



A soil carbon proxy to predict CH₄ and N₂O emissions from rewetted agricultural peatlands



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ABSTRACT

The temporal and spatial variations in greenhouse gas (GHG) emission estimates in wetlands impede our ability to predict and upscale total emissions; thus, a scalar parameter is needed to predict GHG emissions. We investigated the importance of soil organic carbon (SOC) in the prediction of methane (CH₄) and nitrous oxide (N₂O) emissions in rewetted agricultural peatlands, positing that both CH₄ and N₂O production are explained by the quantity and turnover of SOC. Field CH₄ and N₂O fluxes, along with other edaphic and environmental variables, were monitored in rewetted peatlands with a range of SOC (6%, 11%, and 23%) that were recently converted from row crops to flooded rice cultivation to reverse soil subsidence. Nitrogen (N) fertilization reduced annual CH₄ emission by 77.2% in the 6% C field, but this effect was not found in other fields. Annual N₂O emissions were not affected by N fertilization and averaged 8.9, 5.2, and 1.9 kg N₂O-N ha⁻¹ for the 6%, 11%, and 23% C fields, respectively. SOC was the dominant factor controlling both CH₄ and N₂O emissions. The annual emission for both CH₄ and N₂O was accurately described by a decaying power regression with increasing SOC contents ($R^2 > 0.49$). This relationship was also observed after splitting total annual emission of CH₄ and N₂O into growing and fallow seasons. Nitrogen fertilization and the seasonality in CH₄ and N₂O emissions did not change the relationships. The inverse correlation between SOC and CH₄ and N₂O emissions was likely caused by different chemical composition of SOC in various soils. Our results suggest that SOC can be a potential proxy to predict CH₄ and N₂O emissions in rewetted peatlands to better define GHG predictions of wetland restoration efforts.

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1. Introduction

Peatlands are estimated to contain 513 Pg soil carbon (C) or 22% of global soil C to 3 m depth (Maltby and Immirzi, 1993; Jobbágy and Jackson, 2000). Disturbance, mainly from drainage and cultivation of these organic soils has reversed C storage and resulted in extensive emissions of greenhouse gas (GHG), primarily as CO₂ and nitrous oxide (N₂O), together accounting for more than 2 Gt CO₂-eq yr⁻¹ (Maljanen et al., 2010; Couwenberg, 2011; Joosten, 2011). Rewetting (i.e., flooding) these degraded peatlands is considered an important action to mitigate climate change by

the United Nations Framework Convention on Climate Change (UNFCCC) and Inter-Governmental Panel for Climate Change (IPCC) (IPCC, 2014). Despite the growing interest in peatland restoration for its sustainable use and C sequestration, there are few comprehensive studies that reveal the long-term effects restoration activities have on C balance and emission of other GHGs, e.g., methane (CH₄) and N₂O (Schrier-Uijl et al., 2014; Knox et al., 2015). The main limitation to these efforts is both the lack and difficulty in obtaining integrated and continuous GHG measurements to estimate climate warming mitigation potential of restoration approaches.

Greenhouse gas emissions are estimated using various methods dependent on point measurements followed by up-scaling to establish inventories (Montzka et al., 2011; Bridgman et al., 2013). Common measurements of CH₄ and N₂O fluxes by means of the close-chamber techniques can be highly variable across space and

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time (Kasimir-Klemedtsson et al., 1997; Couwenberg et al., 2010; Maljanen et al., 2010), impeding accurate emission scaling to regional scales (Bridgham et al., 2013). Therefore, identifying parameters to effectively extrapolate emissions would greatly benefit regional up-scaling.

Proxies to estimate CH₄ effluxes from natural peatlands have been proposed, but are lacking for N₂O emissions (Klemedtsson et al., 2005; Maljanen et al., 2010; Couwenberg and Fritz, 2012). For example, Couwenberg and Fritz (2012) demonstrated that mean water Table height and leaf area cover of aerenchymous shunts are robust proxies to estimate CH₄ fluxes from natural peatlands. Similarly for N₂O, Klemedtsson et al. (2005) suggested that soil C to N ratio can predict N₂O emissions from drained forested histosols. However, the robustness of these proxies across various peatlands types (i.e., natural, drained, and restored drained) often lose their explanatory powers, especially for restored areas (Berglund and Berglund, 2011; Bridgham et al., 2013; Turetsky et al., 2014).

Methane and N₂O are produced by different microbial processes, but both are often directly or indirectly influenced by soil organic carbon (SOC) content and mineralization (Senbayram et al., 2012; Bridgham et al., 2013). The turnover of SOC can create reduced conditions favorable for CH₄ production and denitrification (Reddy and DeLaune, 2004; Saggar et al., 2013). Addition of C, such as rice residues, has been found to increase CH₄ emissions (Bossio et al., 1999; Ye et al., 2015) and denitrification-derived N₂O emissions (Senbayram et al., 2012), demonstrating a positive relationship to C availability. Other studies have demonstrated that CH₄ emissions in some peat soils are mostly plant-derived, with limited contributions from recalcitrant SOC (Couwenberg, 2009; Bridgham et al., 2013). Similarly, organic amendments with higher labile C contents can result in increased N₂O emissions (Senbayram et al., 2012). These studies suggest that the quality of inputs and SOC likely affect the production of CO₂ and CH₄ (Hodgkins et al., 2014; Medvedeff et al., 2015). In drained peat soils, cultivation degrades SOC resulting in mineralized N that can lead to N₂O production (Silvan et al., 2002; Holden et al., 2004). Under rewetting, the mineralization of SOC can cause reduced conditions and provides substrates for CH₄ production (Hribljan et al., 2014). Therefore, the extent of CH₄ and N₂O emissions are likely highly influenced by SOC stocks and its mineralization. The importance of SOC to predict CH₄ and N₂O emissions in rewetted peatlands has yet to be firmly established (Maljanen et al., 2010; Bridgham et al., 2013; Turetsky et al., 2014).

The Sacramento-San Joaquin Delta (hereafter the Delta) was once a 1400 km² tidal marsh influenced by runoff from the Sierra Nevada Mountains. The area was drained for agriculture in the mid-1800s resulting in extensive soil C loss and subsidence and large continuous CO₂ and N₂O emissions (Drexler et al., 2009; Deverel and Leighton, 2010). The loss of soil C and emissions of GHG has been extremely variable across the Delta (Miller et al., 2008; Deverel and Leighton, 2010; Knox et al., 2015). Restoration of these degraded agriculture systems by rewetting has been increasingly recognized as a regional solution to reduce or reverse soil subsidence and mitigate GHGs emissions. The objectives of the present study were to investigate (1) how SOC affects CH₄ and N₂O emissions, and (2) whether SOC can be used as a proxy to predict both CH₄ and N₂O emissions in rewetted agricultural peatlands.

2. Materials and methods

2.1. Site description

Field studies were conducted from 2013 to 2014 on Twitchell Island (38.1053 N, 121.6542 W) in the Delta. Mean annual precipitation for this region is 380 mm and over 80% occurs from November to March. Yearly average maximum and minimum

temperatures were 22 °C and 9 °C. The soils are classified as poorly drained histosols with organic C contents ranging from less than 5 to greater than 25% depending on the degree of oxidation. Rice (*Oryza sativa* L.) has been grown on the site since 2009 to test its potential as a regional solution to reduce soil subsidence (Kirk et al., 2015), mitigate GHG emissions, and improve Delta water quality.

2.2. Experimental design and field setup

The experiment was embedded in an established N rate trial to evaluate rice yield response across a gradient of SOC (Espe et al., 2015). Three sites with contrasting SOC (6, 11, and 23%) were selected for this study. The distance between each site is less than 1.25 km and mapped as the same soil series. The SOC gradients chosen cover the SOC range across the Delta (Deverel and Leighton, 2010). A total of five N rates ranging from 0 to 160 kg N ha⁻¹ were evaluated as a randomized complete block design with four replicates in each site. Only two rates (0 and 80 kg N ha⁻¹) were chosen for this study. The 80 kg N ha⁻¹ was chosen as it the recommended N rate for rice production in the Delta (Espe et al., 2015). All sites were managed similarly. Each experimental plot was 4 × 5 m². Rice variety 'M-206' was planted in early-April 2013 in all fields, except for the 23% C field, where 'M-104' was planted by accident by the cooperating grower. Both varieties are medium grain having similar yield potential (data available online at <http://www.carrb.com/Variety/M-206.htm>) and N requirements (Mutters et al., 2013). Fields were flooded around May 15 and drained on August 10 to prepare for harvest in mid-September. After harvest the rice residue was left on the soil surface. The field sites were flooded on October 15 with the fallow flooded period ending on February 20 in 2014.

2.3. CH₄ and N₂ emissions

CH₄ and N₂O fluxes were monitored weekly during the growing season and every other day following paddy drainage for harvest and biweekly during the winter. Emissions were measured with closed vented chambers from 10:00 am to 3:00 pm (Parkin et al., 2003). The chamber extensions had an inner diameter of 25 cm and a height of 9, 69, and 99 cm, depending on the height of the rice plants. A PVC ring (25 cm in diameter and 15 cm in depth) was driven into soils one week prior to seasonal measurements and protruded 2–3 cm above the soil surface. The rings were removed at harvest then reinstalled. Before measurements, chamber extensions were placed on rings and sealed with a wide rubber band made from a cross cut section of a tire inner tube that overlapped the chamber and ring by 5 cm. A fan was used to mix the chamber headspace for 10 or 60 s (depending on chamber height) to avoid gas gradients (Parkin et al., 2003), followed by extracting 20 mL of air from the chamber every 10 min during a 30 min period for a total of 4 samples including time 0. Air samples were transferred completely to 12 mL pre-vacuumed vial and subsequently analyzed for CH₄, CO₂, and N₂O on a GC-2014 gas chromatograph (Shimadzu, Columbia, Maryland). CH₄, CO₂, and N₂O emission rates were calculated with a linear regression model using concentration against time and expressed as mg production m⁻² h⁻¹ after adjusting for soil temperature and chamber volume (Pittelkow et al., 2013). If the determinant coefficient (*R*²) for CH₄ was <0.9, emissions were set to zero, which represented 12% of the total data points. Zero emissions were mostly observed prior to paddy flooding or during the drainage events when water levels were below the soil surface, during which low or no CH₄ emission is expected (Reddy and DeLaune, 2004; Turetsky et al., 2014). Changing criteria from *R*² < 0.9 to < 0.8 or < 0.7 did not change the fraction of zero emissions (data not shown). Likewise, N₂O

emissions were set to 0 when R^2 of the linear regression was <0.9 . For N_2O , zero emissions were observed when NH_4^+ concentration was minimal (ranging from 0.07 to 0.52 $mg\ L^{-1}$, with a median of 0.27 $mg\ L^{-1}$, Supplementary Fig. 7) and no NO_3^- was detected. We assumed that N_2O emission was minimal when these substrates for nitrification and denitrification were both limited (Reddy and DeLaune, 2004; Baggs, 2011). Similarly, changes in the criteria from $R^2 < 0.9$ to <0.8 or <0.7 did not change the total flux estimate (data not shown). For CO_2 emissions, data points were discarded when R^2 of the linear regression was <0.9 , assuming that CO_2 production would never be 0 in these soils.

Total integrated flux was calculated assuming the rate changed linearly during two subsequent sampling events,

$$\text{Flux} = \Sigma \left\{ \frac{1}{2} (Y_{i+1} + Y_i) \times (X_{i+1} - X_i) \right\}$$

where Y_i and Y_{i+1} are the emission rates on sampling event X_i and X_{i+1} , while $(X_{i+1} - X_i)$ is the time interval between events. The calculated fluxes were further adjusted by soil bulk density at 0–15 cm depth (see below) and expressed as $mg\ C$ or Ng^{-1} soil C.

2.4. Soil organic carbon

Soil cores were collected nearby each chamber ring at a depth of 0–15 cm in mid-June. In the laboratory, soil samples were dried and ball milled after the removal of plant residues. The SOC content was analyzed at the Analytical Laboratory of the University of California Davis with a combustion method (AOAC, 1997) coupled with an acid fumigation procedure to remove carbonates (Harris et al., 2001).

2.5. Interstitial water sampling and other field measurements

Porewater was collected with a custom sampler for the determination of NH_4^+ , NO_3^- , Fe^{2+} and Fe^{3+} , dissolved organic C (DOC) and inorganic C (DIC), and dissolved CH_4 and N_2O . The sampler was a 15 cm long and 5 mm in diameter polyethylene tube perforated with a row of small holes (2 mm in diameter) equally spaced every 1 cm, covered with a nylon mesh (30 μm) (Genesee Scientific Corp., San Diego, CA) to exclude large plant or soil particles, connected to a 2-way valve via Tygon tubing, and a 5 μm syringe filter attached to the end of the tubing. The sampler was inserted vertically into the soil (0–15 cm) inside the chamber ring

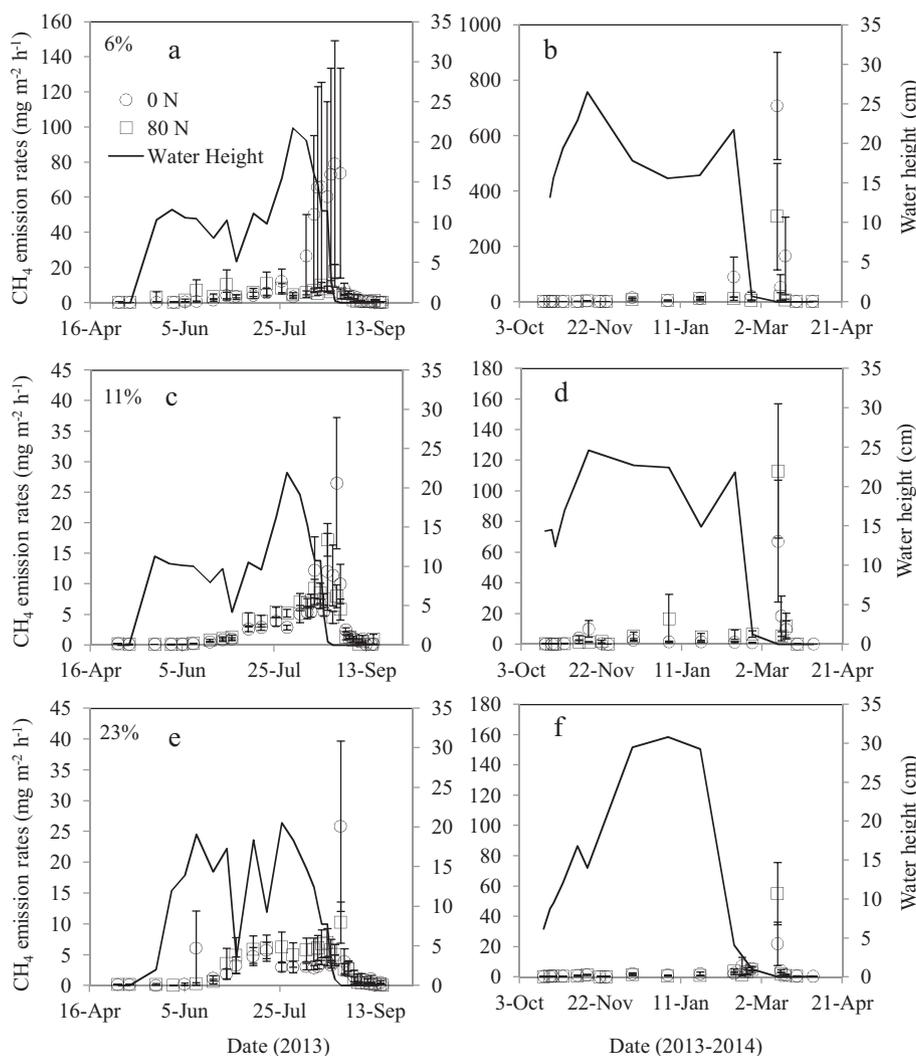


Fig 1. The CH_4 emission rates and water height over the soil surface in rewetted peatlands with contrasting SOC in the growing (a, c and e) and fallow season (b, d and f). The bars represent ± 1 standard error ($n=4$), while the “0N” and “80N” in the legend is the fertilization rate at 0 and 80 $kg\ N\ ha^{-1}$, respectively. The “6%”, “11%”, and “23%” in the legend represent the SOC content.

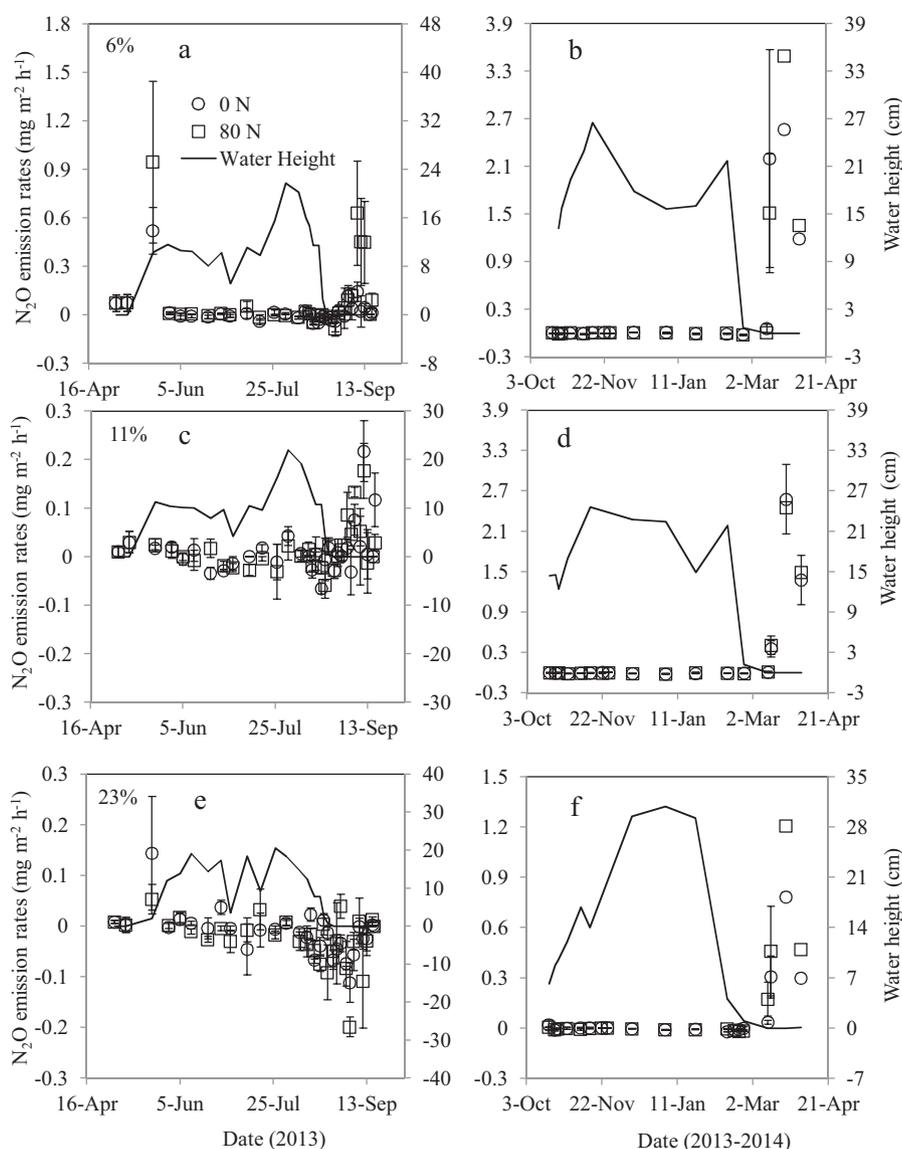


Fig. 2. The N_2O emission rates and water height over the soil surface in rewetted peatlands with contrasting SOC in the growing (a, c and e) and fallow season (b, d and f). The bars represent ± 1 standard error ($n=4$), while the “0N” and “80N” in the legend is the fertilization rate at 0 and 80 kg N ha $^{-1}$, respectively. The “6%”, “11%”, and “23%” in the legend represent the SOC content.

after it was installed and remained there during the seasonal sampling periods. Pore water was collected after attaching a pre-

Table 1

Selected measured variables by stepwise procedure that are potentially important in predicting production rates of CH_4 and N_2O in a re-flooded peatland in the Sacramento-San Joaquin Delta, CA, USA.

Step	Variables	F value	P value	R ²
Log (CH_4 rate)				
1	Log (porewater CH_4)	257	<0.01	0.300
2	Log (CO_2 rate)	122	<0.01	0.455
3	Log (dissolve inorganic C)	13	<0.01	0.470
4	Log (dissolve organic C)	17	0.04	0.479
N_2O				
1	Porewater N_2O	667	<0.01	0.640
2	Log (dissolve inorganic C)	13	<0.01	0.646
1	Log (dissolve organic C)	23	<0.01	0.654
2	Log (total Fe)	11	=0.01	0.662

evacuated 12 mL extainer onto the syringe filter using a syringe needle. The initial porewater sample was discarded, representing >100% of the sampler/tubing volume. A second sample was collected and transported on ice to the laboratory, and stored at 4 °C until analyzed.

Soil temperature during sampling was measured inside the chamber ring with a T type thermocouple at 5 cm depth. Redox potential was determined using an Orion combination ORP probe (Thermo Scientific Orion, USA) at 10 cm below soil surface adjacent to the chamber before each sampling campaign started.

Soil bulk density (0–15 cm) was measured once in the middle of the growing and fallow season. A polyethylene pipe (15 cm in length, 10 cm in diameter) was gently pushed into submerged soils attempting to minimize compaction, it was then capped on the top and bottom (after excavating soil from the side of the tube) and removed. Soils were dried at 100 °C until no further weight change was observed and bulk density was calculated from the dried soil weight and the volume of the pipe. The bulk density was used to

Table 2
Averaged annual and seasonal CH₄ and N₂O emissions in restored peatlands with contrasting SOC contents (means ± standard error, *n* = 4) in the Sacramento-San Joaquin Delta, CA, USA. The control was unfertilized with N and the fertilized plots had 80 kg N ha⁻¹ applied.

	Season	6%		11%		23%	
		Control	Fertilized	Control	Fertilized	Control	Fertilized
CH ₄ (kg CH ₄ -C ha ⁻¹)	Growing	264 ± 163	108 ± 33	66 ± 9	69 ± 10	55 ± 20	70 ± 28
	Fallow	1662 ± 379	332 ± 72	192 ± 54	347 ± 82	85 ± 28	137 ± 34
	Whole	1927 ± 360	439 ± 56	259 ± 52	416 ± 82	140 ± 48	206 ± 54
N ₂ O (kg N ₂ O-N ha ⁻¹)	Growing	1.0 ± 0.2	2.4 ± 0.7	0.2 ± 0.1	0.2 ± 0.1	0.0 ± 0.2	-0.2 ± 0.1
	Fallow	6.8 ± 1.8	7.6 ± 1.8	5.0 ± 1.0	5.0 ± 0.2	1.6 ± 0.6	2.4 ± 0.8
	Whole	7.8 ± 2.1	10.0 ± 1.8	5.2 ± 1.0	5.2 ± 0.3	1.6 ± 0.8	2.2 ± 0.8

adjust total CH₄ and N₂O emissions in the fallow and growing season, while averaged soil bulk density across seasons was used to adjust total annual emissions.

2.6. Porewater chemistry

For dissolved inorganic carbon (DIC) analysis, 0.35 mL of 6 N HCl was added to an empty 12 mL extainer and evacuated, followed by an injection of 4 mL of the porewater and 8 mL helium. The mixture was shaken vigorously and the headspace gas was analyzed for CO₂ concentration using a gas chromatograph (GC-2014, Shimadzu). Porewater CH₄ was determined according to the method described by Bossio et al. (1999). In brief, after the removal of 4 mL porewater for DIC analysis, the headspace of the extainer with the remaining porewater was replenished with helium and shaken vigorously with a vortex mixer for 1 min, followed by the extraction of the headspace gas for CH₄ and N₂O analysis.

Porewater Fe²⁺ was determined with a modified ferrozine method (Gibbs, 1976; Lovley and Phillips, 1987). Approximately, 0.25 mL of the porewater was added to a mixture of 0.5 mL DI water and 0.25 mL of 0.25 M acetic acid (pH 4) with 4 g L⁻¹ of ferrozine, followed by measuring Fe²⁺ concentration at A₅₆₂ with a UV mini 1240 spectrophotometer (Shimadzu, Columbia, Maryland). After the measurement, 50 μL of 10% (w/v) hydroxylamine hydrochloride in 0.25 M HCl was added to the mixture and allowed to equilibrate overnight to reduce any remaining Fe³⁺. The amounts of total Fe (Fe²⁺ plus Fe³⁺) was determined by measuring A₅₆₂ of the mixture with Fe³⁺ calculated as the difference between the total Fe and Fe²⁺.

Dissolved organic C was quantified by the UV-persulfate oxidation (Teledyne-Tekmar Phoenix 8000), while porewater NH₄⁺ (Verdouw et al., 1978) and NO₃⁻ (Doane and Horwath, 2003) was determined colorimetrically.

2.7. Diffuse reflectance of infrared Fourier-transform spectroscopy (DRIFTS)

Soils from each replicate of the fertilizer rate treatment in each soil C gradient block were collected from inside the chamber ring to 15 cm, composited, and air dried at 20 ± 1 °C. Subsamples were ground prior to DRIFTS analysis after the removal of visible plant and root residues. Subsamples were further divided to remove organic matter from a subset in order to conduct spectral subtractions to obtain spectra corresponding to the OM fractions (no mineral component) (Parikh et al., 2014). To estimate the mineral component, the soil was combusted at 400 °C until no further weight change (approximately 8 hours) before DRIFTS analysis (Kaiser et al., 2008). Spectra were collected on a Thermo Nicolet 6700 FTIR Spectrometer (Thermo Scientific) with a DTGS detector and a diffuse reflectance accessory (Pike AutoDIFF, Pike

Technologies, Madison, WI) using a KBr background, 128 averaged scans, and a resolution of 4 cm⁻¹. Spectral Subtraction of the mineral absorbance from the whole soil was conducted using OMNIC 7.0 (Thermo Scientific).

2.8. Data analysis

Repeated measures ANCOVA and one-way ANCOVA were conducted with mixed-model (SAS 9.3, SAS Institute) to detect main effect of N fertilization on emission rates and total emissions of GHG, respectively. The SOC content is listed as the covariate, while N rate is the fixed-effect and the field site and nested experimental plot are treated as random-effect block and nested sub-block, respectively. The relationship between SOC and total emissions were evaluated by plotting emission data against SOC content using Microsoft Excel 2010 and further tested with Fix Y by X function of JMP pro 10 (SAS Institute) after log-transformation of the emission data. Significance level was set at α = 0.05. Stepwise regression with forward procedure (JMP pro 10, SAS Institute) was employed to compare relative importance of measured edaphic and environmental variables in predicting CH₄ and N₂O emission rates. A *p* value of 0.1 and 0.05 was used as the entry and staying values. Log-transformation was performed to scale measured variables prior to the stepwise procedure, except for porewater N₂O concentration and N₂O emission rates as zero and negative values were frequently observed.

3. Results

3.1. CH₄ and N₂ emission rates

Nitrogen fertilizer had a minimal effect (*p* = 0.067) on CH₄ emission rates (Fig. 1). The emission rates were always low at the beginning of the growing season and during most of the fallow period. Methane emissions began to increase following flooding and peaked after the onset of the drainage for harvest activities (Fig. 1a, c and e). The highest rates were observed at the end of the fallow season when water was close to the soil surface following drainage to prepare for planting of the next season crop (Fig. 1b, d and f). In general, CH₄ emissions rates for the 6% C field were higher than the 11% and 23% C fields (Fig. 1).

Nitrogen fertilization did not affect N₂O emissions across all fields when the effect of SOC was controlled (Fig. 2). The emission rates for the 6% and 11% C field were highest during the drainage events in both growing and fallow seasons (Fig. 2a–d). However, in the 23% C field, no N₂O peak was observed during the first drainage event, during which the rate was mostly negative (Fig. 2e). Negative emissions were also frequently observed in the 11% and 6% C fields (Fig. 2a and c). In all fields, the highest N₂O emissions rates were found during the second drainage prior to spring planting (Fig. 2).

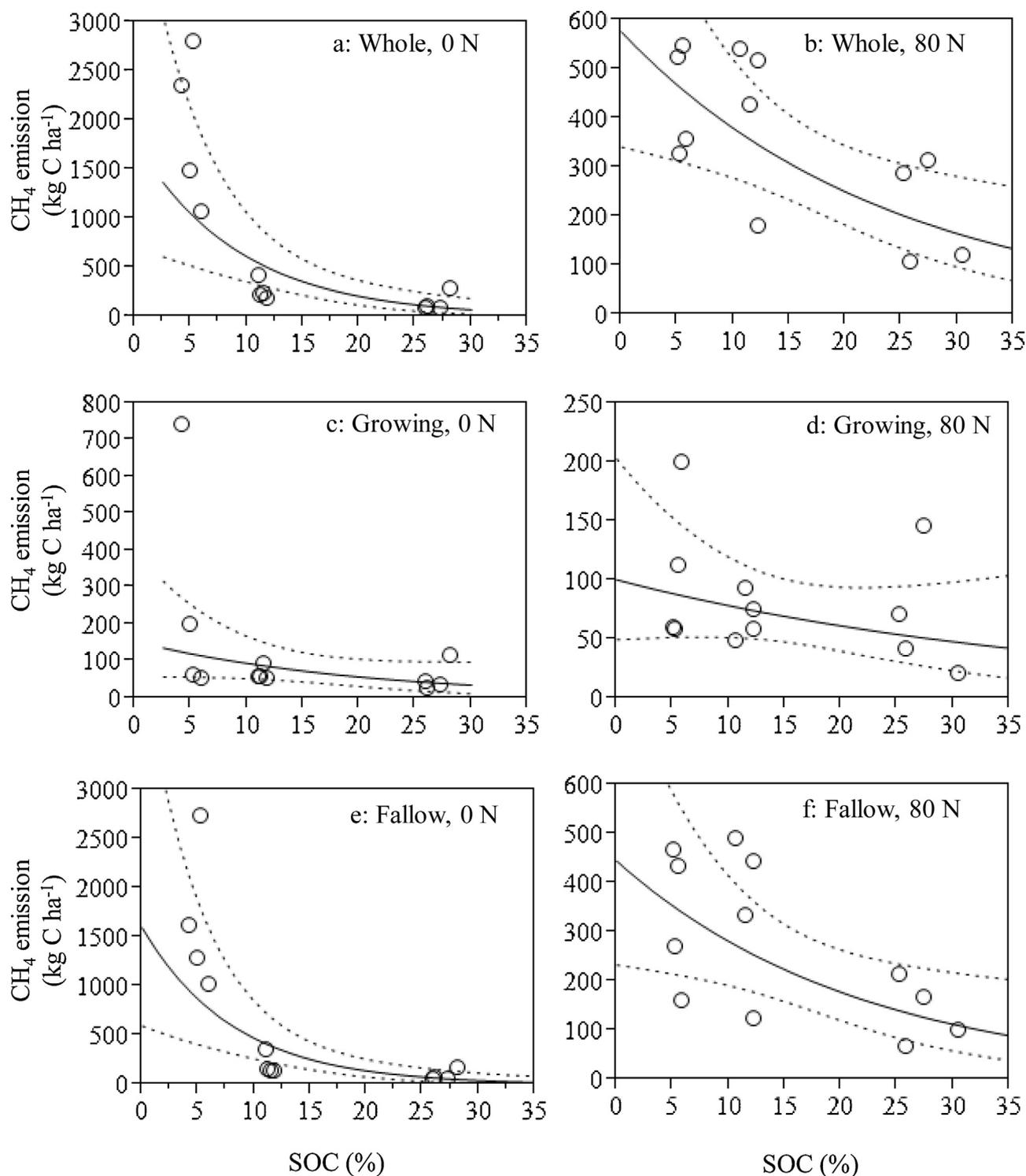


Fig. 3. Relationship between SOC and total CH_4 emissions of the whole (a and b), growing (c and d), and fallow (e and f) seasons when 0 (a, c and e) and 80 kg N ha^{-1} (b, d and f) was applied ($n = 12$). The solid line is the line of fit, while dotted lines display the 95% confidence limits for the expected mean.

Using a stepwise procedure, porewater CH_4 and CO_2 emission rates were identified as the most important measured variables that can be further used to predict CH_4 emission rates, while porewater N_2O were the most important measured variables in predicting N_2O emission rates (Table 1). Water level and soil and air temperature were not selected ($p > 0.05$) in either case. All the measured variables used were presented in the supplementary file (Supplementary Figs. 1–10).

3.2. Annual CH_4 and N_2 emissions

Mean annual CH_4 emissions varied considerably across the soil C gradient, ranging from 140 to $1927 \text{ kg CH}_4\text{-C ha}^{-1}$, with higher emissions generally observed in the fallow season (Table 2). In the 6% C field, N fertilization reduced annual CH_4 emission by 77% when compared to that of the control, but this effect was not found in other fields after controlling for the effect of SOC (Table 2).

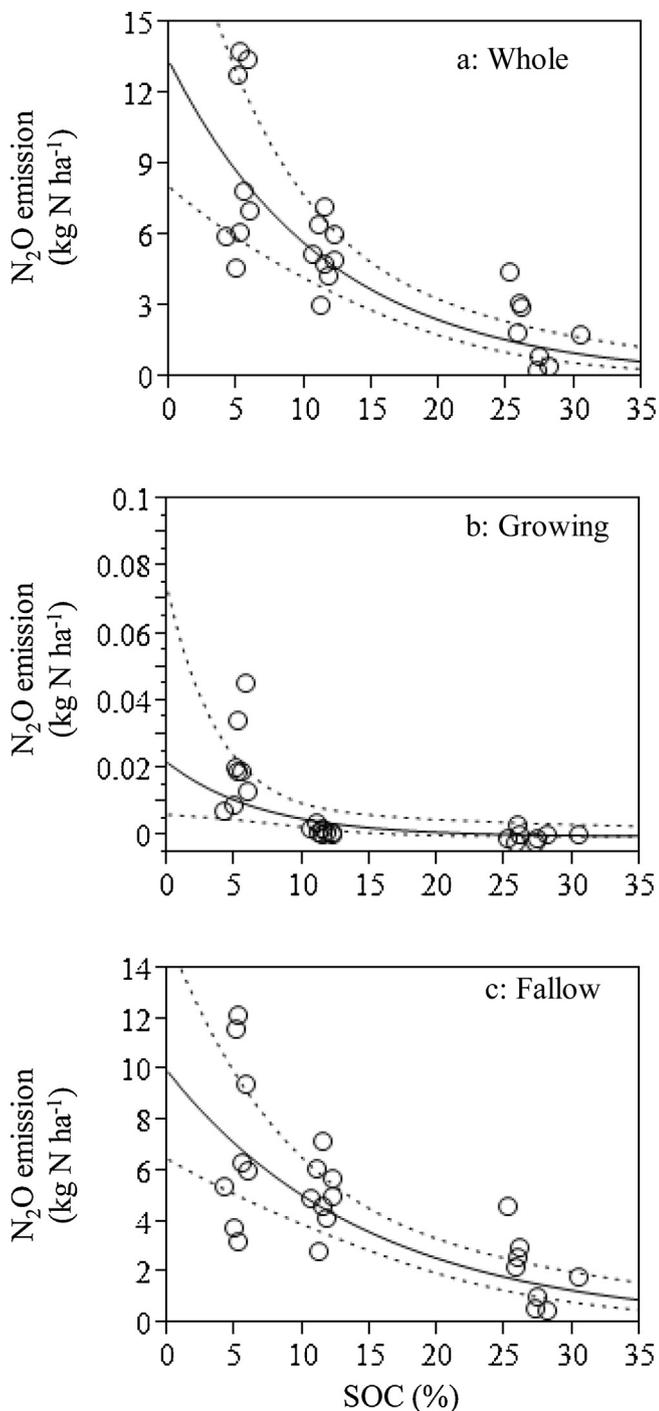


Fig. 4. Relationship between SOC and total N_2O emissions of the whole (a), growing (b), and fallow (c) seasons ($n=24$). The solid line is the line of fit, while dotted lines display the 95% confidence limits for the expected mean.

Similarly, annual N_2O emissions were always higher in the fallow season than in the growing season for all the fields, ranging from 1.6 to 10 $\text{kg N}_2\text{O-N ha}^{-1}$, but no N fertilization effect was found (Table 2). In general, annual CH_4 and N_2O emissions were highest in the 6% C field and smallest in the 23% C field.

3.3. Relationship between SOC and total CH_4 and N_2 emissions

To evaluate the relationship across growing and fallow season, total CH_4 and N_2O emissions within seasons were calculated

(Table 2). Significant N application effects on the combined seasonal total CH_4 emission occurred, so we grouped the data by N rates and used them separately to evaluate the relationship to SOC. Both annual emissions of CH_4 and N_2O were strongly correlated to SOC and can be described by a decaying power regression with increasing SOC content (Figs. 3 and 4). It appears that seasonal emissions of CH_4 and N_2O were also strongly related to the SOC, mostly described by a similar power regression (Figs. 3 and 4). These relationships were also observed when the emissions were corrected for soil C (Supplementary Figs. 1 and 2). Estimate of parameters constraining these relationships are listed in Tables 3 and 4, and Supplementary Tables 1 and 2, respectively.

3.4. DRIFT bands of the peat soils

The analysis of SOC quality across the soil C gradient was done with FTIR. The FTIR spectra were generally similar across the soil C gradient, but some distinct differences are noted for the 23% C soil (Fig. 5). FTIR peaks consistent for all soils were $3000\text{--}2800\text{ cm}^{-1}$ (asymmetric and symmetric aliphatic C—H stretching) (Piccolo et al., 1992; Senesi et al., 2007; Tatzber et al., 2007), 1450 cm^{-1} (aliphatic C—H bend) (Olk et al., 2000; Fernández-Getino et al., 2010), and 914 cm^{-1} (aromatic C—H bending) (Senesi et al., 2007; Tatzber et al., 2007; Cécillon et al., 2012). Specific differences are observed as the C content increases to 23% with decreased peak intensities at 1405 cm^{-1} (COO^- stretch) (Ellerbrock et al., 1999; Ding et al., 2002), a new peak at 1349 cm^{-1} (C—N stretch) (Pearson and Slifkin, 1972), and increased intensities between 1658 and 1600 cm^{-1} (aromatic C=C stretch, C—O asymmetric stretch, C=O stretch) (Haberhauer and Gerzabek, 1999; Senesi et al., 2007; Tatzber et al., 2007), and 1105 and 1040 cm^{-1} (polysaccharide C—O—C, C—OH stretch) (Haberhauer and Gerzabek, 1999; Olk et al., 2000).

4. Discussion

4.1. N fertilization and CH_4 and N_2 emissions

In rice, N fertilization has been observed to be stimulatory (Shang et al., 2011), neutral (Pittelkow et al., 2014), and inhibitory (Dong et al., 2011) to CH_4 emission. It is expected that N fertilization stimulates plant growth leading to organic inputs to soils, such as plant residues and root exudates, providing potential substrates for methanogens (Wu et al., 2009; Banger et al., 2012). Nitrogen application has also been shown to stimulate methanotrophic activity resulting in greater CH_4 oxidation rates and then less emissions (Banger et al., 2012). The N rate used in this study was the optimum rate for grain yield at 23% soil C content, while there was no yield response in soils with 6% and 11% SOC (Espe et al., 2015). However, CH_4 emissions in the 6% SOC soil at the 80 kg N rate were less than half that of the unfertilized control (Table 2). The decrease in CH_4 emission occurred primarily during the draining periods (Fig. 1a and b), suggesting that CH_4 oxidation could have reduced total emissions. During the first draining periods, the abundance of methanotrophs based on quantified 16S rRNA abundance were higher in the 6% C fields when N was applied (data not shown), suggesting that the observed decrease in CH_4 emission was likely due to enhanced CH_4 oxidation (Dong et al., 2011; Banger et al., 2012). Overall, decomposition of rice straw and its potential priming of SOC likely explain the higher CH_4 emission rates during the fallow season across all treatments. Our recent study demonstrated that retention of rice straw in these soils released large amounts of DOC from soil organic matter (SOM) stimulating microbial activities that resulted in priming SOM mineralization and the production of CH_4 and CO_2 (Ye et al., 2015)

Table 3Estimate parameters obtained by fitting observed natural log-transformed CH₄ emissions (kg CH₄-C ha⁻¹) by SOC (%) using JMP Fix Y by X function.

Treatment	Season	R ² _{adjust}	Effect	Estimate	Standard error	t value	p > t	95% confidence interval	
								Lower	Upper
0N	Whole	0.67	Intercept	7.49	0.41	18.24	<0.01	6.58	8.41
			SOC	-0.11	0.02	-4.49	<0.01	-0.16	-0.05
	Growing	0.27	Intercept	5.04	0.43	11.7	<0.01	4.08	6.00
			SOC	-0.05	0.03	-1.94	0.08	-0.10	0.01
	Fallow	0.69	Intercept	7.38	0.44	16.66	<0.01	6.39	8.36
			SOC	-0.12	0.03	-4.74	<0.01	-0.18	-0.06
80N	Whole	0.49	Intercept	6.36	0.23	27.15	<0.01	5.83	6.88
			SOC	-0.04	0.01	-3.10	0.01	-0.07	-0.01
	Growing	0.16	Intercept	4.61	0.32	14.62	<0.01	3.91	5.31
			SOC	-0.02	0.02	-1.36	0.20	-0.06	0.02
	Fallow	0.43	Intercept	6.10	0.29	21.04	<0.01	5.45	6.74
			SOC	-0.05	0.02	-2.76	0.02	-0.08	-0.01

Table 4Estimate parameters obtained by fitting observed natural log-transformed N₂O emissions (kg N₂O-N ha⁻¹) by SOC (%) using JMP Fix Y by X function.

Season	R ² _{adjust}	Effect	Estimate	Standard error	t value	p > t	95% confidence interval	
							Lower	Upper
Whole	0.63	Intercept	2.59	0.24	10.64	<0.01	2.08	3.09
		SOC	-0.09	0.01	-6.08	<0.01	-0.11	-0.06
Growing	0.62	Intercept	1.25	0.55	2.27	0.04	0.07	2.44
		SOC	-0.21	0.04	-4.74	<0.01	-0.30	-0.11
Fallow	0.60	Intercept	2.30	0.21	11.14	<0.01	1.87	2.72
		SOC	-0.07	0.01	-5.69	<0.01	-0.10	-0.04

Fertilizer N applications generally result in increased N₂O emissions (Shang et al., 2011; Linquist et al., 2012). Recent research has further demonstrated that N fertilizer has the greatest effects on N₂O emissions when applied at rates that exceed crop demand and the relationship is logarithmic (Pittelkow et al., 2014). Overall, N₂O production was low with highest emission rates during the fallow season in all treatments (Table 2). There was no significant effect of N fertilizer on N₂O emission compared to the control. Our results showed that the N rate of 80 kg N ha⁻¹ caused an initial increase in porewater NH₄⁺ in all fields, but the effects diminished gradually and disappeared within a month after planting (data not shown). There was no NO₃⁻ detected after a week of flooding, likely due to active plant uptake or denitrification.

4.2. SOC and CH₄ and N₂ emissions

Methane production is the terminal step of anaerobic decomposition, and its emission is a net balance of production, consumption, and transport (Couwenberg, 2011; Bridgman et al., 2013). Consequently, many factors influence CH₄ emission resulting in large variation across soils. The observed CH₄ emission rates and its temporal dynamics observed are comparable to other rice studies (Bossio et al., 1999; Xu et al., 2015). However, the stepwise procedure indicated porewater CH₄ as the most important measured variable for predicting CH₄ emission rates, followed by CO₂ emission rates, while measured environmental and edaphic factors were not selected (Table 1). Given that porewater CH₄ likely represents recent microbial activity (Bellisario et al., 1999) and CO₂ production is a proxy for decomposition (Reddy and DeLaune, 2008), the results indicate that anaerobic decomposition of SOC to CH₄ was likely the main factor regulating the size of emissions in these fields. Our recent attempts to quantify the sources for CH₄ emission in these Delta soils have shown that at least 73% of the emitted CH₄ was derived from the decomposition of old SOC

during the growing season (Morris et al., 2016), suggesting that SOC stocks can predict its emission. Indeed, regardless of N fertilization, we observed a strong relationship between mean annual CH₄ emission and SOC and it also existed after splitting the annual emissions into two seasons (Fig. 3, Table 3), which supports our original hypothesis. However, unexpectedly, all the relationships were negative (Fig. 3, Table 3). A positive relationship between SOC content and CH₄ emission has been demonstrated at SOC contents up to 6% (Yan et al., 2005), suggesting that C quantity or availability can be a main factor controlling methanogenic production in many mineral soils (Bridgman et al., 2013). Nonetheless, peat soils usually contain large amounts of high-molecular weight organic compounds that can be very resistant to microbial degradation (Collins and Kuehl, 2001; Tfaily et al., 2013), and chemical composition and structure of these organic C and the derived DOC are also important in regulating CH₄ production and emissions in peat soils (Bridgman et al., 2013; Hodgkins et al., 2014; Medvedeff et al., 2015). In the present study, FTIR analysis revealed that soils with higher SOC contain relatively higher abundance of lignin and other aromatics, lipid, and aliphatics (Fig. 5), described by higher peak intensity around 1600–1650 cm⁻¹ (aromatic C=C stretch, C—O asymmetric stretch, C=O stretch) (Haberhauer and Gerzabek, 1999; Senesi et al., 2007; Tatzber et al., 2007), which likely are not readily decomposable because of their chemical recalcitrance under anoxic conditions and can also be highly inhibitory to soil microorganisms (Minderlein and Blodau, 2010; Freeman et al., 2012; Bridgman et al., 2013). This likely explained the relatively higher polysaccharide abundance (i.e., less microbial decomposition activity) in higher SOC soils, represented by higher peak intensity around 1105 and 1040 cm⁻¹ (polysaccharide C—O—C, C—OH stretch) (Haberhauer and Gerzabek, 1999; Oik et al., 2000). It is therefore plausible that the negative relationship between CH₄ emission and SOC was partly attributable to the difference in peat chemistry across the fields resulting in

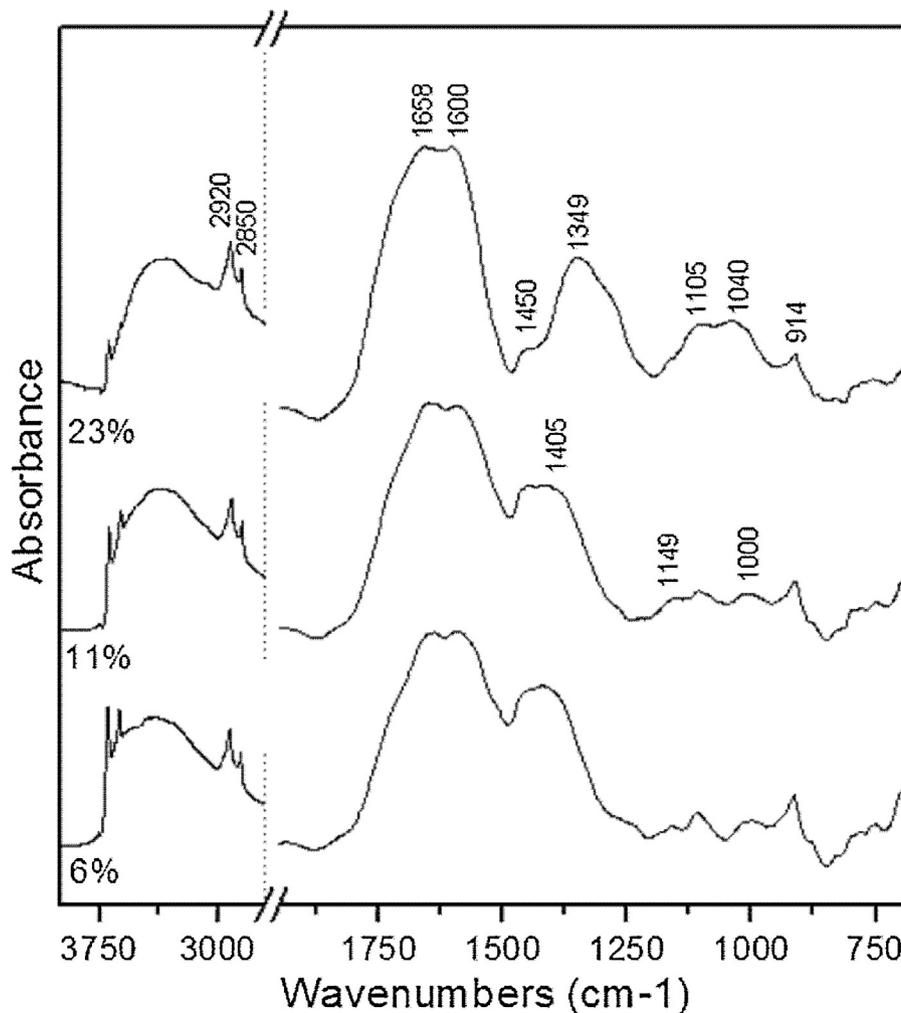


Fig. 5. Average peat DRIFT absorption spectra ($n=4$). The “6%”, “11%”, and “23%” in the legend represent the SOC content.

distinctive decomposition potentials to provide methanogenic substrates, which however requires further investigation to substantiate.

Mean annual and seasonal N_2O emissions were also strongly related to SOC described by a similar regression (Fig. 4, Table 4). Nitrification and denitrification are the main soil sources for N_2O (Baggs, 2011). Nitrification is generally regulated by NH_4^+ supplied from mineralization, while denitrification relies on NO_3^- production from nitrification (Reddy and DeLaune, 2004). Consequently, N_2O emissions are directly or indirectly dependent on mineralization of substrates, especially when exogenous N sources are not available. In the present study, SOC mineralization is seemingly the main available N source and its indigenous supplies can be largely predicted by SOC contents (Espe et al., 2015). It is therefore not surprising that the extent of N_2O emissions were strongly related to SOC (Fig. 4, Table 4).

4.3. SOC as a proxy to predict CH_4 and N_2 emissions

The SOC in surface soils (0–15 cm) appears to be a good predictor for mean annual CH_4 and N_2O emissions from rewetted agricultural Delta peatlands, as evident by the strong relationship between SOC and emissions (Figs. 3a and b, 4a). Surprisingly, N fertilization at recommended levels does not affect the relationship, even after splitting the annual emissions into growing and fallow season (Figs. 3c–f, 4b and c), though the estimate parameters differed substantially between the two seasons

(Tables 3 and 4). With these estimated parameters, we calculated and summed the predicted emissions of CH_4 and N_2O in the growing and fallow season respectively, and compared them with the estimated annual emissions directly calculated from the corresponding equations shown in Tables 3 and 4 and showed the two methods yielded similar results (Fig. 6), further suggesting SOC could be used as a proxy to predict both CH_4 and N_2O emissions. Undoubtedly, the ideal way to evaluate this relationship is to measure field fluxes with higher frequencies and large numbers of chambers across an expanded SOC gradient and time scale, which however is difficult using intensive chamber monitoring. Therefore, like many studies, our estimations of CH_4 and N_2O emissions with measured SOC are influenced by temporal and spatial uncertainties associated with the annual fluxes (Klemmedtsson et al., 2005; Bridgham et al., 2013). However, despite the uncertainties, our results demonstrate strong relationships between SOC and the CH_4 and N_2O emissions (Figs. 3 and 4), and importantly, the power of using SOC in peat derived soils as a predictor of the emissions is significant (Fig. 6, Tables 3 and 4).

The two estimate parameters that restrain the relationship between SOC and log-transformed CH_4 or N_2O emissions differed substantially between the growing and fallow seasons (Tables 3 and 4), which was likely due to the incorporation of rice straw in the fallow season after harvest resulting in higher emission rates (Figs. 1 and 2) (Sander et al., 2014; Ye et al., 2015). The presence of rice plants in the growing season likely contributed to the difference in seasonal CH_4 emission rates since

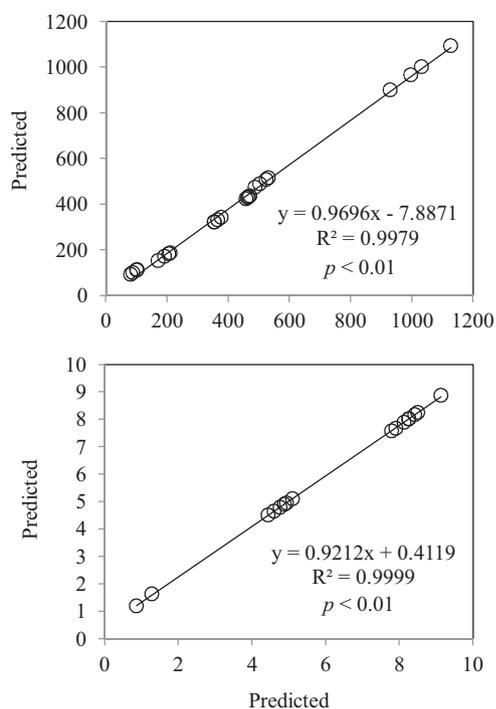


Fig. 6. Correlations between the estimated annual CH₄ and N₂O emissions calculated by adding up the predicted emissions in the growing and fallow season (X axis) and the predicted annual emissions calculated directly from the relationship between SOC and annual CH₄ and N₂O emissions (Y axis). The equation described the overall relationships ($n = 24$).

its transport is primarily through the aerenchyma tissue of rice plants (Couwenberg and Fritz, 2012). Similarly, N fertilization was also able to alter the parameters, especially the ones confining the relationship between SOC and the CH₄ emissions (Fig. 3, Table 3). Despite the changes, the power of SOC to estimate emissions of CH₄ and N₂O was not substantially changed (Figs. 3, 4 and 6, Tables 3 and 4). Nonetheless, a better characterization of how management practices affect CH₄ and N₂O emissions would be beneficial to develop management and seasonal specific parameters to improve the accuracy of the prediction, especially when management practices are different among peatlands.

Water level has been demonstrated to be a good proxy for CH₄ emissions in natural peatlands (Couwenberg and Fritz, 2012), which also influences N₂O emissions from histosols (Jungkunst et al., 2004). However, in their model, water level only explained 34% of variations in CH₄ effluxes and incorporating shunt species (i.e., with or without shunt) and peatland types (i.e., bog or fen) explained 17% more (Couwenberg and Fritz, 2012). Similarly, Turetsky et al. (2014) also found low explanatory power of the water Table as a predictor of CH₄ flux in many wetlands. In the present study, water level during the growing and fallow season was not predictive of emission rates of both CH₄ and N₂O, while water drainage influenced the emissions substantially (Figs. 1 and 2). Inversely, SOC appeared to be the dominant factor, explaining >67% and 63% of variations of annual CH₄ and N₂O emissions in Delta peatlands, respectively (Tables 3 and 4). The ability of SOC to predict CH₄ and N₂O emission is likely associated with its mineralization and effect on C substrate supplies and nutrient availability (e.g., N), which generally stimulates emission of CH₄ and N₂O, respectively. Cultivation following drainage of peat soils causes enhanced decomposition of SOC, and the rate of its decomposition is affected by the intensity of management (Kasimir-Klemetsson et al., 1997; Beetz et al., 2013). It is therefore plausible that SOC may lose its importance in regulating CH₄ and

N₂O emissions in peatlands restored to wetlands in comparison to an intensively managed agricultural crop such as rice. The observed relationship between SOC and the CH₄ and N₂O emissions may change when field data from other restored peatlands are incorporated, but could be constrained with other variables in order to improve reliability and accuracy.

5. Conclusion

Our study estimated CH₄ and N₂O emissions in three rewetted wetlands with contrasting SOC contents of the Sacramento-San Joaquin Delta. Like many other studies, our data used chamber-based data, which may be influenced by temporal and spatial uncertainties when extrapolated to annual fluxes. However, despite these uncertainties, our results indicate that SOC is a good proxy to predict both CH₄ and N₂O emissions. Annual emissions of CH₄ and N₂O were described well by decaying power regressions as a function of SOC content in the range of 6–23% C. Fertilization and seasonal influences did not degrade the relationship, but did alter the estimate parameters that constrained the relationship. The established relationship derived from our field measurements of rewetted agricultural peatlands provides a basic index that could be tested in other restored wetlands for upscaling CH₄ and N₂O emissions and, most importantly, for the evaluation of climate warming mitigation potential of restoration approaches.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.agee.2016.01.008>.

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