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# Redox potential characterization and soil greenhouse gas concentration across a hydrological gradient in a Gulf coast forest

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## Abstract

Soil redox potential (Eh), concentrations of oxygen ($O_2$) and three greenhouse gases ($CO_2$, $CH_4$, and $N_2O$) were measured in the soil profile of a coastal forest at ridge, transition, and swamp across a hydrological gradient. The results delineated a distinct boundary in soil Eh and $O_2$ concentration between the ridge and swamp with essentially no overlap between the two locations. Critical soil Eh to initiate significant $CH_4$ production under this field conditions was about +300 mV, much higher than in the homogenous soils (about −150 mV). The strength of $CH_4$ source to the atmosphere was strong for the swamp, minor for the transition, and negligible or even negative (consumption) for the ridge. Maximum $N_2O$ concentration in the soils was found at about Eh +250 mV, and the soil $N_2O$ emission was estimated to account for less than 4% for the ridge and transition, and almost negligible for the swamp in the cumulative global warming potential (GWP) of these three gases. The dynamic nature of this study site in response to water table fluctuations across a hydrological gradient makes it an ideal model of impact of future sea level rise to coastal ecosystems. Soil carbon (C) sequestration potential due to increasing soil water content upon sea level rise and subsidence in this coastal forest was likely limited and temporal, and at the expense of increasing soil $CH_4$ production and emission.

*Keywords:* Greenhouse gas; Global warming potential; Redox potential; Sea level rise; Wetland

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## 1. Introduction

Carbon dioxide ($CO_2$), methane ($CH_4$) and nitrous oxide ($N_2O$) are the primary greenhouse gases contributing to radiative forcing of the Earth's atmosphere. The 20th century global warming has contributed significantly to the observed sea level rise, through thermal expansion of seawater and widespread loss of land ice. Global mean sea level is projected to rise by 0.09–0.88 m between 1990 and 2100 under different greenhouse gas emission scenarios (IPCC, 2001).

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*Abbreviations:* Carbon dioxide ($CO_2$); Methane ($CH_4$); Nitrous oxide ($N_2O$); Global warming potential (GWP); Redox potential (Eh); Intergovernmental Panel on Climate Change (IPCC); Gas chromatography (GC); Least significant difference (LSD).

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Coastal ecosystems are highly vulnerable to rising sea level. Increasing soil saturation and flooding period will affect a series of biogeochemical processes of ecological importance. The study of greenhouse gas dynamics between coastal wetland ecosystems and the atmosphere is lacking worldwide. It is critical to understand the impacts of rising sea level on such ecosystems to better predict the function and feedback of the ecosystems, and to estimate greenhouse gas emissions. Investigation of this nature in coastal wetland ecosystems will fill the gap in global change research, since most studies of ecosystem response to global climate change have focused on upland systems (Mosier et al., 2002). Forested wetlands cover about 2% of global land surface area (Lugo et al., 1990). High vegetation productivity, frequent flooding, and high soil organic C content make these ecosystems more important to the global C budget than their area alone suggests. Prolonged flooding conditions retard organic matter (OM) decomposition with less $CO_2$ production, but favor methanogenesis. Frequent fluctuation of soil water content may favor $N_2O$ production and emission to the atmosphere, because $N_2O$ efflux is likely to be greatest at moderately reducing conditions (Smith et al., 1983). Soil redox potential (Eh) is a quantitative indicator of anoxic conditions that govern the production and consumption of $CH_4$ and $N_2O$ (Yu and Patrick, 2003).

Despite the prevalence of coastal forests in the southeastern US and their critical locations at land-water margins, our knowledge of their soil biogeochemical processes is very limited. This field study was initiated to investigate the production and mechanistic controls of the three major greenhouse gases ($CO_2$, $CH_4$, $N_2O$) in a representative coastal bottomland hardwood forest in southeastern Louisiana where the rate of relative sea level rise has been accelerated by regional subsidence. We aimed to (1) identify soil Eh characteristics of this study site in different hydrological seasons, (2) quantify the relationship between Eh and greenhouse gas ($CO_2$, $CH_4$, and $N_2O$) concentrations in the soils across an elevation gradient, and (3) qualitatively discuss the overall greenhouse gas emission, in terms of $CO_2$ equivalent, from soils along this transect.

## 2. Methodology

### 2.1. Study Site

The study site is located in the Barataria Unit of the Jean Lafitte National Historic Park and Preserve (N29°48.2′, W90°06.7′), south of New Orleans, Louisiana. This coastal area is undergoing substantial regional subsidence (Conner and Day, 1988), due to oil and gas exploration, sediment consolidation, oxidation of buried OM, changes in sediment deposition patterns, and reduced sediment loading from the Mississippi River. 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). Site hydrology is affected by the topographic gradient and seasonal meteorological conditions. Soil saturation and inundation are due to accumulation of precipitation under insufficient natural drainage and evapotranspiration, and flooding from Bayou Barataria.

The study plot is 100 m wide (N–S) and 500 m long (E–W) with an elevation drop of approximately 1 m across its 500 m length. A hydrological gradient exists with a rarely flooded, mixed forest (dominated by *Ilex decidua* Walt, *Quercus virginiana* Mill, *Liquidambar styraciflua* L., *Acer rubrum* L., *Ulmus americanum* L., and *Quercus nigra* L.) on the elevated natural levee (ridge) and a permanently flooded swamp (dominated by *Acer rubrum* L., and *Fraxinus profunda* Bush) at the lowest elevation. The transition site is dominated by *Acer rubrum* L., *Liquidambar styraciflua* L., and *Ulmus americanum* L. Detail vegetation structure and composition within this study plot is available (Denslow and Battaglia, 2002). If relative sea level rise continues at the current regional rate of about 1 cm $yr^{-1}$, the 1-m elevation gradient of this study site represents approximately 100 years of sea level rise. Thus, the hydroperiod and soil moisture level at the ridge should be similar to the swamp in about one century. Although other factors will be involved with the complex event of future sea level rise, i.e., change of vegetation structure and composition (Denslow and Battaglia, 2002), saltwater intrusion, and variation in soil microbial diversity, this coastal forest ecosystem with a hydrological gradient is a good natural model and provides a platform to study the impact of future sea level rise and increasing hydroperiod on soil biogeochemistry.

### 2.2. Setup of the study plot and measurements

Greenhouse gases ($CO_2$, $CH_4$, and $N_2O$), $O_2$ concentration, and Eh were measured in the soil profile across the hydrological gradient of the study plot. Four replicate sub-plots were established in each of the ridge and swamp locations. An additional set of sub-plots was established at an elevation midway (transition) between the ridge and swamp. Soil samples (6 depths in the soil profile, 10 cm for each depth) at the three locations were collected and analyzed for soil total carbon (C) and nitrogen (N) contents on a CE Elantech CNS analyzer, and soil pH (soil:water = 1:4) on a pH meter in the laboratory. Both soil C and N contents at the three locations showed the same decreasing tendency from the upper to lower depths of the soil (Fig. 1A and B). The results indicated that the soil C and N content generally increased from the ridge to the swamp attributed to the difference in the upper 20 cm soil, but there was almost no difference between 20 and 60 cm soil profiles at the

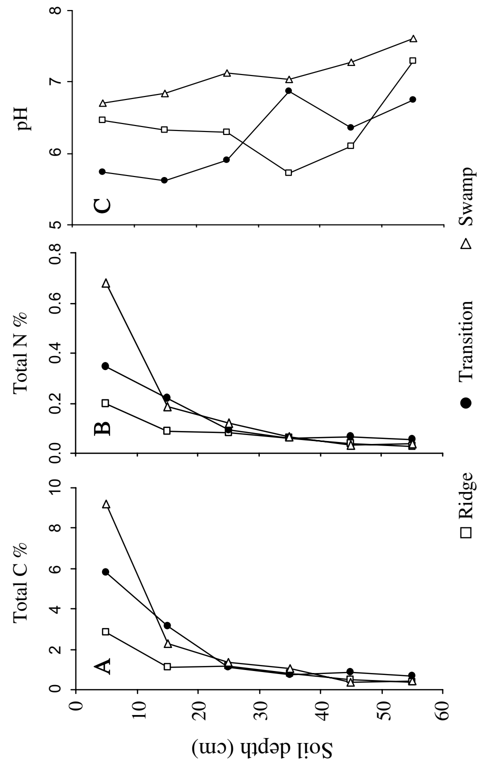

Fig. 1. Major characteristics in the soil profiles at the three locations. Despite of large variation in the soil C and N content at different soil depths and locations, the soil C/N ratio was quite uniform with an average (±standard deviation) of 13.3 ± 0.9 for the ridge, 13.6 ± 1.8 for the transition, and 13.0 ± 1.4 for the swamp, respectively.

three locations regardless of hydrological variations. The turnover time of soil OM increases with depth, ranging from several years for litters to over a century below a depth of about 25 cm (Harrison et al., 1990). The close soil OM content at the lower depths of the soil indicates the same origin in evolution of the three locations in this study site. The average soil C and N contents in the upper 40-cm profiles were 1.13% and 0.08% for the ridge, 2.06% and 0.14% for the transition, and 2.46% and 0.19% for the swamp, respectively. Soil pH tended to be slightly higher at the lower depths of the soil with an average of 6.4 ± 0.5 for the ridge, 6.2 ± 0.5 for the transition, and 7.1 ± 0.3 for the swamp, respectively (Fig. 1C). Soil bulk density (0–10 cm) at the three locations was estimated to be 0.95 ± 0.03 for the ridge, 0.77 ± 0.08 for the transition, and 0.43 ± 0.18 g dry soil $cm^{-3}$ for the swamp, respectively. The bulk density at the swamp represented the best estimate available because of technical difficulty for the measurement under the flooded conditions.

At each sub-plot, 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 (e.g., 10 cm). The chambers were left in the field for at least 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, 20 ml gas samples were drawn from the chambers using gas-tight syringes and transported to the laboratory for rapid analysis. Then, at least 25 ml air was recharged to the chambers to maintain sufficient gas inside the chambers available for next sampling after equilibrium. This system of gas sampling and transport was tested to be leak free for both diffusion chambers and syringes. The actual gas emission rates to the atmosphere at each location depend on the gas concentration gradients between the soil and atmosphere, and the highly variable gas diffusion coefficients under different hydrological conditions. Two platinum (Pt) redox electrodes were installed nearby each diffusion chamber at the same depths for measuring soil Eh with a portable redox meter (Accumet AP62, Fisher Scientific, USA) and a calomel reference electrode. The Pt electrode of this kind can last for several years with necessary replacement when an electrode is suspected to give poor readings (i.e., the readings do not change at different measurements, or are considerably different than that of other replicate electrodes). Detail information on the construction and application of the diffusion chamber and Pt electrode was described in a previous publication (Faulkner et al., 1989). The concentrations of $CO_2$, $CH_4$, $N_2O$, and $O_2$ in the soils were determined with a Tremetrics 9001 gas chromatography (GC) instrument equipped with an electron capture detector (ECD, for $O_2$ and $N_2O$ analysis) and a flame ionization detector (FID, for $CH_4$ and $CO_2$ analysis). The GC was equipped with stainless steel columns packed with Porapak-Q. The system had a back-flush mechanism operated by 10-port Valco valves to prevent moisture in the samples entering into the detectors. Operating temperature was 50 for the oven, 310 for the ECD and 150 °C for the FID. Gas samples were injected through a 2.0 ml and a 0.5 ml sample loop connected to the Valco valves for ECD and FID detections, respectively. A methanizer catalyst column was installed in the GC after a sample separation column, which reduced the $CO_2$ to $CH_4$ for detection. All GC analyses were calibrated individually using certified standards of known concentration (Scott Specialty Gases, Inc., Plumsteadville, PA, USA).

Gas samples in the soils were collected and soil Eh was measured on six sampling dates: May, July, and November 2001, March and August 2002, and April 2003. These sampling dates are representative of the seasonal hydrological conditions present in many bottomland hardwood forests, which are typically inundated and saturated in winter and spring, and are of low water tables and aerobic conditions in late summer and early fall (Faulkner and Patrick, 1992; Hunter and Faulkner, 2001). Therefore four measurements were conducted in the dry season (May, July, November 2001, and August 2002), and two measurements in the wet season (March 2002 and April 2003). Highest water level was found in March 2002 with about 60 cm standing water at the swamp, and the lowest in August 2002 with about 20 cm water above the ground. The ground water table almost reached the soil surface at the transition only on the date with the highest water level (March 2002). The duration of each hydrological season may vary each year under different meteorological and drainage conditions.

### 2.3. Calculation and statistical analysis

Redox potential was calibrated to the standard $H_2$ electrode by adding 247 mV (the correction factor for calomel reference electrode at 20 °C) to the observed instrument reading. The effect of field temperature variation on the correction factor is small and generally ignored. Due 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 per pH unit) as described by the Nernst equation (Bohn, 1971). Statistical analysis was conducted using SAS (V8 for Windows, 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 with four replicates. Simple linear regression (SLR) using PROC REG was conducted to test if the slope of a regression was significantly different from that of a theoretical model. Analysis of variance (AVOVA) using PROC GLM was conducted to determine the least significant difference (LSD) between the different treatments. When the difference of the mean values exceeds the LSD, it represents statistically significant difference. The significant level was chosen at alpha 0.05 for all statistical analyses.

## 3. Results and discussion

### 3.1. Soil redox potential in different hydrological seasons

Soil Eh of the study site generally ranged from +700 to –200 mV, which represents the normal Eh range in natural conditions that support major biogeochemical activities. In different hydrological season, soil Eh status showed a distinctly different pattern along the study transects corresponding to the hydrological gradient and moisture conditions (Fig. 2). In the dry season, the ridge and transition soils were both strongly oxidized with soil Eh higher than +450 mV. The average Eh gradient between the ridge and transition was 92 mV (statistically significant but not strong), while the Eh gradient from the transition to swamp was 410 mV (statistically significant) (Fig. 2A). In the wet season, the soil Eh in the transition was as low as in the swamp soil with no

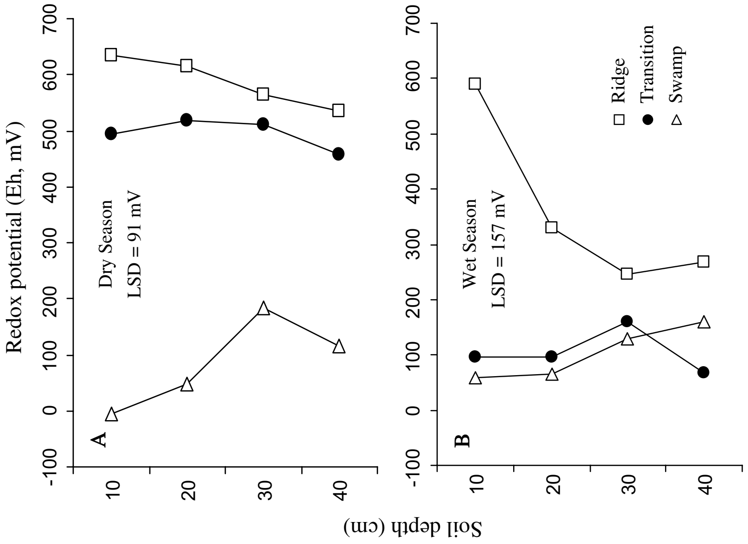

Fig. 2. Redox potentials (Eh) in the soil profiles in different hydrological seasons. Mean Eh values in the soil profiles are used. It represents statistically significant different if the difference of the mean values exceeds the LSD.

significant difference, and the average Eh gradient from the transition to ridge became 253 mV with statistical significance (Fig. 2B). The soil Eh at the swamp remained low due to continuously inundated conditions. The transition site and the lower depths of the ridge soil were obviously affected the most by the seasonal hydrological fluctuation with statistically significant difference observed between the dry and wet seasons for the means of soil Eh at the ridge and transition.

### *3.2. Relationship between soil redox potential and oxygen concentration*

Soil $O_2$ concentration generally showed a similar pattern as the soil Eh measurement during each hydrological season with a statistically significant correlation between the soil Eh values and $O_2$ concentrations. The only insignificant relation ($P = 0.07$) was found at the swamp where the Eh and $O_2$ concentrations were at the extreme lower ends of the scale (Table 1 and Fig. 3). The relatively weak correlation between the soil Eh and $O_2$ concentration at the swamp was partially due to (1) the limitation of the diffusion chamber technique that the equilibrium between the chambers and surroundings may take longer time to reach at the swamp and (2) the error in $O_2$ analysis using a sample loop for sample injection to the GC where contamination with the ambient $O_2$ (21%) is unavoidable, especially for the swamp samples with lower $O_2$ concentration (less than 10%). Thus, the soil $O_2$ concentrations measured at the swamp were likely higher than the actual values. There was almost no overlap in the range of the soil Eh and $O_2$ concentration between the ridge and swamp under all hydrological conditions studied (Figs. 2 and 3). The transition soil spanned almost the entire range of soil Eh and $O_2$ concentration due to water table fluctuations. However, the soil Eh values at the transition never decreased below +20 mV (Table 1), indicating that the reducing conditions at this location could only be established for a short period of time.

### *3.3. Soil greenhouse gas concentrations and potential exchange with the atmosphere*

Due to the distinct Eh characteristics of the study site, soil greenhouse gas concentrations at the three locations were plotted against the soil Eh with a vertical line to denote the critical Eh boundary (about +250 mV) between the ridge and swamp (Fig. 4). On each particular date and location, the lower soil depths generally showed higher concentrations of gas probably because of higher resistance in gas diffusion (and ebullition for the swamp site) through the soil/water layer to the atmosphere when the soil gases were beyond saturation (Chareonsilp et al., 2000). The ability of wetland plants to transport the atmospheric $O_2$ into the root zone has been well documented (Armstrong, 1979; Grosse et al., 1992). Gases produced in soils can be released to the atmosphere through the same pathway (Higuchi, 1982; Yu et al., 1997). However, existing evidence on $O_2$ and greenhouse gas exchange through wetland plants mainly came from the studies on rice with little information on trees available due to technical difficulties, which is also why we couldn't cover this issue.

Both soil and plant root respirations contribute to $CO_2$ production, resulting in a large amount of $CO_2$ accumulation in the soils (Fig. 4A). Significant $CO_2$ emissions through soil/water surface to the atmosphere were expected at all three locations, because the soil $CO_2$ concentrations were 1 or 2 orders of magnitude higher than the atmospheric $CO_2$ level. Substantial increase of the soil $CO_2$ concentration when the soil Eh decreased from +700 to +400 mV was mainly due to slower release of $CO_2$ to the atmosphere at the ridge and transition under higher soil moisture conditions. When the soil Eh was lower than +400 mV, soil $CO_2$ concentrations generally accounted for 4–10% of the soil gas volume, as the balance of (1) increasing soil $CO_2$ concentration due to higher resistance of $CO_2$ release to the atmosphere under higher soil moisture conditions and (2) deceasing soil $CO_2$ concentration due to less $CO_2$ production from anaerobic soil (Yu and Patrick, 2003)

Table 1
Linear regression between soil redox potentials (Eh) and $O_2$ concentrations

| Gradient location | Soil depth (cm) | Eh range (mV) | $O_2$ range (%) | Linear regression | | |
|---|---|---|---|---|---|---|
| | | | | Equation | $r^2$ | $P$-value[a] ($n$) |
| All | All | −136 to +669 | 0.6–20.5 | $\text{Eh} = 32.5 \times O_2 - 57.8$ | 0.73 | < 0.001 (72) |
| Ridge | All | +219 to +669 | 8.3–20.3 | $\text{Eh} = 28.7 \times O_2 + 99.0$ | 0.46 | < 0.001 (24) |
| Transition | All | +22 to +646 | 2.2–20.5 | $\text{Eh} = 32.2 \times O_2 - 61.1$ | 0.74 | < 0.001 (24) |
| Swamp | All | −136 to +262 | 0.6-12.9 | $\text{Eh} = 12.2 \times O_2 - 12.4$ | 0.14 | 0.070 (24) |
| All | 10 | −136 to +667 | 1.0–20.2 | $\text{Eh} = 37.3 \times O_2 - 119.1$ | 0.82 | < 0.001 (18) |
| All | 20 | −40 to +669 | 1.5–20.5 | $\text{Eh} = 35.2 \times O_2 - 138.8$ | 0.70 | < 0.001 (18) |
| All | 30 | +58 to +646 | 2.3–20.0 | $\text{Eh} = 27.4 \times O_2 + 47.4$ | 0.74 | < 0.001 (18) |
| All | 40 | +22 to +612 | 0.6–20.2 | $\text{Eh} = 30.5 \times O_2 - 34.2$ | 0.75 | < 0.001 (18) |

[a] $P$-value was the statistic of the slope test (SLR) against zero (no relationship).

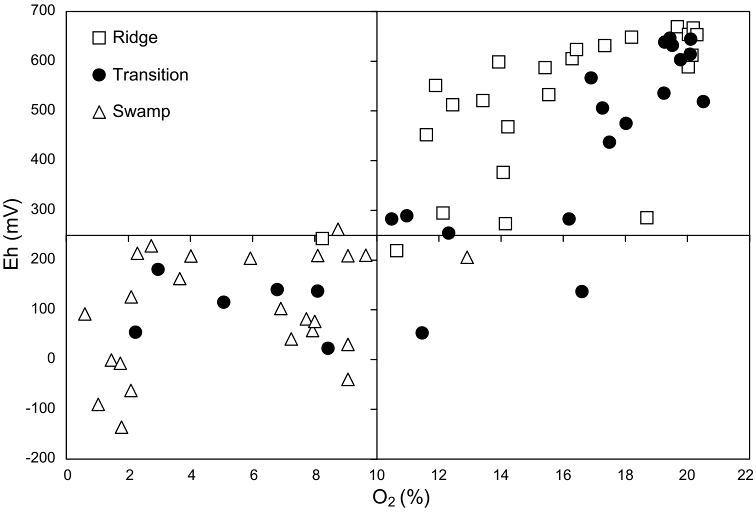

Fig. 3. Measurements of soil redox potential (Eh) and $O_2$ concentrations at the three locations. A distinct boundary was found between the ridge and swamp in soil Eh and $O_2$ concentration. The ridge soil showed an oxidizing characteristic with the $O_2$ concentrations higher than 10% and the Eh values higher than +250 mV, while the swamp soil located in the opposite Eh and $O_2$ range with a reducing characteristic.

and plant root respirations. The $CO_2$ emission to the atmosphere was expected much smaller at the swamp than at the ridge and transition, and largely depended on the water table fluctuations, since the $CO_2$ gradients between the soil and the atmosphere were rather constant at the three locations (Table 2).

Significant $CH_4$ production can only occur under strongly reducing conditions. Critical Eh values for $CH_4$ production in homogenous soils are normally below −150 mV (Cicerone and Oremland, 1988; Yu et al., 2001; Yu and Patrick, 2003). In this study, Eh values of as high as +300 mV seemed to be sufficient to initiate significant $CH_4$ production in the field. Soil $CH_4$ concentrations reached higher than the atmospheric level when the soil Eh was lower than +300 mV, and then increased greatly as the soil Eh decreased further (Fig. 4B). Unlike dispersed soil conditions, the strictly reducing conditions favorable for methanogenesis can be developed in inner soil microenvironment when the surrounding soil Eh is still high. The swamp soils were below this Eh point (+300 mV) in all seasons, but only the lower depths of the ridge soil in the wet season (Fig. 2). The transition soils showed a reducing Eh characteristic favorable for methanogenesis in the wet season, but the Eh level was never below +20 mV (Table 1), indicating the reducing conditions could only exist temporally at this location. In the dry season, however, the ridge and transition soils actually showed a potential of $CH_4$ consumption activity, because more than half of the measurements at the ridge (58%) and transition (50%) showed the soil $CH_4$ concentrations below the atmospheric level (Fig. 4B; Table 2). Methane oxidation in aerated soils has been evaluated for its important role in the global $CH_4$ budget (King, 1992). Such $CH_4$ consumption activity in soils can substantially abate the amount of $CH_4$ emitted to the atmosphere from where it is produced. Therefore, in this study transect, the swamp represented the only major $CH_4$ source to the atmosphere. The strength of $CH_4$ source to the atmosphere for the transition was probably not strong in the wet season, and was partially compensated by the $CH_4$ consumption activity in the dry season. The ridge might act as a net sink of the atmospheric $CH_4$, since the soil $CH_4$ concentrations in the wet season were only slightly higher than the atmospheric $CH_4$ level.

Atmospheric dry and wet depositions (and possible biological nitrogen fixation) represent the only external N source to this oligotrophic natural ecosystem. Unlike fertilized agriculture ecosystems (Armstrong and Davidson, 1990), such a coastal forest is probably not a strong source of $N_2O$ to the atmosphere. Nitrogen cycle is mainly in form of plant internal cycle with a limited external cycle between the standing vegetations and the soils. Nitrification and denitrification activities, as the major sources of $N_2O$, are probably limited by mineral N because of competition with plant assimilation. Soil $N_2O$ concentrations tended to exponentially increase with the soil Eh decrease (a liner relation in the logarithm scale) at the ridge and transition, but decrease with the soil Eh at the swamp (Fig. 4C). Consequently, the average soil $N_2O$ concentrations were higher in the wet season for the ridge and transition, but lower in the dry season for the swamp (Table 2). Such a relationship between the soil $N_2O$ concentration and Eh sug-

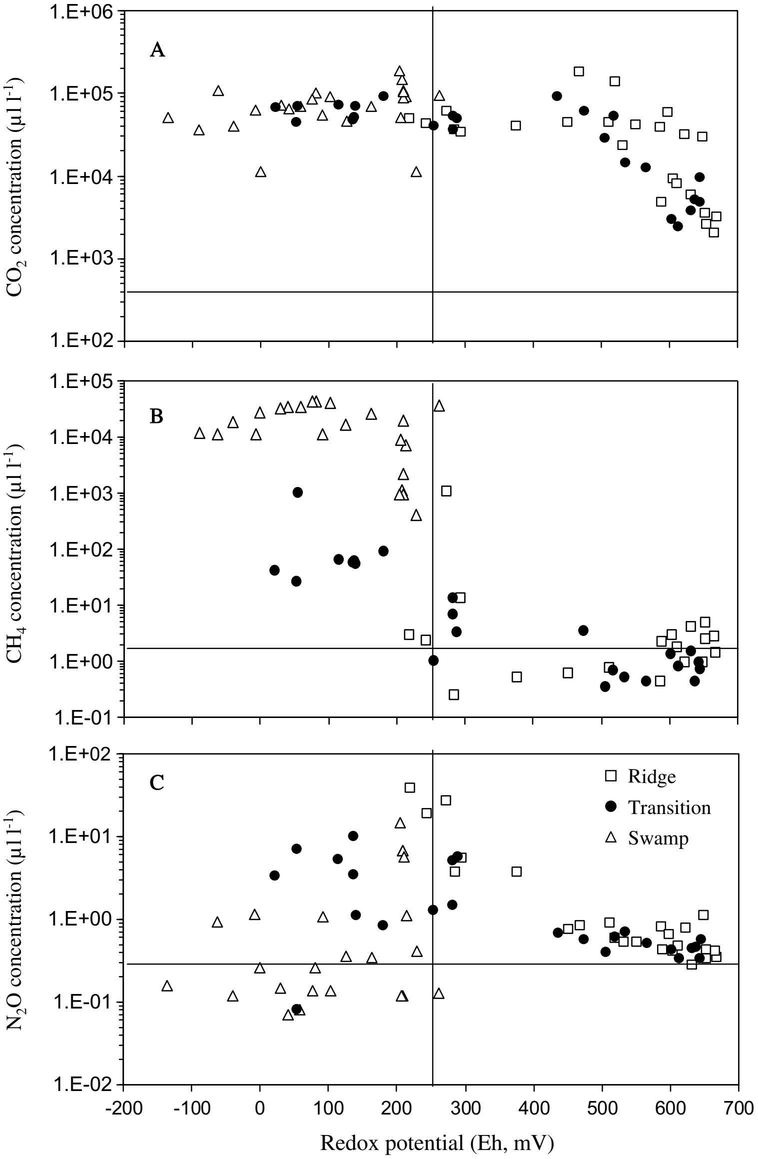

Fig. 4. Soil carbon dioxide, methane and nitrous oxide concentrations at the three locations. The horizontal lines in the three panels of the figure denote the atmospheric concentration (year 1998) of $CO_2$ (365 µl $l^{-1}$), $CH_4$ (1.7 µl $l^{-1}$), and $N_2O$ (0.3 µl $l^{-1}$), respectively (IPCC, 2001).

gested that denitrification was probably the major mechanism for $N_2O$ production (Smith et al., 1983; Yu and Patrick, 2003). The maximum soil $N_2O$ concentration was found at about Eh +250 mV, the boundary Eh between the ridge and swamp, which is in good agreement with the laboratory studies using homogeneous soils (Yu et al., 2001; Yu and Patrick, 2003). Why was the soil Eh level to initiate significant $CH_4$ production in the field (about +300 mV) was much higher than in the laboratory homogeneous soils (about −150 mV), while the maximum soil $N_2O$ concentration was found at approximately the same Eh level (about +250 mV) for both the field and laboratory studies? Microenvironment in structured soil aggregates consists of an outer aerobic layer (characterized with high Eh), and an inner anaerobic, reducing core (characterized with low Eh) (Tiedje et al., 1984). The Eh level in the inner core of the soil aggregates can be low enough for significant methanogenesis to occur when the Eh level at the outer layers and the surroundings still show moderately reducing or even oxidizing characteristics (high Eh). Nitrous oxide can be produced at the outer oxidizing (for

Table 2
Summary of the soil gas measurements

| Location | Season | Mean (median) of soil gas concentration ($\mu l\, l^{-1}$)[a] | | | $CO_2/CH_4$ ratio[b] |
|---|---|---|---|---|---|
| | | $CO_2$ | $CH_4$ | $N_2O$ | |
| Ridge | Dry | $38.8\ (20.0) \times 10^3$ | 1.6 (1.2) | 0.6 (0.5) | $22.6\ (16.7) \times 10^3$ |
| | Wet | $39.2\ (38.3) \times 10^3$ | 132.1 (1.7) | 12.3 (4.6) | $42.1\ (23.2) \times 10^3$ |
| Transition | Dry | $29.0\ (21.3) \times 10^3$ | 2.2 (0.9) | 1.2 (0.6) | $22.2\ (24.4) \times 10^3$ |
| | Wet | $64.1\ (67.8) \times 10^3$ | 177.0 (59.7) | 3.9 (3.4) | $1.1\ (1.1) \times 10^3$ |
| Swamp | Dry | $76.1\ (65.1) \times 10^3$ | $11.9\ (11.3) \times 10^3$ | 2.5 (0.7) | 37.3 (5.8) |
| | Wet | $76.8\ (78.3) \times 10^3$ | $31.5\ (34.5) \times 10^3$ | 0.1 (0.1) | 2.9 (2.3) |
| LSD[c] | Dry | $31.0 \times 10^3$ | $5.0 \times 10^3$ | 1.8 | $18.0 \times 10^3$ |
| | Wet | $14.7 \times 10^3$ | $6.9 \times 10^3$ | 8.6 | $31.1 \times 10^3$ |

[a] Due to skew distribution of some of the original data, median values were also calculated and provided in parenthesis ($n = 16$ for the dry season, $n = 8$ for the wet season).

[b] $CO_2/CH_4$ ratio was the mean (median) value of $CO_2/CH_4$ concentration ratios of each measurement in the soil profiles of each location.

[c] It represents statistically significant different if the difference of the mean values exceeds the LSD.

nitrification) and moderately reducing (for denitrification) layers of the soil aggregates where the soil Eh levels are close to what can be conventionally measured using a Pt-electrode. Large amount of the $CH_4$ produced in the inner core of the soil aggregates is oxidized when it moves through the outer oxidized layers into the soil air before it emits to the atmosphere (Mosier et al., 1986; Khalil et al., 1998). However, $N_2O$ produced at the outer layers probably can move through the oxidizing soil pore space and emit to the atmosphere without significant loss, because $N_2O$ can only be consumed by reduction to $N_2$ (the last step of denitrification) under more reducing conditions. Such an Eh stratification in the soil microenvironment is likely disappeared in continuously flooded soils (e.g., at the swamp) when the entire soils become reducing with low Eh measured. When the reducing conditions in the soils are intense enough, a complete denitrification is likely to occur with $N_2$, instead of the intermediate product of $N_2O$, as the end product. About 54% of the measurements at the swamp showed that the soil $N_2O$ concentrations were lower than the atmospheric level, but such $N_2O$ consumption potential was greatly limited by the flooding nature of the swamp that prevented the atmospheric $N_2O$ from reaching the reducing soils. Global warming potentials (GWP) provide a measure of the cumulative radiative forcing of various greenhouse gases relative to $CO_2$ (IPCC, 2001). If the three greenhouse gases emitted to the atmosphere at the same ratio as found in the soils, $N_2O$ emission would account for less than 4% for the ridge and transition, and almost negligible for the swamp in cumulative GWP (in a 100-year time horizon, both mass and molar GWP conversion factor is 310 for $N_2O$ in $CO_2$ equivalent (IPCC, 2001), because of the same molecular weight of $N_2O$ and $CO_2$).

### *3.4. Concentration ratio of carbon dioxide to methane and its implication in cumulative GWP*

Carbon (C) cycle is of prominent interest for such a coastal forest ecosystem where integrated effects of future sea level rise on C sequestration potential (of both soil and vegetation) and soil greenhouse gas production are unknown. Atmospheric C (in form of $CO_2$) enters into the ecosystem through photosynthesis of the vegetations, and returns to the atmosphere mainly through plant and soil respirations (in form of $CO_2$), as well as through methanogenesis (in form of $CH_4$). We hypothesized that the relative emission ratios of these three greenhouse gases were probably approximate to their concentration ratios in the soils (Fig. 5), which would allow a qualitative analysis of their contributions from the soils. Our preliminary measurements on the surface emission of these three greenhouse gases to the atmosphere showed a good agreement for the $CO_2/CH_4$ ratios at the swamp (but not for the other two sites) where the hydrological condition (continuous flooding, Fig. 2) was relatively constant (unpublished data). Molar ratio of $CO_2/CH_4$ emission to the atmosphere was reported to be about 100 in a marsh field with a 5–15 cm standing water (Whiting et al., 1991), and about 10 in a swamp soil column with the water table close to the soil surface (Moore and Dalva, 1993), which is in the same magnitude as our measurement in the soils (Table 2).

The relative contribution of $CH_4$ to the cumulative GWP of these three greenhouse gases increased dramatically from the ridge to swamp, as indicated by the decrease of soil $CO_2/CH_4$ concentration ratios and generally small quantity of $N_2O$ accumulation (Table 2). The swamp was a significant source of $CH_4$ to the atmosphere in this ecosystem, since the soil Eh was continu-

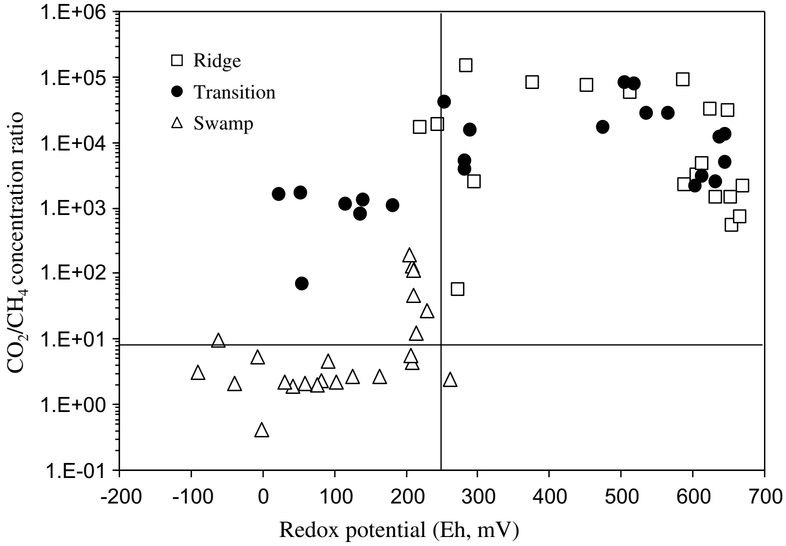

Fig. 5. Ratios of soil carbon dioxide to methane concentrations at the three locations. The horizontal line in the figure denotes the critical $CO_2/CH_4$ concentration ratio (8.4, also equals molar ratio) below which $CH_4$ exceeds $CO_2$ in GWP contribution, based on 1 g of $CH_4$ (molecular weight 16) is equivalent to 23 g of $CO_2$ (molecular weight 44) in GWP on a 100-year basis (IPCC, 2001). Globally, molar ratio of $CO_2/CH_4$ emission is 636.4, based on the estimated annual soil emission of $70 \times 10^{15}$ g $CO_2$–C, and $110 \times 10^{12}$ g $CH_4$–C (Mosier, 1998).

ously low (Fig. 2), and new OM was available from the plant root turnover and annual leaf litter fall (and occasional branch and tree falling). Carbon storage potential in the soils, due to retarded OM decomposition under higher soil moisture conditions as found from the ridge to swamp (Fig. 1A), will be greatly compensated by the increasing $CH_4$ production and emission. Carbon turnover in peatlands that are generally considered as a significant $CO_2$ accumulator is a good example for this case. Globally, annual $CO_2$ accumulation in peatlands is estimated to be $100 \times 10^{12}$ g C (Gorham, 1991) with $CH_4$ emission of $23 \times 10^{12}$ g C (Fung et al., 1991). Such amount of $CH_4$ emission is equivalent to about $190 \times 10^{12}$ g C in GWP (multiplying molar conversion factor 8.4 for $CH_4$, see note in Fig. 5), largely exceeds the annual C accumulation in $CO_2$ equivalent. Increase of the soil OM content from the dry to wet end of this transect (Fig. 1A) suggested a soil C sequestration potential under increasing soil moisture conditions. From dynamic perspective, however, soil C sequestration potential in this coastal forest is likely limited and temporal, because (1) at each location, the soil C content decreased dramatically with the soil depth (Fig. 1A), indicating a significant loss of soil organic C over time. Higher C content found at the upper depths of the soil was mostly maintained by the annual leaf litter fall to replenish the soil C pool; (2) future increase of the soil C content at the ridge, due to increasing soil water content upon sea level rise, will be at the expense of losing soil $CH_4$ consumption potential and increasing soil $CH_4$ production and emission; (3) C pool in the standing vegetations may be relatively constant at the ridge over a century time frame. The survey on stand composition and structure at the same study transect showed that the mean stem size were getting smaller, and stem densities getting greater from the ridge to swamp with similar total basal area ($m^2\,ha^{-1}$) at the three locations (Denslow and Battaglia, 2002).

Sea level rise, carbon sequestration, and greenhouse gas productions and emissions in wetlands are interrelated through multiple biogeochemical processes that will vary depending on wetland type and hydrological regime. The dynamic nature of this study site in response to water table fluctuations across a hydrological gradient makes it an ideal model of impact of future sea level rise to coastal ecosystems. Soil Eh will be a key factor to monitor across this gradient over time as relative sea level continues to rise rapidly in this region. The transition zone will be the most vulnerable to changes in hydrological conditions. More frequent and prolonged flooding in the transition is expected in the future, which will ultimately make the transition function as the present swamp in about half a century. Future studies on change of carbon storage in both soils and vegetations, and greenhouse gas emissions to the atmosphere will improve our understanding of the ecological functions and feedbacks of coastal wetlands and their role in global climate change.

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