Soil greenhouse gases emissions reduce the benefit of mangrove plants to mitigating atmospheric warming effect

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Abstract

Mangrove soils have been recognized as sources of atmospheric greenhouse gases, but the atmospheric fluxes are poorly characterized, and their adverse warming effect has scarcely been considered with respect to the role of mangrove wetlands in mitigating global warming. The present study balanced the warming effect of soil greenhouse gas emissions with plant carbon dioxide (CO_2) sequestration rate derived from net primary production of plants in a productive mangrove wetland in South China to assess the role of mangrove wetland in mitigating atmospheric warming. Seasonal flues of the three greenhouse gases, nitrous oxide (N_2O), methane (CH_4) and CO_2, were measured at three mangrove sites in Jiulong River Estuary, and net primary productions of mangrove plants were estimated from the litter fall production (9 replicates for these samplings in each site). Soil characteristics were also studied in the summer to examine their relationships with gas fluxes. Soil to atmosphere gas fluxes ranged from -1.6 to 50.0 μg N_2O m^{-2} h^{-1}, from -1.4 to 3215.3 μg CH_4 m^{-2} h^{-1} and from -31 to 512 mg CO_2 m^{-2} h^{-1} in the present study, indicating that soils release significant greenhouse gases into atmosphere. The results also showed that gas fluxes were significantly higher in the summer and also different among mangrove sites. Gas fluxes in summer were positively correlated with the soil organic carbon, total nitrogen, and NH_4^+-N contents. The mangrove plants were able to sequester a considerable amount of atmospheric CO_2 at rates between -3652 g CO_2 m^{-2} yr^{-1} and -7420 g CO_2 m^{-2} yr^{-1}. The ecosystem was a source of methane (CH_4) and nitrous oxide (N_2O) gases but meanwhile more intense CO_2 sink. However, the total CO_2-equivelent flux of the three gases indicating their warming effect accounted for 9.3-32.7 % of the plant CO_2 sequestration rate, indicating that the warming effect of soil greenhouse gas emissions could partially offset the benefit of mangrove plants to in mitigating atmospheric warming. We therefore propose the assessment of the direct mitigation of atmospheric warming by mangrove ecosystem that take into account both soil greenhouse gases emissions and plant CO_2 sequestration. Moreover, the contribution of two trace gases, N_2O and CH_4, was also relevant, comprising 9.7-33.2 % of the total warming effect.

1 Introduction

The global atmospheric concentrations of greenhouse gases, carbon dioxide (CO_2), and other two trace gases, methane (CH_4) and nitrous oxide (N_2O) have all shown large increases since the pre-industrial times and contribute the global warming. The atmospheric concentrations of CO_2, CH_4 and N_2O have increased from 278 ppm in 1750 to 391 ppm in 2011, by a factor of 2.5 from 722 ppb to 1803 ppb, and from 270 ppb to 342 ppb, respectively (IPCC, 2014a). The CO_2 concentration is increasing at the fastest observed decadal rate of change in the past ten years, and unfortunately the atmospheric greenhouse gas concentrations continue to rise. In order to maintain global temperature warming below 2°C over the 21st century relative to pre-industrial levels, a reduction by 40% to 70% of global anthropogenic greenhouse gases emissions by 2050 compared to 2010, and increasing the existing biological carbon pools for carbon sequestration have been proposed (IPCC, 2014a).

Mangroves grow along the coastlines of most of the world's tropical and subtropical regions. Despite the limited area occupied by mangrove wetlands compared to terrestrial forests (0.32%, Mcleod et al. 2011), these highly productive ecosystems are ecologically important on the global scale, and have been suggested to be responsible for 10-11% of global terrestrial carbon export to the ocean (Dittmar et al., 2006; Alongi, 2014a) and 11-14% of carbon sequestration in the world's oceans (Duarte et al., 2005; Alongi, 2014b). Recent studies have also highlighted the valuable role that mangrove wetlands play in carbon sequestration, and estimated the carbon burial rate in mangrove soil as 226 g C m^{-2} yr^{-1} from 34 sites (Mcleod et al., 2011; Alongi, 2014b). Plants sequester CO_2 from the atmosphere through photosynthesis and store it in their biomass and as detritus in soil. The capability of mangrove plants to sequester CO_2 from atmosphere is therefore related to their net primary production (NPP). The overall global mangrove NPP recently estimated by Bouillon et al. (2008) is 1362.5 g C m^{-2} yr^{-1}, indicating that the CO_2 sequestration capability of global mangrove is equal to 4996 g CO_2 m^{-2} yr^{-1}.

Being inter-tidal, mangrove wetlands are regularly flooded by incoming tides and their soils alternate between oxic and anoxic conditions, which favors microbial processes like nitrifcation, denitrification and methanogenesis that produce greenhouse gases. Numerous studies have recognized mangrove soil as sources of atmospheric greenhouse gases (Allen et al., 2007; Chauhan et al., 2008; Chen et al., 2010). The biogenic emission of greenhouse gases from mangrove soil to the atmosphere could be further enhanced by anthropogenic nitrogen input (Purvaja and Ramesh, 2001; Muñoz-Hincapié et al., 2002; Kreuzwieser et al., 2003; Chen et al., 2011). These gas emissions contribute to atmospheric warming and reduce the overall mitigation of global warming by mangroves. Therefore, the role that mangrove wetlands play in directly mitigating atmospheric warming is reflected by the exchange of greenhouse gases between mangrove ecosystem and the atmosphere as it relates to the ecosystem reducing or contributing to the atmospheric radiative forcing (Chmura et al., 2011). Assessments of the direct effect of mangrove wetlands in mitigating atmospheric warming on the ecosystem scale are important but still lacking. Although some studies have focused on the net ecosystem production (NEP) that combined the net primary production and gaseous carbon emissions from soil respiration in mangrove wetlands, for assessing the contribution of mangrove wetlands to atmospheric carbon gas exchange on the ecosystem scale (Golley et al., 1962; Komiyama, 2008), these studies are inadequate for assessing the contribution of mangroves to mitigating atmospheric warming as the contributions of N_2O emission and the warming effect of gas emissions were not taken into account.

According to a global carbon budget quantified by Bouillon et al. (2008), the mean soil CO_2-C flux represents ~20% of the mangrove NPP, indicating that the soil CO_2 emission from mangrove wetland offsets 20% of the CO_2 sequestration rate by mangrove plant. Although the atmospheric fluxes of CH_4 and N_2O are generally 2 or 3 orders of magnitude lower than CO_2 flux in mangrove wetlands (Chen et al., 2010), their contributions to global warming could also be substantial and are worthy attention because they are more stable and have considerably higher radioactive forcing than CO_2, with direct global warming potential (GWP) 298 and 34 times as that of CO_2, respectively (Myhre et al., 2013). For instance, the annual mean fluxes of CH_4 could be up to 3899 μg CH_4 m^{-2} h^{-1} (Allen et al., 2007), with a warming effect of 1161 g CO_2 m^{-2} yr^{-1}. Our previous studies have demonstrated that some mangrove wetlands in South China subjected to exogenous nutrient inputs were significant sources of greenhouse gases (Chen et al., 2010, 2011). The warming effect of N_2O and CO_2 emissions in Mai Po mangrove in Hong Kong equated to 507 and 3279 g CO_2 m^{-2} yr^{-1}, respectively (Chen et al., 2011). Given that the NPP of the Mai Po mangrove was 1107 gDW m^{-2} yr^{-1} (Lee, 1989) and a carbon content of 44% in plants is assumed (Bouillon et al., 2008), the warming effect of gas emissions, totalled 70 % of the plant CO_2 sequestration. However, the greenhouse gas emissions from mangrove soils remain poorly characterized, and to what extend the gas emissions would offset the benefit of plant carbon sequestration is still unclear. In this study, we compared the warming effect of the gas emissions against the plant CO_2 sequestration rate to estimate the mitigating effect of mangrove wetland on atmospheric warming, and this balancing is based on the exchange of greenhouse gases between the mangrove ecosystem and the atmosphere.

The Jiulong River Estuary in South China is considered as the distribution centre of *Kandelia obovate* (Wang and Wang, 2007), which is wide-spread and well suited for use in restoration of areas of north Asia's coastline (Field, 1996). Previous studies have examined the production in this area and reported the litter fall production ranging from 852-1249 g m^{-2} yr^{-1}, similar to those in tropical mangroves (Lin et al., 1985; Lu et al., 1988; Ye et al., 2013); this finding indicates that the mangrove forests in this region are productively and ecologically important in the sequestration of atmospheric CO_2. However, mangroves in this area are affected by a wide variety of human activities, including the mariculture that intermittently discharges pond effluents into the coastal water and potentially impact mangrove forest. Alongi et al. (2005) has reported rapid mineralization rates of soil carbon and nitrogen in this area; for instance, soil denitrification rate ranged from 1106 to 3780 mmol N_2 m^{-2} d^{-1}, and equated to 11-20% of total soil nitrogen inputs. These rapid mineralization processes suggest significant greenhouse gas emissions from the mangrove soils. In this study, spatial and seasonal variations in soil greenhouse gas emissions were investigated, and the warming effect of the gas emissions was quantified and then balanced with the plant CO_2 sequestration rate to estimate the mitigating effect of mangrove wetland on atmospheric warming. We also evaluated the effects of soil characteristics on greenhouse gas emissions. We hypothesized that (1) the mangrove soils in this region could be sources of greenhouse gases, and the gas emissions would to a certain offset the benefits of mangrove plants to mitigating atmospheric warming; (2) the contribution of the two trace gases, N_2O and CH_4, to atmospheric warming might be relevant and were considered; and (3) the mitigating effects might vary spatially among different mangrove sites.

2 Materials and Methods

2.1 Study area

Soil greenhouse gas emissions and plant CO_2 sequestration rates were studied in the subtropical mangroves in the Jiulong River Estuary. The region is subtropical has a mean annual temperature of 20.9 °C, and most of the annual rainfall (1284 mm) is derived from summer typhoons. Tides are semi-diurnal, with an average range of 4 m (Alongi et al., 2005). The majority of the primary mangrove forests in this region were destroyed for aquaculture activity and sea wall construction. Plantation of *K. obovata*.was carried out near Caoputou Village to protect the shoreline in 1960s and 1980s (Chen et al., 2007). Most mangrove forests (~32 ha) in this region now are located on the southwestern shore (Alongi et al., 2005), and are narrow fringing forests due to the destruction. The mangrove soils are mainly composed of silt and clay (Alongi et al., 2005).

As some mangrove dominated shores were subjected to erosion, *Spartina alterniflora* invasion or garbage from upstream, the present study chose sites in good conditions for comparison study so as to eliminate such exogenous impacts. Samplings were carried out in three mangrove sites (Fig. 1) located near Caoputou Village (CPT, 24°23'40.89"N, 117°54'42.90"E), Xiaguo Village (XG, 24°23'36.24"N, 117°55'19.48"E) and on Haimen Island (HMI, 24°24'24.05"N, 117°56'28.51"E). CPT mangrove was a rehabilitated and now mature *K. obovata* forest planted in 1962 at the high intertidal zone on the south bank with a density of 1.0 stem m^{-2} (Chen et al., 2007) and had the highest canopy height (7.8m). XG mangrove was at the mid intertidal zone, based on its intertidal elevations and the intertidal zonation scheme in Jiulong River Estuary, as described by Chen et al. (2006); this mangrove was composed of natural and dense *K. obovata* tress (6.2m-high, 1.7 stem m^{-2}). The lowest vegetation density (0.9 stem m^{-2}) and canopy height (5.5m) occurred in the mid-low natural mangrove site on Haimen Island. The width of each sampling area was ~40 m, ~90 m and ~90 m from the landward to seaward fringes in the three mangrove sites, respectively, and the sampling length was around 20 m for each site.

2.2 Soil to atmosphere greenhouse gas fluxes

Soil to atmosphere fluxes of greenhouse gases were quantified in January, April, August and October 2012, representing the seasons winter, spring, summer and autumn, respectively. All samplings were conducted two hours before the lowest ebb tide during the daytime as the study areas are subject to semi-diurnal tides and the exposure times of mangrove wetlands are relative short. The tidal range, tidal flooding and exposure duration were comparable among the sampling days and the three mangrove sites. Nine replicate plots were chosen at each mangrove site during each sampling campaign to achieve more accurate estimation of gas emissions because of high levels of spatial variation, even on a small scale (Allen et al., 2007; Chen et al., 2010).

Gas flux in this study was quantified using the static (closed) chamber technique followed by gas chromatography as described by Chen et al. (2010). The circular and transparent chambers were placed between the trees, in locations without mangrove seedlings, aboveground roots or litter fall to avoid the influences of these factors on gas fluxes, and the open end of the chamber was inserted 3 cm into the soil. The chambers had a basal area of 0.025 m^2, an internal volume (headspace volume over the soil) of 1.25 l, and did not include a fan (Corredor et al., 1999; Bauza et al., 2002). The volume/basal area ratio was similar to those (1l vs. 0.02 m^2) used by previous researchers (Corredor et al., 1999; Bauza et al., 2002) which is sufficiently small for the rapid increase in gas concentrations. A comparison study by Moore and Roulet (1991) showed that the fluxes measured using static chambers (0.053 m^2 basal area and 40cm height) has no difference from those using dynamic chamber (the insider air was circulated) with similar height, indicating that the gas mixing in the static chamber was as efficient as the dynamic chamber even with a height of 40 cm. The chambers used in this study have a hole at their top. When pushing the chambers into soils, these holes were left open to eliminate the pressure disturbance, and were closed using rubber stoppers for first gas collection. The deployment time was set to 30 minutes, with sampling at 10-minute intervals. At each sampling time, a 5-ml gas sample was collected with a hypodermic needle attached to a 10-ml glass syringe from the chamber and then injected into a 20-ml gas sampling bag. Previous study by Chen et al. (2012) revealed that gases were continuously released and their concentrations were significantly and linearly related to the deployment time (with regular sampling at 15-20 minutes' intervals), even in event that the gas concentrations in the chamber were very high. In this study, the gas flux was much lower than those reported by Chen et al. (2010), and the dimension of sampling chamber was the same as that used by them. Therefore, the samplings at 10-minute intervals were appropriate and the rapid gas accumulations in the chamber (especially for CO_2) would not result in significant underestimation of gas flux.

Gas concentrations were analysed in parallel with a gas chromatography system (7890A, Agilent Technologies, Santa Clara, California, USA) configured with a single channel and two detectors, by comparing the peak areas of samples against an Agilent Greenhouse Gas Checkout Sample (1 ppm

N_2O, 5 ppm CH_4 and 600 ppm CO_2 in N_2). The N_2O and CH_4 concentrations were determined with a 63Ni electron capture detector and a flame ionization detector (FID), respectively. The CO_2 concentration was analyzed by FID after methanization. During the measurement, the standard sample was analyzed in every 15-20 samples to ensure data quality. The relative standard deviations of replicate standard measurements were 3.6%, 2.5% and 3.4% for N_2O, CH_4 and CO_2, respectively.

The soil to atmosphere fluxes of greenhouse gases were calculated using the following formula:

$$F_m = V\Delta M/A\rho$$

where F_m is the interfacial gas flux (mol m^{-2} h^{-1}), V is the internal air volume (m^3) in the chamber after being placed, ΔM (h^{-1}) is the change in gas concentration in the container, A is the surface area of the soil (m^2) and ρ is the volume of per mol gas (m^3 mol^{-1}). During each sampling, the open air temperature was simultaneously measured with a mercury thermometer to calculate the ρ value.

2.3 Sampling and analysis of soil

Soil parameters were also measured at these sampling sites in summer to examine their relationship with gas fluxes as the fluxes have been found to be higher in summer in subtropical mangroves (Chen et al., 2012) which is conducive this examination. Soil redox potential (E_h) under the chamber was measured using a pH/E_h meter (WP-81, TPS, Australia) after gas sampling, by inserting the platinum probe directly into the soil at a depth of 5 cm from the surface. A soil sample to a depth ~5cm was collected at each plot using a steel tube (i.d. 1.75cm) with the open end sharpened, and the bulk density was estimated from the soil volume and 105 ^oC oven-dried weight. Independent soil cores to a depth of 15 cm (6 cores for each mangrove site) were then collected using hand-held PVC corers. Soil organic carbon (OC) concentration was analyzed using rapid dichromate oxidation procedure. Total Kjeldahl nitrogen (TKN) content after Kjeldahl digestion and NH_4^+-N and NO_3^--N contents in the KCl (2M) extracts were measured by the Continuous Flow Analyzer (CFA, Futura II, Alliance Instruments). All soil analyses were based on the standard methods for soil analyses described by Page et al. (1982), and the data were expressed in terms of 105 ^oC oven-dried weight.

In addition to the soil analysis, salinity of the soil porewater was only measured at the seaward fringe of each mangrove site (three replicates for each site) as porewater sample was not available for all sample sites. The salinity was measured using a pocket refractometer (0–100 parts per thousands, Atago PAL-06 S, Japan). Such measurement does not reveal the salinities within the mangrove wetlands, but could reflect the salinity gradient among the three mangrove sites.

2.4 Plant CO_2 sequestration rate

Plant CO_2 sequestration rate was calculated from the NPP, the carbon content and the formula weights of CO_2 and C. Mangrove NPP was estimated using the litter fall technique proposed by Teas (1979), which postulates that 1/3 of mangrove NPP is returned as litter fall. A global extrapolation by Bouillon et al. (2008) also showed a clear relationship between litter fall and wood production and further suggested that litter production amounts to ~32% of the total mangrove NPP including root production. This rapid and direct method was also applied in other studies (e.g. Lee, 1990; Alongi, 2009), but its accuracy depends on the availability of a good conversion factor (Odum et al., 1982). In this study, a conversion factor 2.75 was applied for the estimation of NPP, which was calculated from previously reported NPP (including root production) and the concurrent litter fall production of *K. obovata* mangrove in the Jiulong River Estuary (Lin et al., 1985). The mean carbon content in various plant fractions was 47% for *K. obovata* in the Jiulong River Estuary (Zheng et al., 1995).

Litter fall samples were collected using metal-framed litter traps (Φ=70 cm for surface area, 30 cm depth) with 2-mm mesh. Nine traps were placed randomly under canopies at similar height above the maximum tide level (1.5m above the sediment) at each mangrove site. Trap contents were collected monthly and sorted into the categories of leaves, woods and reproduction (flowers and propagules), and were then dried at 60 °C to a constant weight and weighed. The total litter fall production was expressed as the sum of these components.

2.5. Mitigating effect of the mangrove ecosystem on atmospheric warming

The gas fluxes were converted to CO_2-equivalent fluxes to indicate their respective contributions to global warming using the GWP value of each gas (1, 34 and 298 for CO_2, CH_4 and N_2O, respectively, over a 100-year timeframe) according to Myhre et al. (2013). The annualized warming effect of gas emissions at each site was then compared against the CO_2 sequestration rate of plants to estimate the ecosystem mitigation effect. Net ecosystem productions of the three mangrove sites were also estimated by subtracting soil respiration rate from NPP, and the soil respiration rate expressed as the total carbon-gas flux was calculated as the sum of CO_2-C and CH_4-C fluxes.

The annual fluxes of the three gases and their warming effects were calculated from the fluxes measured in the four seasons during exposure periods for each site (n=36) or the three sites (n=108). This estimation was subjected to the assumptions that the fluctuations in soil-atmosphere fluxes were insignificant during exposure period and the water-atmosphere fluxes during inundation were similar to those during exposure. The assumption was based on the following findings from previous studies (Chang and Yang, 2003; Bouillon et al., 2008; Tong et al., 2013). Although tidal effect on gas flux was observed during the exposure in previous study (Chang and Yang, 2003), the results were inconsistent across different measurement campaigns. The study by Chang and Yang (2003) showed that gas fluxes in a *K. obovate* wetland had significantly more emission after ebb tide than before flooding in August 1996, but the fluxes before flood were significantly higher than that after ebb tide in May and August 1998. Our preliminary study also showed that the temporal variation in gas flux was insignificant during the exposure (unpublished data). On the other hands, gases released from soils could be dissolved in tides during the flood, partial of which is released to atmosphere from the seawater (Tong et al., 2013). Bouillon et al. (2008) reported that there was no significant difference in the CO_2 emission between exposed and inundated periods. A diurnal measurement of CH_4 and N_2O fluxes in an estuarine marsh in Fujian Province also showed no clear difference between the inundation and exposure periods (Tong et al., 2013). Therefore, the calculations of annual emissions from fluxes during exposure time obtained from imitated measurement would not affect the findings of the present study.

Since the carbon sequestration by mangrove plants is estimated based on net primary production, the CO_2 released due to autotrophic respiration of mangrove roots should not be included. Although CO_2 emissions from some soils include the CO_2 efflux from plant roots and heterotrophic respiration (Lovelock, 2008; Bulmer et al., 2015), Komiyama et al. (2008) concluded that most metabolic respiration from mangrove roots is considered to be released through the lenticels and underground roots of mangroves may only make a small contribution to the soil respiration when soil respiration chambers are placed where there is no peumatophore, because the aerenchyma tissues of underground roots are connected with lenticels on pneumatophores, prop roots, and buttresses above the ground (Tomlinson, 1986). In the present study, *K. obovate* develops no pneumatophore. The sampling points located between the trees, and there was no obvious root biomass observed in the soil under the chambers. Thus, the CO_2 flux was more likely to represent metabolism of microbes (including microalgae) in this study.

2.5 Statistical analysis

The normality of variables was checked using the Kolmogorov-Smirnov test, and the gas fluxes that did not follow a normal distribution were transformed to improve normality and homoscedasticity prior to analysis. Two-way ANOVA was used to test the differences in greenhouse gas flux among the four seasons and the three sites. If the difference was significant ($p<0.05$), a post hoc Tukey test was then used to determine what the difference was. Differences in litter fall production and soil characteristics among different mangroves were compared by using one-way ANOVA. Pearson correlation coefficients were calculated to determine the relationships between soil properties and greenhouse gas fluxes in the summer. All statistical analyses were performed using SPSS 18.0 for Windows (SPSS Inc., USA).

3 Results

3.1 Soil to atmosphere greenhouse gas fluxes

The soil to atmosphere N_2O fluxes ranged from -1.6 to 50.0 μg m^{-2} h^{-1} in Jiulong River Estuary (Fig. 2), with annualized CO_2-equivelent flux ranging from 24.3 to 88.9 g CO_2 m^{-2} yr^{-1} in the three mangrove sites. According to the two-way ANOVAs, N_2O flux and its CO_2-equivelent flux (proportional to gas flux) varied significantly among the three mangrove sites ($F=10.63$, $p=0.000$) and among the four seasons ($F=17.21$, $p<0.001$). However, no significant interaction was found between these two factors ($F=1.28$, $p>0.05$). The highest N_2O flux was measured in the summer, while the lowest was observed in the winter and autumn. XG mangrove had higher N_2O flux than the other two sites with similar fluxes.

The CH_4 flux and its CO_2-equivelent flux showed significantly spatial ($F=15.36$, $p<0.001$) and seasonal ($F=26.03$, $p<0.001$) variations. The lowest flux was -1.39 ug m^{-2} h^{-1} (measured in HIM in winter), while positive fluxes in other measurements indicated sources of CH_4 in the mangroves. Significant interaction was also found between the two factors ($F=3.83$, $p<0.001$). The flux was significantly higher in summer while the winter flux was generally the lowest. However, the highest value of CH_4 flux was measured in autumn (in XG), when the CH_4 flux had a greatly spatial variation (40.5-5360.5 ug m^{-2} h^{-1}).

For CO_2, the flux also varied significantly among the mangrove sites (F=10.24, $p<0.001$) and the four seasons (F=73.25, $p<0.001$), and the interaction between these two factors was also significant (F=4.42, $p<0.01$). Sinks of CO_2 were measured in the winter in the three mangrove sites; however, mangrove soils in the warmer seasons acted as significant CO_2 sources. Significantly higher CO_2 flux was measured in the summer, varying from 108.0 to 511.8 mg m^{-2} h^{-1}, irrespectively the mangrove sites. The annual mean CO_2 fluxes were 1015.3 g m^{-2} yr^{-1}, 1470.3 g m^{-2} yr^{-1} and 307.4 g m^{-2} yr^{-1} in CPT, XG and HMI, respectively.

3.2 Soil characteristic in summer and their relationship with gas fluxes

HMI mangrove had slightly higher porewater salinity while there was no difference in salinity between the other two sites (Fig. 3). Soil characteristics, except NO_3^--N concentration, bulk density and E_h, varied significantly among the three mangrove sites in Jiulong River Estuary (Fig. 3). Lower soil water content was measured in CPT than in other two sites ($p<0.01$). Soil NH_4^+-N content was lower in CPT and HMI ($p<0.05$). XG mangrove site had the highest soil OC and TKN concentrations and the lowest concentrations were measured at HMI. Among the measured soil parameters measured, NH_4^+-N, OC and TKN concentrations were positively correlated with fluxes of the three gases and the total CO_2-equivelent flux (Table 2). No significant effect was detected for other soil parameters on the gas fluxes.

3.3 Litter fall and net primary productions

Litter fall productions ranged from 771 gDW m^{-2} yr^{-1} to 1565 gDW m^{-2} yr^{-1} (Table 2) in Jiulong River Estuary mangroves. Leaf fall and reproduction components were 550 and 514 gDW m^{-2} yr^{-1}, comprising 44% and 41% of the total litter fall production, respectively. Using the conversion factor 2.75, the net primary production of mangrove calculated from litter fall production was 2119-4306 gDW m^{-2} in the three mangrove sites. Due to its lower leaf and twig productions, the litter fall production and NPP measured in HMI were lower compared to the other two mangrove sites,.

3.4 Mitigating effect of the mangrove ecosystem on atmospheric warming

In case of high primary productions and low soil carbon gas emissions, the mangrove wetlands in this study had NEP rates ranging from 912 to 1746 g C m^{-2} yr^{-1} (Table 3), with a mean as 1358 g C m^{-2} yr^{-1}.

The carbon gas emission accounted for 8.4-22.7 % of the total mangrove NPP, and the CH_4 made a negligible contribution (0.2 %-3.4 %) to the total carbon gas emission.

Based on the CO_2-equivelent fluxes of the three gases (Fig. 2), the total CO_2-equivalent fluxes indicating the warming effect of gas emission, were 1125, 2200 and 340 g CO_2 m^{-2} yr^{-1}, respectively, in the three sites (Table 3). The two trace gases, CH_4 and N_2O, contributed as much as 33.2% of the total CO_2-equivalent flux in XG, but contributed less than 10% in the other two sites. When balancing the warming effect of the gases and the concurrent CO_2-sequestration rate of the mangrove plants, the effect of the mangrove ecosystem on atmospheric warming was equal to -4708 g CO_2 m^{-2} yr^{-1} (Table 4), further indicating the mangrove wetland as an affirmative role in mitigating global warming.

4 Discussion

The subtropical *K. obovata* mangrove forest in Jiulong River Estuary had high net primary productivity, close to or higher than amounts reported in tropical regions, and higher than the global mean production (Bouillon et al., 2008). This is consistent with the summary by IPCC (2014b), which shows that some subtropical mangroves have higher growth rates than the tropical. This high NPP and low carbon gas emissions from soil in the present study indicated that the mangrove wetlands have strong sequestration capability of atmospheric carbon on the ecosystem scale. The NEP in Jiulong River Estuary (912-1747 gC m^{-2} yr^{-1}) was also higher than the global mean value of 1100 g C m^{-2} yr^{-1} reported by Bouillon et al. (2008), and those estimated in a *Rhizophora mangle* forest (561 gC m^{-2} yr^{-1}) in Puerto Rico (Golley et al., 1962) and in the mangrove in western Florida Everglades (1170 gC m^{-2} yr^{-1}, Barr et al., 2010). Although CH_4 emission was also significant in the estuarine mangrove wetlands in this study, it accounted for a small proportion (0.2-3.4%) of the soil gaseous carbon emission.

The soil to atmosphere gas fluxes in the Jiulong River Estuary fell within the ranges previously reported for other mangrove wetlands (Chauhan et al., 2008; Chen et al., 2010). The results further demonstrated that mangrove soils can be sources of greenhouse gases which contribute to the warming effect. With both plant CO_2 sequestration (showed in Table 3) and soil gas emissions considered, mangrove wetlands were small sources for CH_4 and N_2O (0.08–0.30 g N_2O m^{-2} yr^{-1} and 0.25–18.86 g CH_4 m^{-2} yr^{-1}) and significant CO_2 sinks at rates from -6405 g CO_2 m^{-2} yr^{-1} to -3345 g CO_2 m^{-2} yr^{-1}. However, when considering their warming effect, soil greenhouse gas emissions accounted for 9.3-32.7

% of the plant CO_2 sequestration rate in this study, indicating that greenhouse gas emissions from mangrove soils could reduce the benefit of mangrove plants. The net mitigating effect of the mangrove ecosystem on atmospheric warming was estimated to be from -6295 g CO_2 m^{-2} yr^{-1} to -3312 g CO_2 m^{-2} yr^{-1} in the three mangrove sites. As the three sites in this study locate at different areas (north-shore mangrove and island mangrove) in the estuary and cover both the rehabilitated and natural sites in this region, we considered they are representative of the larger entire estuary. The mitigation effect of the mangroves in Jiulong River Estuary could be estimated as 4708 g CO_2 m^{-2} yr^{-1}, suggesting that mangrove wetland in this region, in term of the radioactive forcing, is important sinks of atmospheric CO_2. Given that the CO_2 sequestration capability of global mangrove is equals to 4996 g CO_2 m^{-2} yr^{-1} and that soil CO_2 flux offsets 20% of the CO_2 sequestration rate (Bouillon et al., 2008), the mitigating effect of global mangrove is assumed to be less -4000 g CO_2 m^{-2} yr^{-1} when the warming effect of non-CO_2 emission is considered. In the present study, the greenhouse gas fluxes were measured at the clear surface soils, and the fluxes were mainly derived from soil metabolisms. If Take into account of the CO_2 emissions from other source like decompositions of litter fall and dead wood as important carbon pools in the mangroves (IPCC, 2014b), the contribution of greenhouse gas emissions would be more significant. Alongi (2014a) suggested that the CO_2 loss to air due to faunal respiration could also be considerable. Further studies are therefore needed with consideration of CO_2 emissions from these sources. Globally, mangrove NPP decreases with increasing latitude and the highest litter fall rates occur in the tropical areas (Bouillon et al., 2008; Alongi, 2009). Some studies on the other hand reported low greenhouse gas emissions from soils in tropical mangroves (Chen et al., 2014; Nóbrega et al., 2016). These suggest that the tropical mangrove could be more relevant in mitigation global warming, and their roles deserve detailed studies as the tropical mangroves (e.g. Indonesian mangrove) comprise the majority of global mangroves (Giri et al., 2010).

Despite their low fluxes compared to CO_2, the contributions of the trace CH_4 and N_2O gases are also relevant (up to 33.2%) to global warming in the mangrove wetlands considering their warming effect. When subjected to anthropogenic nutrient inputs, the emissions of these two gases and CO_2, could be more considerable (Muñoz-Hincapié et al., 2002; Chen et al., 2011), which would largely enhance their contributions to the warming effect. High gas emission rates have been reported from mangrove soils, and N_2O and CH_4 contributed twice the global warming potential as CO_2 in the Futian mangrove in South China which receives discharges and anthropogenic nutrient inputs from Pearl River Delta and nearby polluted rivers (Chen et al., 2010). As the fluxes of the CH_4 and N_2O are not still poorly quantified, their fluxes from mangrove soils therefore should receive more attentions and should also be documented in addition to that of CO_2 to quantify the contribution of greenhouse gas emissions from mangrove soil, especially for those receiving exogenous nutrients. Liu and Greaver (2009) have also suggested that although the addition of N increased the global terrestrial C sink, CO_2 sequestration could be largely offset by N stimulation of global CH_4 and N_2O emissions. N_2O was found to dominate the total warming effect of gas emissions in some agro-ecosystems (Mosier et al., 2005).

Mangrove production, gas fluxes and the ecosystem mitigation effect in this study varied spatially with mangrove sites, with a lower fluxes and mitigation effect observed at HMI due to a much lower plant CO_2 sequestration rate. The variation was greater for gas fluxes, with CO_2 flux ranging between as low as 307 g m^{-2} yr^{-1} and up to 1470 g m^{-2} yr^{-1}, and even greater spatial variation was found in CH_4 flux. Warming effect of the gas emissions in XG was about 6 times of that in HMI. Moreover, gas fluxes also varied seasonally. Such spatial and seasonal variations in gas fluxes, which are suggested to be mainly due to fluctuations in temperature in subtropical mangroves and moisture in tropical mangroves (Chen et al., 2012), therefore should be taken into account for the inventory of greenhouse gas emissions. We also measured a lower primary production accompanied by low gas emission rates in this study. Similarly, the soil respiration rate was found to be correlated with litter fall production on a large range of latitude extending from 27°N to 37°S (Lovelock, 2008). This pattern suggested that the more CO_2 is sequestrated by mangroves, the more substantial the effect of the soil greenhouse gas emissions might be, and their warming effect should not be ignored.

The spatial variations of greenhouse gas fluxes could be partly attributed to the differences in soil characteristics among the study sites as the gas fluxes are related to mangrove soil properties including concentrations of organic carbon, total and inorganic nitrogen, bulk density, salinity and redox potential (Purvaja and Ramesh 2001; Allen et al., 2007; Chen et al., 2010, 2012). The higher gas fluxes were attributed to higher soil organic carbon, nitrogen and NH_4^+-N concentrations in mangrove soils (Table 2). This is similar to the findings in our previous studies in other subtropical *K. obvota*-dominated wetlands in South China (Chen et al., 2010). Positive soil E_h in the mangrove soil and significant correlation between N_2O flux and soil NH_4^+-N concentration indicated the importance of nitrification process in mangrove soil that is responsible for the N_2O production. Nevertheless, the results didn't exclude the potential of denitrification for N_2O production as the soil E_h in this study was below 350 mv, below which denitrification usually starts (Pitty, 1979). Similarly to some other studies (e.g. Allen et al., 2007; Chen et al., 2010), high soil NH_4^+-N concentration also enhanced the CH_4 emission into the atmosphere in this study, probably due to the inhibition effect of soil NH_4^+-N on CH_4 oxidation under high concentration (Bosse et al., 1993). Methane emission from the coastal soils has been known to be limited by high salinity as the presence of high sulphate in coastal soils allows sulphate-reducing bacteria to outcompete methanogens for energy sources (Biswas et al., 2007; Poffenbarger et al., 2011; IPCC, 2014b). Lower soil CH_4 flux and higher porewater salinity in HMI was also consistent with such inhibition effect.

Soil temperature and soil moisture were the two key environmental factors affecting soil greenhouse gases fluxes and driving their seasonal and spatial variations (Lovelock, 2008; Poungparn et al., 2009; Chen et al., 2012). The CO_2 flux can be suppressed by elevated soil moisture (Poungparn et al., 2009; Chen et al., 2014; Lewis et al., 2014), because the high degree of soil saturation reduces the exposure of soil to air and decomposition rate of organic matter. On the opposite, the high moisture can stimulate anaerobic respiration in soils and enhance the CH_4 flux (Lu et al., 1998). However, in this study, the soil water moisture fluctuated in a narrow range and had no significant impact on gas fluxes. No significant correlations were found between soil E_h (indicator of oxidation-reduction potential) and the gas fluxes in the present study, and flux variabilities were more related to the C/nutrient availabilities. Variations in soil temperature have been reported to influence gas fluxes (Lovelock, 2008; Poungparn et al., 2009; Chen et al., 2012; Leopold et al., 2015), and higher temperature generally induce higher gas fluxes. Although not measured in this study, we consider that soil temperature drives the seasonal variation in gas fluxes in the mangroves in Jiulong River Estuary.

Some other studies in saltmarshes also quantified the potential global warming feedbacks based on the soil carbon sequestration rate and non-CO_2 gas emission rates (e.g. Chmura et al., 2011; Yuan et al., 2014). Considering the rapid soil accumulation rate in the mangrove wetland in Jiulong River Estuary (33.7 mol C m^{-2} yr^{-1}, equivalent to 1482.8 g CO_2 m^{-2} yr^{-1}, Alongi et al., 2005), the global warming potential of this mangrove area is determined to be ~1190 g CO_2 m^{-2} yr^{-1} (the CO_2-equivelent flux of CH_4 and N_2O fluxes had a sum of 290 g CO_2 m^{-2} yr^{-1}). This value was higher than those in northern and northwestern Atlantic saltmarshes estimated in the growing season (574-1000 g CO_2 m^{-2} yr^{-1}, Chmura et al., 2011) and in the marshes in eastern China (114-1130 g CO_2 m^{-2} yr^{-1}, Yuan et al., 2014). Unlike the salt marsh, the carbon accumulation of which through plant growth is roughly balanced by losses through grazing, decomposition and fire (IPCC, 2006, 2014b), a majority of C captured by mangrove plant is stored in their biomass and as detritus in soil. Taking these carbon sequestrations into account, it can be suggested that the mangrove wetland plays a more substantially potential role in mitigating global warming.

Mangrove ecosystem is open and dynamic in the carbon processes. Majority of mangrove NPP is stored in plant biomass; partial litter fall production can be decomposed, retained and buried in the mangrove soil, while the rest is exported to the adjacent coastal water. On the other hand, mangrove ecosystem could also bury the exogenous carbon during flooding periods (Twilley et al., 1992, Bouillon et al., 2008). Mangrove ecosystem also loses significant organic carbon in dissolved (DOC) and particulate forms with tidal water (Dittmar et al., 2006; Bouillon et al., 2008; Ye et al., 2011), while the majority of carbon export from mangroves might occur as dissolved inorganic carbon (DIC, Bouillon et al., 2008; Maher et al., 2013). Alongi (2014a) recently suggested that loss of DIC in mangrove soils via subsurface pathways to adjacent waterways is large, at a potential rate up to 40% of annual primary production. These processes determine the carbon sequestration potential within mangrove wetland, which is related to the potential of mangrove wetland in reducing carbon gas emissions and mitigating global warming, as the loss of carbon pool is equivalent to relevant carbon dioxide emission to atmosphere (IPCC 2014b). The present study assessed the role of mangrove wetland in mitigating atmospheric warming based on the greenhouse gas exchange between mangrove ecosystem and atmosphere. Considering the potential of carbon sequestration of mangrove ecosystem in reducing carbon gas emissions, we further propose assessment of the potential of mangrove wetland in mitigating global warming by considerations of both the greenhouse gas emissions and the carbon sequestration potential as a synthesis of the above comprehensive carbon processes.

5 Conclusions

The present study showed that mangrove soils are significant sources of greenhouse gases, and the warming effect of gas emissions could partially offset the benefit of plant CO_2 sequestration to mitigating atmospheric warming. We therefore propose that any assessment of the mitigation effect on atmospheric warming should take into account soil greenhouse gas emissions. The contributions of trace amounts of CH_4 and N_2O gases to the warming effect are also significant and should not be ignored in mangrove wetlands, especially in those nutrient-enriched. Moreover, the temporal and spatial variations in gas fluxes and plant CO_2 sequestration rate should be taken into account to improve the accuracy of inventory of greenhouse gas emissions and the estimates of mitigating effect of mangroves on atmospheric warming.

Author contribution

G. Chen designed the experiments, and S. Chen and D. Yu carried out the field sampling and laboratory analysis. B. Chen performed the data analysis. G. Chen wrote the first draft of the manuscript, and all authors contributed substantially to revisions.

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Table 1. Litter fall production and net primary production (gDW m^{-2} yr^{-1}) in the three mangrove sites in the Jiulong River Estuary.

Mangrove	Leaf	Twig	Reproduction	Total	NPP
CPT	683±101 a	241±105 a	641±234 a	1565±246 a	4306±676 a
XG	692±86 a	267±164 a	458±177 a	1417±189 a	3899±519 a
HMI	275±121b	52±72 b	444±160 a	771±143 b	2119±393 b
JRE	550±222	187±151	514±207	1251±355	3441±1098

CPT: Caoputou; XG: Xiaguo; HMI: Haimen Island; JRE: Jiulong River Estuary; NPP: Net primary production. Different letters in one column indicate a significant difference among the three mangrove sites. Data are mean ± SE of each site or the three sites (n =9 for each site and n=36 for JRE, the same as for Table 3)

Table 2. Pearson correlation coefficient values (r) between soil properties and summer fluxes of greenhouse gases in Jiulong River Estuary.

Soil parameter	Fluxes of gases			Total CO_2-equivelent flux
	N_2O	CH_4	CO_2	
Redox potential	-0.323	-0.126	-0.130	-0.157
Bulk density	0.406	0.311	0.152	0.160
Water content	0.424	0.329	0.175	0.359
NH_4^+-N	0.575*	0.730**	0.618*	0.720**
NO_3^--N	-0.199	0.008	-0.205	-0.175
OC	0.756***	0.838***	0.713**	0.831***
TKN	0.812***	0.541*	0.724**	0.789***

OC: organic carbon, TKN: total Kjeldahl nitrogen. *, ** and *** indicate significant r value at $p<0.05$, 0.01 and 0.001, respectively ($n=18$). No correlation was done between porewater salinity and gas flux as the porewater samples were collected out of the sampling areas.

Table 3. Net ecosystem production and the mitigating effects of wetlands on global warming in the Jiulong River Estuary

Study site	Soil C-gas flux ($g\ C\ m^{-2}\ yr^{-1}$)	Net primary production ($g\ C\ m^{-2}\ yr^{-1}$)	Net ecosystem production ($g\ C\ m^{-2}\ yr^{-1}$)	Plant CO_2 sequestration rate ($g\ CO_2\ m^{-2}\ yr^{-1}$)	CO_2 equivalent flux ^{A} ($g\ CO_2\ m^{-2}\ yr^{-1}$)	Ecosystem mitigation effect ^{B} ($g\ CO_2\ m^{-2}\ yr^{-1}$)
CPT	278±515	2024±317	1746	7420±1165	1125±2050 (9.8 %)	6295 (15.2%)
XG	415±572	1832±244	1417	6719±894	2200± 3032 (33.2 %)	4519 (32.7%)
HMI	84±133	996±185	912	3652±677	340± 513(9.7 %)	3312 (9.3%)
JRE	259±468	1617±516	1358	5930±1893	1222± 2249(23.8 %)	4708 (20.6%)

CPT: Caoputou; XG: Xiaguo; HMI: Haimen Island; JRE: Jiulong River Estuary. Data are means ±SD for each site or for the JRE (for gas flux, n=36 for each site and n=108 for JRE).

Net primary production was derived from litter fall production (Table 2) and the carbon content in plants (47 %). Net ecosystem production was estimated through NPP minus soil respiration rate, i.e. soil C-gas flux (the sum of CO_2-C and CH_4-C fluxes). The ecosystem mitigation effect was estimated by comparing the annualized warming effect of gas emissions against the CO_2 sequestration rate of plants.

A: Value in the bracket represents the proportion of N_2O and CH_4 gases to the total CO_2-equivelent flux.

B: Value in the bracket represents the proportion of warming effect of gas emissions to the plant CO_2 sequestration rate.

Figure captions

Fig. 1 Map of the Jiulong River Estuary, China and the typical scene of the mangrove forest (A and B). Numbers 1-3 indicate the positions of the three sampling sites in this study, 1: Caoputou; 2: Xiaguo; 3: Haimen Island;

Fig. 2 Soil to atmosphere greenhouse gas flux (mean±SE, n=9 for the seasonal fluxes and 36 for the annual mean fluxes) at the mangrove sites in Jiulong River Estuary. Same abbreviation as Fig. 1. In each season, different letters (in lower case) indicated significant difference among the three mangrove sites according to ANOVA test. For each mangrove site, different letters (in capital) indicated significant difference among the four seasons.

Fig. 3 Soil characteristics (mean±SE, n=6) at the mangrove sites in Jiulong River Estuary. Same abbreviation as Fig. 1. Different letters indicated significant difference among the three mangrove sites according to ANOVA test.

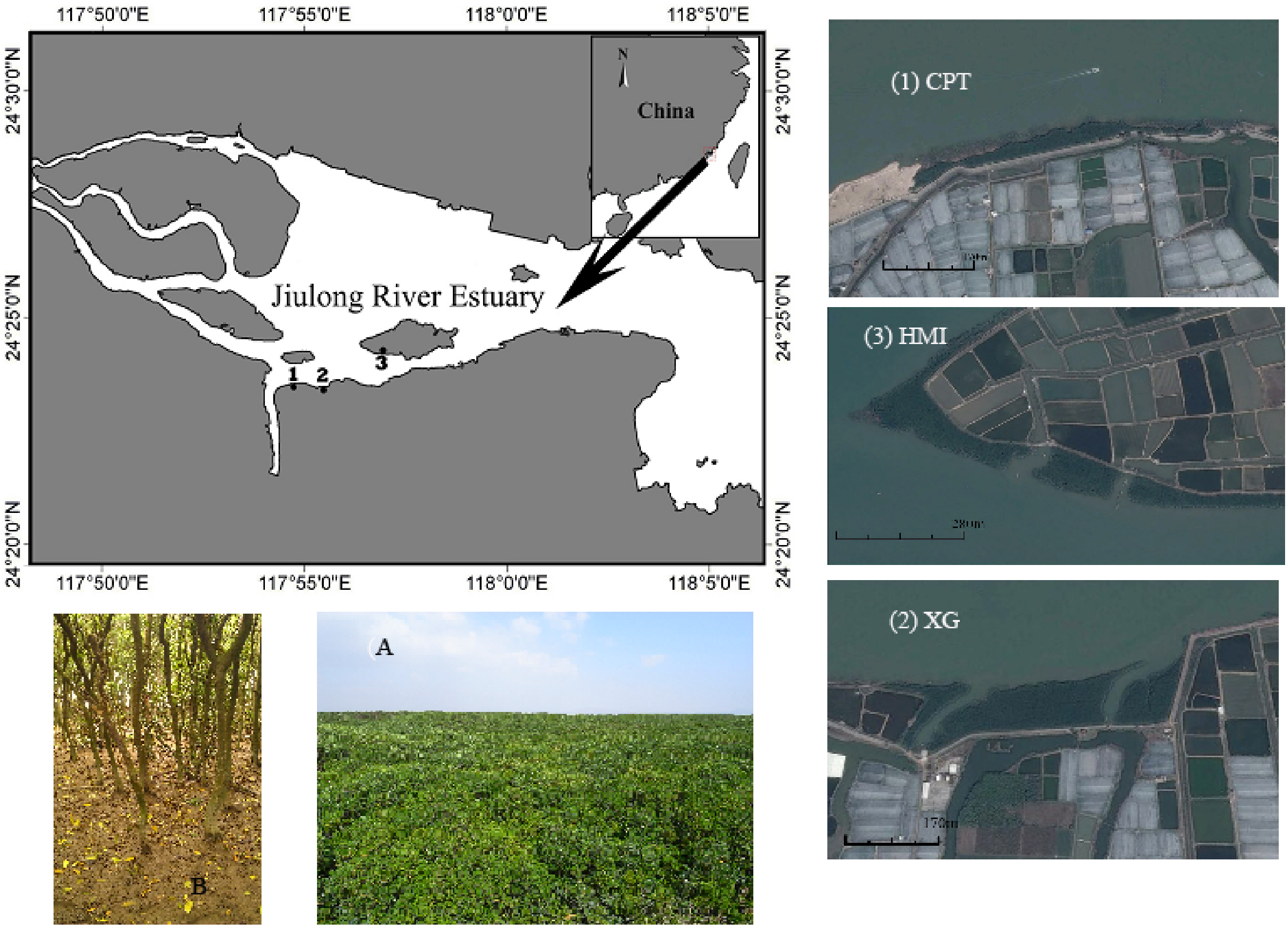
117°50'0"E
117°55'0"E
118°0'0"E
118°5'0"E
24°30'0"N
24°25'0"N
24°20'0"N
N
China
Jiulong River Estuary
1
2
3
A
B
(1) CPT
(3) HMI
280m
(2) XG
170m

Fig. 1

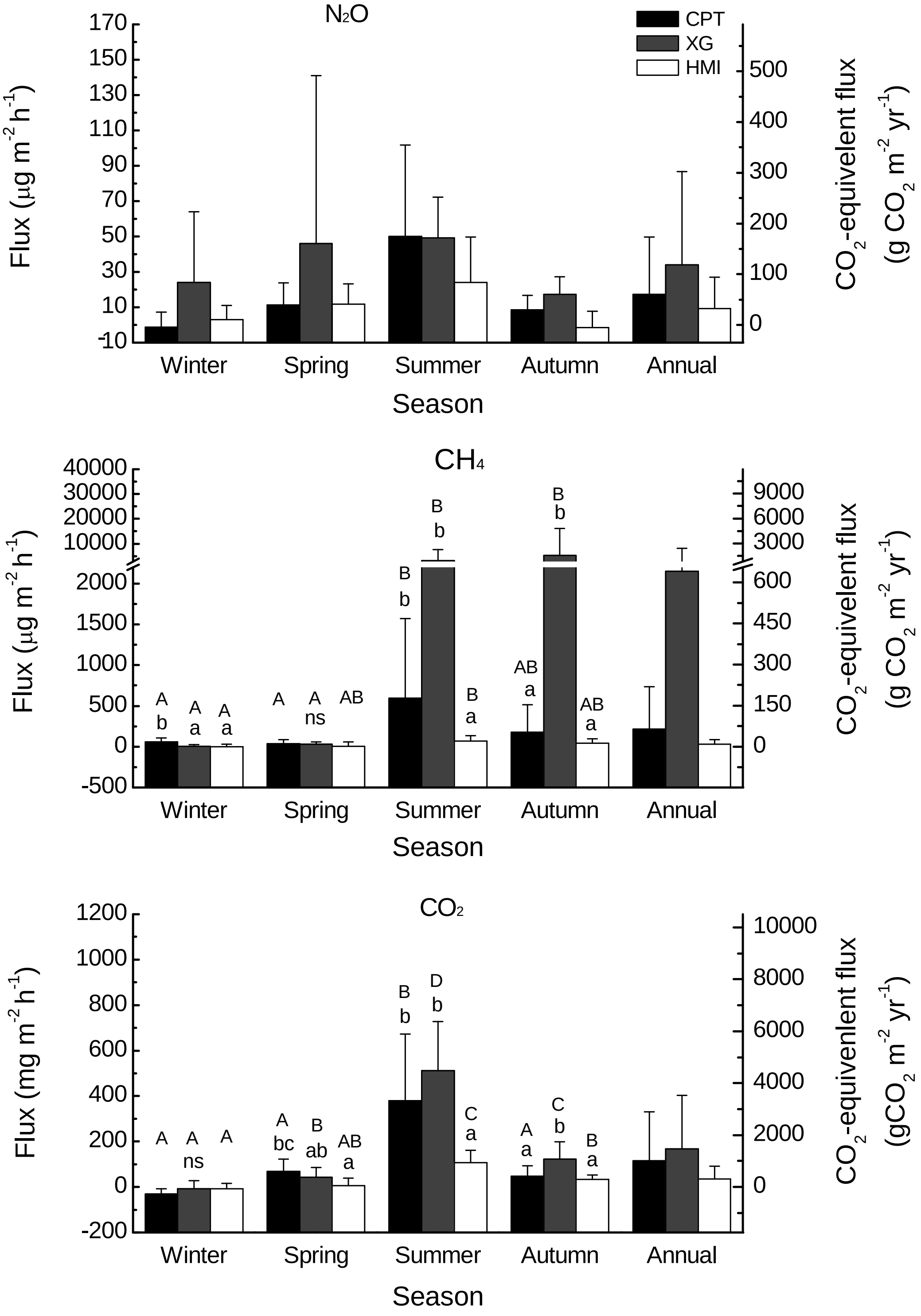
N₂O
CPT
XG
HMI
Flux (µg m-2 h-1)
CO2-equivelent flux (g CO2 m-2 yr-1)
170
150
130
110
90
70
50
30
10
-10
500
400
300
200
100
0
Winter
Spring
Summer
Autumn
Annual
Season
CH₄
Flux (µg m-2 h-1)
CO2-equivelent flux (g CO2 m-2 yr-1)
40000
30000
20000
10000
2000
1500
1000
500
0
-500
9000
6000
3000
600
450
300
150
0
A b
A a
A a
A
A ns
AB
B b
B b
B a
AB a
B b
AB a
Winter
Spring
Summer
Autumn
Annual
Season
CO₂
Flux (mg m-2 h-1)
CO2-equivenlent flux (gCO2 m-2 yr-1)
1200
1000
800
600
400
200
0
-200
10000
8000
6000
4000
2000
0
A
A ns
A
A bc
B ab
AB a
B b
D b
C a
A a
C b
B a
Winter
Spring
Summer
Autumn
Annual
Season

Fig. 2

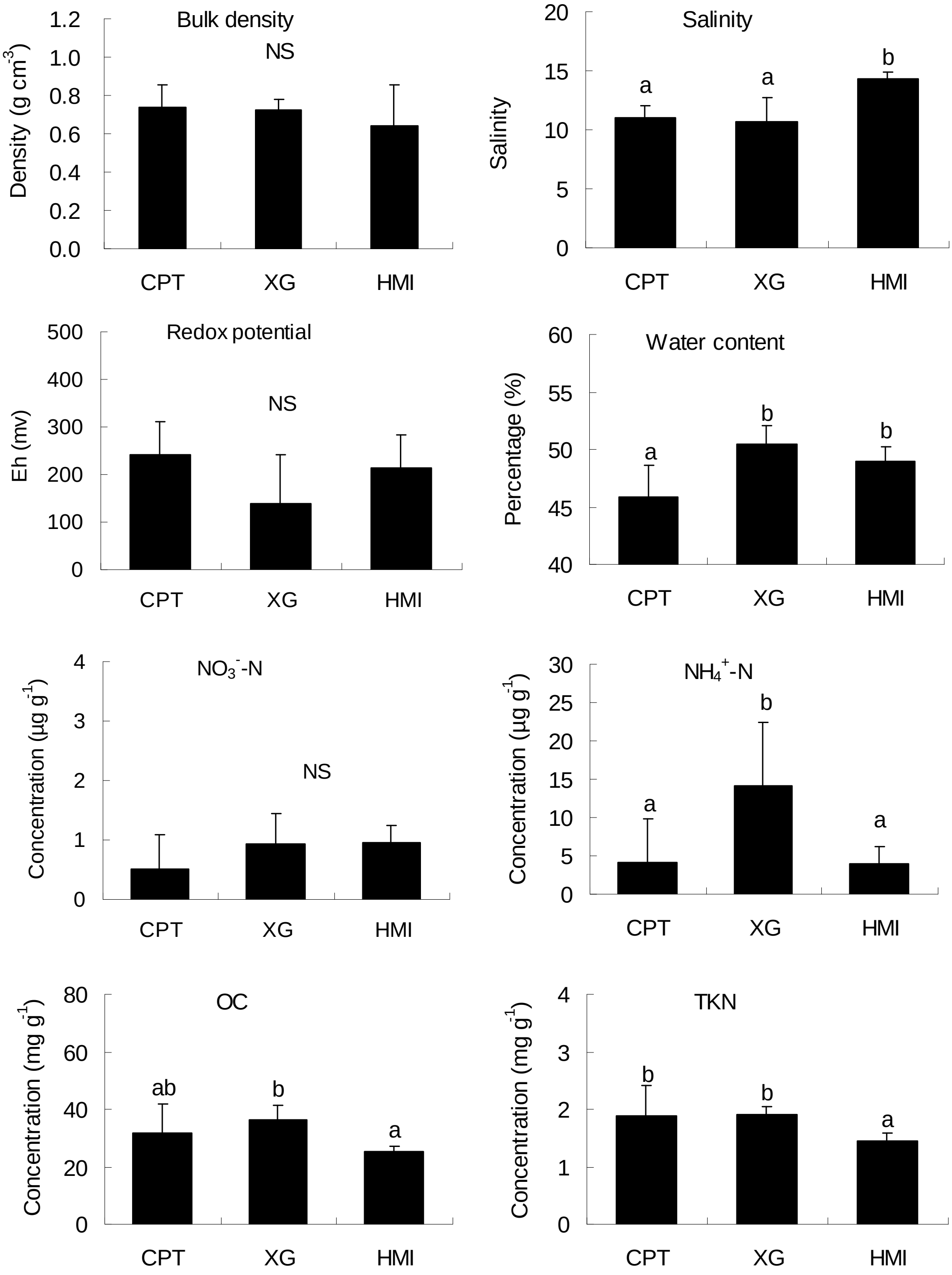
Bulk density
NS
Density (g cm^{-3})
1.2
1.0
0.8
0.6
0.4
0.2
0.0
CPT
XG
HMI
Salinity
Salinity
20
15
10
5
0
a
a
b
CPT
XG
HMI
Redox potential
NS
Eh (mv)
500
400
300
200
100
0
CPT
XG
HMI
Water content
Percentage (%)
60
55
50
45
40
a
b
b
CPT
XG
HMI
NO_3^--N
NS
Concentration (µg g^{-1})
4
3
2
1
0
CPT
XG
HMI
NH_4^+-N
Concentration (µg g^{-1})
30
25
20
15
10
5
0
a
b
a
CPT
XG
HMI
OC
Concentration (mg g^{-1})
80
60
40
20
0
ab
b
a
CPT
XG
HMI
TKN
Concentration (mg g^{-1})
4
3
2
1
0
b
b
a
CPT
XG
HMI

Fig. 3