Effect of hydrological conditions on nitrous oxide, methane, and carbon dioxide dynamics in a bottomland hardwood forest and its implication for soil carbon sequestration

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Abstract

This study was conducted at three locations in a bottomland hardwood forest with a distinct elevation and hydrological gradient: ridge (high, dry), transition, and swamp (low, wet). At each location, concentrations of soil greenhouse gases (N_2O , CH_4 , and CO_2), their fluxes to the atmosphere, and soil redox potential (Eh) were measured bimonthly, while the water table was monitored every day. Results show that soil Eh was significantly (P < 0.001) correlated with water table: a negative correlation at the ridge and transition locations, but a positive correlation at the permanently flooded swamp location. Both soil gas profile analysis and surface gas flux measurements indicated that the ridge and transition locations could be a sink of atmospheric CH_4 , especially in warm seasons, but generally functioned as a minor source of CH₄ in cool seasons. The swamp location was a major source of CH_4 , and the emission rate was higher in the warm seasons (mean 28 and median $23 \text{ mg m}^{-2} \text{ h}^{-1}$) than in the cool seasons (both mean and median 13 mg m⁻² h⁻¹). Average CO₂ emission rate was 251, 380 and 52 mg m⁻² h⁻¹ for the ridge, transition and swamp location, respectively. At each location, higher CO₂ emission rates were also found in the warm seasons. The lowest CO₂ emission rate was found at the swamp location, where soil C content was the highest, due to less microbial biomass, less CO₂ production in such an anaerobic environment, and greater difficulty of CO₂ diffusion to the atmosphere. Cumulative global warming potential emission from these three greenhouse gases was in an order of swamp>transition>ridge location. The ratio CO₂/CH₄ production in soil is a critical factor for evaluating the overall benefit of soil C sequestration, which can be greatly offset by CH₄ production and emission.

Keywords: carbon sequestration, global warming potential, greenhouse gas, methane, redox potential, sea level rise, wetland

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Introduction

The steady increase in global mean surface temperature over the last 150 years has caused a wide concern on its impact on the Earth's environment. The scale of impact can be global, such as observed sea level rise through thermal expansion of seawater and widespread loss of

Correspondence: Kewei Yu, Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, USA, tel. +1 225 5788832, fax +1 225 5786423, e-mail: kyu1@lsu.edu land ice; and can be regional, such as the frequent occurrence of extreme temperature and precipitation events. Global climate change is driven by complex feedback mechanisms amongst the atmosphere, ocean and land. Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the primary atmospheric trace gases contributing to the enhanced global warming. Increases in the atmospheric abundance of these trace gases are significantly correlated with the intensifying anthropogenic activities since industrialization (Intergovernmental Panel on Climate Change, 2001). Coastal regions around the world are the most developed and populated areas, and are highly vulnerable ecosystems to climate change (Gambolati *et al.*, 1999). Global mean sea level is projected to rise by 0.09–0.88 m between 1990 and 2100 as predicted by the Intergovernmental Panel on Climate Change (2001). Rising sea level will inundate nonflooded areas, prolong soil saturation and flooding duration in currently flooded areas, and may increase salinity levels, all of which will significantly affect soil biogeochemical processes and the ecosystem's functions (Pezeshki *et al.*, 1987; Patrick & Jugsujinda, 1992).

Wetland ecosystems play an important role in the global C budget. Few studies worldwide are conducted in coastal ecosystems on major greenhouse gas fluxes between the soils and the atmosphere and soil C sequestration potentials. Prolonged flooding conditions retard soil organic matter (OM) decomposition with less CO₂ production in wetland ecosystems, resulting in high soil organic C content in the soils and sediments. However, the overall benefit of C sequestration in wetland soils deserves careful evaluation because productions and emissions of CH4 and N2O (more effective greenhouse gases than CO₂) may significantly offset the gains made by greater soil C storage. Both aerobic and anaerobic conditions exist in wetland ecosystems, due to hydrological fluctuations and the presence of wetland plants that transport atmospheric oxygen (O₂) to the soil (Armstrong, 1979; Grosse et al., 1992). Intensity of soil oxidation and reducing status can be characterized by soil redox potential (Eh). Previous laboratory (Yu & Patrick, 2003, 2004) and field studies (Yu et al., 2004, 2006a) have shown that soil Eh provides a quantitative measure of soil oxidizing and/or reducing conditions that govern the dynamics of CO₂, N₂O, and CH₄ production. Soil CO2 comes from both plant root respiration and aerobic and/or anaerobic soil respirations. Biological N₂O can be produced from nitrification under aerobic conditions (high Eh), and denitrification under moderately reducing conditions. Denitrification is generally believed to be the major source of soil N_2O . Significant CH₄ formation (methanogenesis) in soils generally occurs under strictly reducing conditions (low Eh).

Coastal wetlands in southeastern Louisiana are experiencing rapid regional land subsidence caused by anthropogenic activity, sediment consolidation, oxidation of soil OM, and reduced sediment loading from the Mississippi River leading to a rapid decline in land elevation (Conner & Day, 1988). A field study in a representative coastal bottomland hardwood forest of this region was initiated in 2001. Soil profile analysis of N₂O, CH₄, and CO₂ concentrations across a hydrological gradient (ridge, transition, and swamp) indicates a

close relation between soil redox conditions and the potential of soil as a source or sink of N_2O and CH_4 (Yu *et al.*, 2006a). In the study reported here, water level was automatically recorded at the three locations of the study site to monitor changes of hydrological conditions. Measurements of soil gas profiles and surface gas fluxes to the atmosphere were conducted simultaneously to link gas dynamics between soil and atmosphere. Soil C sequestration potential upon increasing soil inundation and the overall benefits in terms of CO_2 equivalents will be discussed.

Methodology

Study site and plot setup

The study site is a typical natural bottomland hardwood forest, located in Jean Lafitte National Historic Park and Preserve (N29°48.2′, W90°06.7′), south of New Orleans, Louisiana. At Barataria Bay, south of the study site, relative sea level rise is estimated to be 1.2 cm yr^{-1} , only 0.2 cm yr⁻¹ of which is due to eustatic global sea level rise (Bourne, 2000), and 1.0 cm yr^{-1} due to regional subsidence (Conner & Day, 1988).

The study plot is 100 m wide (N–S), and 500 m long (E-W) with an elevation gradient of approximately 1 m across its 500 m length (Fig. 1). Both topographic gradient and seasonal meteorological conditions affect hydrology on this plot. The study site is a freshwater ecosystem with salinity less than 1‰ and no indication of salt water intrusion. Soil saturation and inundation are due to accumulation of precipitation under insufficient natural drainage and evapotranspiration, and flooding from Bayou Barataria. Three locations are classified according to their distinct hydrological conditions along the elevation gradient: (1) ridge - rarely flooded, (2) transition – occasionally flooded, and (3) swamp - permanently flooded. Without interference of salt water intrusion, water table is the major driving force of soil biological function and dynamics. Such a unique study site provides an excellent natural platform to study the impact of increasing inundation on soil biogeochemical processes. If land subsidence continues at the current regional rate, such an elevation drop represents approximately 100-year relative sea level rise in this region. In other words, before salt water intrusion, field conditions at the ridge and transition locations would be similar to the swamp location in about 100 and 50 years, respectively. Vegetation structure and composition is of typical freshwater bottomland hardwood forest for this region, and detailed analysis of species and changes within this study plot has been previously reported (Denslow & Battaglia, 2002).



Fig. 1 Setup of the study plots. Position of each replicate subplot at ridge, transition and swamp locations was determined by GPS coordinates. Circles denote the locations for water table monitoring wells.

Four replicate sub-plots (about 20 m apart) were established at the ridge, transition, and swamp locations (Fig. 1). A water table monitoring device was setup at each of the three locations. At each subplot (12 subplots in total), measurements of soil Eh profile, N₂O, CH₄, and CO₂ concentrations in soil profile and gas fluxes to the atmosphere were conducted bimonthly over a 2-year period (April 2003 to March 2005).

Major soil characteristics analysis

Soil pH and total C and N contents were determined for the upper 40 cm of the soil profile at each subplot. Soil samples were taken from 0–10 cm, 10–20 cm, 20–30 cm, to 30–40 cm of the soil profile. Surface leaf litter layer was removed before soil sampling at the ridge and transition locations. No litter layer was found at the swamp location (below water). Soil pH was measured in a soil slurry with a soil : water ratio of 1 : 4. Soil C and N contents were analyzed on a Thermo Finnigan Flash EA 1112 elemental analyzer. Soil bulk density was estimated only for top 10 cm of the soil profile by measuring soil dry weight of known volume.

Gas measurement and analysis

Soil gas profiles were determined using a diffusion chamber technique (Faulkner *et al.*, 1989). At each subplot, a single gas diffusion chamber was installed at depths of 10, 20, 30, and 40 cm. The diffusion chamber consisted of a PVC cap (5 cm in diameter, 70 cm^3 in volume) connected to a three-way sampling valve (located above the soil/water surface) with a gas impermeable Tygon plastic tubing of various length. The opening of the cap was located at the desired depth of the soil profile (e.g. 10 cm). The chambers were left in the field for about two months to allow equilibrium between the gas inside the chamber and the surroundings of each depth. After purging about 5 mL gas from the tubing, a 20-mL gas sample was drawn from the chamber using a gas-tight syringe and transported to the laboratory for rapid analysis. Then, at least 25 mL ambient air was recharged to the chamber to maintain sufficient volume of gas inside the chamber available for the next sampling after equilibrium. This system of gas sampling and transport has been successfully applied in a previous study (Yu *et al.*, 2006a). The diffusion chamber technique was later modified (Yu & DeLaune, 2006) for soil gas profile measurement at the swamp location in this study.

Surface gas flux to the atmosphere was measured using a closed chamber technique. At each subplot, a closed chamber was installed adjacent to the diffusion chambers. The closed chamber consisted of two parts: a chamber body made of a PVC pipe (30.5 cm in diameter, 35 cm in height for the ridge and transition locations, and 120 cm in height for the swamp location), and a chamber PVC cap (12 cm in height). The chamber body was inserted 20 cm into the soil, and remained during the study period. Eight holes (2 cm in diameter) were evenly drilled around the bottom 20 cm of the chamber body. The holes were below ground after installing the chamber body in the field to assist exchange between inside and outside the chamber. For the swamp location, additional eight holes were drilled around central part of the chamber body to allow standing water exchange. The eight additional holes were usually below the water table, but could be exposed when the water table was low, in which case the exposed holes were closed by rubber stoppers during the gas measurement. Both the chamber body and cap have screw connections that formed a closed system during the measurement. The chamber was uncovered at the end of each measurement. The chamber is not transparent to light, and there was generally no live vegetation inside the chamber to interfere with CO₂ concentration measurements. An advantage of such a dark chamber is to prevent temperature rise inside the chamber due to solar irradiation. The gas samples were withdrawn through a rubber stopper on top of the chamber cap at 0 and 60 min after covering the cap. Gas flux rate was determined by calculating gas concentration change over time. The calculation of gas flux rate is independent of chamber area, but a larger area will minimize the disturbance of inserting the chamber into soil. No soil cracking around the edge of the chamber body was found during the study period.

The concentrations of N₂O, CH₄, and CO₂ were determined using a two-channel Tremetrics 9001 gas chromatograph (GC) equipped with an electron capture detector (ECD, for N₂O analysis) and a flame ionization detector (FID, for CH₄ and CO₂ analysis). A methanizer catalyst column was installed in the FID channel after a sample separation column, which reduced CO₂ to CH₄ for detection. The system has a back-flush mechanism operated by a 10-port Valco valve for each channel to prevent moisture in the samples from entering into the detector. Gas samples were injected through a 2.0 and a 0.5-mL sample loop connected to the Valco valves for the ECD and FID channel, respectively. The operating temperature was 50 °C for the oven, 310 °C for the ECD, and 150 °C for the FID. All GC analyses were calibrated individually using certified standards of known concentration (Scott Specialty Gases Inc., Plumsteadville, PA, USA).

Redox potential measurement

Two platinum (Pt) redox electrodes were installed, near each diffusion chamber at the same depths, for measuring soil Eh with a calomel reference electrode using a portable redox meter (Accumet AP62, Fisher Scientific, Pittsburgh, PA, USA). The Pt electrode consisted of a 2cm Pt tip welded to a copper wire of various lengths, and sealed with water-proof Epoxy cement (Faulkner et al., 1989). Redox potential was calibrated to the standard H₂ electrode by adding a correction factor for the calomel reference electrode at the corresponding temperature [Calomel correction factor (mV) = $-0.66 \times \text{temperature} \ ^{\circ}\text{C} + 260, \ R^2 = 0.9996$] to the observed instrument reading (DeLaune & Reddy, 2005). Owing to the variations of soil pH in the study transect, the Eh values at each soil depth and location were calculated and reported as the corresponding values at pH 7 according to the inverse relationship of Eh and pH (59 mV pH unit⁻¹) as described by the Nernst equation (Bohn, 1971).

Water table measurement

At each of the three locations along the transect, a perforated PVC pipe (10 cm in diameter) was installed for water table measurements down to 60 cm below soil surface. The relative position of the water well is denoted in Fig. 1. Measurements were automatically taken every 4 h by a built-in pressure sensor inside the

perforated PVC pipe, and data were downloaded using a hand-held data logger (Infinities USA Inc., Port Orange, FL, USA) on every field visit.

Statistical analysis

Statistical analysis was conducted using SAS 9.1 (SAS Institute Inc., Cary, NC, USA). For each soil depth and location, the results were reported in mean values for Eh with eight replicates, and for gas concentration and surface flux rate with four replicates. Simple linear regression (SLR) using PROC REG was conducted to test if there was a statistically significant relationship between the variables. Analysis of variance (ANOVA) using PROC GLM was conducted to determine the least significant difference (LSD) between the different treatments. When the difference of the mean values exceeded the LSD, it represented a statistically significant difference. The significance level was chosen at $\alpha = 0.05$ for all analyses.

Results and discussion

Soil characterization, and weather and hydrological conditions

Major soil characteristics are summarized in Table 1. The results indicate that the soil C and N contents increased from the ridge to swamp location, mainly due to the difference in upper 20 cm soil profile. Both the soil C and N contents decreased with soil depth at each location, but the C/N ratios remained quite uniform at different soil depths and at different locations. Soil pH was generally in an order of swamp>ridge> transition location. Further observation showed that the soil pH at the bottom layer (30-40 cm) of the ridge location was similar to that at the top layer (0-10 cm) of the transition location. Similarly, the soil pH at the bottom layer of the transition location was similar to that at the top layer of the swamp location. This is likely due to the unique hydrological gradients along this transect (i.e. the bottom layer of the ridge location experiences similar hydrological conditions as the top layer of the transition location, and so on).

Rainfall and daily mean air temperatures during the study period are displayed in Fig. 2. The recorded water tables at the three locations are displayed in Fig. 3. Hydrologic regime of a given site may vary from year to year depending on precipitation and drainage conditions. In most bottomland hardwood forests of southeastern Louisiana, higher water tables and surface flooding typically occur in winter and spring when cooler temperature and dormant vegetation reduce evapotranspiration. As temperature rise and evaporative losses increase in summer and fall, surface flooding

	Depth (cm)	Total C%	Total N%	C/N ratio	pН	Bulk density
Ridge	10	2.84 ± 0.01	0.20 ± 0.000	14.22	6.5 ± 0.03	0.95 ± 0.03
0	20	1.12 ± 0.00	0.09 ± 0.000	13.13	6.3 ± 0.02	
	30	1.16 ± 0.08	0.08 ± 0.004	14.02	6.3 ± 0.02	
	40	0.80 ± 0.01	0.06 ± 0.000	13.70	5.7 ± 0.02	
Transition	10	5.80 ± 0.02	0.35 ± 0.002	16.69	5.7 ± 0.03	0.77 ± 0.08
	20	3.15 ± 0.05	0.22 ± 0.000	14.51	5.6 ± 0.04	
	30	1.12 ± 0.01	0.09 ± 0.002	12.40	5.9 ± 0.02	
	40	0.75 ± 0.02	0.06 ± 0.000	12.06	6.9 ± 0.01	
Swamp	10	9.19 ± 0.11	0.68 ± 0.004	13.52	6.7 ± 0.01	0.43 ± 0.18
	20	2.30 ± 0.06	0.19 ± 0.002	12.31	6.8 ± 0.03	
	30	1.38 ± 0.02	0.12 ± 0.001	11.23	7.1 ± 0.03	
	40	1.05 ± 0.00	0.07 ± 0.001	15.36	7.0 ± 0.01	

Table 1 Major soil characteristics at the three locations of the study site (Yu et al., 2006a, Fig. 1)

Data represent mean \pm standard deviation (n = 4). Soil bulk density (g dry soil cm⁻³) was only estimated for the top 10 cm soil profile. Soil bulk density was inversely correlated with soil total C content, soil bulk density = $-0.08 \times C\% + 1.21$ (P < 0.001, $R^2 = 0.98$, n = 12).



Fig. 2 Daily precipitation and mean air temperature during the study period. Weather records are from New Orleans international airport, the closest weather station to the study site. Average temperature during the study period was 21.4 °C and denoted by a horizontal line in the figure. Daily mean temperatures were generally above the average in warm seasons (May–October), and below the average in cool seasons (November–April).

and water tables recede (Faulkner & Patrick, 1992; Hunter & Faulkner, 2001). In this study, we defined the warm season from May 1 to October 31, and cool season from November 1 to April 30. Temperature was generally above annual average in the warm season, below in the cool season. Larger variations in tempera-



Fig. 3 Water table measurement at the three locations. Warm season: May–October; cool season: November–April. Water tables above soil surface are in positive values, below soil surface in negative values.

ture were found in the cool seasons than in the warm seasons (Fig. 2). Examination of the temperature record over the past 50 years revealed a similar pattern for this region. Owing to the elevation gradient, water tables showed a consistent order of swamp > transition > ridge location (Fig. 3). Water tables at the ridge and transition locations were higher in the cool seasons, even though total rainfall in the warm seasons was about 20% more than that in the cool seasons (Table 2). There was almost no difference in average water table at the swamp location between the two seasons. However, the median water depth at the swamp location was much higher in the cool seasons than in the warm seasons, indicating longer periods of higher water in the cool seasons. Lower water tables found in the warm seasons at the ridge and transition locations were probably due to greater evapotranspiration. The water table at the swamp location may be more controlled by the drainage pattern and water stage at the Barataria Bay.

Soil redox potential and its relationship with hydrological conditions

Redox potential variations in the soil profile during the study period are displayed in Fig. 4. Soil redox status

shows a general pattern of ridge>transition>swamp location (Table 3), a reverse order of water table. Water table is a dominant factor for soil redox status at the ridge and transition locations; thus, soil Eh was generally lower during the cool seasons (higher water table) and higher during the warm seasons (lower water table). The occurrence of lower water tables in the cool seasons could significantly elevate soil redox status, as in the case of December 10, 2003 (water table was <-60 cm at the ridge and transition locations, and only 13.5 cm at the swamp location). Such a seasonal pattern of soil Eh with water table did not apply to the swamp location, probably due to two major reasons: (1) there was no significant seasonal difference in the water table at the swamp location (Fig. 3 and Table 2), and (2) the soil redox status at the swamp location was more likely controlled by temperature and soil OM content, resulting in lower soil Eh in the warm seasons and at the upper soil layers (Fig. 4). Higher soil OM content in the surface layers provided a source of electrons which generated stronger reducing conditions (lower Eh) and also supported greater soil respiration. Unlike the swamp location, soil Eh at the ridge and transition locations showed a significant control by the water table (Table 3), and generally lower soil Eh was found at

	Parameter	Location	Mean	Median	Minimum	Maximum	Total (mm)	
Warm season	Precipitation (mm day ⁻¹)		5.8	0	0	111.8	2130.8	
	Temperature (°C)		26.7	27.2	16.7	31.1		
	Water table (cm)	Ridge	-47.3	-61.5	-64.8	5.6		
		Transition	-35.7	-50.9	-62.1	9.2		
		Swamp	24.0	21.7	-1.5	74.8		
Cool season	Precipitation (mm day $^{-1}$)	1	4.9	0	0	194.8	1772.9	
	Temperature (°C)		15.9	16.1	1.11	26.7		
	Water table (cm)	Ridge	-41.2	-46.8	-76.2	4.3		
		Transition	-22.6	-15.2	-60.7	10.4		
		Swamp	24.2	24.8	-0.7	54.2		

Table 2 Statistical summaries of precipitation, air temperature, and water table

Warm season: May-October; cool season: November-April. Water tables above soil surface are in positive values, below surface in negative values. Total precipitation represents the accumulated rainfall during the study period (April 1, 2003 to March 31, 2005).

deeper soil layers (Fig. 4). Surprisingly, the swamp soil Eh was positively correlated with the water table change (Table 3), and such a discrepancy might be due to the presence of wetland plants that can transport O_2 from the atmosphere into soil, which can cause poor correlations between soil Eh and water table (Yu *et al.*, 2006b).

Seasonal variations of soil N₂O and CH₄ profile

Soil consumption potential is an important factor for the residence time of N_2O and CH_4 in the atmosphere (King, 1992). Previous soil gas profile analysis at this study site indicated that the ridge and transition locations showed consumption potential of atmospheric CH_4 , and the swamp location might occasionally function as a sink of atmospheric N_2O (Yu *et al.*, 2006a). When soil CH_4 and N_2O concentrations are below atmospheric levels, the soils will uptake CH_4 and N_2O according to their concentration gradients. Oxidation by methanotrophs is the major mechanism of CH_4 consumption (Conrad, 1995). Denitrification is generally recognized as the major process for N_2O production in soils, but also a mechanism for N_2O consumption by further reducing N_2O to N_2 (Firestone *et al.*, 1980).

Seasonal soil N₂O (Fig. 5) and CH₄ (Fig. 6) profile results were comparable to the previous findings at the same study site (Yu *et al.*, 2006a). In most of 2003, the swamp soil N₂O concentrations were below atmospheric levels. For the remaining period, the swamp soils probably emitted N₂O, because soil N₂O concentrations exceeded atmospheric levels (Fig. 5). The transition soil N₂O was only occasionally below atmospheric levels, as in October 2003. In the aerated ridge location, soil N₂O concentrations were consistently above atmospheric levels, probably due to (1) N₂O production from nitrification and (2) unfavorable conditions for bacterial conversion of N₂O to N₂, which requires more reducing conditions (Table 3). Methanotrophy (CH₄ oxidation) occurs mainly under aerobic conditions driven by methanotrophs that have two major oxidation pathways, high CH₄ affinity type-I, and low affinity type II. Consumption of atmospheric CH₄ has been reported mainly through type-I methanotrophy activity (Conrad, 1995; Hanson & Hanson, 1996; Jackel *et al.*, 2001). Soil CH₄ emission rate may largely depend on methanotrophic activity, since it has been reported that strong methanogenic activity may still occur in well-oxidized environments (Teh *et al.*, 2005). A study of methanotrophs in this study plot using molecular techniques is ongoing and is expected to reveal the linkage between hydrological conditions of the soil and the two types of methanotrophy.

The CH₄ compensation point, where CH₄ concentration becomes constant due to equilibrium between CH₄ production and consumption, is a critical factor for soil acting as a source or sink of ambient CH₄. A recently completed laboratory study showed that the CH4 compensation point exponentially decreased with increasing soil Eh. At pH 7, the critical Eh above which soils consumed atmospheric CH_4 (1.75 µL L⁻¹) was generally above +400 mV (Yu et al., 2007). In this field study, soil Eh above + 400 mV were only found in the ridge (n = 30) and transition (n = 20) soils where soil CH₄ concentrations were all lower than the atmospheric levels. When the soil Eh was < +400 mV, only 40% of the soil measurements at the ridge (n = 10) and 20% at the transition (n = 20) showed soil CH₄ concentrations lower than the atmospheric levels. The ridge soil showed a significant potential to consume atmospheric CH₄ with soil CH₄ concentrations lower than the atmospheric levels observed in most of the study period (Fig. 6). The transition soil exhibited similar CH₄ consumption potential only in the warm seasons. In the cool season, higher water table decreased soil Eh, favoring CH₄ production instead of CH₄ oxidation. Long periods



Fig. 4 Redox potential (Eh) measurement in the soil profile during the study period. Warm season: May–October; cool season: November–April. Note: Eh legend at swamp location is different than at ridge and transition locations.

Table 3 Statistical summaries of soil redox potential (Eh) and correlation with water table (cm) and air temperature (°C)

Location	Eh (mV)			Linear regression			
	Mean	Median	Minimum	Maximum	Equation	R^2	
Ridge	+ 511	+ 534	+ 174	+ 722	$Eh = -5.3 \times WT - 4.6 \times T + 466$	0.51	
Transition	+403	+456	+ 29	+ 694	$Eh = -7.2 \times WT - 2.7 \times T + 356$	0.71	
Swamp	-66	-69	-241	+ 161	$Eh = 3.6 \times WT - 4.8 \times T - 136$	0.35	

Relative water table (WT) = measured water table + absolute value of soil depth (positive value).

Such a conversion allows a simultaneous comparison of Eh variations with the water tables in the entire soil profile. All above multiple regressions (n = 44) were significant statistically (P < 0.001). Single linear regressions of Eh with WT were also significant (P < 0.001) with R^2 of 0.47, 0.70, and 0.27 for the ridge, transition, and swamp locations, respectively. However, single linear regressions of Eh with air temperature (T) yielded R^2 of 0.05 (P = 0.15), 0.10 (P = 0.03), and 0.03 (P = 0.3) for the ridge, transition, and swamp locations, respectively.



Fig. 5 Seasonal variation of soil N₂O concentrations. N₂O concentration above ambient level $(0.3 \,\mu L L^{-1}, Log_{10} 0.3 = -0.52)$ is denoted by dark color, below ambient level by light color. Soil gas profile sampling was not conducted for the June 2003 field visit.

of inundation at the swamp location provided desirable conditions for vigorous CH₄ production. Methane concentrations in the swamp soil profile were several orders of magnitude higher than atmospheric levels, indicating the swamp location was a significant source of CH_4 (Fig. 6). It is important to understand that type II methanotrophy activity likely exists in reducing conditions where large amount of CH_4 is produced. Such



Fig. 6 Seasonal variation of soil CH₄ concentrations. CH₄ concentration above ambient level $(1.75 \,\mu\text{L}\,\text{L}^{-1}, \text{Log}_{10} 1.75 = 0.24)$ is denoted by dark color, below ambient level by light color. Gas profile analysis was not conducted for the June 2003 field visit.

 CH_4 oxidizing activities can significantly abate the actual CH_4 emission to the atmosphere (Jackel *et al.*, 2001). Soil CO_2 concentrations were several orders of magnitude higher than atmospheric levels at all three locations, indicating the study site was a significant source of CO_2 (figure not shown).

Seasonal variations of N_2O , CH_4 , and CO_2 fluxes and their relative contribution to overall global warming potential

The direction and magnitude of gas fluxes corresponded well with soil gas concentrations, with increased emissions associated with periods of higher soil gas concentrations. CH₄ and N₂O uptake was observed during periods when soil gas concentrations fell below atmospheric levels (Fig. 7). Flux rates of N₂O (both emission and consumption) were generally low, probably due to limited N source available for denitrification activity in this natural environment. Extraordinarily high N₂O concentrations in soil and surface emissions at the swamp location were observed in June 2004 (Figs 5 and 7), possibly due to higher nitrate inputs from runoff following higher rainfall levels in April and May (Fig. 2). Both the swamp and transition locations occasionally showed consumption of atmospheric N2O. However, it did not exactly match the soil profile prediction (Fig. 5). This may be because soil gas concentrations between 10 cm soil depth to the surface, which is probably the most active soil layer, were not determined. Unknown information on gas production and/or consumption within the top 10 cm soil layer may be of interest for future investigation.

The swamp location functioned as a major source of CH_4 , and the intensity was stronger in the warm seasons than in the cool seasons (Fig. 7 and Table 4). Since no obvious hydrological difference was found at the swamp location, the higher CH₄ emission rate was likely due to the higher temperatures in the warm seasons (Table 2). Correlation between CH_4 emission rates at the swamp location and air temperatures was positive but not statistically significant. Both the ridge and transition locations showed a general consumption of atmospheric CH₄ in the warm seasons, but functioned as a minor source of CH₄ in the cool seasons (Table 4). Large variations in gas production (Moore & Dalva, 1993) and other biogeochemical reactions (Tiedje et al., 1984) are expected in this study site due to seasonal variations in the temperature (Fig. 2) and frequent fluctuation of the water table (Fig. 3). For example, CH₄ emission rates varied annually, as noticed by comparing the emission rates measured in the same month (i.e. June 2003 and June 2004) (Fig. 7). Methane emission rates found in this study are substantially

higher than the reported CH₄ fluxes measured at similar ecosystems in southeastern United States: $2.5 \text{ mg m}^{-2} \text{h}^{-1}$ (forested wetland, Florida, Harriss *et al.*, 1988), $2.6 \text{ mg m}^{-2} \text{h}^{-1}$ (bottomland hardwoods/ swamp, Georgia, Pulliam, 1993), and $6.1 \text{ mg m}^{-2} \text{h}^{-1}$ (swamp forest, Louisiana, Alford *et al.*, 1997).

All three locations showed significant CO₂ emissions, and the emission rates were higher in the warm seasons than in the cool seasons (Fig. 7 and Table 4). The CO_2 emission rates were in an order of transition>ridge> swamp. Recent phospholipid fatty acid (PLFA) study using the soils from this study plot revealed that soil microbial biomass was in the same order as in CO₂ emission rates (unpublished results). The highest CO2 production and emission at the transition location may contribute to the observed lowest soil pH (Table 1). Soil CO_2 production is of a complex nature because both plant root and microbial respiration processes generate CO2. To some extent, soil microbial activities at the ridge location were probably limited by water stress, while flooding conditions at the swamp location limited O₂-using soil microbial activities. Limitation of gas transfer through soil and/or water layer is another important factor governing gas emission rates. Thus, despite having the highest soil OM content, the lowest CO₂ emission rates were at the swamp location mainly due to (1) less microbial biomass in the soil, (2) less CO_2 production in such an anaerobic environment, and (3) greater difficulty of CO₂ diffusion through the soil and water layer to the atmosphere. Statistical analysis showed no significant correlation between N2O, CH4 and CO₂ emission rates and temperature, water table and soil Eh, due to the complex nature of gas production and emission. However, the detailed measurements in this study will help calibrate trace gas emission rates under different hydrological conditions by process-based models.

GWP was introduced by the Intergovernmental Panel on Climate Change (IPCC) to compare the overall radiative forcing of different greenhouse gases, by converting other gas (e.g. N₂O and CH₄) fluxes into CO₂ equivalent (Intergovernmental Panel on Climate Change, 2001). The results from this study indicate that the contributions from the three greenhouse gases to overall GWP were highly site dependent. Fluxes of N_2O , CH_4 , and CO_2 contributed to 1.0%, <0.1%, and 99.0%, respectively, to overall GWP at the ridge location, 6.9%, 0.1%, and 93.0% at the transition location, and 2.8%, 88.2%, and 9.0% at the swamp location (calculation based on the median values to avoid the interference of extraordinary values). The cumulative GWP emission from these three greenhouse gases was in the order of swamp>transition>ridge location, and warm season > cool season (Table 4). Nitrous oxide was



Fig. 7 Seasonal N₂O, CH₄, and CO₂ fluxes at the three locations. Warm season: May–October; cool season: November–April. Variations of the four replicate measurements are denoted by standard deviation (SD) bars. An unusual high N₂O emission (actual rate and SD are labeled) was found at the swamp location on June 21, 2004. Surface gas flux measurement was not conducted on March 31, 2005.

a less important contributor to GWP at this study site, due to the tight internal N cycling in the vegetation and limited N input into the system. Significant CH_4 (a stronger greenhouse gas than CO_2) emission turned the swamp location into the greatest source of GWP, despite of the lowest CO_2 emissions from this location.

Implications for soil C sequestration

The role of wetland ecosystems in mitigating global climate change is complicated by the interaction between higher soil C densities resulting from slowed decomposition and potentially higher GWPs from N₂O

		$N_2O \ (mg \ m^{-2} \ h^{-1})$		$CH_4 (mg m^{-2} h^{-1})$			$CO_2 (mg m^{-2} h^{-1})$			GWP		
		Mean	SD	Median	Mean	SD	Median	Mean	SD	Median	Mean	Median
Warm season	Ridge	0.06	0.04	0.05	-0.02	0.12	0.00	310.20	176.15	391.91	327.5	406.7
	Transition	0.19	0.32	0.11	-0.03	0.08	0.00	504.14	315.43	587.15	559.7	619.7
	Swamp	2.22	4.96	0.06	28.39	24.75	22.53	59.77	34.16	63.21	1369.9	599.2
	LSD $(n = 5)$	3.96			19.71			288.72			1041.8	
Cool season	Ridge	-0.05	0.11	-0.01	0.01	0.06	0.00	192.39	136.31	190.87	177.8	187.9
	Transition	0.07	0.06	0.06	0.45	0.87	0.02	238.80	207.19	190.36	269.9	208.6
	Swamp	0.05	0.05	0.03	13.26	11.78	13.18	43.60	34.39	24.81	363.4	336.8
	LSD $(n = 5)$	0.11			9.40			199.24			329.2	

Table 4 Summary of N₂O, CH₄, CO₂ fluxes, and cumulative GWP from these greenhouse gases

Warm season: May–October; cool season: November–April. Global warming potentials (GWP) were calculated by taking mass factors, in a 100-year time horizon, 1 for CO₂, 23 for CH₄, and 296 for N₂O (Intergovernmental Panel on Climate Change, 2001). All GWP results were expressed as mg CO₂ equivalent $m^{-2}h^{-1}$. It represents statistically significant difference if the difference of the mean values exceeds the least significant difference (LSD).

and CH₄ emissions generated by the same anaerobic conditions responsible for the soil C accumulation (Fung et al., 1991; Gorham, 1991). Reduction in gaseous C production in soil (mainly in form of CO₂ and CH₄) is an important mechanism for soil C sequestration, as found at the swamp location with higher C content in soil (Table 1) and lower gaseous C emission (Table 4) than at the other two locations. This is a freshwater coastal ecosystem, as indicated by the vegetation and salinity, and future relative sea level rise will move freshwater inland increasing flooding depths and soil saturation in areas similar to the transition and ridge locations of this study. According to the hydrological gradient of the study site and regional relative sea level rise, the hydrological conditions at the transition location would likely become the current conditions at the swamp location in about half a century. The sums of CO2 and CH4 emission rates were 51 and $212 \text{ mg Cm}^{-2} \text{h}^{-1}$ for the swamp and transition locations, respectively. Meanwhile, average GWP (from CO₂ and CH₄ only) emission rates were 248 and $212 \text{ mg} \text{ Cm}^{-2} \text{ h}^{-1}$ for the swamp and transition locations, respectively. Even though less gaseous C was emitted from the swamp location, more GWP emission actually occurred due to the stronger effect of CH4 on Earth radiative forcing (Table 4). Carbon sequestration potential due to less gaseous C emission would be $161 \text{ mg C m}^{-2} \text{h}^{-1}$ (212–51) for the transition location, if it became the current swamp location in about half a century. However, the compensation of GWP by CH₄ emission would be $197 \text{ mg C m}^{-2} \text{h}^{-1}$ (248–51), which exceeds the C sequestration potential $(161 \text{ mgCm}^{-2}\text{h}^{-1})$ for the transition location. Thus, there would be no net benefit to GWP from increased C sequestration if the transition converted to the swamp upon future regional subsidence and sea level rise. Only soil CO₂ and CH₄ emissions are taken into account in this example, but N₂O must be considered in an ecosystem with significant N input, (e.g. fertilizer inputs in agricultural watersheds). It is important to note, other factors need to be considered to reach an affirmative conclusion, such as change of C pool in above ground vegetation, other forms of C in the systems and their fates, and possible gas fluxes through wetland plants (Grosse *et al.*, 1992).

Nevertheless, the ratio of CO₂/CH₄ production in soil is a critical factor for evaluating soil C sequestration potential. Without CH₄ production, any mechanisms leading to less CO₂ production will have a net benefit for C sequestration in soils (assuming no N₂O involved). With significant CH₄ production and emission, the soil C storage potential is greatly offset, and can even become a negative benefit overall (as in the swamp location in this study). Median values of soil CO₂/CH₄ ratio at the swamp location were 5.8 and 2.3 in the warm and cool seasons, respectively, in a previous study (Yu et al., 2006a), and 0.85 and 0.75 in this study. Surface CO₂ and CH₄ emissions at the swamp location (Table 4) exhibited the same order of CO_2/CH_4 ratio in the warm (2.81) and cool (1.88) seasons. Although large variations in CO₂/CH₄ ratio exist in the soil gas concentrations and surface emissions, CH₄ and CO₂ production in the swamp soil was approximately of the same order of magnitude. In this case, CH₄ exceeded CO₂ becoming the leading greenhouse gas emitted from the swamp location, because of the larger radiative forcing factor for CH₄. The larger CO₂/CH₄ ratio in the surface gas emission than in the soil gas concentration at the swamp location is probably due to CH₄ oxidation while moving through the soil/water layer. No obvious consumption mechanism of CO₂ can be identified during this movement. Soil CH₄ consumption capacity is a critical factor for the potential of soil as a sink of atmospheric CH₄ (as seen at the ridge and transition locations). This is also true for abating the intensity of a CH₄ source (as seen at the swamp location), because a large amount of CH₄ can be consumed before it is emitted to the atmosphere (Cicerone & Oremland, 1988; Khalil et al., 1998). The overall benefit of soil C sequestration under different scenarios needs to consider the changes not only in production potential, but also in consumption potential of greenhouse gases in soils. Without interference of salt water (mainly high salinity and high sulfate content) on greenhouse gas dynamics, the information obtained in this study is valuable to most terrestrial ecosystems under different hydrological conditions. In the future, the swamp location may be inundated by brackish water, the implications of which deserve further investigation in the effects on soil biogeochemical processes.

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