*, *S. alterniflora* coastal marsh; *ACP*, aquaculture pond

Values are means (±S.E.) of samples ($n=60$ for air temperature, ground temperature and water temperature; $n=12$ for water content) collected from WSS, OF, SCM and AP. Statistically significant differences among study sites ($p<0.05$) were calculated for multiple comparisons using ANOVA and are indicated by different letters within each row

Table 2 Spearman correlation analysis between CO_2, CH_4 fluxes and environmental factors

Environmental parameters	CO_2				CH_4			
	WSS	OF	SCM	ACP	WSS	OF	SCM	ACP
Air temperature (°C)	0.448^b	0.356	0.699^b	0.024	0.042	0.147	0.674^b	0.147
5 cm ground temperature (°C)	0.645^b	0.645^b	0.641^b	–	0.062	0.230	0.695^b	–
10 cm ground temperature (°C)	0.648^b	0.375	0.642^b	–	0.102	0.177	0.677^b	–
15 cm ground temperature (°C)	0.653^b	0.419	0.713^b	–	0.132	0.260	0.753^b	–
20 cm ground temperature (°C)	0.654^b	0.374	0.678^b	–	0.159	0.230	0.757^b	–
Water content (%)	0.252	0.140	0.224	–	0.692^a	0.587^a	0.713^b	
0–10 cm water temperature (°C)	–	–	–	0.173	–	–	–	0.302
10–20 cm water temperature (°C)	–	–	–	0.132	–	–	–	0.329

[a] Correlation is significant at the 0.05 level (2-tailed), [b] correlation is significant at the 0.01 level (2-tailed). WSS, west side of the seawall; OF, oil field; SCM, *S. alterniflora* coastal marsh; ACP, aquaculture pond

ratio between CH_4 production and oxidation is controlled by soil moisture which regulates the relative extent of oxic and anoxic environment within soils. Our result showed that CH_4 emissions were positively correlated with soil moisture in WSS, OF, and SCM (Table 2).

CO_2 and CH_4 fluxes across the air-water interface of ACP had obvious seasonal variations (Figs. 2 and 3). Xing et al. (2005) also pointed that the fluxes of CH_4 and CO_2 showed strong seasonal dynamics from a shallow hypereutrophic subtropical Lake in China, CH_4 emission rate was the greatest in summer, whereas CO_2 was adsorbed from the atmosphere in spring and summer, but underwent a large-scale emission in winter. In our study, CO_2 flux over the entire sampling period from ACP ranged from −71.14 to −3.96 mg CO_2 m^{-2} h^{-1}, indicating that ACP was a sink for CO_2, with the greatest CO_2 consumption occurred in August. Previously, $^{13}C_{DIC}$ and pCO_2 measurements suggested that respiration and decomposition of organic sediments were the primary sources of CO_2 in the water column (Striegl et al. 2001). Del Giorgio et al. (1999) reported that in the water column of temperate lakes the baseline respiration, fueled by allochthonous C, was independent of phytoplankton production. When primary production was high, baseline respiration was insignificant and algal activity usually dominated the CO_2 exchange across air-water interface. Therefore, we consider ACP in our study to be a highly autotrophic water body with high primary production, and the baseline respiration supported by external organic matter was insignificant, which corresponded to the measured CO_2 flux that ranged from −71.14 to −3.96 mg CO_2 m^{-2} h^{-1}. Moreover, the insignificant relationship between CO_2 flux and air temperature or water temperature (Table 2) confirmed the conclusion that ACP was an autotrophic water body where algal photosynthesis, rather than the mineralization of organic matter, played a more important role in CO_2 flux, because an increase in air temperature favored the CO_2 production derived from the mineralization of organic matter (Huttunen et al. 2003). Xing et al. (2005) observed that, in a subtropical lake (Donghu, China), exponential relationships between CH_4 emission and air, water surface, and sediment surface temperature were observed in a subtropical lake (Donghu, China) (Xing et al. 2005). However, in our study, CH_4 emission from ACP was not affected by seasonal variability of temperature. CH_4 emission in air-water interface resulted from the balance of two opposing processes: methanogenesis in anoxic conditions and the oxidation of the generated CH_4. The production of CH_4 is dependent on the concentration of PO_4^{3-} (Schrier-Uijl et al. 2011), phytoplankton primary production (Xing et al. 2005), electron donors and acceptors (Van Bodegom and Scholten 2001). In addition, the CH_4 could be oxidized to CO_2 during any stage of its travel from the sediment through the water column to the atmosphere (Whiting and Chanton 2001). A large fraction of the unoxidized CH_4 was likely to be emitted to the atmosphere by diffusion.

Spatial Variation of CO_2 and CH_4 Fluxes

Vegetation type and species composition affected the carbon dynamics and the formation and emission of the GHG in wetlands (Van Der Nat and Middelburg 2000; Ström et al. 2005). The significant higher fluxes of CO_2 and CH_4 from SCM than other three sites indicated that the invasion by exotic *S. alterniflora* had resulted in increase in CO_2 and CH_4 fluxes sharply, which was consistent with the result of Tong et al. (2012), who found that CH_4 cycling in *S. alterniflora* marshes was high CH_4 production in Min River estuary in southern China. The same conclusion was obtained in the Yangtze River estuary (Cheng et al. 2007) and in Jiangsu province (Zhang et al. 2010).

Plants have three main functions in the regulation of CO_2 and CH_4 emissions. Firstly, plants act as an important source of methanogenic substrate through excreting labile carbohydrates as exudates and root debris. Minoda et al. (1996) and

Watanabe et al. (1999) pointed out that substrates derived from plants contributed up to 90 % of the total CH_4 emission. Roots can directly regulate most aspects of rhizosphere C flow either by regulating the exudation process itself or by directly regulating the recapture of exudate from soil (Jones et al. 2004). Zhang et al. (2010) found that increase of CH_4 emissions was mainly due to a rise in porewater CH_4 concentrations in the *S. alterniflora* mesocosm, therefore concluded that *S. alterniflora* could fix and allocate more organic carbon, such as root exudates and debris inputs to the soil. Therefore, when compared with *S. salsa*, the presence of *S. alterniflora* ensured enhanced CH_4 production and emission in wetlands. In our study, the WSS, OF and SCM were predominated by *T. chinensis*, *S. salsa*, and *S. alterniflora*, respectively. Rhizospheres in these sites were different due to different vegetations and that probably affected the emission of CH_4 and CO_2. It is likely that the slightest change in the chemistry of the soil or physiology of the plant induced rapid shifts in the quantity and quality of the exudative flux (Jones et al. 2004).

Secondly, numerous reports demonstrated that CH_4 emission was well correlated with aboveground living biomass of vegetation (Hirota et al. 2007; Tong et al. 2012). In this study, the maximum aboveground biomass of *T. chinensis*, *S. salsa*, and *S. alterniflora* were 200.1131±15.8172, 376.8582±31.5023, and 1281.9200±176.9304 g m^{-2}, respectively. The high aboveground biomass of *S. alterniflora* matched with the high emission of CO_2 and CH_4 from the SCM, therefore supporting the conclusion that aboveground live plant biomass was a key factor controlling carbon production and emission. Tong et al. (2012) also found that *S. alterniflora* could fix and then allocate more carbon to the soil, which in turn resulted in higher CH_4 production and emission when compared with native species.

Thirdly, plants act as a conduit for CO_2 and CH_4 transport through the aerenchyma system, and as a source of oxygen stimulating CH_4 oxidation. Using ^{14}C labeling techniques, Christensen et al. (2003) observed that the emission of CH_4 was dependent on the amount of vascular plants. Other studies also found that 39.7–90.0 and 48.8–90.0 % of CH_4 emission were transported by *S. alterniflora* and *Phragmites australis* (Cheng et al. 2007). *S. salsa* adapts to tidal inundation because the transportation mechanism carries oxygen from aboveground parts to the roots via the aerenchyma (Han et al. 2005). But we found that CO_2 and CH_4 emissions from OF (dominated by *S. salsa*) were lower than those from SCM (dominated by *S. alterniflora*). That may be due to the difference of vegetations in the two sites. *S. salsa* is a succulent halophytic herb (Song et al. 2009) while *S. alterniflora*, which belongs to the perennial grass family, has visibly evident lacunae in its stems (Tong et al. 2012), which may explain why the CH_4 transport potentials of *S. alterniflora* was higher than that of *S. salsa*. However, *S. alterniflora* has a thick stem

Table 3 CO_2 and CH_4 flux rates from this study and literature

Location	Vegetations	CO_2 (mg m^{-2} h^{-1})	CH_4 (mg m^{-2} h^{-1})	Observation period	References
Yellow River estuary, China	*Tamarix chinensis* (WSS)	125.3625	−0.0110	June~December 2013	This study
	Suaeda salsa (OF)	111.0289	−0.0165		
	Spartina alterniflora (SCM)	241.9720	0.2012		
	aquaculture pond (AP)	−39.4909	0.0034		
Yellow River estuary, China	*Suaeda salsa* [a]	ND	−0.0128	October 2009~July 2010	Sun et al. 2013
Yellow River estuary, China	*Suaeda salsa*	20.86~45.31	ND	May 2012	Zhang et al. 2014
Min River eatuary, China	*Spartina alterniflora*	ND	15.1	January 2007~Decenber 2009	Tong et al. 2012
Yangtze River estuary	*Spartina alterniflora*	ND	0.64 (0.16~1.12)	April~October 2004	Cheng et al. 2010
Jiangsu, China	*Spartina alterniflora*	ND	0.88	May~October 2009	Zhang et al. 2010
	Suaeda salsa	ND	0.54		
Brisbane River estuary, Australia	*Avicennia marina*	ND	0.003~17.4	April 2004~July 2005	Allen et al. 2007
Peat, Netherlands	Lake	61.6±7.1	3.9±1.6	June 16th~July 6th 2009	Schrier-Uijl et al. 2011
Bay of Fundy, Germany	*Spartina alterniflora* etc.	104.167 [b]	6.667 [b]	July~Semperber	Magenheimer et al. 1996
Min River estuary, China	Shrimp pond	−48.79	1.00	October 20th, 21th 2011	Yang et al. 2012
	Polyculture pond of fish and shrimp	−105.25	5.74		
Québec's reservoirs, Canadian	Reservoirs	62.83 [b]	0.367 [b]	1993~2003	Tremblay et al. 2005
Switzerland	Reservoirs	40.417 [b]	0.0083 [b]	September 2003~August 2006	Diem et al. 2012
Temmesjoki River, Finland	River	225 [b]	2.75 [b]	2003~2004	Silvennoinen et al. 2008

[b] Mean values after unit conversion

and well-developed aerenchyma tissue, which can deliver more oxygen into the rhizosphere and lead to higher rates of CH_4 oxidation under *S.alterniflora* stands. But CH_4 emission from *S. alterniflora* was still higher than others because this effect was outweighed by the higher CH_4 production.

Soil moisture in SCM was greater than that in WSS and OF. This was a result of the construction of seawall, which blocked the transport of sea water into the study area and the low coverage of vegetation in WSS and OF under the strong evaporation (evaporation/precipitation ratio, 3.52) condition. Significantly positive impact of moisture on CH_4 emission was observed in WSS, OF, and SCM, but the relationship between CO_2 fluxes and moisture was not significant (Table 2). In our study, soil moisture in SCM was greater than these in WSS and OF, and was inundated occasionally by tide on the neap tide day. The consumption of CH_4 from WSS and OF and the emission from SCM in our study consisted with the conclusion that soil moisture controlled CH_4 emission from sites where the water table fluctuates below the soil surface (Christensen 1993). On other hand, low soil moisture make O_2 diffuse into soil to oxygen CH_4 to CO_2.

Comparisons with Other Studies

At present, reports which focused on GHG emission in Yellow River estuary are scarce. Sun et al. (2013) and Zhang et al. (2014) studied GHG emission in natural wetlands and found that fluxes of CH_4 and CO_2 were -0.0128 mg CH_4 m^{-2} h^{-1} (Sun et al. 2013) and 20.86 to 45.31 mg CO_2 m^{-2} h^{-1} (Zhang et al. 2014), respectively (Table 3). Compared with CO_2 and CH_4 fluxes from natural wetlands where is affected minimally by human mentioned in these two studies, we found that CO_2 fluxes recorded from WSS and OF in our study were greater, while CH_4 fluxes were close to the reported values. That might due to the construction of seawall leading to low moisture which accelerated CO_2 emission. CO_2 and CH_4 emissions from *S. alterniflora* marsh (SCM) in our study were also greater compared with that from natural wetland, differences in vegetation may be the main reason. CH_4 flux from *S. alterniflora* marshes in Yellow River estuary was smaller than these from *S. alterniflora* marshes in Min River estuary (Tong et al. 2012), Yangtze River estuary (Cheng et al. 2010), and Jiangsu province, China (Zhang et al. 2010), which might due to the different latitudes that study areas located. The emission of CH_4 and consumption of CO_2 in aquaculture pond, similar to the result of Yang et al. (2012), which different from natural water body (lakes, reservoirs) act as a source of CO_2 and CH_4 (Tremblay et al. 2005; Silvennoinen et al. 2008; Schrier-Uijl et al. 2011; Diem et al. 2012). Aquaculture ponds are significantly influenced by human activities, therefore nutrient substance content and physicochemical property of these will be different from natural water bodies (lakes, reservoirs), which can lead to differences in GHG emissions.

Conclusion

Human activities have profound impact on greenhouse gas emission in the Yellow River estuary. Exotic-specie *S. alterniflora* invasion significantly increased CO_2 and CH_4 emissions due to its strong gas transportation capacity and excreting large amounts of substrates for methanogens. The construction of seawall blocked sea water transporting into the study area leading to low soil moisture which accelerated CO_2 emission. Aquaculture pond was a source of CH_4 and a sink of CO_2. However, the results of this study are preliminary and need to be validated with further studies. More investigations and long-term measurements (including year-to-year variations) on CO_2 and CH_4 exchanges between ecosystem and atmosphere are needed in order to gain a better understanding of human activities on CO_2 and CH_4 emissions in the Yellow River estuary.

Acknowledgments The authors would like to acknowledge the financial support of the National Basic Research Program of China, (No. 2013CB430401).

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