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Component greenhouse gas fluxes and radiative balance from two deltaic marshes in Louisiana: Pairing chamber techniques and eddy covariance

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RESEARCH ARTICLE

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Key Points:

- A brackish marsh was a source and a freshwater marsh was a sink for net ecosystem fluxes of C
- CH₄ and CO₂ emission estimates were different using eddy covariance versus static flux chambers
- Radiative balance of marshes varied by accounting technique applied

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Component greenhouse gas fluxes and radiative balance from two deltaic marshes in Louisiana: Pairing chamber techniques and eddy covariance

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Abstract Coastal marshes take up atmospheric CO₂ while emitting CO₂, CH₄, and N₂O. This ability to sequester carbon (C) is much greater for wetlands on a per area basis than from most ecosystems, facilitating scientific, political, and economic interest in their value as greenhouse gas sinks. However, the greenhouse gas balance of Gulf of Mexico wetlands is particularly understudied. We describe the net ecosystem exchange (NEE_c) of CO₂ and CH₄ using eddy covariance (EC) in comparison with fluxes of CO₂, CH₄, and N₂O using chambers from brackish and freshwater marshes in Louisiana, USA. From EC, we found that 182 g C m⁻² yr⁻¹ was lost through NEE_c from the brackish marsh. Of this, 11 g C m⁻² yr⁻¹ resulted from net CH₄ emissions and the remaining 171 g C m⁻² yr⁻¹ resulted from net CO₂ emissions. In contrast, -290 g C m⁻² yr⁻¹ was taken up through NEE_c by the freshwater marsh, with 47 g C m⁻² yr⁻¹ emitted as CH₄ and -337 g C m⁻² yr⁻¹ taken up as CO₂. From chambers, we discovered that neither site had large fluxes of N₂O. Sustained-flux greenhouse gas accounting metrics indicated that both marshes had a positive (warming) radiative balance, with the brackish marsh having a substantially greater warming effect than the freshwater marsh. That net respiratory emissions of CO₂ and CH₄ as estimated through chamber techniques were 2–4 times different from emissions estimated through EC requires additional understanding of the artifacts created by different spatial and temporal sampling footprints between techniques.

1. Introduction

CO₂ is currently building in the atmosphere at a rate of approximately 1.9 ppm yr⁻¹, representing roughly 45% (4 of 8.6 Pg C yr⁻¹) [Ciais *et al.*, 2013] of the CO₂ being emitted from anthropogenic activities such as fossil fuel combustion, cement production, and land use change [Ciais *et al.*, 2013]. CO₂ is responsible for the majority of the current global warming trend [Archer, 2010], and overall, approximately 68 Pg C yr⁻¹ results from global soil CO₂ emissions [Raich and Schlesinger, 1992]. Similarly, CH₄ concentrations have risen at roughly 0.013 Pg C yr⁻¹ [Ciais *et al.*, 2013], with this increase accounting for approximately 25% of the current global warming trend [Archer, 2010], due in large part to the high radiative efficiency of CH₄.

A discussion of wetland processes has long been germane to climate issues because wetlands emit 20–25% of CH₄ globally to the atmosphere [Whalen, 2005], but wetlands are also particularly efficient CO₂ sinks. Peatlands alone store approximately 16–33% of the terrestrial soil carbon pool yet occupy only about 3% of the Earth's surface [Gorham, 1991; Bridgman *et al.*, 2006]. However, the climatic influence of a particular wetland (i.e., does a site have a net warming or cooling effect?) depends on the rate and direction of greenhouse gas fluxes as well as the time frame of interest. The radiative balance of a site may be positive (i.e., net warming) over a defined time period, but wetlands that sequester C will eventually become net radiative sinks, with that time frame ranging from decades to thousands of years depending on the ratio of net CO₂ uptake to emissions of CH₄ and N₂O [Frolking *et al.*, 2006; Neubauer, 2014]. Greenhouse gas fluxes and climatic influences for specific wetlands could change rapidly with shifts in the oxidation of soil C stores, acute emissions from storms or human activity, increased microbial respiration, and increased root respiration [Hanson *et al.*, 2000]. Furthermore, ecosystem respiration (from both CO₂ and CH₄) often intensifies as atmospheric CO₂ concentrations rise [Meronigal and Schlesinger, 1997; Schlesinger and Andrews, 2000].

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How we assess C sequestration relative to the climatic influence of wetland ecosystems is critical. Many techniques developed for measuring greenhouse gas emissions are more useful in upland systems, where CO₂ flux from soil and organic matter provides a major component of the radiative C flux [Raich and Schlesinger, 1992]. Even in upland systems, rates of greenhouse gas fluxes vary widely among location and among the technique used [e.g., Edwards and Sollins, 1973; Cropper et al., 1985; Raich et al., 1990; Knoepp and Vose, 2002; Rochette et al., 1992, 1997]; variability in the assessment of greenhouse gas flux is indeed inherent to the process. Accurately assessing spatial variation in greenhouse gas emissions is particularly problematic in wetlands, where diverse biogeochemical conditions (i.e., anoxic to suboxic soils) and hydrological regimes (i.e., seasonally, permanently, and tidally flooded) produce not only CO₂ emissions but also CH₄ emissions in appreciable quantities. The majority of wetland greenhouse gas studies also use single techniques, which limit assessments to a specific scale.

However, comparisons of greenhouse gas fluxes at different spatial scales, e.g., hundreds of square meters or greater with eddy covariance methods versus ~1 m² with chambers [Christensen et al., 1996; Norman et al., 1997; Teh et al., 2011; Budishchev et al., 2014], are particularly valuable, can provide insight into which components of the ecosystem might be contributing to specific gas emissions, may differ considerably, and are scarce in wetlands [Mejjide et al., 2011]. For example, CH₄ emissions are often routed through vegetation [Garnet et al., 2005; Pangala et al., 2013], a process discernable only at small spatial scales. Yet the cumulative balance of CO₂:CH₄ exchange across an entire wetland (per hectare) and net ecosystem exchange of carbon (NEE_c) are best determined through larger scale approaches, such as eddy covariance. We often use chambers to represent components of NEE_c across large spatial scales. Although other studies have assessed NEE_c of CO₂ in natural tidal, restored, and agricultural wetlands through eddy covariance techniques [Kathilankal et al., 2008; Rocha and Goulden, 2009; Moffett et al., 2010; Hatala et al., 2012; Schäfer et al., 2014; Artigas et al., 2015; Anderson et al., 2016], there are limited studies from the northern Gulf Coast region that can be drawn upon to understand C sequestration of coastal wetlands versus the influence that those wetlands might have on the climate by releasing greenhouse gases. The existing greenhouse gas flux data for the northern Gulf Coast region are from chamber studies, and it is uncertain whether these studies are representative of broad-area fluxes from brackish and freshwater marshes.

In this study, we measured NEE_c of CO₂ and CH₄ using eddy covariance (hereafter, eddy covariance (EC)) techniques for two marsh types in coastal Louisiana. Simultaneously, we measured and modeled rates of respiratory CO₂, CH₄, and N₂O fluxes through small chambers. We wanted to explore three questions relative to brackish and freshwater marshes. First, how do rates and patterns of NEE_c and soil/vegetation respiratory fluxes of C and N₂O differ seasonally to influence carbon dynamics for each marsh? Second, how do estimates of CH₄ and CO₂ emissions differ between EC and chamber techniques? Third, how do these marshes contribute to radiative forcing through suppressing or enhancing greenhouse gas emissions when assessed over broad spatial scales?

2. Methods

2.1. Study Sites

This study focuses on two marsh sites in coastal Louisiana (Figure 1). Both sites were selected with three primary criteria in mind. First, both sites needed to be representative of similar marsh types in Louisiana. The coastal zone of Louisiana has approximately 2144 km² of brackish marsh and approximately 2837 km² of freshwater marsh [Enwright et al., 2015], and both sites have vegetation assemblages and hydrological signatures consistent with these wetland types. Many brackish marshes in Louisiana dominated by *Spartina patens* (Aiton) Muhl. are undergoing stress and peat collapse from persistent submergence and salt-water intrusion [DeLaune et al., 1994], and our brackish marsh is representative of such deterioration. Second, marsh coverage needed to be fairly continuous within a circular radius of approximately 200 m (12.5 ha) to attempt EC measurements and avoid open water. Third, sites needed to be accessible both in the physical and legal sense.

The first site (hereafter referred to as “brackish marsh”) is adjacent to Pointe-aux-Chenes Wildlife Management Area (WMA), approximately 24 km southeast of Houma (29°30′04.77″N; 90°26′41.65″W; Coastwide Reference Monitoring System (CRMS-Wetlands) site 2825). Soils are organic (40–70% organic content) with low bulk density

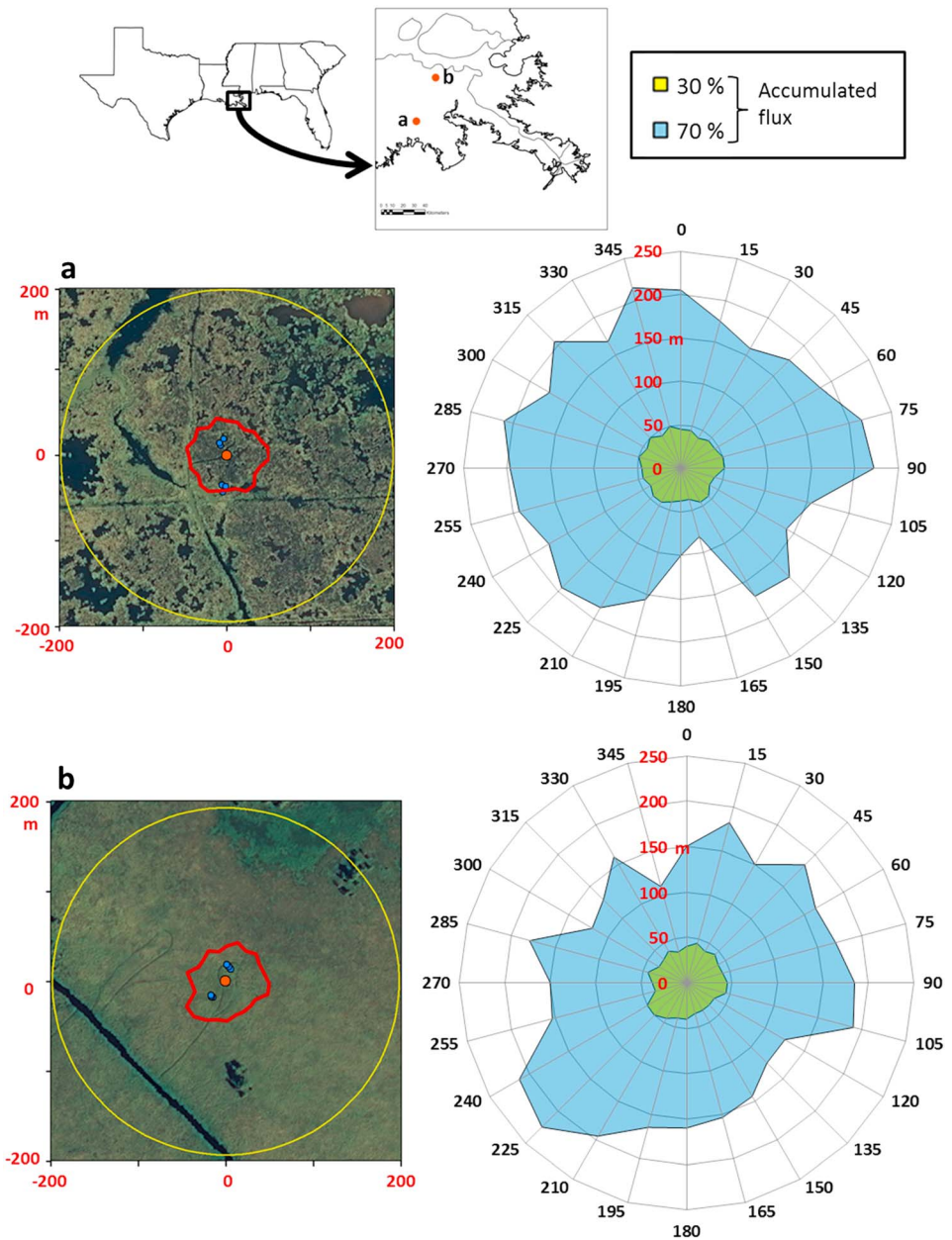


Figure 1. (a) Location of the brackish marsh study site adjacent to Pointe-aux-Chenes Wildlife Management Area (WMA) and (b) location of the freshwater marsh study site at Salvador WMA, Louisiana, USA. (left column) Aerial images depict actual marsh distribution within a 12.5 ha area (yellow circle), the location of the EC tower (orange dot), region corresponding to 30% accumulated fluxes of CO₂ and CH₄ (red polygon), and the location of static flux chambers (blue dots) within the EC footprint. For the (right column) footprint diagram, yellow shading and blue shading correspond to 30% and 70%, respectively, of accumulated NEE_c calculated over the duration of EC measurements.

(<0.2 g cm⁻³) and have a live rooting depth ≤ 30 cm (G. Holm, unpublished data, 2012). The site is characterized as mesohaline (salinity of 9.15 ± 1.5 SE practical salinity unit (psu) during the period of study). Our study was conducted in a fairly intact marsh area dominated by *S. patens*; small areas of open water between vegetation patches are common for *P. patens* marshes in Louisiana (see Figure 1a).

The second site (hereafter referred to as “freshwater marsh”) is on Salvador WMA, which is approximately 19 km southeast of New Orleans (29°51’31.29”N; 90°17’12.80”W; CRMS-Wetlands site 3166). The freshwater marsh (salinity of 0.23 ± 0.1 SE psu during the period of study) is typical of freshwater deltaic plain wetlands [Swarzenski *et al.*, 1991; Sasser *et al.*, 1996] which have semibuoyant mats capable of adjusting to moderate changes in water level.

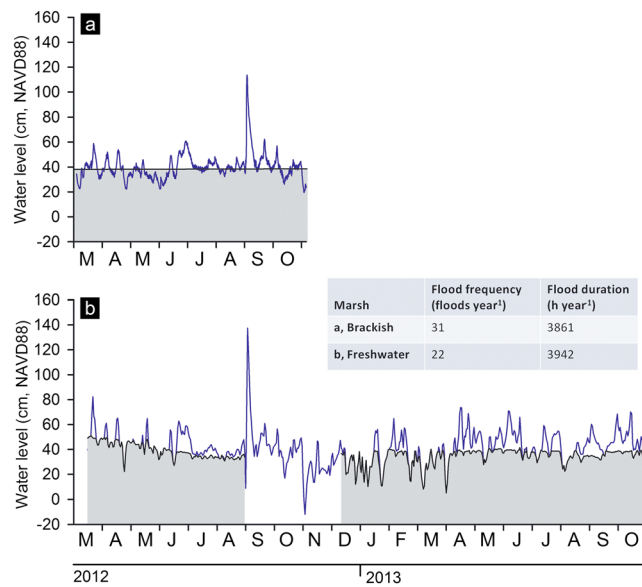


Figure 2. Hydrologic characteristics of the (a) brackish marsh and (b) freshwater marsh for periods where hydrology data overlap with EC and chamber measurements, including hydroperiod summaries (flood frequency and duration). Shaded areas represent water levels below the soil surface, depicting a static surface for the brackish marsh and a dynamic surface for the semibuoyant freshwater marsh, both to approximately NAVD 88. The interval where shading is omitted from the freshwater marsh corresponds to missing vertical motion data for the floating mat (G. Holm, unpublished data, 2012).

The dominant species are *Sagittaria lancifolia* and *Leersia oryzoides*, with patchy areas of *Typha domingensis*. The soils are >75% organic matter with a bulk density of <math> <0.10 \text{ g cm}^{-3}</math>, live rooting depth of up to 60 cm (G. Holm, unpublished data, 2012), and basal peats as deep as 2–4 m [Kosters *et al.*, 1987]. This site is also within the receiving basin of a freshwater diversion (Davis Pond) from the Mississippi River, which is designed to reintroduce seasonal pulses of fresh water, nutrients, and sediments from the river to the Barataria estuary. Our study was conducted in a healthy freshwater marsh with near-continuous vegetation coverage (see Figure 1b).

Both sites are microtidal (range <math> <30 \text{ cm}</math>) with major wind events influencing duration of flooding (Figure 2). Mean annual temperature for coastal Louisiana (Houma) is 20.8°C, with annual means ranging from 15.6 to 26.0°C, and a mean annual rainfall of 1580 mm [U.S. Climate Data, 2016].

2.2. Static Flux Measurements

We used static flux chambers (in the sense of Livingston and Hutchinson [1995]) (hereafter referred to as “chambers”) to measure respiratory fluxes of greenhouse gases (CO₂, CH₄, and/or N₂O) from the soil and through vegetation within 40 m of EC systems operating on the same sites (Figure 1). Two elevated boardwalks were constructed approximately 0.7 m above the marsh surface at each site to prevent investigator disturbance during sampling. A set of three chambers was installed along the two separate boardwalks, for a total of six chambers per site split between two replicate areas ($n=3$ per replicate; $n=2$ replicates). Chambers were placed as far from the boardwalk as possible. The square chambers (29.4 × 29.4 cm or 864 cm²) were made of white plastic material to reflect sunlight and limit heating during sampling, and inserted 5 cm into the soil by cutting through the marsh and sealing edges by pressing cut soils. Chambers were installed and left to settle for 1 month before the first set of measurements were made and left in place between 9 (brackish marsh) and 21 months (freshwater marsh) for a total of 5 and 11 sampling periods, respectively. The chambers were 30.5 cm tall and remained opened when measurements were not underway. Each chamber had small ports (0.64 cm) on each of the four sides just at the soil surface to allow for natural water exchange during tidal cycles when chambers were not being sampled. The holes were plugged with Nalgene stoppers during sampling.

During sampling, portable 27 cm tall tops were placed on the chambers, increasing sample chamber height to approximately 57 cm above the soil. Chamber tops simulate dark conditions allowing little to no light into the chamber. All chambers included existing vegetation on sites; while no vegetation was removed, at times larger plants had to be bent slightly, folded, or cut (infrequently). The top of each chamber base was outfitted with a trough that held water during sampling. Chamber tops were inserted into the water trough to prevent significant egress of gases and were not otherwise vented. Chamber tops were fitted with two brass, 0.9 cm inlets with rubber septa from which gases were collected with a needle and syringe and injected into 5 mL vacuum-evacuated vials. Tygon tubing was attached to each septum and suspended into the chamber at 15 cm below the chamber top. The volume of air in the head space (including tubing) of each chamber was mixed manually by sucking air into a 30 mL syringe and forcefully injecting that air back into the chamber

at the tubing depth of 15 cm at least 3 times prior to each gas extraction to ensure a well-mixed chamber volume. Initial samples were collected seconds before tops were emplaced by lowering the syringe directly to the center of the open chamber approximately 5–10 cm above ground and at intervals of 30 and 60 min thereafter from the chamber inlets. All samples were taken during daylight hours between 1000 and 1600. Samples were transported back to the U.S. Geological Survey (USGS) Wetland and Aquatic Research Center in Lafayette, Louisiana, and analyzed within 24 h for CO₂, CH₄, and N₂O with a multicolumn gas chromatograph (model CP-3800, Varian, Inc., Palo Alto, CA, USA) calibrated using certified standards (Scott Specialty Gases, Inc., Plumsteadville, PA, USA). Rates of flux were determined from the linear portion of fit saturation curves contrasting time with volume-adjusted gas concentrations.

2.3. EC Data Collection and Processing

We used EC techniques to determine NEE_c in the form of CO₂ and CH₄ above the wetland surface. Elevated tripods comprising a Li-Cor closed path CO₂/H₂O sensor (LI-7200), Li-Cor open path CH₄ sensor (LI-7700, Li-Cor Biosciences, Nebraska, USA), and a sonic anemometer (Gill Windmaster Pro, Gill Instruments Ltd, Lymington, England) were installed on both sites. The EC systems were located on 3 × 3 m platforms elevated 1.0 m above the soil surface within uniform wetland areas of similar roughness and a 200 m fetch where wind directions could be accessed in all directions to maximize data capture (Figure 1). Both sites had herbaceous canopy heights of 0.5 to 1.2 m. EC data were collected from 3.4 m and 3.6 m above the soil for the brackish and freshwater marsh sites, respectively; EC system heights were chosen to limit the flux footprint to ≤200 m (70% of the footprint contribution) (Figure 1). EC sensor height was selected with a footprint estimator using the following assumptions: the standard deviation of vertical velocity fluctuations was 0.3 m s⁻¹; surface friction velocity was 0.3 m s⁻¹; planetary boundary layer height was 1000 m; and roughness length was 0.1 m [Kljun *et al.*, 2004].

For EC systems, we report data from 8 October 2011 to 5 December 2012 for the brackish marsh and 15 December 2011 to 18 November 2013 for the freshwater marsh. Raw data were collected at 10 Hz frequency, binned in 30 min data files and downloaded monthly when serviced. All instruments (CO₂/H₂O sensor, CH₄ sensor, and sonic anemometer) were factory calibrated prior to initial deployment and cleaned at 4–6 week intervals. Given the remote nature of the sites, gas quantities needed for the calibration shroud, and adequate environmental stability in the field, the CH₄ sensors were retrieved after 6 months and checked for zero and span in the laboratory using zero grade and 10 ppm CH₄ primary standard gases (MESA Specialty Gases and Equipment, Santa Ana, CA, USA). The CO₂ sensors were checked approximately every 8 weeks in the field with zero certified standard gas and then checked/calibrated for zero and span in the laboratory with zero grade and 500 ppm CO₂ primary standard gases, after 6 months in the field. After 8 weeks, drift due to contamination was biased on the order of ≤35 ppm CO₂. The freshwater site CO₂ sensor malfunctioned and was replaced with a new factory calibrated sensor, resulting in a data gap from 25 July to 9 August 2012. Sensors at both sites were removed from the field prior to Hurricane Isaac resulting in a data gap from 26 August to 5 September 2012. Other intermittent gaps in data for CH₄ and CO₂ were due to data removal when instruments malfunctioned, lost power, were contaminated, or were subjected to poor atmospheric conditions (see below).

Fluxes of CO₂ and CH₄ were determined by incorporating mean air density, mean covariance of instantaneous deviations of vertical wind velocity, and the mixing ratio of CO₂ or CH₄ in the air:

$$f_{\text{CO}_2/\text{CH}_4} = (\overline{p\bar{a}w's'}) \quad (1)$$

where

$f_{\text{CO}_2/\text{CH}_4}$ = CO₂ or CH₄ flux (μmol m⁻² s⁻¹);

$\overline{p\bar{a}}$ = mean air density (μmol air m⁻³);

$\overline{w's'}$ = mean covariance of instantaneous vertical wind velocity and mixing ratio of CO₂ or CH₄ in air;

w' = instantaneous vertical wind velocity (m s⁻¹);

s' = instantaneous mixing ratio of CO₂ or CH₄ in air (μmol gas (μmol air)⁻¹).

We used open source, Eddy Pro 4.0 software [Li-Cor Biosciences, 2012], to process data from EC systems. Data were preconditioned and corrected, and quality control tests were run according to the processing options

Table 1. Methods Used for Conditioning and Correcting 30 min Eddy Covariance Flux Measurements in Eddy Pro Software for Determining CH₄ and CO₂ Fluxes From Brackish and Freshwater Marshes in Louisiana, USA

Data Conditioning, Corrections, and Quality Control	Selection/Method
Compensation for air density fluctuations	<i>Webb et al.</i> [1980] and <i>Ibrom et al.</i> [2007]
Correction for frequency response	<i>Moncrieff et al.</i> [1997, 2004]
Axis rotation for sonic anemometer tilt correction	Double rotation
Detrending of raw time series	Block averaging
Time lag compensation between wind and gas terms	Time lag optimization and maximum covariance
Statistical control tests for fluxes	<i>Vickers and Mahrt</i> [1997]
Quality control tests for fluxes	<i>Foken et al.</i> [2004] and <i>Göckede et al.</i> [2008]
Flux footprint estimation	<i>Kljun et al.</i> [2004] and <i>Kormann and Meixner</i> [2001]

defined in Table 1 [see also *Holm et al.*, 2016]. Data were subjected to two quality control tests for steady state and turbulence (based on *Foken and Wichura* [1996], *Foken et al.* [2004], and *Mauder and Foken* [2006]), which determines if the assumptions of the EC method are not strongly violated for a particular half hour. Thus, under this scheme, we retained only data that were flagged “0” (excellent) and “1” (suitable for general budget estimation), while poor quality data not satisfying these assumptions were discarded. The processed 30 min data resulted in mean CO₂ and CH₄ fluxes, which were filtered further, to eliminate potentially spurious values based on the following thresholds: CH₄ < -0.1 and >0.5 μmol m⁻² s⁻¹; CO₂ < -25 and >20 μmol m⁻² s⁻¹; sensible heat < -100 and >500 W m⁻²; and latent heat < -100 and >600 W m⁻². Half-hourly fluxes were also removed during periods of heavy precipitation, sensor contamination (<15% signal strength for CH₄ and automatic gain control >70% CO₂/H₂O), and extreme friction velocity events (0.05 > u* > 1.5 m s⁻¹). Most of the data that were retained for analysis (i.e., >80%) had a friction velocity > 0.1 m s⁻¹. Other studies, with level terrain and short canopy (e.g., prairie, pasture, and grassland) similar to our study, have demonstrated that flux data were considered reliable also during relatively low friction velocity (u* < 0.1 m s⁻¹) compared to other sites (e.g., forested and tall canopy) [*Gu et al.*, 2005; *Papale et al.*, 2006; *Meijide et al.*, 2011; *Wolf et al.*, 2011; *Galvagno et al.*, 2013].

To develop daily integrated CO₂ estimates, missing 30 min data were gap filled with an algorithm [*Reichstein et al.*, 2005], which used the covariance of meteorological variables and the covariance of fluxes to provide an estimate of CO₂ flux based on similar meteorological conditions for those 30 min periods. All algorithm calculations based on *Reichstein et al.* [2005] were processed using the eddy covariance gap-filling and flux-partitioning tool (Max Planck Institute for Biogeochemistry, <http://www.bgc-jena.mpg.de/~MDIwork/eddyproc/>, accessed 4 April 2016). The algorithm provided estimates of ecosystem respiration (R_{eco}) and gross ecosystem production (GEP) based on the short-term temperature sensitivity of respiration in order to extrapolate respiration from nighttime to daytime periods. We selected air temperature from the EC tower (T_{a-tower}) as the input for flux partitioning instead of water/soil temperature given the more complete data stream of T_{a-tower}.

The gap-filled data were assigned a Quality of A, B, or C (high, medium, and low, respectively) based on availability of meteorological data and the time window of extrapolation. Further description of the flux-partitioning and gap-filling method is described by *Reichstein et al.* [2005]. For the brackish marsh there were a total of 20,399 half-hourly CO₂ measurements, of which 10,931 were gap filled, resulting in 53.6% rejected. Of these gap-filled data, 64%, 16%, and 20% were categorized as Filling Quality A, B, and C, respectively. For the CO₂ data from the freshwater marsh, there were a total of 35,328 half-hourly measurements, of which 16,986 fluxes were gap filled, resulting in 48.1% rejected. Of these gap-filled data, 65%, 20%, and 15% were categorized as Filling Quality A, B, and C, respectively. We rejected 10–18% more CO₂ and CH₄ half-hourly measurements at night than during the day for the brackish marsh and 21–23% more measurements at night than during the day for the freshwater marsh.

Uncertainties were estimated for gap-filled data based on average standard deviations by simulating gaps and applying gap-filling procedures in comparison to actual data retained using online algorithms. Uncertainty for NEE_c is provided for each 30 min interval, and overall annual model uncertainty for actual versus gap-filled data was calculated using a derivation of *Shoemaker et al.* [2015], assuming random uncertainty is part of the 30 min uncertainty term provided by the eddy covariance gap-filling and flux-partitioning tool:

$$U = \sqrt{\sum_{t=0}^{\text{year}} (\text{SE}^2)}. \quad (2)$$

where U is annual uncertainty in NEE_c ($\text{g C m}^2 \text{ yr}^{-1}$) and SE ($\text{g C m}^2 \text{ d}^{-1}$) is the average of 30 min uncertainty values (error) scaled to daily values. For the brackish marsh, maximum U was $67.9 \text{ g CO}_2\text{-C m}^2 \text{ yr}^{-1}$ for 2011 and 2012, ranging from 11.8 to 13.2% of NEE_c . For the freshwater marsh, maximum U was $43.4 \text{ g CO}_2\text{-C m}^2 \text{ yr}^{-1}$ for 2012 and 2013, ranging from 10.5 to 13.2% of NEE_c .

Given the complications of developing subdaily CH_4 correlations with hydrometeorological data [Shoemaker *et al.*, 2015], 30 min CH_4 fluxes were averaged by day to estimate daily flux. To gap fill missing days, stepwise regression analysis was performed using meteorological and environmental covariates to predict daily CH_4 flux (see *Statistical Analysis*) [Holm *et al.*, 2016]. Of the 30 min CH_4 samples collected using EC, we retained 38% from the brackish marsh and 55% from the freshwater marsh. Predicted to observed error based on daily CH_4 fluxes equated to 14.3% (or $1.5 \text{ g CH}_4\text{-C m}^2 \text{ yr}^{-1}$) of NEE_c of CH_4 for the brackish marsh and 19.5% (or $9.1 \text{ g CH}_4\text{-C m}^2 \text{ yr}^{-1}$) of NEE_c of CH_4 for the freshwater marsh [Holm *et al.*, 2016].

2.4. Meteorological and Environmental Measurements

In addition to $T_{a\text{-tower}}$, we installed two combination air and soil temperature probes. Air temperature was also measured just at the top of the marsh grass ($T_{a\text{-marsh}}$) and soil temperature (T_s) was measured just below the soil surface (10 cm) near each boardwalk at 15 min intervals using a data logger (model HOBO Pro v.2, Onset Computer Corp., Bourne, MA, USA). Water vapor mole fraction and relative humidity was measured with the LI-7200. Vapor pressure deficit (D) was then calculated as the difference between ambient water vapor partial pressure (derived from the ideal gas law, using ambient water vapor mass density, the water vapor gas constant, and temperature) and the water vapor partial pressure at saturation. On-site water table depth (WTD) was measured at hourly intervals on each site using a continuous water level recorder (model #138, Infinities USA Inc., Port Orange, FL, USA) inserted into a 7.6 cm diameter PVC pipe to a soil depth of approximately 0.8 m. Continuous in-stream salinity, water temperature (T_w), and supplemental water level data (water elevation) from the brackish marsh were acquired from CRMS-Wetlands Station 2825 and from the freshwater marsh were acquired from CRMS-Wetlands Station 3166. All elevations relative to North American Vertical Datum (NAVD 88) were acquired from CRMS-adjusted water levels. Discharge data from the Davis Pond Mississippi River diversion, which influences the freshwater marsh at Salvador WMA, came from U.S. Geological Survey Station 295501090190400 near Boutte, Louisiana. Photosynthetically active radiation (PAR) data were derived from the nearest UV-B Monitoring and Research Program (UVMRP) site in Baton Rouge, Louisiana.

2.5. Analyses

2.5.1. Statistical Analyses

All data were analyzed using SAS (Version 9.1, SAS Institute, Cary, North Carolina, USA). For chamber data, differences by site in instantaneous elemental fluxes (g C or N) of CO_2 , CH_4 , and N_2O over time were determined ($n = 6$ per day) at hourly intervals (e.g., $\text{g C m}^2 \text{ h}^{-1}$) using a repeated measures analysis of variance. Chamber data were then converted to daily flux rates through summation and analyzed as elemental flux rates per unit area at daily intervals (e.g., $\text{g C m}^{-2} \text{ d}^{-1}$).

For EC measurements, gap filling 30 min CO_2 data produced a continuous data set for all days. Specifically, the meteorological variables sensible heat, latent heat, PAR, $T_{a\text{-tower}}$, T_s , relative humidity, and D were used in combination to gap fill. For days with no acceptable CH_4 data, missing data were estimated by interpolation based upon statistically significant relationships between daily CH_4 flux and measured meteorological or environmental variables [Holm *et al.*, 2016]. Daily CH_4 fluxes exhibited the strongest correlation ($p < 0.001$ for all) with T_w , T_s , salinity, and $T_{a\text{-tower}}$ for the brackish marsh, and with T_w , T_s , salinity, $T_{a\text{-tower}}$, and discharge from the freshwater diversion at Davis Pond for the freshwater marsh. The residuals of the models selected were then tested for normality and homogeneity of variance ($\alpha = 0.01$) and further tested for autocorrelation, and then an appropriate autoregressive integrated moving average model was fit ($\alpha = 0.01$).

2.5.2. Formulation for Daily Gas Flux Determinations From Chambers

To scale chamber fluxes, linear correlation analyses were first conducted on daily fluxes versus average T_s , $T_{a\text{-marsh}}$, $T_{a\text{-tower}}$, and WTD. Linear correlations were retained and further tested using square root and natural logarithmic transformations of these variables, along with salinity, discharge, and T_w data when applicable, over quarterly time intervals (Q) to improve model fit using stepwise multiple regression procedures (Proc GLMSelect). Q was defined as March to May, June to August, September to November, or December

to February. Groupings for Q corresponded to time periods when fluxes were similar, reflecting seasonal activity in these fluxes. When significant, multifactorial models were used to predict chamber fluxes of CO_2 , CH_4 , and N_2O on an annual basis. Otherwise, hourly flux data were summed to yield daily fluxes.

Q and T_s were useful for predicting CO_2 fluxes from the brackish marsh:

$$\text{CO}_2 = [-37555.41 + Q + 12001.18 \times \ln(T_s + 1)]/1000, \quad (3)$$

where CO_2 is in $\text{g C m}^{-2} \text{d}^{-1}$, T_s is in $^\circ\text{C}$, and Q equals 2567.29 for predictions from March to May and 0.00 for predictions from June to August for the period sampled ($R^2 = 0.83$; $p = 0.002$). No significant equations were identified for CH_4 or N_2O from the brackish marsh so we were not able to predict these fluxes for days not sampled.

For the freshwater marsh, the following predictive equation was developed:

$$\text{CO}_2 = [-990.09 + 4.15(T_s)^2 - 123.62(\text{WTD})]/1000, \quad (4)$$

where CO_2 is in $\text{g C m}^{-2} \text{d}^{-1}$ and WTD is in centimeters ($R^2 = 0.79$; $p < 0.001$). Q was not significant such that equation (4) can be used for prediction throughout the year. In contrast, fluxes of CH_4 from the freshwater marsh were affected by Q and mean WTD:

$$\text{CH}_4 = [211.67 + 14.297(\text{WTD}) + Q]/1000, \quad (5)$$

where CH_4 is in $\text{g C m}^{-2} \text{d}^{-1}$ and Q describes a step function equating to 156.25 for predictions from March to May, -68.56 for predictions from June to August, -12.36 for predictions from September to November, and 0.00 for predictions from December to February ($R^2 = 0.79$; $p < 0.001$). No significant predictive equations were identified for N_2O from the freshwater marsh, so we were not able to predict these fluxes for days not sampled.

3. Results

3.1. Hydrological Characterization

Available hydrologic records over the study period indicated that major pulses of high water transcended the coastline to affect both brackish and freshwater marsh sites simultaneously, especially during a southern swell (June) and tropical storm event in late August (Hurricane Isaac) of 2012 (Figure 2). For the southern swell event, water levels increased by about 20 cm on both sites and persisted for approximately 1 month without dewatering, while the surge from Hurricane Isaac caused approximately 70–100 cm of flooding, gradually decreasing over the following week. While sites differed considerably in salinity regime— <0.5 versus 9 psu—mean flood frequency differed by only nine events per year. The freshwater marsh influenced by a freshwater diversion at Salvador WMA was flooded for only 81 hr^{-1} more than the brackish marsh at Pointe-aux-Chenes WMA, which had no diversion. An additional difference was that the surface of the freshwater marsh was semibuoyant (Figure 2), a common condition of this marsh type in Louisiana. While these sites are characterized as tidal (micro-), diurnal fluctuations are more obvious for the brackish marsh than for the freshwater marsh, which was dominated by wind tides. On-site, realized tidal range was extremely low for both sites (Figure 2).

3.2. Instantaneous CO_2 , CH_4 , and N_2O Fluxes From Chambers

Instantaneous fluxes of CO_2 ranged from 0.027 to 0.188 $\text{g C m}^{-2} \text{h}^{-1}$ among five measurement periods for the brackish marsh and from -0.065 to 0.135 $\text{g C m}^{-2} \text{h}^{-1}$ among 11 measurement periods for the freshwater marsh (Figure 3). Fluxes of CO_2 differed significantly over time for both the brackish ($F = 17.35$; $p = 0.002$) and freshwater marsh ($F = 32.13$; $p < 0.001$), highlighting a net efflux of CO_2 from chambers most prominently in April–June. In fact, only once was CO_2 taken up during dark chamber measurements (freshwater marsh in March 2012), perhaps related to site flooding.

Neither fluxes of CH_4 ($p = 0.094$) nor fluxes of N_2O ($p = 0.166$) differed significantly over time for the brackish marsh. Measurements for both were most variable in May 2012 (Figure 3) when marsh vegetation established high biomass for the first time that season and flooding was persistent. Fluxes of CH_4 ($F = 14.35$; $p < 0.001$), but not N_2O ($p > 0.05$), differed over time for the freshwater marsh and were highest in March and April of 2012. Fluxes of CH_4 ranged from 0.001 to 0.026 $\text{g C m}^{-2} \text{h}^{-1}$ for the brackish marsh and from 0.002 to 0.029 $\text{g C m}^{-2} \text{h}^{-1}$ for the freshwater marsh, while fluxes of N_2O ranged from -32.0 to 54.5 $\mu\text{g N m}^{-2} \text{h}^{-1}$

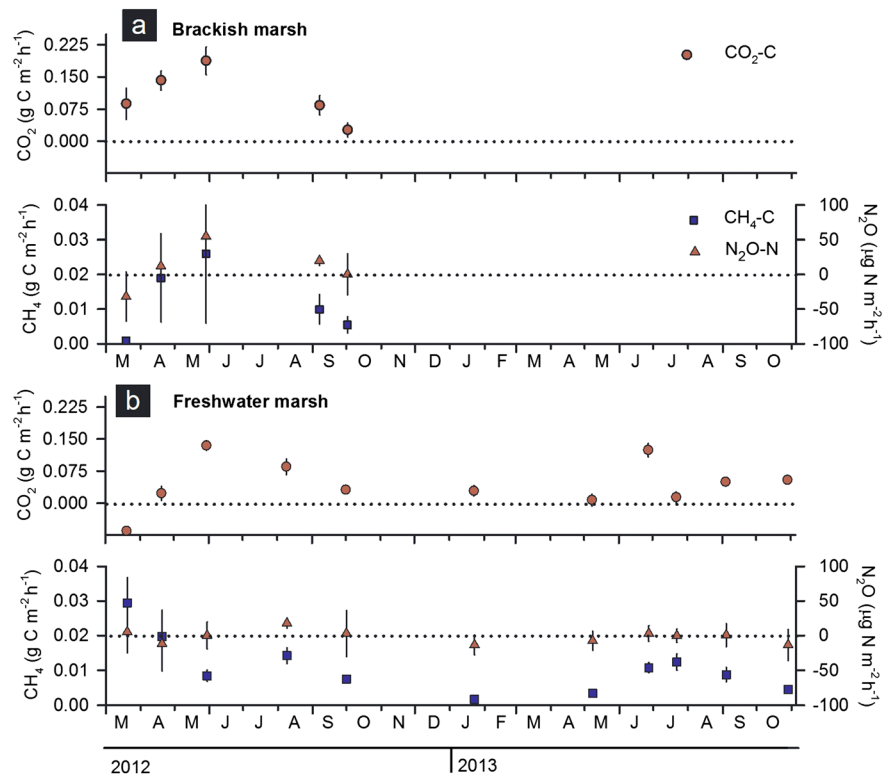


Figure 3. Mean instantaneous, hourly elemental chamber fluxes (± 1 SE) of gaseous carbon (CO_2 and CH_4) and nitrogen (N_2O) from (a) brackish marsh and (b) freshwater marsh study sites in Louisiana. Negative CO_2 , CH_4 , or N_2O flux values signify uptake by the marsh; positive values signify emissions from the marsh.

for the brackish marsh and from -13.7 to $17.9 \mu\text{g N m}^{-2} \text{h}^{-1}$ for the freshwater marsh (Figure 3). While CH_4 fluxes were consistently positive and vectored out of the soil, N_2O fluxes were bidirectional.

Correlation analysis was used to identify the meteorological and environmental variables influencing CO_2 , CH_4 , and N_2O fluxes through chambers. For the brackish marsh, two meteorological variables were autocorrelated, $T_{a\text{-marsh}}$ related to both T_s and $T_{a\text{-tower}}$ (Table 2). Of the three greenhouse gases measured by chambers, CO_2 was the only gas that correlated linearly to a meteorological or environmental variable, in this case WTD. More exposed soils (i.e., lower WTD) gave rise to greater fluxes of CO_2 . CH_4 and N_2O correlated to nothing for the brackish marsh site (Table 2). For the freshwater marsh, the same meteorological variables that autocorrelated for the brackish marsh were observed, as well as two additional variables (Table 2), where $T_{a\text{-tower}}$ also correlated with T_s . In addition, WTD correlated positively to CH_4 fluxes and negatively to CO_2 fluxes (Table 2), indicating that lower water tables give rise to greater CO_2 fluxes relative to CH_4 fluxes from chambers as soils became more exposed. Fluxes of N_2O did not correlate to any meteorological or environmental variable.

3.3. Daily Fluxes of CO_2 , CH_4 , and N_2O From Chambers

Over the record of chamber measurements, modeled daily CO_2 fluxes from the brackish marsh mirrored seasonal patterns from instantaneous measurements in being highest in May–June, ranging from -1.78 to $5.11 \text{ g C m}^{-2} \text{ d}^{-1}$. We were not able to determine CH_4 fluxes through modeling. However, based on individual hourly samples summed (Figure 3), CH_4 fluxes from the brackish marsh averaged $0.14 \text{ g C m}^{-2} \text{ d}^{-1}$; this includes the exclusion of two outlier values (>3 standard deviation of mean) from individual chambers over time. From the freshwater marsh, modeled CO_2 fluxes ranged from -5.38 to $3.83 \text{ g C m}^{-2} \text{ d}^{-1}$ and CH_4 fluxes ranged from -0.02 to $0.95 \text{ g C m}^{-2} \text{ d}^{-1}$ through chambers.

N_2O fluxes through chambers were very low for both marshes and also had to be estimated based on individual hourly samples summed. Despite fewer samples for the brackish marsh than for the freshwater marsh,

Table 2. Pearson Correlation Coefficients and *p* Values for Daily Averaged Soil Greenhouse Gas Fluxes of CO₂, CH₄, and N₂O Collected From Static Flux Chambers Versus Mean Daily Soil Temperature (*T_s*), Air Temperature Measured Just Above the Marsh (*T_{a-marsh}*), Air Temperature at the Eddy Covariance Tower (*T_{a-tower}*), and Water Table Depth (WTD) for (A) a Brackish Marsh Adjacent to Pointe-Aux-Chene WMA and (B) a Freshwater Marsh on Salvador WMA, Louisiana, USA^a

	(A) Brackish Marsh							(B) Freshwater Marsh						
	CH ₄	CO ₂	N ₂ O	<i>T_s</i>	<i>T_{a-marsh}</i>	<i>T_{a-tower}</i>	WTD	CH ₄	CO ₂	N ₂ O	<i>T_s</i>	<i>T_{a-marsh}</i>	<i>T_{a-tower}</i>	WTD
CH ₄	1.0000	--	--	--	--	--	--	1.0000	--	--	--	--	--	--
CO ₂	0.2059	1.0000	--	--	--	--	--	-0.4253	1.0000	--	--	--	--	--
	0.568							0.062						
N ₂ O	0.4553	0.2130	1.0000	--	--	--	--	-0.0046	0.0669	1.0000	--	--	--	--
	0.186	0.555						0.985	0.779					
<i>T_s</i>	0.1955	0.3897	0.4698	1.0000	--	--	--	0.3227	0.3204	0.3232	1.0000	--	--	--
	0.588	0.266	0.171					0.165	0.168	0.165				
<i>T_{a-marsh}</i>	0.3036	0.4352	0.3608	0.7832	1.0000	--	--	0.3306	0.2917	0.3359	0.9368	1.0000	--	--
	0.394	0.209	0.306	0.007				0.155	0.212	0.148	<0.001			
<i>T_{a-tower}</i>	0.3149	0.5807	0.3225	0.6299	0.9427	1.0000	--	0.3853	0.3327	0.2629	0.9405	0.9794	1.0000	--
	0.376	0.078	0.364	0.051	<0.001			0.093	0.152	0.263	<0.001	<0.001		
WTD	-0.5573	-0.7148	-0.4784	-0.5320	-0.4510	-0.4301	1.0000	0.7867	-0.6706	0.2214	0.3169	0.3214	0.2828	1.0000
	0.094	0.020	0.162	0.114	0.191	0.215		<0.001	0.001	0.348	0.174	0.167	0.227	

^aBold font indicates significant correlations

N₂O fluxes ranged more broadly from the brackish marsh (-420 to 1310 μg N m⁻² d⁻¹ versus -330 to 430 μg N m⁻² d⁻¹ for the freshwater marsh). N₂O fluxes did not differ significantly from 0 on individual sampling days for either the brackish marsh (*t* test, *n* = 10; *p* = 0.359) or the freshwater marsh (*n* = 20; *p* = 0.596).

3.4. Daily Fluxes of CO₂ and CH₄ From EC

Over the record of EC measurements, CO₂ fluxes ranged from -0.91 to 3.15 g C m⁻² d⁻¹ and CH₄ fluxes ranged from -0.01 to 0.15 g C m⁻² d⁻¹ from the brackish marsh (Figure 4). Patterns depict some interannual variability. First, CO₂ emissions were higher in October–November of 2011 than in the same months in 2012. Second, CH₄ emissions were generally highest when CO₂ emissions were lowest, corresponding to periods of low salinity in April–October of 2012 not as prevalent in 2011. Third, *R_{eco}* gradually increased from October 2011 to mid-February 2012 and decreased until March 2012. Then, *T_s* and *T_{a-tower}* increased to an apparent threshold level when rates of *R_{eco}* nearly doubled rapidly over the ensuing 8 days to reach growing season values in April and into the summer.

Accordingly, CO₂ fluxes ranged from -5.92 to 2.39 g C m⁻² d⁻¹ and CH₄ fluxes ranged from -0.06 to 0.42 g C m⁻² d⁻¹ from the freshwater marsh (Figure 5). Patterns were fairly consistent between years. CO₂ uptake was highest in April–August during the active growing season, which did tend to occur slightly before major CH₄ emissions in June–September of 2012. CO₂ uptake and CH₄ efflux coincided much better in 2013. Higher rates of *R_{eco}* tended to coincide with greater CO₂ uptake and higher *T_s* and *T_{a-tower}*. *NEE_c* of CO₂ and *R_{eco}* balanced during winter months, concomitant also with near zero CH₄ fluxes. Furthermore, CH₄ emissions tended to be inversely related to discharge from the Davis Pond diversion, although this is confounded somewhat by the correspondingly lower *T_s* and *T_{a-tower}* during higher winter discharge periods (Figure 5). However, discharge and WTD were not strongly connected for the freshwater marsh site [Holm *et al.*, 2016].

Specific drivers of CH₄ and CO₂ flux are highlighted through univariate analyses (Figure 6). Emissions of CH₄ from both marshes increased exponentially with increasing *T_s*, while CO₂ uptake increased with increased *T_s*, reflecting increased photosynthetic activity by plants on both sites. *D* had no influence on CH₄ emissions or CO₂ flux from the brackish marsh; however, increasing *D* yielded greater CH₄ emissions and CO₂ uptake from the freshwater marsh (Figure 6), highlighting the relative health of the freshwater marsh versus the brackish marsh. Increasing salinity from ~2 to 16 psu decreased CH₄ flux from the brackish marsh, as well as from the freshwater marsh, even though salinity from the freshwater marsh ranged to only 0.41 psu. The relationship between salinity and CO₂ flux was either highly variable without obvious pattern (brackish marsh) or not significant (freshwater marsh). Finally, increased water elevation stimulated CH₄ emissions and CO₂ uptake on both sites, although an inflection from higher to lower CO₂ uptake at water elevations of >0.6 m (NAVD 88) for both sites was observed, highlighting potentially greater flood stress on marsh vegetation growing on both sites.

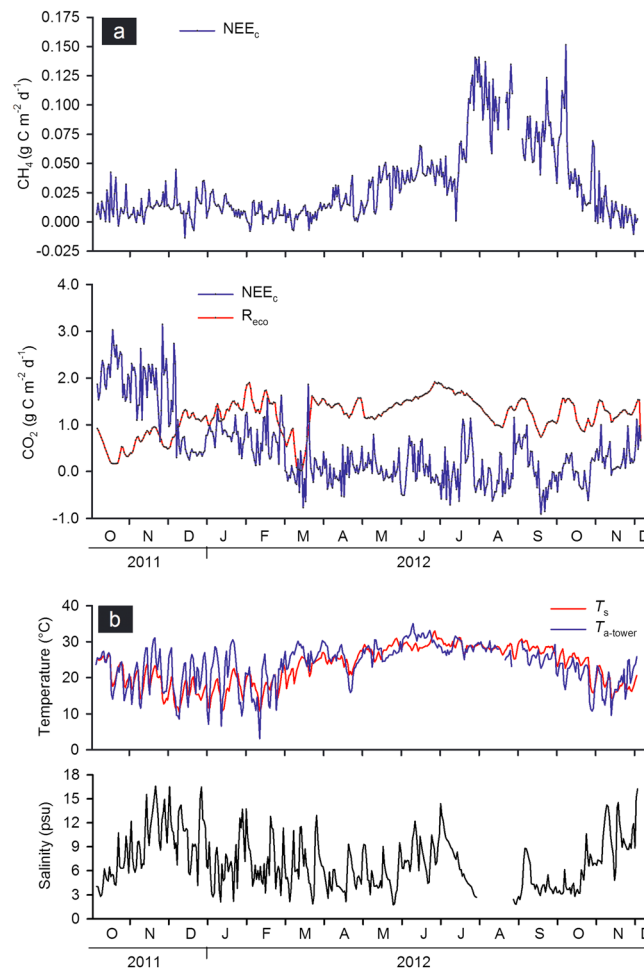


Figure 4. Overview of NEE_c (from EC techniques) for the brackish marsh, Louisiana, USA, including (a) daily elemental fluxes of carbon from CH_4 and CO_2 , along with ecosystem respiration of CO_2 (R_{eco}), and (b) daily summary of relevant meteorological and/or environmental variables, including soil temperature (T_s), air temperature measured from the EC tower ($T_{a-tower}$), and salinity. Negative CO_2 or CH_4 flux values signify uptake by the marsh; positive values signify emissions from the marsh.

Of the NEE_c of $-289.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ taken up by the freshwater marsh, $47.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ was lost from CH_4 emissions and $-337.0 \text{ g C m}^{-2} \text{ yr}^{-1}$ of CO_2 was taken up. R_{eco} emissions of CO_2 were $893.0 \text{ g C m}^{-2} \text{ yr}^{-1}$, suggesting that plant photosynthetic uptake (or \sim GEP) accounts for approximately $-1230.0 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the freshwater marsh. Respiratory CH_4 fluxes from chambers were $91.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ or 26% of chamber CO_2 fluxes of elemental C. Together, CO_2 and CH_4 emissions from chambers equated to $449.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the freshwater marsh and represented only 48% of the combined respiratory emissions of CO_2 ($893.0 \text{ g C m}^{-2} \text{ yr}^{-1}$) plus CH_4 ($47.1 \text{ g C m}^{-2} \text{ yr}^{-1}$) through EC (Table 3). N_2O uptake rate was estimated from chambers as $-0.02 \text{ g N m}^{-2} \text{ yr}^{-1}$ for the freshwater marsh.

4. Discussion

4.1. EC Fluxes of Gaseous C From Coastal Louisiana Marshes and Other Locations

Carbon was emitted to the atmosphere at a rate of $182 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the brackish marsh, comparing favorably with EC-based C emissions assessments from grazed degraded peatlands ($178\text{--}302 \text{ g C m}^{-2} \text{ yr}^{-1}$) [Hatala et al., 2012] and drained agricultural wetlands in the Sacramento-San Joaquin Delta of California

3.5. Annual NEE_c From EC Versus Chamber Fluxes

Daily fluxes from EC and chambers were summed separately over the period of record and annualized. Using EC, the brackish marsh lost $181.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ and the freshwater marsh took up $-289.9 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Table 3). Of the NEE_c of $181.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the brackish marsh, $11.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ is from CH_4 emissions and the remaining $170.6 \text{ g C m}^{-2} \text{ yr}^{-1}$ is from CO_2 emissions. R_{eco} emissions of CO_2 were $434.4 \text{ g C m}^{-2} \text{ yr}^{-1}$, suggesting that plant photosynthetic uptake (or \sim GEP) accounts for approximately $-263.8 \text{ g C m}^{-2} \text{ yr}^{-1}$ on the brackish marsh despite marsh deterioration. In contrast, respiratory CO_2 emissions as estimated from chambers equated to an even higher C emissions rate of $1011.0 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the brackish marsh. Respiratory CH_4 fluxes through chambers were estimated at $49.6 \text{ g C m}^{-2} \text{ yr}^{-1}$ or $<5\%$ of chamber CO_2 fluxes of elemental C. Together, CO_2 and CH_4 emissions from chambers equated to $1060.6 \text{ g C m}^{-2} \text{ yr}^{-1}$ from the brackish marsh and were approximately 2.4 times higher than the combined respiratory emissions of CO_2 ($434.4 \text{ g C m}^{-2} \text{ yr}^{-1}$) plus CH_4 ($11.1 \text{ g C m}^{-2} \text{ yr}^{-1}$) through EC (Table 3). N_2O emissions were estimated from chambers as $0.12 \text{ g N m}^{-2} \text{ yr}^{-1}$ for the brackish marsh.

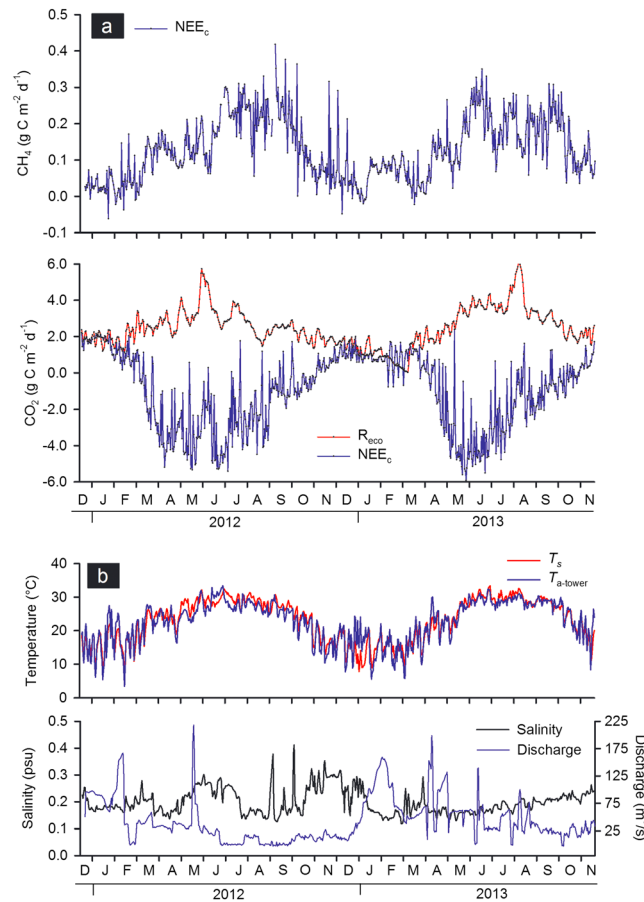


Figure 5. Overview of NEE_c (from EC techniques) for the freshwater marsh, Louisiana, USA, including (a) daily elemental fluxes of carbon from CH₄ and CO₂, along with ecosystem respiration of CO₂ (R_{eco}), and (b) daily summary of relevant meteorological and/or environmental variables, including soil temperature (T_s), air temperature measured from the EC tower (T_{a-tower}), salinity, and discharge from the Davis Pond freshwater diversion. Negative CO₂ or CH₄ flux values signify uptake by the marsh; positive values signify emissions from the marsh.

from CO₂ emitted to 11 g C from CH₄ emitted) among those marshes reported by Mitsch *et al.* [2013], while on the flip side, this ratio was also fairly low (EC ratio: -337 g C from CO₂ taken up to 47 g C from CH₄ emitted) for the freshwater marsh. These ratios are likely related to a combination of degradation of the brackish marsh facilitating organic matter mineralization and erosion and low salinity in the freshwater marsh facilitating high productivity with appreciable CH₄ emissions. In more saline marshes, especially at salinity concentrations above 18 psu [Poffenbarger *et al.*, 2011], CH₄ emissions are universally suppressed. For example, C emissions from CH₄ were only 0.02–0.11% of C emissions from CO₂ in a Canadian tidal salt marsh [Chmura *et al.*, 2011].

Even short-term experimental additions of salinity to freshwater marshes can change the balance of CO₂ versus CH₄ fluxes; CH₄ emissions were reduced from 53 to 37 g C m⁻² yr⁻¹ in a tidal freshwater marsh where the salinity was experimentally raised from freshwater to oligohaline levels for over 18 months [Neubauer, 2013]. Thus, fluctuating short-term salinity concentrations from 1.8 to 16.6 psu was likely responsible for reducing the respiratory emissions of CH₄ in our brackish marsh (Figure 6), an observation expected by past results in marshes developing along salinity gradients [Bartlett *et al.*, 1987; DeLaune *et al.*, 1983; Magenheimer *et al.*, 1996; Poffenbarger *et al.*, 2011]. Emissions of CH₄ along our salinity gradient at the ecosystem level mirrored a statistical relationship developed from chamber-based studies [Poffenbarger *et al.*, 2011; Holm *et al.*, 2016], suggesting that the greater availability of sulfate (SO₄²⁻) as salinity concentrations increase also suppress CH₄ emissions at the spatial scale measured by EC (Figure 6).

(up to 352 g C m⁻² yr⁻¹) [Knox *et al.*, 2014]. However, C emissions from our brackish marsh were much lower than emissions of 984 g C m⁻² yr⁻¹ registered for a single year from a managed urban tidal marsh in New Jersey [Schäfer *et al.*, 2014]. In contrast, net C uptake from the atmosphere by our healthy freshwater marsh was -290 g C m⁻² yr⁻¹. From other EC tower-based annual estimates of C uptake, the natural freshwater marsh in Louisiana compared similarly to other natural and restored tidal wetlands. For example, C was taken up at a rate of -130 g C m⁻² yr⁻¹ in a *Spartina alterniflora* marsh in Virginia [Kathilankal *et al.*, 2008], -65 to -310 g C m⁻² yr⁻¹ for 2 of 3 years in a managed urban tidal marsh in New Jersey [Schäfer *et al.*, 2014], and -231 g C m⁻² yr⁻¹ in a restored *Spartina patens* marsh in New Jersey [Artigas *et al.*, 2015]. However, uptake rates of up to -397 to -804 g C m⁻² yr⁻¹ were reported from restored coastal wetlands in California [Knox *et al.*, 2014; Anderson *et al.*, 2016], suggesting that the potential for wetland C uptake is much higher than what we documented in Louisiana.

Interestingly, the brackish marsh in Louisiana represented among the highest flux ratio of CO₂ to CH₄ on an elemental basis (EC ratio: 171 g C

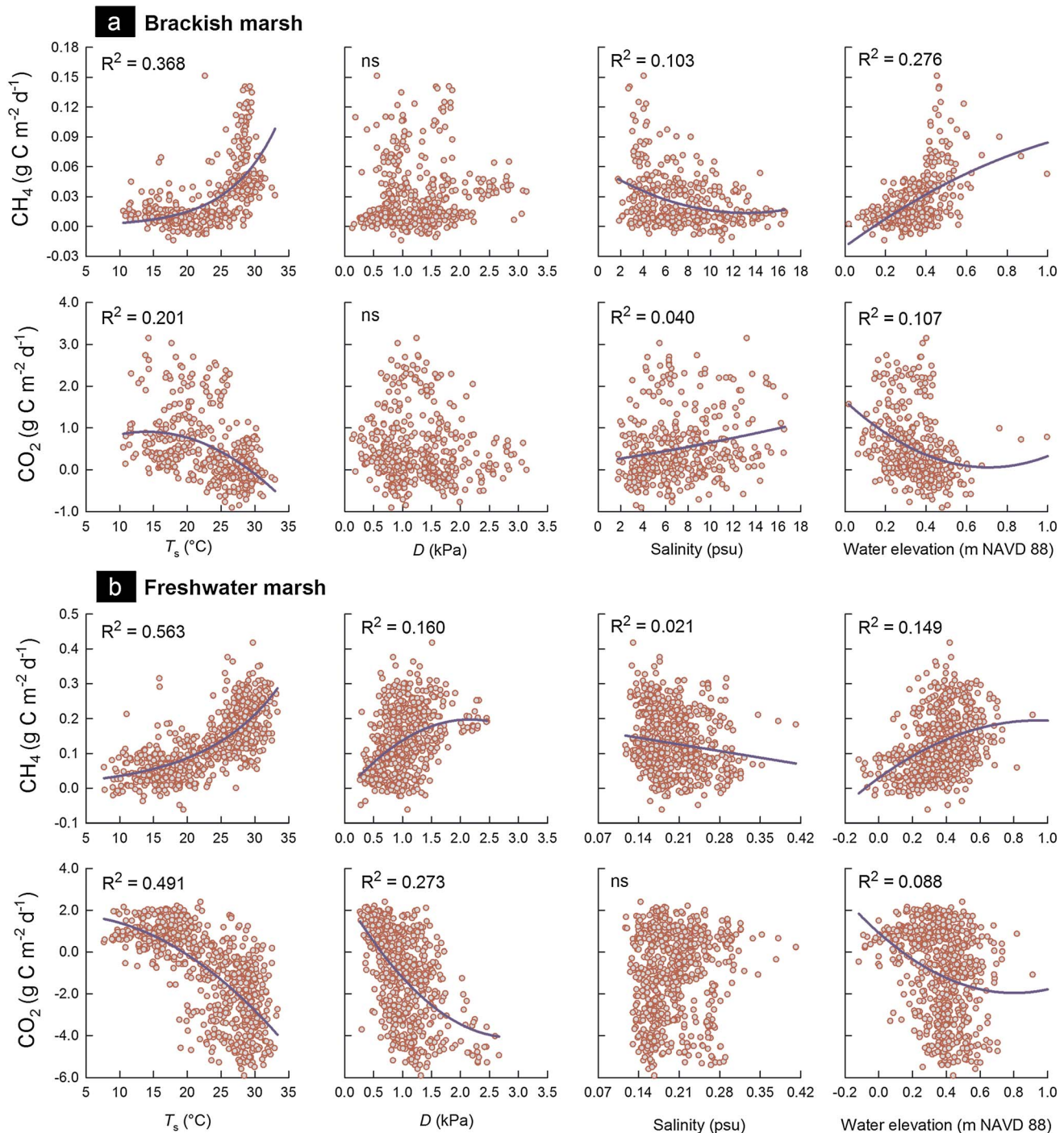


Figure 6. Mean daily NEE_c of CH_4 and CO_2 as measured from EC techniques for the (a) brackish marsh and (b) freshwater marsh in Louisiana, USA, versus soil temperature (T_s), vapor pressure deficit (D), salinity, and water elevation. Negative CO_2 or CH_4 flux values signify uptake by the marsh; positive values signify emissions from the marsh.

Crozier and DeLaune [1996] showed that the most important factors for predicting CH_4 emissions in these microtidal systems in Louisiana were temperature, labile C availability, and SO_4^{2-} concentration. With the greater availability of SO_4^{2-} with seawater, SO_4^{2-} reduction becomes the dominant pathway for organic matter oxidation prompting increases in CO_2 fluxes [Weston et al., 2006] and forcing the depletion of soil organic C stores [Weston et al., 2011]. Surprisingly, salinity also affected CH_4 emissions in the freshwater marsh even though salinity remained below 0.5 psu (Figure 6). In this case, perhaps CH_4 emissions were responding

Table 3. Summary of Elemental Fluxes of C or N From CO₂, CH₄, and N₂O Separated by Ecosystem Contribution Using Eddy Covariance (NEE_c) and Static Chambers for a Brackish Marsh Adjacent to Pointe-aux-Chene WMA and a Freshwater Marsh on Salvador WMA, Louisiana, USA^a

Spatial Scale	Flux	Elemental Fluxes (g C or N m ⁻² yr ⁻¹)	
		Brackish Marsh	Freshwater Marsh
NEEc	CH ₄	11.1	47.1
	CO ₂	170.6	-337.0
	Net C flux ^b	181.7	-289.9
	R _{eco}	434.4	893.0
	GEP ^c	-263.8	-1230.0
Chamber	CH ₄	49.6	91.9
	CO ₂	1011.0	357.9
	Net soil C flux ^b	1060.6	449.9
	N ₂ O	0.12	-0.02

^aNegative values correspond to net uptake.

^bNet C flux is calculated as the sum of CH₄ emissions and CO₂ uptake/release.

^cGross ecosystem productivity (GEP) is calculated as NEE_c of CO₂ minus R_{eco}.

more to differences in specific conductivity from the river diversion in lieu of salinity per se; there is no direct evidence that such a low salinity range would influence CH₄ emissions appreciably.

4.2. Comparing EC Versus Chamber Techniques

We expected emissions of CH₄ to be similar among techniques since both techniques measure mostly the net loss of CH₄ from wetland ecosystems; plants do not take up CH₄. That CH₄ fluxes were 2–4 times higher when measured by chambers versus EC in our study is important to note, especially when reviewing the literature. Other studies have also documented

greater CH₄ emissions when assessed by chambers versus EC. For example, CH₄ emissions ranged from 18 to 91% higher (mean, 30% higher) as assessed by small chambers versus EC from a rice field in Northern Italy [Mejjide *et al.*, 2011]. Since CH₄ has an atmospheric lifetime of approximately 12 years [Myhre *et al.*, 2013], CH₄ released from the soil would not oxidize to CO₂ appreciably before reaching the EC sensor at 3.4–3.6 m. However, at least three other explanations for the disparate values between EC and chamber techniques can be proposed. First, along with CH₄ emitted directly from the soil surface, wetland plants vector CH₄ to the atmosphere from deeper soils [Whiting and Chanton, 1993; Vann and Magonigal, 2003; Gauci *et al.*, 2010; Pangala *et al.*, 2013]. In locations with a prominent methanotrophic bacterial community, such as strongly tidal freshwater wetlands, up to 52–81% of CH₄ produced in situ undergoes re oxidation back to CO₂ prior to being released from the soil [Magonigal and Schlesinger, 2002]. Both of our marshes were tidal, but with smaller lunar tides, larger wind tides, and longer flood durations than is typical of Atlantic coastal tidal freshwater marshes, with some exception. The use of dark chambers might influence the role of the plant in vectoring CH₄ from deeper soils to the atmosphere by bypassing zones of bacterially mediated methanotrophy; however, one would hypothesize that the effect would be to further reduce fluxes of CH₄ from chambers (in the sense of Magenheimer *et al.* [1996]) relative to EC techniques, not enhance them as we show here.

Second, the spatial footprint of EC and chambers are vastly different. This should be noted since the majority of CH₄ (and CO₂) assessments are point based using chambers that are rarely replicated well over time, including our current study [see also Neubauer *et al.*, 2000]. We used six chambers per site for each measurement period as our sample unit, which represents a total area of 0.52 m² (0.0864 m² per chamber), and only measured fluxes 5–11 times. While chambers include some exposed water associated with culms of vegetation, the percentage of open water, bare soils, and vegetation differs greatly over larger spatial scales targeted by the EC system [e.g., Budishchev *et al.*, 2014]. Likewise, only a fraction of the temporal environmental variability is included in chamber studies.

Third, and related, chamber data were collected exclusively during midday (1000–1600) when CH₄ fluxes are inherently higher overall. For example, respiratory CH₄ emissions were at least twice as high during the day as compared to night emissions in a tidal freshwater marsh in Virginia, USA [Neubauer *et al.*, 2000]. EC calculations integrate night and day. Issues associated with spatial and temporal sampling resolution are also quite prevalent when comparing R_{eco} data from EC with respiratory CO₂ emissions from chambers for both sites (Table 3); yet applying chambers as we did to estimate soil CO₂ emissions is common [Livingston and Hutchinson [1995], Yu *et al.* [2008], Moseman-Valtierra *et al.* [2011], Krauss and Whitbeck [2012], Olsson *et al.* [2015], etc.). With chamber estimates of respiratory CO₂ emissions ranging from less than half to more than twice as high as EC estimation of R_{eco}, disparities may be quite difficult to reconcile in the literature if these results are repeated. Greater replication of chamber measurements from our sites over time may have closed

the gap in CH_4 and R_{eco} (CO_2 emissions) estimates from chambers versus EC (as in *Mejjide et al.* [2011]). Part of the issue for our brackish marsh, where the EC versus chamber fluxes varied the greatest, was certainly related to fairly limited temporal sampling from chambers ($n = 5$). More studies that compare these techniques are critical; however, good discussion of spatial sampling variability is already becoming more and more the focus of greenhouse gas emissions research [e.g., *Forbrich et al.*, 2011; *Mejjide et al.*, 2011; *Budishchev et al.*, 2014].

4.3. Relating Greenhouse Gas Fluxes to the Process of Marsh Degradation

Brackish and freshwater marshes in Louisiana have inherently different capacities for regulating fluxes of CO_2 and CH_4 , as we document here. Earlier studies showed that brackish marshes of the Barataria Basin, Louisiana, emitted $73 \text{ g C m}^{-2} \text{ yr}^{-1}$ as CH_4 , while freshwater marshes emitted $160 \text{ g C m}^{-2} \text{ yr}^{-1}$ as CH_4 [*DeLaune et al.*, 1983]; these rates were about 1.5–1.7 times higher than our chamber fluxes and much higher than our EC fluxes (Table 3). On the other hand, CO_2 emissions were lower from cores collected from brackish marshes ($228 \text{ g C m}^{-2} \text{ yr}^{-1}$) versus freshwater marshes ($780 \text{ g C m}^{-2} \text{ yr}^{-1}$) in past study [*Nyman and DeLaune*, 1991], better echoing our R_{eco} results from EC towers than from chambers. It is uncertain exactly why our chamber data were opposite to this trend (Table 3), but we suspect that it has to do with the observation that our brackish marsh was not healthy with tremendous spatial variability in response. *Nyman and DeLaune* [1991] related differences between their marsh types to plant species composition and to the quality of soil organic matter, where the latter is most applicable to our results.

We also determined GEP (or gross photosynthetic uptake) of CO_2 from EC. The brackish marsh took up $-264 \text{ g C m}^{-2} \text{ yr}^{-1}$ as GEP (Table 3). This is considerably lower than chamber-based estimates of GEP (uptake of -650 to $-1000 \text{ g C m}^{-2} \text{ yr}^{-1}$) in mesohaline and polyhaline marshes along the Atlantic and Gulf coasts of the U.S. [*Miller et al.*, 2001; *Weston et al.*, 2014; *Wilson et al.*, 2015]. Technique disparity aside, reduced GEP from the Louisiana brackish marsh suggests that reductions in ecosystem carbon fixation is an important factor in the net emissions of C ($182 \text{ g C m}^{-2} \text{ yr}^{-1}$) as our brackish marsh site is challenged to keep up with land submergence. Deposition of vegetative debris (wrack) from storms onto a brackish marsh caused a similar reduction in GEP (to $-280 \text{ g C m}^{-2} \text{ yr}^{-1}$) and led to net C emissions of $222 \text{ g C m}^{-2} \text{ yr}^{-1}$ in coastal Virginia [*Miller et al.*, 2001]. However, it is important to note that net emissions of C to the atmosphere do not necessarily mean that a site is deteriorating. In healthy tidal marshes in Alabama and Virginia, R_{eco} exceeded gross production due to high inputs of allochthonous carbon that subsequently was mineralized in the marsh [*Neubauer et al.*, 2000; *Wilson et al.*, 2015].

In contrast to the brackish marsh, the plant community of the freshwater marsh took up $-1230 \text{ g C m}^{-2} \text{ yr}^{-1}$ as GEP as estimated using EC (Table 3). This rate is typical of tidal freshwater marshes from New Jersey to Alabama, which had GEP rates of -750 to $-1500 \text{ g C m}^{-2} \text{ yr}^{-1}$ [*Neubauer et al.*, 2000; *Neubauer*, 2013; *Weston et al.*, 2014; *Wilson et al.*, 2015]. Instead of losing C to the atmosphere, the freshwater marsh at Salvador WMA is taking up $-290 \text{ g C m}^{-2} \text{ yr}^{-1}$, a rate that is similar to long-term rates of soil C sequestration in tidal freshwater marshes (typically ~ 100 – $300 \text{ g C m}^{-2} \text{ yr}^{-1}$ as calculated from *Neubauer* [2008]). Therefore, our freshwater marsh was taking up atmospheric C at a high rate fed by a much higher rate of photosynthesis than observed at the brackish marsh to facilitate net C sequestration.

As tidal marshes deteriorate, they can experience reduced primary production, enhanced carbon emissions, net loss of surface elevation, and subsurface changes. A deteriorating salt marsh in New York was found to have less root and rhizome biomass, larger diameter rhizomes, reduced soil consolidation, and, like our brackish marsh, higher soil CO_2 emissions than a nearby stable marsh [*Wigand et al.*, 2014]. Stability of the deteriorating marsh was attributed to a balance among surface accretion of sediments, enhanced individual rhizome diameters, and swelling of surficial peats to facilitate greater soil volume expansion to survive submergence in the New York marsh system. Indeed, the root production for brackish *S. patens* marsh at Pointe-aux-Chenes probably was contracting as the plants formed shrinking clumps with bare areas between clumps, although aboveground tissue was still relatively prolific. This growth pattern may be a negative belowground response of this species to inundation [*Snedden et al.*, 2015], driving an overall loss of C to the atmosphere, and, while unmeasured in this study, perhaps even greater losses to dissolved organic C through export [*Bergamaschi et al.*, 2012].

4.4. Perspectives on Radiative Forcing From Louisiana Deltaic Marshes

In the simplest terms, the climatic role of ecosystems is determined using global warming potentials (GWPs) to convert rates of greenhouse gas uptake and emissions to a common currency (g CO_2 equivalents). CH_4 and N_2O

Table 4. The Radiative Balance of the Brackish and Freshwater Marsh Sites Based on Ecosystem CH₄, Net C Fluxes, and Soil N₂O Fluxes (Table 3)^a

Flux (g CO ₂ -eq m ⁻² yr ⁻¹)	Radiative Fluxes (GWP)		Radiative Fluxes (SGWP/SGCP)	
	Brackish	Freshwater	Brackish	Freshwater
CH ₄	444.0	1885.2	666.0	2827.8
Net C flux	666.2	-1063.0	666.2	-1063.0
N ₂ O	50.4	-9.6	51.3	-12.6
Net radiative balance	1160.6	812.7	1383.6	1752.2

^aWe first calculated radiative fluxes with the older approach of using global warming potentials (GWPs), which assumes that gases are emitted only as a single pulse at the beginning of the period of interest. We used 100 year GWP values of 30 and 265 for CH₄ and N₂O, respectively [Myhre *et al.*, 2013]. Positive numbers indicate a net warming effect; negative numbers indicate net cooling. For comparison, radiative fluxes (g CO₂-eq m⁻² yr⁻¹) were also calculated using sustained-flux global warming and global cooling potentials (SGWP and SGCP), which are based more appropriately on continuous fluxes of gases over a 100 year period [Neubauer and Magonigal, 2015].

are greenhouse gases with 100 year GWP values 30 times and 265 times greater than CO₂, respectively [Myhre *et al.*, 2013]. Using these GWPs and applying them to EC data, we calculate that the brackish marsh is contributing the equivalent of 1161 g CO₂-eq m⁻² yr⁻¹ to the atmosphere and the freshwater marsh is contributing the equivalent of 813 g CO₂-eq m⁻² yr⁻¹ to the atmosphere (that is, both are contributing to net warming, not cooling) (Table 4). However, the application of GWPs assumes that greenhouse gas emissions involve simple pulses that are not sustained annually, that uptake and emissions contribute similarly to radiative forcing with opposite signs, and that forcing occurs over specified time frames [Frolking *et al.*, 2006; Neubauer and Magonigal, 2015].

In contrast, Neubauer and Magonigal [2015] proposed the use of the sustained-flux global warming potential (SGWP) [see also Fuglested *et al.*, 1996] for gas emissions and the sustained-flux global cooling potential (SGCP) for gas uptake. These metrics consider persistent greenhouse gas fluxes (rather than a single pulse) and account for asymmetry in radiative behavior between uptake and emissions fluxes. Over a 100 year period at our freshwater marsh site, the sustained-flux metrics indicate that this site emits the equivalent of 1752 g CO₂-eq m⁻² yr⁻¹ to the atmosphere (net warming) whereas the GWP suggested that this influence is 54% less (Table 4), a disparity driven by CH₄ accounting. In a qualitative sense, both sets of metrics also indicated that the brackish marsh had a strong net warming effect, although the strength of that warming differed by roughly 19% depending on the choice of sustained-flux (1384 g CO₂-eq m⁻² yr⁻¹) versus pulse metrics (1161 g CO₂-eq m⁻² yr⁻¹). Both marshes were net radiative sources over a 100 year period (Table 4), despite appreciable rates of GEP in both systems and net C sequestration in the freshwater marsh (Table 3).

In the longer term, the warming from wetland greenhouse gas emissions eventually will be offset by long-term C sequestration [Neubauer, 2014; Petrescu *et al.*, 2015]. The time when the marsh switches from having a lifetime net warming effect to a net cooling effect is known as the radiative forcing switchover time (in the sense of Frolking *et al.* [2006]), which happens because CH₄ and N₂O burdens will eventually reach steady state in the atmosphere, whereas the cumulative C storage in wetlands will increase from year to year. The switchover time for our freshwater marsh site is 376 years (calculated following the model in Neubauer [2014], as updated in Neubauer and Magonigal [2015]). Since the age of Holocene basal peat depths in the upper Barataria Basin exceeds this switchover time (>2250 years B.P. versus 376 years) [Kosters *et al.*, 1987], we conclude that over the lifetime of the freshwater marsh, the cooling effect due to its C sequestration and N₂O uptake has exceeded the warming due to its CH₄ emissions. A switchover time could not be calculated for the brackish marsh since there was no net uptake for any of the three greenhouse gases we considered. In other words, unless processes change in the brackish marsh such that there is net C sequestration, this site will continue to have a positive (warming) radiative effect.

5. Conclusions

When scaled, emissions of C to the atmosphere equated to 1817 kg C ha⁻¹ yr⁻¹ from the brackish marsh, and uptake of C equated to 2899 kg C ha⁻¹ yr⁻¹ from the freshwater marsh. Partitioning between uptake of CO₂ and emissions of CO₂ and CH₄ was quite different between these two marsh types, driven by much greater GEP from the freshwater versus brackish marsh. We also discovered that net fluxes of CH₄ and of respiratory

CO₂ emissions as estimated through EC differed from emissions as estimated with chamber techniques, identifying a potentially prominent source of variation in greenhouse gas flux estimation within the wetland literature. Emissions of N₂O were insignificant from both marshes. As calculated using sustained-flux greenhouse gas metrics, the radiative balance over a 100 year time frame was positive (net warming) for both marshes but was considerably larger from the brackish marsh. Assuming that the fluxes described herein were maintained over time, the freshwater marsh would switch to having a net cooling effect after 376 years, implying that there are climatic benefits associated with preserving healthy wetlands.

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