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RESEARCH ARTICLE

Greenhouse gas emissions from intact riparian wetland soil columns continuously loaded with nitrate solution: a laboratory microcosm study

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Abstract

In this study, we aimed at determining greenhouse gas (GHG) (CO_2, CH_4, and N_2O) fluxes exchange between the soil collected from sites dominated by different vegetation types (*Calamagrostis epigeios*, *Phragmites australis*, and *Carex schnimdtii*) in nitrogenous loaded riparian wetland and the atmosphere. The intact soil columns collected from the wetland were incubated in laboratory and continuously treated with NO_3^- -enriched water simulating downward surface water percolating through the soil to become groundwater in a natural system. This study revealed that the soil collected from the site dominated by *C. epigeios* was net CO_2 and N_2O sources, whereas the soil from *P. australis* and *C. schnimdtii* were net sinks of CO_2 and N_2O, respectively. The soil from the site dominated by *C. schnimdtii* had the highest climate impact, as it had the highest global warming potential (GWP) compared with the other sites. Our study indicates that total organic carbon and NO_3^- concentration in the soil water has great influence on GHG fluxes. Carbon dioxide (CO_2) and N_2O fluxes were accelerated by the availability of higher NO_3^- concentration in soil water. On the other hand, higher NO_3^- concentration in soil water favors CH_4 oxidation, hence the low CH_4 production. Temporally, CO_2 fluxes were relatively higher in the first 15 days and reduced gradually likely due to a decline in organic carbon. The finding of this study implies that higher NO_3^- concentration in wetland soil, caused by human activities, could increase N_2O and CO_2 emissions from the soil. This therefore stresses the importance of controls of NO_3^- leaching in the mitigation of anthropogenic N_2O and CO_2 emissions.

Keywords Greenhouse gas · Fluxes · Riparian wetland · Vegetation type · Microcosm experiment · Soil columns · Nitrate

Introduction

It is increasingly recognized that methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) are important GHGs contributing to global warming (Change 2001; Lashof and Ahuja 1990; Song et al. 2012). The global warming potential of N_2O and CH_4 for a 100 years is 298 and 25 times higher than that of carbon dioxide, respectively (Myhre et al. 2013). Moreover, the global mean concentrations of N_2O and CH_4 has risen from 270 ± 7 ppb in 1750 to 324.2 ± 0.1 ppb in 2011, and from 722 ± 25 ppb in 1750 to 1803 ± 2 ppb by 2011, respectively (Myhre et al. 2013). Although the percentage of land surface covered by natural wetland is very small, much of the global carbon is stored in the wetland soil, sediments, and their accumulated detritus (Kayranli et al. 2010). It is increasingly recognized that wetlands have great influence on the dynamics and cycles of greenhouse gases in nature (Bhullar et al. 2014; Xu et al. 2014). As a result, numerous studies have been conducted on GHG's emission from natural wetlands globally (Beringer et al. 2013; Kayranli et al. 2010), including coastal saline wetlands (Xu et al. 2014), tropical and temperate wetlands (Couwenberg et al. 2010; Juszczak and Augustin 2013), and subarctic and boreal wetlands (Huttunen et al. 2003; Ström and Christensen 2007). In China, studies on CO_2, N_2O, and CH_4 emissions have been conducted in Yancheng coastal saline wetland in southeast China (Xu et al. 2014), mangrove ecosystems (Chen et al. 2010; Xu et al. 2014), Yangtze River estuary (Cheng et al. 2010; Zhang et al. 2010), and in natural marsh wetlands such as

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Sanjiang Plain (Song et al. 2006; Song et al. 2009; Yang et al. 2013). However, similar studies is lacking on CO_2, N_2O, and CH_4 emissions within Qixing River Wetland National Nature Reserve (QRWNNR) located in Northeast China.

It has been demonstrated that GHG emission greatly varies temporally and spatially in different wetlands and within wetlands (Jacinthe et al. 2012; Jørgensen et al. 2012). Temporally, the variation of GHG emission has been related to different factors, among which are soil moisture, temperature, and water level, whereas spatial variation has been documented to be influenced mainly by vegetation composition (Dinsmore et al. 2009; Liu et al. 2017; Sun et al. 2013). For example, Nag et al. (2017) reported that CO_2 emitted from wetland soils dominated by *Typhus latifolia* in central Ohio was much higher compared with the reference site (upland site). While assessing the response of greenhouse gas emissions from three types of wetland soils in the Qinghai-Tibetan Plateau, Liu et al. (2017) observed that N_2O production was remarkably higher in palustrine wetlands compared with riverine and lacustrine wetlands. Sun et al. (2013) also revealed that the coastal marsh dominated by *Suaeda salsa* in the Yellow River estuary acted as source of N_2O and sink of CH_4 at interseasonal scales. Xu et al. (2014) investigated the spatial dynamics of GHG fluxes under various vegetation covers in a coastal saline wetland in southeast China. The authors concluded that the spatial variations of CO_2, N_2O, and CH_4 gases in the coastal wetland primarily depended on vegetation type. Sites dominated by *S. alterniflora*, *S. glauca*, and grass flats in the coastal wetland had higher greenhouse gas flux than those from the mud flat. Under laboratory microcosms, Lind et al. (2013) found that nitrate load was a significant factor that controlled both nitrate reduction and N_2O emission in riparian wetlands in central and northern Jutland, Denmark. However, no studies have been conducted to determine greenhouse gas emission from QRWNNR riparian wetlands receiving surface runoff rich in nitrogenous fertilizer and dominated by different vegetation types.

Qixing River Wetland National Nature Reserve (QRWNNR) is located in Sanjiang Plain, the agricultural hub of China. The wetland is located at the heart of farmlands and it receives surface runoff rich in nitrogenous fertilizers. QRWNNR is characterized by high environment heterogeneity with some sites purely dominated by mono-stands of *C. epigeios*, *P. australis*, and *C. schnimdtii* plants. The wetland plays a major part in environmental functions, such as protecting water quality, erosion control, sheltering and feeding different plants and animals, and recharging groundwater (Wang et al. 2015). Moreover, it provides significant socioeconomic and cultural benefits. However, despite its heterogeneous nature created by different vegetation types and being the recipient of agricultural runoff rich in nitrogenous fertilizers, there exist uncertainties on GHG emission in the QRWNNR. In this study, a laboratory microcosm was conducted to determine GHG's emissions from intact soil columns collected from sites dominated by different vegetation types in the nitrogenous loaded riparian wetland. The aims of this study were (i) to quantify and compare CO_2, N_2O, and CH_4 gases emissions from wetland soil collected from sites dominated by different vegetation types, and (ii) to assess the effect of nitrate availability and environmental factors on CO_2, N_2O, and CH_4 emissions. A clear understanding of the spatial variability and factors influencing GHG's emission in this important and critical environmental system is very crucial for management, and even for re-establishing wetlands within the greater Sanjiang plain. To unravel this, undisturbed soil columns collected from sites dominated by different vegetation types (*C. epigeios*, *P. australis*, and *C. schnimdtii*) were incubated in the laboratory and treated with NO_3^- -enriched water. Unlike other studies which simulate an upward groundwater flow through the wetland soils (Laverman et al. 2010; Lind et al. 2013), in this study, the experiment was set to simulate downward surface water percolating through the soil to become groundwater in a natural system. This experimental design is unique in that not only the gas emission is monitored but also the fate of NO_3^-–N -enriched solution from the different soil columns.

Study site and sampling procedure

Study area

The QRWNNR is a typical representative of riparian natural freshwater marsh type located in the Northeastern part of Heilongjiang Province, China, and ranges from 46° 39′ 45″–46° 48′ 24″ N and 132° 00′ 22″–132° 24′ 46″ E. The wetland was designated as site of international importance in 2011. Its size is approximately 20,000 ha, sub-divided into a buffer zone (3600 ha), core zone (7960 ha), and experimental zone (8440 ha). The experimental zone is an area set aside by the QRWNNR administration for the purposes of conducting research. QRWNNR lies in an area which is under the influence of a temperate humid monsoon climate with an average yearly temperature and rainfall of about 1.9 °C and 500 mm, respectively. Moreover, the average evaporation of the study area is approximately 3.84 mm. The soil in QRWNNR is characterized by mires soils, including peat-boggy soils, humus, meadow, and peat soils. The most dominant plant species in this wetland are *C. epigeios*, *P. australis*, and *C. schnimdtii*. Other companion species include *Quercus mongolica*, *Glyceria spiculosa*, and *Betulla platyphylla*, among many others. More details about the study site can be found in Mwagona et al. (2019).

Field sampling procedure

In order to allow for comparison of the GHG emission, three georeferenced sites were selected from the experimental zone based on dominant vegetation types; *C. epigeios*, *P. australis*, and *C. schnimdtii* within the wetland. During the soil sampling period, the standing water depth in sites dominated by *P. australis* and *C. schnimdtii* ranged approximately from 0.4 to 0.7 m and from 0 to 0.2 m in site dominated by *C. epigeios.* Triplicate intact soil cores were collected at each site using polyvinylchloride (PVC) pipes (4.5 cm internal diameter, 100 cm in length). The pipes were manually drilled to a depth of 40 cm into the soil. Immediately after retrieving the soil, all PVC pipes containing the soil content were sealed at both ends with corks to avoid water leakage. Soil samples for determination of total nitrogen (TN), total organic carbon (TOC), and bulk density were collected at every sampling site, following the same procedure. The samples were then transported to the laboratory for experiment setup and sample testing.

Experiment setup and measurement methods

Since QRWNNR receives surface runoff rich in nitrogenous fertilizers from the larger Sanjiang Plain, the experiment was designed to simulate the downward surface water flow through the intact soil column. The experiment consists of two storage reservoirs, A and B positioned at different heights and connected to each other using tubes (Fig. 1). The bigger reservoir A was filled with nitrate solution (60 mg/L NO_3^-−N) prepared in the laboratory by dissolving potassium nitrate (KNO_3 99% Junsei Chemical Co., Ltd Japan) in distilled water. The nitrate solution concentration used in this experiment is typical for the most of the marsh wetlands in Northeast China (Zhang et al. 1996). The purpose of reservoir B was to ensure that a constant water head in each intact soil column was maintained using a tube level adjuster connected to the reservoir. The flow of the solution from reservoir A to reservoir B was aided by air pressure generated when the solution level in reservoir B reduced below the tube level adjuster. The PVC pipes were connected to a common supplier of nitrate solution from the small reservoir B. The inlet was placed 5 cm above the 0 cm depth (soil-water surface) in all the cores (Fig. 1).

Gas sampling

Prior to sampling, the system was allowed to attain equilibrium with the chosen flow rate (0.042 mL/second) set using a valve for 5 days. Gas sampling was done after every 5 days for a period of 30 days. During each sampling period, gas samples were collected using a 20-ml nylon syringe at 0-, 10-, 20- and 30-min intervals after closing the PVP pipe ends with rubber stoppers. The extracted gas was then injected in gas sampling bags (aluminum-multi-layer foil composite film gas bags) and stored for 3–7 days in the dark at room temperature until analysis. The CH_4, CO_2, and N_2O gas concentration was measured using gas chromatograph (Agilent 7890A, Agilent Co., Santa Clara, CA, USA) equipped with an electron capture detector (ECD); then, the slope of the gas concentration during sampling was used to compute the gas flux according to the equation from Zhang et al. (2013) and Song et al. (2008)

$$Flux = \frac{\mathrm{dc}}{\mathrm{dt}} \frac{M}{V_0} \frac{P}{P_0} \frac{T_0}{T} H$$

where dc/dt is the slope of the gas concentration change, along with time (μmol/mol/h). M is the molar mass of each gas measured (g/mol). P is the atmospheric pressure in the sampling site (kPa). T is the absolute temperature during the sampling (°C). V_0, T_0, and P_0 are the gas molar volume, air absolute temperate, and atmospheric pressure under standard conditions, respectively. H is the height of the PVC column during sampling (m). Positive values mean efflux to the atmosphere and negative values mean the gas flux from the atmosphere to the soil.

Water sampling

Water samples were collected at the inlet (5 cm above the soil-water surface) and outlet (− 20 cm below the soil-water surface) of every soil column using a 20-mL nylon syringe. The water samples were immediately filtered through 0.45-μm GD/X Whatman filters and stored at − 20 °C until analysis. Nitrate $\left(NO_3^-\right)$ from the water was analyzed according to the standard method described in Federation and Association (2005). The assumption made in this study is that NO_3^- concentration in soil water is the concentration at the outlet of the soil columns.

Global warming potential (GWP)

According to fifth assessment report of intergovernmental panel on climate change, the strength of source and sinks for GHGs are expressed as GWP. GWP is determined through the GHG fluxes from and to the atmosphere (IPCC 2013). Generally, CO_2 is considered as the reference gas in estimating GWP, and an increase or decrease in the CH_4 and N_2O emissions is converted into "CO_2 equivalents" through the CH_4 and N_2O GWPs. For sometimes now, GWP has been used to understand how ecosystems such as wetlands influence radiative forcing (Kayranli et al. 2010; Xu et al. 2014). Based on a 100-year time horizon, CH_4 and N_2O has 25 and 298 times more heat absorbing capacity than CO_2 (IPCC 2013). The GWP of the three sites dominated by

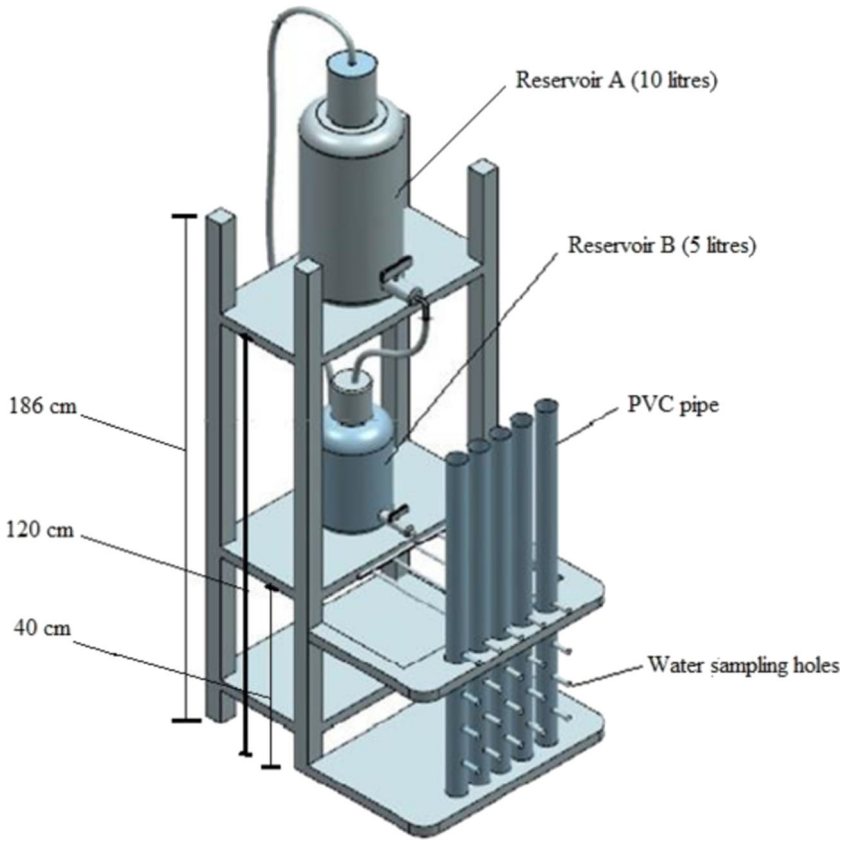

Fig. 1 A schematic diagram of the laboratory experiment set up (not drawn to scale)

different vegetation types was calculated using the following equation (IPCC 2013):

$$GWP = CO_2 + (CH_4 \times 25) + (N_2O \times 298).$$

Statistical analyses

Statistical analyses were performed using the R software (version 3.4.1) (Team 2014). Analysis of variance was used to determine site differences for soil characteristics (with Tukey's HSD for post hoc comparisons). Repeated-measures ANOVAs was conducted with NO_3^- concentration in soil water, N_2O, CO_2, and CH_4 emission being the response variables and site and time (days) and their interaction being fixed factors. Since some data sets of the gas flux values were negative, a constant was added to the fluxes before log transform to satisfy the normality and variance assumption. Spearman non-parametric correlation was used to explore the relationships between CH_4, CO_2, and N_2O gas emission and NO_3^- concentration at the outlet (here after referred as NO_3^- concentrations in soil water). In addition, the relationships between the GHG fluxes and the NO_3^- concentrations in soil water were analyzed by linear regression according to standard formula. Unless otherwise indicated, results are reported as mean value ± standard error (SE).

Results and discussion

Soil characteristics

Figure 2 shows the soil characteristics from the three sites within QRWNNR. From our results, bulk density increased with increasing depth. Spatially, no significant difference was observed for the mean bulk density among the sites. However, the mean bulk density was relatively high in the site dominated by *C. epigeios* (1.12 g/cm^3), followed by *P. australis* (1.04 g/cm^3), then *C. schnimdtii* (1.03 g/cm^3). A significant difference among depth in all sites was observed for bulk density (F = 68.147 p = 0.000). The Tukey HSD post hoc test indicated that the mean bulk density determined in 0–10 cm depth was significantly lower than that in the other depths. This is because soil bulk density is considered to be the basic property that varies with the soil structural conditions (Chaudhari et al. 2013) and increases with soil depth, due to changes in porosity, soil texture, and organic matter content.

Unlike bulk density (Fig. 2a), the total organic carbon and total nitrogen reduces with increasing depth (Fig. 2b, c). The mean total organic carbon in the site dominated by *C. epigeios* (27.14 mg C/g DW) was significantly higher compared with *P. australis* (18.29 mg C/g DW) and *C. schnimdtii* (17.60 mg C/g DW). Moreover, total organic carbon in the top soil profile (0–10 cm) and the other soil profiles had significant

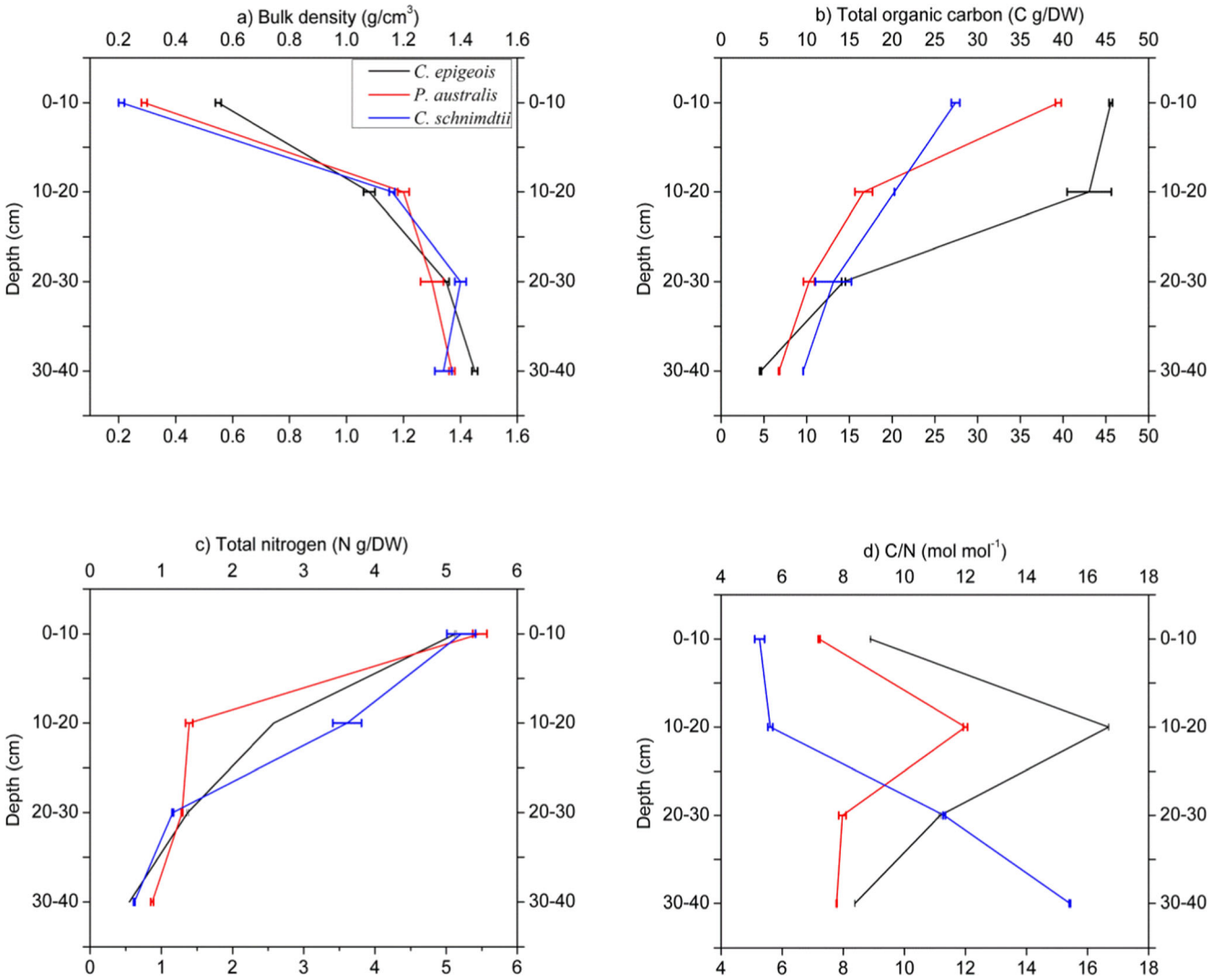

Fig. 2 Vertical profile of soil characteristics collected from sites dominated by different vegetation types in QRWNNR (values are means, error bars represent standard error). DW, dry weight. **a** Bulk density (g/cm^3). **b** Total organic carbon (C g/DW). **c** Total nitrogen (N g/DW). **d** C/N (mol mol^{-1})

differences among the sites, in order of *C. epigeios* > *P. australis* > *C. schnimdtii* (Fig. 2b). Huang et al. (2015) noted that the difference between organic matter input and output determines the amount of soil organic matter and carbon. The vertical profile of total organic carbon from the soil collected in sites dominated by different vegetation types showed that the plants detritus decreased with depth. When plants detritus decompose, most of their organic matter is mineralized (Brinson et al. 1981) and a new soil layer which contains a greater amount of organic matter is formed (Huang et al. 2015). This therefore led to higher total organic carbon in the top soil profile than in the lower soil profile. Our results further indicate that soil from the site dominated by *C. epigeios* had more organic carbon than the other sites. The reasons for this observation may be that: firstly, high organic carbon in the soil from the site dominated by *C. epigeios* can probably be explained by additional organic matter supply by *C. epigeios* through litter fall associated with their relative high productivity (Li et al. 2017). Secondly, probably there were low microorganism activities in *C. epigeios* which leads to decrease of soil organic carbon decomposition rate hence increases the accumulation of soil organic carbon. Mean total nitrogen varied significantly with depth with remarkably higher values being recorded in the top soil profile (0–10 cm depth). However, no significant differences were observed for total nitrogen among sites (Fig. 2c).

Nitrate (NO_3^-) concentration in soil water

Over the 30-day study period, the mean NO_3^- concentration at the inlet was 59.36 mg/L for *C. epigeios*, 59.37 mg/L for *P. australis*, and 59.36 mg/L for *C. schnimdtii*, while the mean outlet concentration was 20.06, 0.89, and 0.92 mg/L for

C. epigeios, *P. australis*, and *C. schnimdtii*, respectively. The NO_3^- concentration in soil water from the site dominated by *C. epigeios* was significantly higher about 20 times compared with the other sites (*P. australis* and *C. schnimdtii*). This implies that different sites within the QRWNNR have different capacities to remove NO_3^-. The observed sites variation of NO_3^- concentration in soil water may potentially be attributed to difference in total organic carbon. The quality and composition of organic carbon has been identified as the major factor limiting denitrification process in wetland soils (Rivett et al. 2008). While doing a comparison of different organic carbon sources for groundwater denitrification, Lorrain et al. (2004) reported that the organic carbon compound may affect the rate of denitrification and the amount of carbon required to denitrify a given amount NO_3^- in soil water. Even though the soil collected from the site dominated by *C. epigeios* had a higher amount of organic carbon, the NO_3^- concentration in soil water at the outlet was significantly higher, suggesting that NO_3^- removal capacity was relatively low, compared with the other sites. Probably the denitrification process was very low in the site dominated by *C. epigeios* due to quality of organic carbon. Organic carbon from *C. epigeios* has been shown to contain proteins, lipids, and lignin which are not readily bioavailable to heterotrophic microorganisms in the soil hence limiting denitrification rate (Rivett et al. 2008; Song et al. 2018). On the other side, organic carbon in *P. australis* contains substrates such as sugars, amino acids, and organic acids that are readily bioavailable to heterotrophic microorganisms (Uddin and Robinson 2017). This could potentially explain the high removal of NO_3^- in soils from *P. Australis*.

The temporal variation of NO_3^- concentration in soil water reveals that the ability of the wetland soil to remove NO_3^- decreases with time (Fig. 3). In the first 10 days of the experiment, the NO_3^- concentration in soil water was low implying high removal of NO_3^- from the initial concentration at the inlet compared with the other days. Likely, during the first few days, the soil microbial activity was very high in the microcosm experiment but then reduced over time due to carbon limitation (Micks et al. 2004).

Greenhouse gases fluxes from soil column

Carbon dioxide (CO_2) fluxes

This study revealed that CO_2 fluxes differed significantly among the sites (Table 1). The mean CO_2 flux from soil collected in the site dominated by *C. epigeios* was significantly higher (98.24 mg $CO_2/m^2/h$) compared with *P. australis* (− 1.25 mg $CO_2/m^2/h$) and *C. schnimdtii* (2.97 mg $CO_2/m^2/h$). The higher CO_2 emission in *C. epigeios* was likely due to higher decomposition of soil organic carbon and litter (Song et al. 2011). Yang et al. (2013) and Chimner and Cooper (2003) documented that in wetland soil, a large available carbon source of decomposition contributes to large emission of CO_2 when exposed to electron acceptor such as NO_3^-. The higher NO_3^- concentration in soil water in *C. epigeios* may have enhanced the quality of organic matter and stimulated decomposition activities (Melillo et al. 1982; Song et al. 2011), hence higher production of CO_2. Nitrate input affects organic matter decomposition by changing the organic matter quality (Song et al. 2018). For example Zhang et al. (2017) showed that nitrate input stimulate decay of *C. epigeios* leaves during the standing and lying-dead phase. Wang et al. (2018) found that nitrogen input increase litter nitrogen concentration which in turn decreases lignin to nitrogen ratios which is important parameter that affects litter decomposability. Moreover, high NO_3^- concentration in soil water as observed in *C. epigeios* has been reported to increase CO_2 emission by promoting CH_4 oxidation (Kögel-Knabner et al. 2010). Anaerobic CH_4 oxidation has been assumed to be restricted to marine environments; however, it has also been described in enriched freshwater wetlands with nitrate as an electron acceptor (Ettwig et al. 2009; Kögel-Knabner et al. 2010). The fact that CO_2 fluxes and NO_3^- concentration in soil water were related positively further confirms the idea that high NO_3^- availability stimulates decomposition of soil organic matter and litter and increase CO_2 fluxes (Table 2, Fig. 4a). On the other hand, low NO_3^- concentration in soil water as observed in *P. australis* and *C. schnimdtii* could have inhibit CH_4 oxidation leading to low CO_2 fluxes.

The fluxes of CO_2 in sites dominated by *P. australis* and *C. schnimdtii* showed a similar temporal pattern with their emission rate ranging between − 5.56 mg $CO_2/m^2/h$ to 6.11 mg $CO_2/m^2/h$ (Fig. 5a). Note that, also the soil characteristics, (i.e., bulk density, total organic carbon, and NO_3^- concentration in the soil water from these sites (*P. australis* and *C. schnimdtii*) were not statistically different. Unlike in *P. australis* and *C. schnimdtii*, the emission of CO_2 from the site dominated by *C. epigeios* varied temporally. From Fig. 5a, the emission of CO_2 in *C. epigeios* increased remarkably from 44.12 mg $CO_2/m^2/h$ on day 5 until it reached to a peak on day 15 (160.39 mg $CO_2/m^2/h$) and then reduced gradually up to 90.19 mg $CO_2/m^2/h$ on day 30. While studying soil respiration and NO_3^- immobilization response to NO_3^- application, Micks et al. (2004) found that the addition of NO_3^- would stimulate soil microbial activity early in the experiment but over time would result in a carbon limited state. Therefore, the evident decline of CO_2 emission after the first 15 days could be rationally explained by decline in organic carbon. The mean CO_2 flux from all sites in this study is much lower to what was reported by Zhaofu et al. (2005) of 620 mg $CO_2/m^2/h$ for soil-surface CO_2 emission in a *C. epigeios* wetland in Sanjiang Plain. Note that unlike our laboratory microcosms study, Zhaofu et al. (2005) conducted their study in the field with

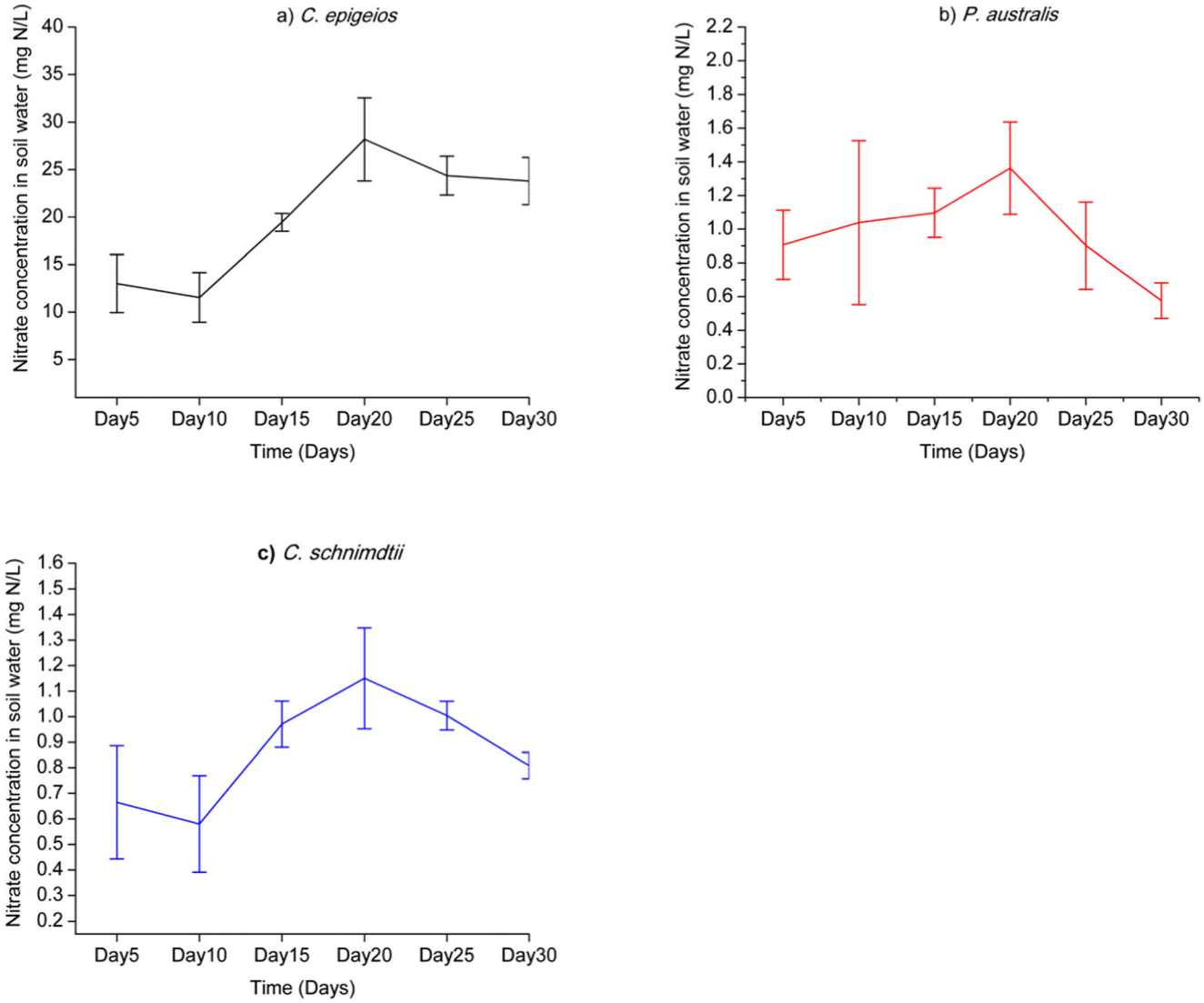

Fig. 3 Temporary variation of NO_3^- concentration in soil water in the soil columns collected from different vegetation types. **a** *C. epigeios*. **b** *P. australis*. **c** *C. schnimdtii*

Table 1 Results from repeated-measures ANOVAs with the response variables NO_3^- concentration in soil water, N_2O, CO_2, and CH_4 fluxes, respectively, the fixed factors site and time (days), and their interaction

Response variable	Factor	Df	*F* ratio	*p*
NO_3^- concentration in soil water (mg/L)	Site	2	47.16	0.000
	Time (days)	5	0.57	0.726
	Site × time	10	2.54	0.020
CO_2 (mg/m^2/h)	Site	2	3.82	0.031
	Time (days)	5	1.21	0.326
	Site × time	10	1.74	0.115
CH_4 (mg/m^2/h)	Site	2	2.45	0.101
	Time (days)	5	0.61	0.694
	Site × time	10	0.64	0.771
N_2O (mg/m^2/h)	Site	2	7.72	0.002
	Time (days)	5	3.28	0.015
	Site × time	10	4.78	0.000

Table 2 Correlation coefficients between NO_3^- concentration in soil water, CO_2, N_2O, and CH_4 fluxes; *$p < 0.05$; **$p < 0.01$

	NO_3^- (mg/L)	CO_2 (mg /m^2/h)	CH_4 (mg /m^2/h)	N_2O (mg /m^2/h)
NO_3^- (mg/L)	1	0.246*	− 0.298*	0.346*
CO_2 (mg/m^2/h)	0.146	1	0.172	0.376*
CH_4 (mg/m^2/h)			1	− 0.110
N_2O (mg/m^2/h)				1

soil temperature and soil water contents being the main parameters in their study model.

Methane (CH_4) fluxes

Over the study period, the mean CH_4 fluxes were − 2.66 mg CH_4/m^2/h in *C. epigeios*, 1.72 mg CH_4/m^2/h in *P. australis*, and 2.01 mg CH_4/m^2/h in *C. schnimdtii*. This means some sites within the wetland acted as CH_4 sink (*C. epigeios*) and others as CH_4 source (*P. australis* and *C. schnimdtii*). The fact that some sites within the wetland acted as net source or sink of CH_4 is not strange because studies in different wetlands have documented spatial variation in CH_4 emission. For instance, while assessing the spatial variation of CH_4 emission and ecosystem respiration in the Liaohe Delta wetlands, Northeast China, Olsson et al. (2015) observed that sites covered by *Suaeda salsa* acted as CH_4 sink whereas those covered by *P. australis* (common reed) and rice paddy were net CH_4 source. Analysis of variance reveals that CH_4 fluxes were not significantly different among sites and over time (Table 1). However, sites *P. australis* and *C. schnimdtii* had relatively higher CH_4 fluxes than *C. epigeios.* This should have been otherwise, i.e., ideally relatively higher CH_4 should have been observed in *C. epigeios* than in *P. australis* and *C. schnimdtii*,

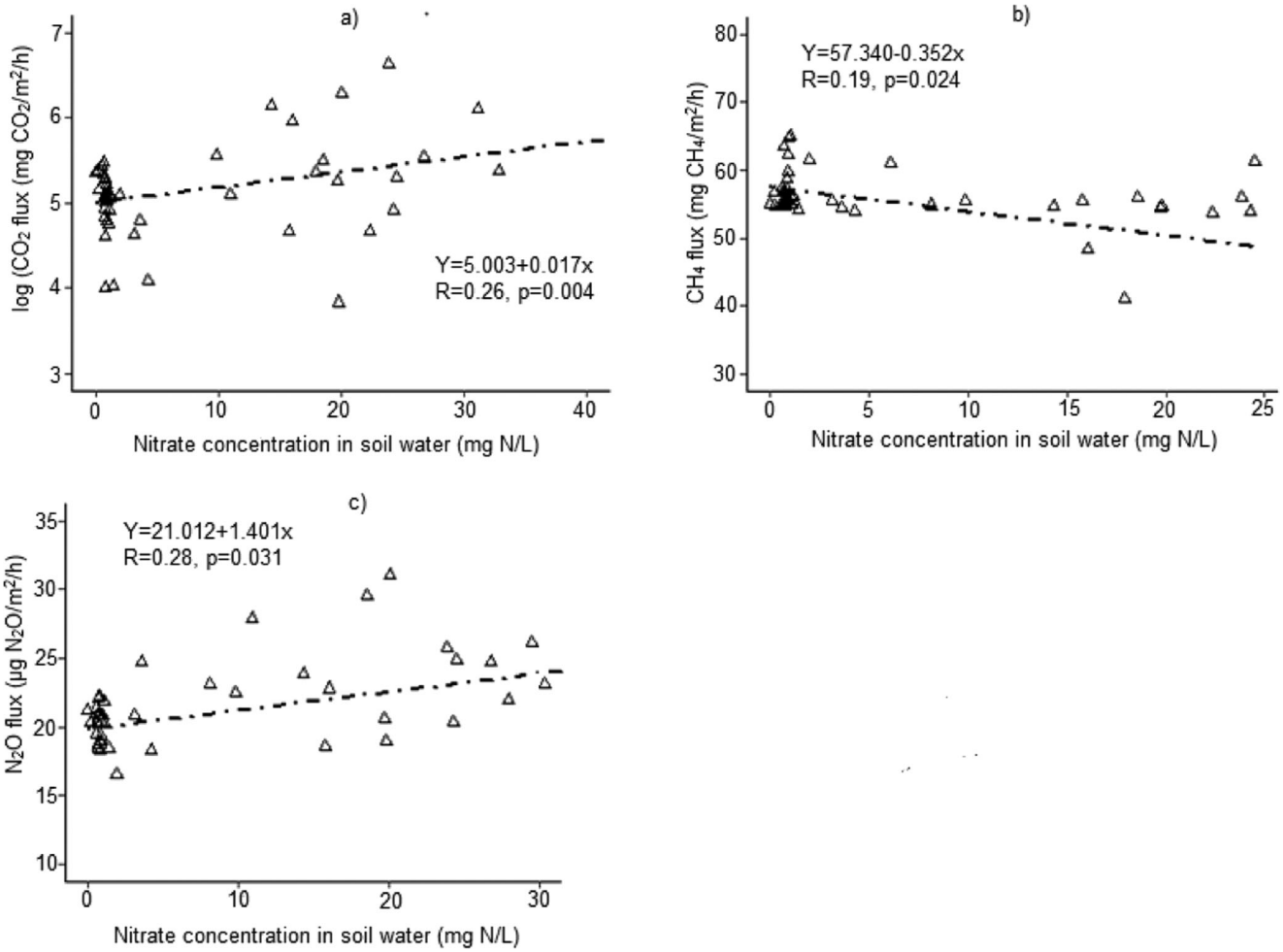

Fig. 4 Relationship between **a** CO_2 flux, **b** CH_4 flux, and **c** N_2O flux with NO_3^- concentrations of soil water

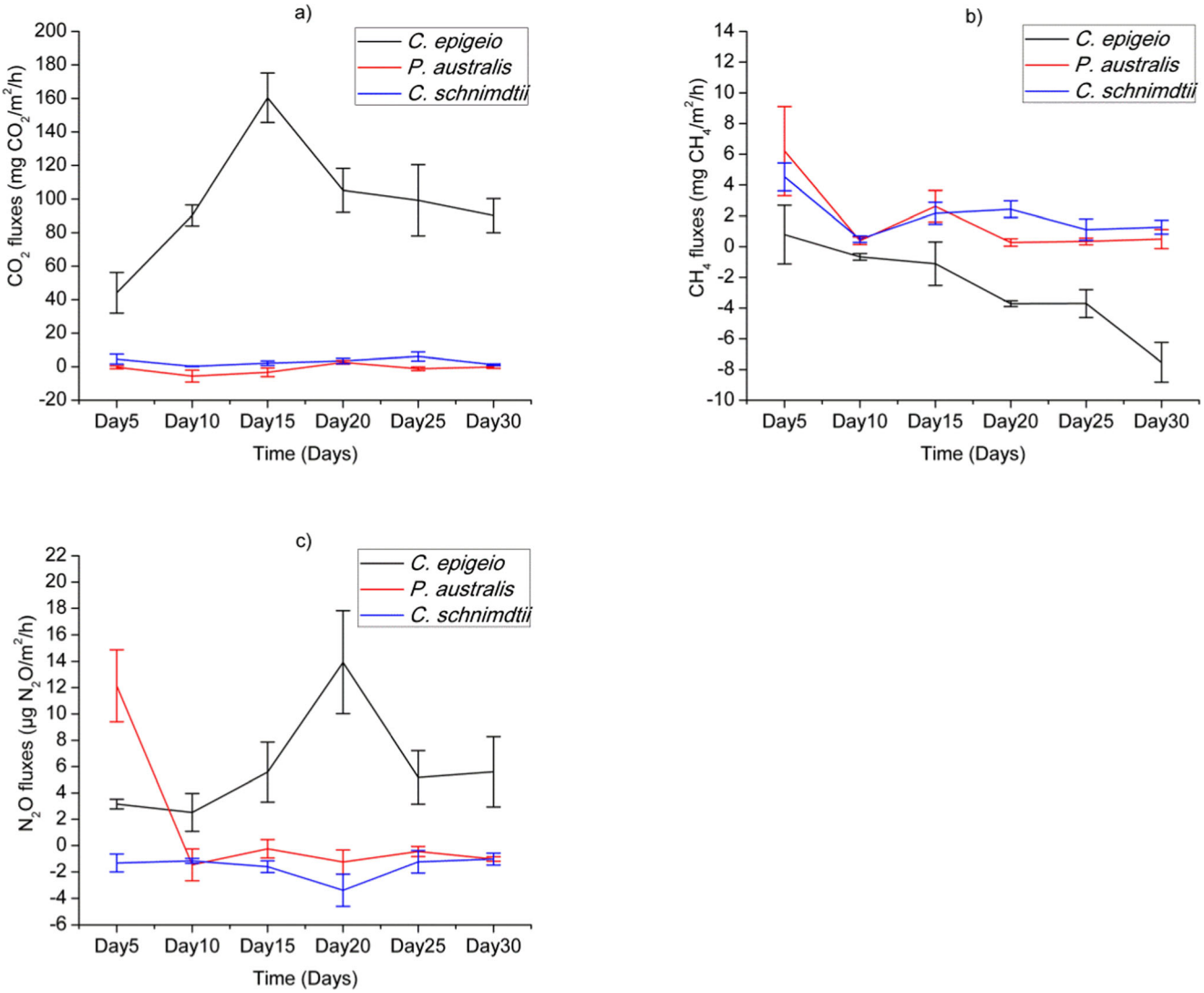

Fig. 5 Temporary variation of GHG fluxes from soil columns collected from different vegetation types. **a** CO_2 fluxes, **b** CH_4 fluxes, and **c** N_2O fluxes

as the presence of significantly higher total organic carbon could act as driver for CH_4 production (Olsson et al. 2015). This observation could be explained by the presence of high NO_3^- concentration (an electron acceptor) in the *C. epigeios* soil water, which could have potentially favors CH_4 oxidation hence the low CH_4 production. While investigating the role of NO_3^- as electron acceptor for CH_4 production (methanogenesis) and oxidation, Jugsujinda et al. (1995) noted that NO_3^- is one of the main electron acceptors for anaerobic respiration. The authors observed that addition of NO_3^- resulted in increase of inorganic carbon content, stimulation of denitrifier activities, and decrease of CH_4 production. Klüber and Conrad (1998) showed that the reduction process of NO_3^- in anoxic rice field soil significantly decreases hydrogen partial pressure hence oxidation of CH_4 and lowering its production. The fact that CH_4 flux is negatively related to NO_3^- concentration in soil water (Table 2, Fig. 5b) further supplements the idea that methanogenesis may be inhibited by electron acceptors such as NO_3^- (Mata-Alvarez et al. 2000). Generally, the mean CH_4 fluxes recorded in this present study are almost in the same range to those reported by Xu et al. (2014) of − 0.368 to 4.959 mg $CH_4/m^2/h$ in Yancheng wetland in southeast China dominated by *Phragmites Spartina alterniflora* and *Suaeda glauca*. Furthermore, the positive mean value of 2.01 mg $CH_4/m^2/h$ recorded in *P. australis* is comparable to the one reported by Olsson et al. (2015) for the wetlands in Liaohe Delta, Northeast China.

Nitrous oxide (N_2O) fluxes

Soils are regarded as source of about 70% of N_2O emitted to the atmosphere (Conrad 1996). However, little is known about

the spatial variability of N_2O production from riparian wetlands characterized by different vegetation types (Sun et al. 2013). Variability in N_2O production is not only observed between wetland ecosystems but also within wetland. In this study, variations in N_2O fluxes both among sites and over time within the same wetland were observed, and these variations were statistically significant (Table 1, Fig. 5c). The N_2O fluxes from the sites dominated by *C. epigeios*, *P. australis*, and *C. schnimdtii* ranged between 0.76 to 13.93 μg $N_2O/m^2/h$, − 1.25 to 12.14 μg $N_2O/m^2/h$, and − 3.40 to − 0.35 μg $N_2O/m^2/h$, respectively. The mean N_2O fluxes over the study period were 5.99 μg $N_2O/m^2/h$ for *C. epigeios*, 1.28 μg $N_2O/m^2/h$ for *P. australis* and − 1.03 μg $N_2O/m^2/h$ for *C. schnimdtii*, indicating that different sites within the wetland act as a source or sink of N_2O. The mean N_2O fluxes from sites dominated by *C. epigeios* were significantly higher than *P. australis* and *C. schnimdtii.* The differences may be due to variations in soil characteristics such as total organic carbon and NO_3^- concentration in soil water. In this study, the soil from sites dominated by *C. epigeios* had a higher amount of organic carbon compared with the other sites. Studies have shown that organic carbon can affect the ability of soil to produce N_2O (Giles et al. 2012). While assessing spatial variability of N_2O emissions and their soil-related driving factors in an agricultural field, Yanai et al. (2003) reported that organic matter-related factors could explain about 20% of the variance of N_2O fluxes. In three experimental boreal forest reservoirs, Hendzel et al. (2005) observed that soils from sites with high organic carbon acted as net sources of N_2O emissions, while low organic carbon sites were N_2O sinks. This is in agreement with the findings of this current study. A positive correlation between N_2O fluxes with NO_3^- concentration in the soil water was observed in this study (Table 2, Fig. 4c). This could imply that the higher NO_3^- concentration of soil water observed in *C. epigeio* hinders the final reduction of N_2O reduction to nitrogen gas during denitrification (Audet et al. 2014; Butterbach-Bahl et al. 2013). In a much more detailed study at chronically nitrate-loaded riparian buffer zones, Hefting et al. (2003) found that NO_3^- loading results in enhancement of N_2O flux to the atmosphere. Similar observations were reported by Muñoz-Hincapié et al. (2002) in red mangrove sediment on the southwest coast of Puerto Rico in the northeastern Caribbean Sea. Other researchers found a similar relationship between N_2O emissions and NO_3^- concentration in the soil water (Weier et al. 1993; Yan et al. 2000). It is tempting to conclude that higher NO_3^- concentration in wetland soil as a result of human activities could increase the N_2O fluxes from the soil. This, therefore, stresses the importance of controls of NO_3^- leaching in the mitigation of anthropogenic N_2O emissions.

The mean N_2O fluxes from all sites in this study are much lower to what was reported in other freshwater marshes. Yang et al. (2013) reported a mean N_2O flux of 12.84 μg $N_2O/m^2/h$ for the freshwater marsh of Northeast China which is relatively higher than the findings of this study. Note, however, that Yang et al. (2013) performed their study in the natural marsh and microcosms of three manipulated water table treatments. Interestingly, the negative range of N_2O fluxes in *P. australis* and *C. schnimdtii* are comparable to what was reported by Zhang et al. (2005) from Sanjiang Plain wetland in sites dominated by *Deyeuxia angustifolia* (− 0.011 to − 0.061 μg $N_2O/m^2/h$) and *Carex lasiocarpa* (− 0.009 to − 0.019 μg $N_2O/m^2/h$). In their study, Yang et al. (2012) noted that when the soil/sediment is in intensive reduced state, microorganisms could assimilate N_2O from air to soil/sediment hence negative N_2O fluxes were measured. Moreover, when NO_3^- concentration in soil water is as low as those observed in *P. australis* and *C. schnimdtii* (Fig. 3b, c) and denitrification rates are high, N_2O is more likely reduced, hence the low fluxes can be observed (Groffman et al. 2000). Other studies have also confirmed the ability of soils to act as N_2O sinks (Syakila et al. 2010) and are based on the consumption of N_2O during denitrification or during nitrification, especially under low NO_3^- concentration (Schlesinger 2013; Wu et al. 2013).

Temporally, the N_2O fluxes in the site dominated by *C. epigeios* increased remarkably from 3.15 μg $N_2O/m^2/h$ on day 5 to 13.92 μg $N_2O/m^2/h$ on day 20, then reduced and remained almost constant at 5.19 μg m^{-2} h^{-1} on day 25 and day 30 (Fig. 5c). This could be attributed to reduction of substrate (i.e., organic carbon). In *P. australis*, the N_2O fluxes reduced dramatically from 12.14 μg $N_2O/m^2/h$ on day 5 to − 1.46 μg $N_2O/m^2/h$ on day 10, then oscillated between − 0.24 μg $N_2O/m^2/h$ and − 1.02 μg $N_2O/m^2/h$ for the other days. Unlike *C. epigeios* and *P. australis*, the N_2O fluxes in *C. schnimdtii* was − 1.32 μg $N_2O/m^2/h$ on day 5 and gradually it became more negative until day 20 (− 3.40 μg $N_2O/m^2/h$). From day 10 to day 30, the N_2O fluxes for both *P. australis* and *C. schnimdtii* were below zero and showed almost a similar pattern ranging between − 3.40 and − 0.24 μg $N_2O/m^2/h$ (Fig. 5c). This further indicates that the soil characteristics of these two sites (*P. australis* and *C. schnimdtii*) were also similar.

Global warming potential (GWP)

From Table 3, the estimated GWP was positive which means that all the sites had negative climatic impact. The GWP of *C. schnimdtii* was the highest in the QRWNNR wetland followed by *P. australis* and then *C. epigeios* (Table 3). Among the GHGs fluxes, CO_2 was the most dominant gas in determining the GWP in QRWNNR wetland. This observation is in agreement with the findings of Xu et al. (2014) from wetlands in the southeast China. Similarly, while examining how net exchange of GHGs from China's ecosystems

Table 3 Global warming potential (GWP) of greenhouse gas fluxes in intact soil samples collected from sites dominated by different vegetation types in QRWNNR wetland

Sites	CO_2-equivalent flux (kg CO_2/ha/y)			
	CO_2	CH_4	N_2O	GWP
C. epigeios	8605.43	− 5820.51	156.46	2941.38
P. australis	− 109.50	3773.10	33.53	3697.13
C. schnimdtii	259.78	4401.90	− 26.89	4634.79

determines GWP, Tian et al. (2011) found that CO_2 was the most dominant gas in determining the GWP from natural wetland and paddy land. Note, however, that the CO_2-equivalent flux of the current study are much lower compared with that of Xu et al. (2014) and Tian et al. (2011) likely because the current study was conducted using intact soil columns continuously loaded with nitrate solution in a laboratory while, Xu et al. (2014) and Tian et al. (2011) conducted their study in the field. Our study suggested that if we omit the most dominant gas CO_2 in estimating the GWP, the fluxes of CH_4 from *C. schnimdtii* and *P. australis* would be remarkable higher than that from *C. epigeios*, and the fluxes of N_2O from *C. epigeios* would have higher proportion of the GWPs. This study reveals that, although the CO_2 fluxes were quite high in *C. epigeios*, when the total CO_2-equivalent fluxes are considered, the site dominated by *C. schnimdtii* was discovered to emit more CO_2-equivalent than *P. australis* or *C. schnimdtii.* It is important to note that this is laboratory microcosm experiment which does not include plants and therefore, it is hard to assess the net effect of the whole site on wetland due to unknown net ecosystem production of the sites.

Conclusions

Over the study period, our study confirmed that soil collected from the site dominated by *C. epigeios* was net CO_2 and N_2O sources, whereas the soil from *P. australis* and *C. schnimdtii* were net sinks of CO_2 and N_2O, respectively. The soil from the site dominated by *C. schnimdtii* had the highest climate impact, as it had the highest GWP compared with the other sites. Our study indicates that total organic carbon and NO_3^- concentration in soil water has great influence on GHG emission. CO_2 and N_2O emission are accelerated by the availability of higher NO_3^- concentration in soil water. On the other hand, higher NO_3^- concentration in soil water favor CH_4 oxidation hence the low CH_4 production. Temporally, CO_2 emission was relatively higher in the first 15 days and decreased gradually likely due to decline in organic carbon. The finding of this study implies that higher NO_3^- concentration in wetland soil as a result of human activities could increase N_2O and CO_2 emissions from the soil. This, therefore stresses the importance of controls of NO_3^- leaching in the mitigation of anthropogenic N_2O and CO_2 emissions.

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