Wetlands
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ORIGINAL RESEARCH

Ecosystem Level Methane Fluxes from Tidal Freshwater and Brackish Marshes of the Mississippi River Delta: Implications for Coastal Wetland Carbon Projects

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Abstract Sulfate from seawater inhibits methane production in tidal wetlands, and by extension, salinity has been used as a general predictor of methane emissions. With the need to reduce methane flux uncertainties from tidal wetlands, eddy covariance (EC) techniques provide an integrated methane budget. The goals of this study were to: 1) establish methane emissions from natural, freshwater and brackish wetlands in Louisiana based on EC; and 2) determine if EC estimates conform to a methane-salinity relationship derived from temperate tidal wetlands with chamber sampling. Annual estimates of methane emissions from this study were 62.3 g $CH_4/m^2/yr$ and 13.8 g $CH_4/m^2/yr$ for the freshwater and brackish (8–10 psu) sites, respectively. If it is assumed that long-term, annual soil carbon sequestration rates of natural marshes are ~200 g $C/m^2/yr$ (7.3 $tCO_2e/ha/yr$), healthy brackish marshes could be expected to act as a net radiative sink, equivalent to less than one-half the soil carbon accumulation rate after subtracting methane emissions (4.1 $tCO_2e/ha/yr$). Carbon sequestration rates would need case-by-case assessment, but the EC methane emissions estimates in this study conformed well to an existing salinity-methane model that should serve as a basis for establishing emission factors for wetland carbon offset projects.

Keywords Methane · Tidal wetland · Carbon sequestration · Eddy covariance

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Introduction

Methane currently has a global warming potential 30 times that of carbon dioxide (Myhre et al. 2013), and wetlands are the dominant natural source of methane comprising an estimated one-third of the global emissions (Bridgham et al. 2013). For tidal wetlands, there is a need to refine the understanding of the environmental variables that constrain methane emissions to improve regional-ecoystem emissions predictions and to reduce uncertainty for blue-carbon wetland restoration projects.

Tidal wetlands typically have high rates of carbon sequestration, burying approximately 200 g $C/m^2/yr$, which is equivalent to 7.3 $tCO_2e/ha/yr$ (Mcleod et al. 2011). Herbaceous tidal marshes of the northern Gulf of Mexico and Louisiana generally have similar baseline burial capacity regardless of salinity regime (Nyman et al. 2006; Piazza et al. 2011; Hansen and Nestlerode 2014). In Louisiana alone, there are 1.47 million ha of freshwater to saline herbaceous coastal wetlands (Sasser et al. 1996); these coastal wetlands are subject to recent loss rates of 4290 ha/yr (Couvillion et al. 2011). While tidal herbaceous and forested wetlands have high

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capacities for carbon accumulation, from a global warming perspective, it is recognized that climate benefits from wetland restoration generally increase, or become more predictable, as salinity increases and methane emissions decrease (Poffenbarger et al. 2011). Thus, low salinity freshwater wetlands or those that have reduced availability of terminal electron acceptors that suppress methanogenesis, could emit enough methane to offset annual rates of carbon accumulation (Poffenbarger et al. 2011).

Aside from the differences among wetland types with respect to annual rates of carbon sequestration and greenhouse gas (GHG) emissions, the continued loss of deltaic wetlands in the Mississippi River Delta Plain (MRDP) may be resulting in accelerated emissions from organic-rich soils that took centuries to form (DeLaune and White 2011). The wetland loss, while partially attributable to natural delta decay, has been linked to systematic hydrologic alteration of interior wetlands (i.e. oil and gas canals; Bass and Turner 1997) and the reduction in sediment delivery from the river to the wetlands (Blum and Roberts 2009). Current wetland restoration measures are being planned and implemented to reduce the wetland loss rate, commonly including wetland creation with dredged sediment, hydrologic restoration, shoreline protection, and Mississippi River sediment diversions (CPRA 2012). These measures, to varying degrees, may have positive climate regulation benefits in the form of increasing sequestration capacity and avoiding the future emissions of eroded soil carbon.

There has been a renewed interest in wetland carbon cycling research, as different groups are advancing the monitoring and verification methods required to support wetland restoration as eligible carbon offset projects. The voluntary markets, through the Verified Carbon Standard (VCS 2014) and American Carbon Registry (ACR 2012), have approved wetland offset methodologies that apply to wetland creation and hydrologic restoration project types. Currently, the onus is on the project developer to provide a high level of confidence to a verifier on the legitimacy of the carbon offset. This process requires intensive monitoring on a project-by-project basis, which can reduce the return on investment to the point that developing a carbon offset project is not attractive to investors, thus, limiting the resources needed for additional restoration. To improve the viability of a project and advance needed restoration, developers require region-specific research and tools to build more robust estimates for carbon sequestration rates and GHG emission factors.

A primary uncertainty is the potential for wetlands to emit nitrous oxide and methane under different baseline (un-restored) and restoration scenarios. Given the atmospheric lifetimes, it is currently understood that nitrous oxide and methane have single-pulse Global Warming Potentials of 265 and 30 over a 100 yr time horizon (Myhre et al. 2013). It is also becoming clearer that methane flux from restored freshwater wetlands may have a warming effect on climate over decadal periods, but across century scales wetlands can be expected to act as net radiative sinks (Whiting and Chanton 2001; Mitsch et al. 2013; Neubauer 2014; Bridgham et al. 2014). Thus, the current guidance for voluntary wetland carbon offset projects (ACR and VCS) is that GHG emissions will be monitored or estimated for periods of 20–100 years to calculate the net carbon benefits of a project versus the baseline condition.

The classic field studies from Virginia and Louisiana tidal wetlands (DeLaune et al. 1983, Bartlett et al. 1985, 1987) formed the basis of our understanding on the importance of salinity and methane interactions across a fresh to saline gradient (0.4 to 26 psu). This inverse log-linear relationship was further improved by the meta-analysis of Poffenbarger et al. (2011) who compiled data from 31 tidal marshes covering a broad geographic extent. Their updated relationship was interpreted in the context of methane emissions relative to the potential wetland carbon accumulation rate. Based on this analysis, the researchers concluded, in general, that wetlands with salinity above 18 psu could reliably act as a net radiative sink, because methane emissions are inhibited. They identified the need to refine estimates of methane emissions from wetlands within the salinity range of 5–15 psu, which are under-represented and exhibit high variability in methane emissions. Recognizing that a large portion Louisiana tidal wetlands fall below 18 psu salinity, the main impetus for this study was to refine methane emission estimates from these deltaic systems using the Eddy Covariance (EC) technique (Baldocchi 2014), which has been applied in other wetland systems (Rinne et al. 2007; Teh et al. 2011; Hatala et al. 2012). This study was designed to:

1) Develop annual estimates of ecosystem-scale methane emissions from natural, tidal freshwater and brackish (mesohaline) wetlands in Louisiana;
2) Evaluate how annual methane emissions estimates from eddy covariance compare to those from a geographically broader chamber-based salinity-methane relationship to assess the use of salinity as a predictor of methane emissions across a salinity gradient;
3) Compare the influence of low and moderate freshwater discharges from a riverine source on methane emissions from a freshwater wetland; and,
4) Understand the interactions of water level, temperature, and salinity on methane emissions to refine predictive relationships.

Methods

Study Sites

This study was conducted on two herbaceous tidal wetland sites in coastal Louisiana, which has a subtropical humid climate (Trewartha and Horn 1980; Fig. 1). Both sites experience astronomical tides (range < 30 cm), with wind tides that dominate long duration water level fluctuations. The freshwater site was established on Salvador Wildlife Management Area, which comprises approximately 12,000 ha of cypress-tupelo forest, emergent marsh, and shallow open water, and is located 19 km southwest of New Orleans (29° 51′31.29″ N; 90° 17′ 12.80″ W) (Fig. 1). This site is located near the outfall of a freshwater diversion (Davis Pond, discharge capacity =280 m^3/s) from the Mississippi River, which was designed to manage salinity in the Barataria Basin through a controlled introduction of freshwater from the river (Day et al. 2014). The marsh is typical of freshwater deltaic plain wetlands (Swarzenski et al. 1991; Sasser et al. 1996) in that it has a semi-buoyant mat that is capable of adjusting to moderate changes in water level. The dominant species were *Sagittaria lancifolia*, *Leersia oryzoides*, with patchy areas of *Typha domingensis*. The upper 24 cm of soils were 75–85% organic matter and 0.08–0.10 g/ cm^3 dry bulk density.

The brackish marsh site was established 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) (Fig. 1). The brackish site comprised marsh dominated by *Spartina patens* and *Schoenoplectus americanus* as well as shallow open water areas. The upper 24 cm of the soils

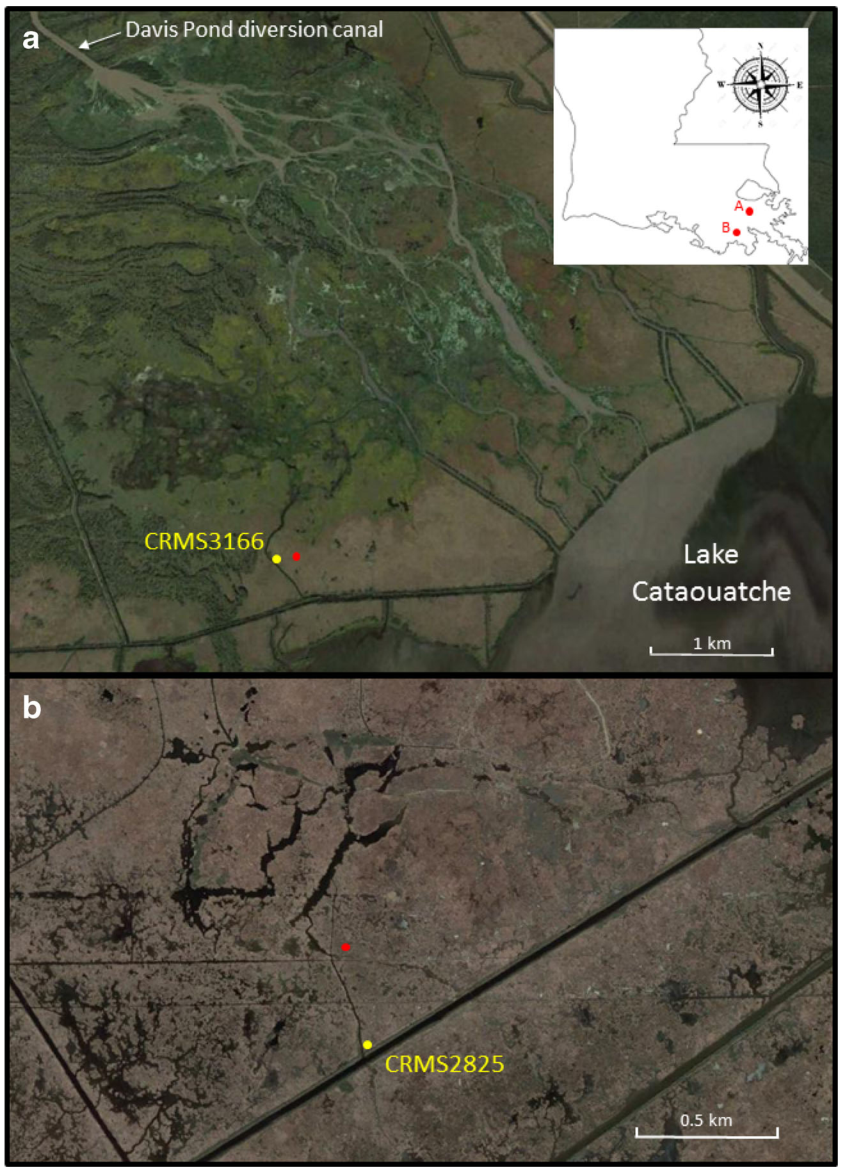

Fig. 1 Location of the freshwater (**a**) and brackish (**b**) eddy covariance study sites (*red*) in coastal Louisiana and the location of Coastwide Reference Monitoring System stations (*yellows*). (Aerial image © 2015 Google Earth. Annotation © 2015 CH2M HILL)

were 40–70% organic matter and 0.10–0.18 g/cm^3 dry bulk density.

Data Collection and Processing

Both sites were instrumented with towers comprising a LI-COR open path methane sensor (LI-7700, LI-COR Biosciences, Nebraska, USA), LI-COR closed path CO_2/H_2O sensor (LI-7200), and a sonic anemometer (Gill Windmaster Pro, Gill Instruments Ltd., Lymington, England), along with a logger and air pump. The Eddy Covariance (EC) system was located on 3 × 3 m platforms, which were elevated 1.0 m above the soil surface. The towers were located in a central region of a homogeneous wetland area with similar roughness (or canopy height) within a 200 m fetch, and where wind directions could be accessed in all directions to maximize data capture. Both sites had similar emergent herbaceous canopy heights that ranged from 0.5 to 1.2 m throughout the year. The instrument measurement heights from the soil surface were 3.6 m and 3.4 m for the freshwater and brackish sites, respectively. The measurement heights were chosen to limit the footprint within a longitudinal distance of ~100 m (70% of the footprint contribution) of the tower during normal daytime conditions, assuming the following: standard deviation of vertical velocity fluctuations (0.3 m/s); surface friction velocity (0.3 m/s); measurement height 3.5 m; planetary boundary layer height (1000 m); and roughness length (0.1 m) (Kljun et al. 2004).

The instruments were installed and recorded from 12 Dec 2011 to 20 Dec 2013 for the freshwater site, and 7 Oct 2011 to 12 Dec 2012 for the brackish site. Raw data were collected on a 10 Hz frequency, binned in 30-min files, and stored on a USB drive. The data were retrieved and instruments were serviced approximately monthly. All instruments were factory calibrated prior to deployment, and standard gas (10 ppm CH_4) checks were run every six months in the laboratory.

Methane eddy fluxes were calculated by multiplying the mean air density with the mean covariance of instantaneous deviations of vertical wind velocity and the mixing ratio of methane in air (Burba 2012):

$$f_{CH4} = \left(\overline{\rho a}\, \overline{w' s'} \right)$$

where,

f_{CH4} = CH_4 flux (μmol/m^2/s)

$\overline{\rho a}$ = mean air density (μmol air/m^3)

$\overline{w' s'}$ = mean covariance of instantaneous vertical wind velocity and mixing ratio of CH_4 in air

w' = instantaneous vertical wind velocity (m/s)

s' = instantaneous mixing ratio of CH_4 in air (μmol gas/μmol air)

The raw data were processed using the open source Eddy Pro 4.0 software (LI-COR 2012) and mean concentrations and fluxes were output in 30-min intervals. Data were pre-conditioned, corrected, and quality control tests were run according to the processing options in Table 1. The quality control process further included removing flux measurements due to instrument malfunction/contamination and poor atmospheric conditions, such as when the following conditions were present: heavy precipitation; extremes in friction velocity ($u^* < 0.05$ or >1.5 m/s); poor signal strength (<15% for methane; and AGC >70% CO_2/H_2O); and methane concentration anomalies (<1.7 or >35 umol/mol).

In addition to the air temperature data measured by the EC system, water level, water temperature, electrical conductivity, and salinity, were measured at both sites for the entire study through the Coastwide Reference Monitoring System (CRMS 2015) program. Water level, temperature, salinity, and electrical conductivity measurements were collected at one hour intervals in a nearby open water channel with a multi-probe data sonde (YSI Model 600LS YSI Inc., Yellow Springs, OH, USA; see Fig. 1 for the location of the CRMS station locations relative to the EC tower location). In addition to the semi-continuous conductivity measurements, monthly soil pore water samples were collected at 10 and 30 cm depths at the CRMS stations and also adjacent to the EC tower. Soil and air temperature were measured on 15-min intervals with replicate data loggers (HOBO Pro v.2, Onset Computer Corp., Bourne, MA, USA) located within 50 m of the EC tower. Diversion discharge data for the freshwater site was obtained from the U.S. Geological Survey gage (295501090190400) at the conveyance channel that flows into to the study site wetland. For each year, cumulative diversion discharge (m/yr) was calculated using daily mean discharge estimates and the area (4050 ha) of the receiving wetland.

Statistical Analyses

A data set of daily means was created from the environmental and methane flux data for exploring relationships among covariates and also to create gap-filling algorithms to integrate annual methane fluxes from both sites. For the freshwater site, the primary environmental covariates included: air/water temperature, water elevation, river diversion discharge, and salinity. For the brackish site, the same covariates were examined, except for river diversion discharge. All data were analyzed using SAS (2015). Linear correlation analyses were first conducted on daily methane fluxes versus temperature variables and water elevation. Linear correlations were retained. Step-wise linear regression (PROC GLMSELECT) was used to further explore the relationships of covariates with methane fluxes, as well as the square-root and natural logarithmic transformations of methane fluxes and salinity and river diversion

Table 1 Methods used to condition the data and calculate 30-min flux measurements in the Eddy Pro software

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

discharge data (when applicable) over daily and quarterly time intervals. For predictive purposes, we declared the relationships significant at $\alpha = 0.15$. The residuals of the models selected were then tested for normality and homogeneity of variance ($\alpha = 0.01$). The final model was the one that fit the best and met the model diagnostic requirements at $\alpha = 0.05$. Furthermore, the residuals of the final model were tested for auto correlation and an appropriate autoregressive integrated moving average model (ARIMA) model was fit (α =0.01).

Results

Freshwater Site

Over the two years of data collection at the freshwater site, 16, 970 30-min samples of the 30,715 samples were retained for analysis, resulting in a 55% retention of quality data. For the whole study period, the median methane concentration was 2.21 parts per billion (ppb) and flux was 0.114 μmol/m^2/s. For both years, a pattern of peak methane emissions (0.25–0.30 μmol/m^2/s) occurred during the Jun-Aug period (Fig. 2). Several brief periods of methane consumption were observed during cold-air outbreaks during Jan.-Feb. in both years (Fig. 2).

Daily methane flux means were calculated for 564 of 701 days, resulting in 137 days that required gap filling with correlation analyses and step-wise regression. The model showed significant contributions to methane flux from the following environmental covariates: air temperature ($p < 0.001$), water temperature ($p < 0.001$), salinity ($p < 0.001$), and river diversion discharge ($p < 0.001$). By excluding water temperature or air temperature in the model, there was only a 2% difference in explaining methane emissions, with water temperature providing the better fit ($R^2 = 0.66$). Water elevation was an insignificant variable ($p > 0.15$) for predicting methane emissions. For most environmental variables, the relationship with methane flux changed over the year, which we accounted for by applying different adjustments by quarter. The root mean squared error (RMSE) of the overall model relationship among observed and measured methane flux was 0.048 μmol/m^2/s, and the overall goodness of fit was $R^2 = 0.67$.

Using the measured and predicted data (during missing days), an integrated estimate of methane emissions was calculated for years 2012 and 2013 (Table 2).

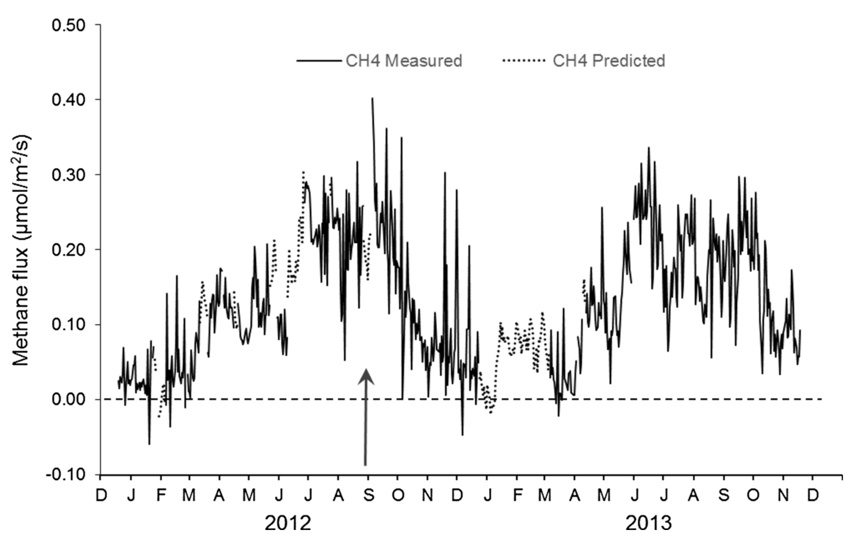

Fig. 2 Mean daily methane flux from the freshwater site. The arrow indicates the passage of Hurricane Isaac which flooded (>1.0 m) the marsh surface

Table 2 Annual methane flux estimates from the freshwater and brackish tidal wetlands. At the freshwater site, 2012 was a low discharge year and 2013 was an average discharge year

Site	Year	Cumulative Annual Diversion Discharge (m/yr)	Methane Emissions (g CH_4/m^2/yr)	Methane Emissions CH_4 GWP = 30 (MT CO_2e/ha/yr)
Freshwater	2012	23	63.0	18.9
Freshwater	2013	41	61.6	18.5
Brackish	2012	N/A	13.8	4.1

Methane emissions estimates for 2012 and 2013 were 63.0 and 61.6 g CH_4/m^2/yr, respectively. Thus over the two years mean methane emission was 62.3 g CH_4/m^2/yr, with a predicted to observed error of ±12.1 g CH_4/m^2/yr, or 19.5% of the mean. Despite the difference in cumulative annual river discharge (23 vs 41 m/yr), methane emissions were practically identical among years. Assuming that radiative forcing by methane is 30 times greater than that of carbon dioxide on a mass basis, the freshwater marsh emitted methane equivalent to 18.5–18.9 tCO_2e/ha/yr each year.

Based on a reduced multiple regression model (similar to the gap filling model, but using only water temperature, salinity, and river diversion discharge as covariates), monthly means of the environmental covariates provided comparable annual methane estimates compared to estimates derived from daily means (Table 3; see Supplemental Electronic Material, Appendix A for equations). The reduced monthly model underestimated the measured annual budget by less than 7%; such that, predicted annual flux was 59.3 and 57.3 g CH_4/m^2/yr as compared to measured annual flux of 63.0 and 61.3 g CH_4/m^2/yr, respectively, for 2012 and 2013.

Examining bivariate trends, methane flux from the freshwater site was most strongly related to temperature, which explained approximately 45% of methane variation (Fig. 3). Methane emissions related positively to water level increase, explaining 16% of the methane variation. Over the course of the study, salinity varied between 0.15–0.40 psu, which corresponded to 250 to 800 μS/cm (Fig. 3). Despite the expected inverse relationship, only 6% of the variation in methane emissions could be attributed to salinity or conductivity (Fig. 3). The river diversion discharge had the effect of

Table 3 Monthly mean methane flux (observed and predicted) with corresponding environmental data for the freshwater site. The reduced multiple regression model contained the covariates of water temperature, water elevation, salinity, and river diversion discharge (see SEM, Appendix A for predictive equations). Environmental data source: Coastwide Reference Monitoring System (CRMS-*Wetlands*)

Year	Month	Water Temperature	Salinity	Water Level	Diversion Discharge	Observed Methane Flux	Predicted Methane Flux
		(°C)	(psu)	(m NAVD88)	(m^3/s)	(g CH_4/m^2/mo)	(g CH_4/m^2/mo)
2011	Dec	15.0	0.19	0.37	93	1.17	1.75
2012	Jan	16.0	0.18	0.28	83	1.13	1.62
	Feb	16.4	0.18	0.30	64	1.44	1.44
	Mar	22.5	0.20	0.41	40	4.25	3.51
	Apr	24.0	0.16	0.41	34	4.74	4.94
	May	28.3	0.25	0.37	55	5.96	5.91
	Jun	29.2	0.25	0.43	16	7.19	7.33
	Jul	29.4	0.20	0.39	4	10.09	8.50
	Aug	28.3	0.17	0.43	6	8.60	8.83
	Sep	27.7	0.18	0.48	1	9.64	8.94
	Oct	22.9	0.23	0.32	13	4.89	4.13
	Nov	17.1	0.29	0.26	15	3.14	2.45
	Dec	15.0	0.25	0.24	20	1.84	2.21
2013	Jan	14.2	0.18	0.29	107	2.30	1.69
	Feb	15.1	0.14	0.35	95	3.15	2.63
	Mar	16.4	0.19	0.19	53	1.47	1.85
	Apr	21.8	0.16	0.51	100	4.64	4.09
	May	25.3	0.15	0.46	57	5.81	5.98
	Jun	30.5	0.16	0.42	45	10.15	8.56
	Jul	29.8	0.18	0.40	39	7.74	8.49
	Aug	29.4	0.19	0.41	46	7.21	7.50
	Sep	28.6	0.20	0.46	24	8.40	7.12
	Oct	23.5	0.22	0.45	20	5.27	5.00
	Nov	17.7	0.24	0.34	31	3.99	2.32

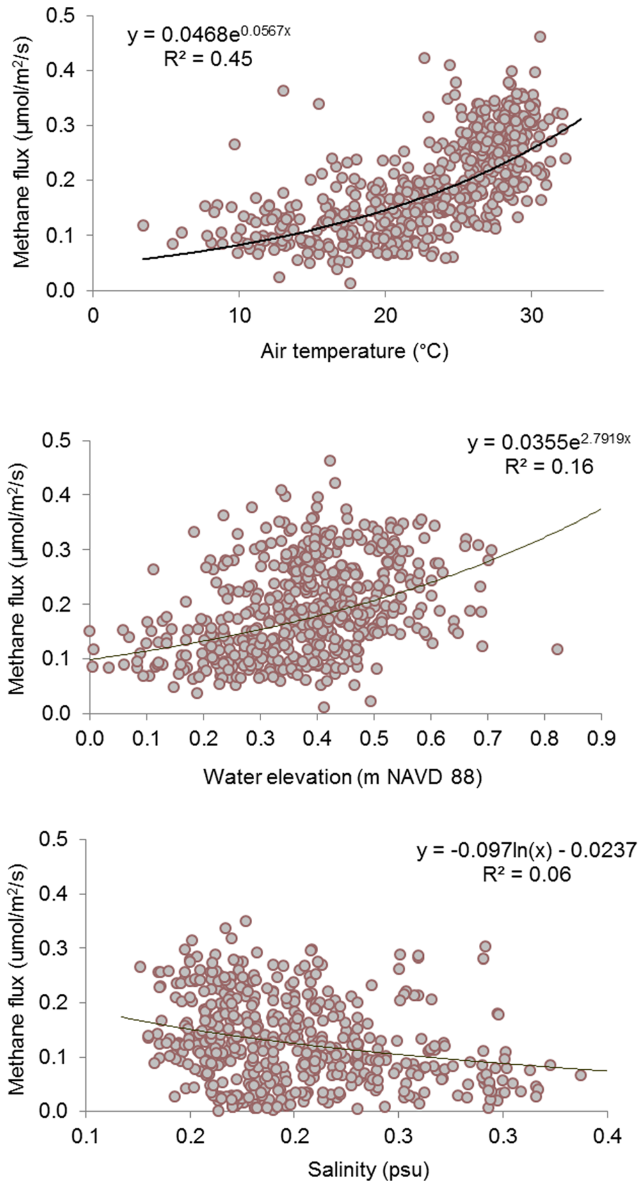

Fig. 3 Mean daily methane flux trends with air temperature, water elevation, and salinity from the freshwater study site over two years. For these relationships, methane flux was adjusted by +0.06 μmol/m^2/s to accommodate negative values

reducing salinity, and there was a weak inverse effect of diversion discharge on methane emissions (R^2 = 0.07; y = −0.019*Ln(x) + 0.1892). There was no difference in monthly methane emissions during April of both years, even when diversion discharge was three-fold greater (34 m^3/s during 2012 and 100 m^3/s during 2013; Fig. 4, Table 3).

Brackish Site

For the one year of data collection at the brackish site, 7524 30-min measurements of the 19,684 samples were retained for analysis, resulting in a 38% acquisition of quality data. For the study period, the median methane concentration was 2.06 ppb and flux was 0.022 μmol/m^2/s (Fig. 5). A protracted period of low level emissions (<0.05 μmol/m^2/s) extended from Oct 2011 until Jul 2012, after which methane emissions pulsed (0.15 μmol/m^2/s). This period of increased methane release corresponded in general with a marked reduction in salinity, increased inundation, and high summer temperatures (Table 4).

Daily means of methane flux were calculated for 325 out of 424 days resulting in 99 days that were gap filled. The model showed significant contributions to methane flux from the following environmental covariates: air temperature (p = 0.013), water temperature (p = 0.009), and salinity (p < 0.001). Water elevation was not a significant variable (p > 0.15) for predicting methane emissions. For most environmental variables, the relationship with methane flux changed over the year, which we accounted for by applying different adjustments by quarter. By excluding water temperature or air temperature in the model, there was a 6% difference in explaining methane emissions, with water temperature providing an improved fit (R^2 = 0.69).

The best model had a RMSE of 0.0344 μmol/m^2/s, and the overall goodness of fit was R^2 = 0.71. Using the measured and predicted data (during missing days), the integrated estimate of methane emissions was 13.8 g CH_4/m^2/yr for the year 2011–2012, with a predicted to observed error of ±2.0 g CH_4/m^2/yr, or 14.3% of the mean (Table 2). Assuming that the radiative forcing of methane is 30 times greater than that of carbon dioxide on a mass basis, the brackish marsh emitted methane equivalent to 4.1 tCO_2e/ha/yr.

Based on a reduced monthly multiple regression model (similar to the gap filling model, but using just water temperature and salinity as covariates), monthly means of the environmental covariates provided a comparable annual methane budget that was derived from daily means (Table 4; see Supplemental Electronic Material, Appendix B for equations). The reduced monthly model overestimated the annual budget by 9% predicting an annual flux of 15.0 g CH_4/m^2/yr as compared to the measured annual flux of 13.8 g CH_4/m^2/yr.

With respect to bivariate trends, methane flux from the brackish site was strongly related to salinity, which explained approximately 25% of the methane flux variation (Fig. 6). For the course of the study, salinity varied from 2 to 17 psu. Porewater salinity was more stable (mean = 9.3 ± 1.0) than the continuously recorded salinity (mean = 7.0 ± 3.5) (Fig. 7). Methane emissions were positively related to water level, which explained 18% of the methane emissions variation (Fig. 6). The highest emissions occurred when the water elevation exceeded the soil surface (Fig. 6). Only 17% of the methane flux was explained by air temperature (Fig. 6). The peak of monthly methane flux corresponded to the highest water level (0.56 m NAVD88) and the lowest salinity

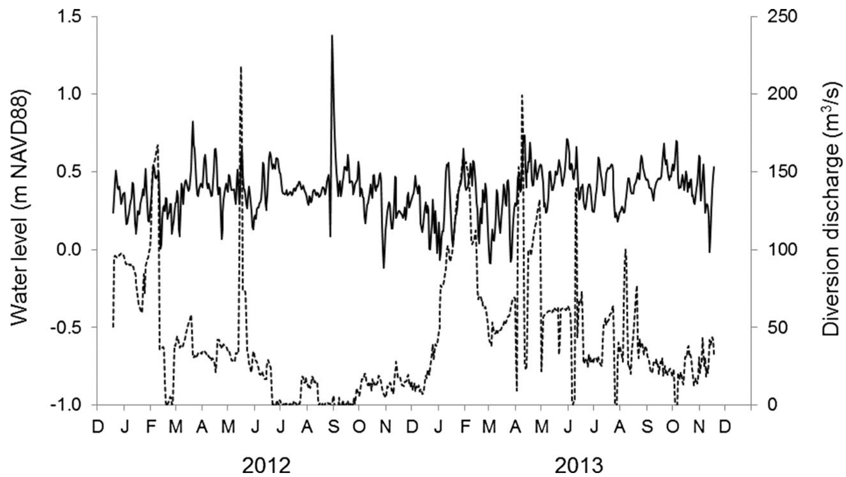

Fig. 4 Mean daily water level (solid) and river diversion discharge (dashed) at the freshwater study site over two years

(3.7 psu) recorded for the study period (Aug 2012; Table 4; Fig. 7).

Discussion

Applicability and Limitations of Methane-Salinity Relationship

The methane flux estimates from the eddy covariance technique for our freshwater and brackish sites conformed to a methane-salinity gradient that was developed from chamber-based annual budgets from regularly inundated tidal wetlands (Poffenbarger et al. 2011; Fig. 8). When data from our study were combined with those from Poffenbarger's meta-analysis, the relationship varied only by 1%, demonstrating agreement to the original relationship. While continued research results will likely refine the relationship further, the data from this study demonstrate that Louisiana wetlands are within the normal range of observation from a spatially broad selection of study areas. We had expected that the annual methane flux estimates from this study would be reasonably greater than the data derived from the meta-analysis using chamber data, given the ability of EC methods to capture ebullition events which may be more difficult to capture with intermittent chamber sampling events (Petrescu et al. 2015) as well as methane efflux from a greater proportion of shallow open water environments than is commonly included in chambers. Seasonal trends and the annual magnitude of methane emissions, however, have been shown elsewhere to agree reasonably between eddy covariance and chamber based measurements, although discrepancy at shorter scales is not uncommon (e.g. diurnal; Schrier-Uijl et al. 2010; Zhang et al. 2012; Wang et al. 2013; Yu et al. 2013).

From a practical perspective, the existing methane-salinity relationship (Poffenbarger et al. 2011) should be considered as an acceptable predictor variable to develop default methane emissions factors across natural tidal marshes in Louisiana, especially when complemented with continuous water temperature and salinity measurements, which are collected at more than 390 sites in coastal Louisiana through the Coastwide Reference Monitoring System (CRMS-*Wetlands*).

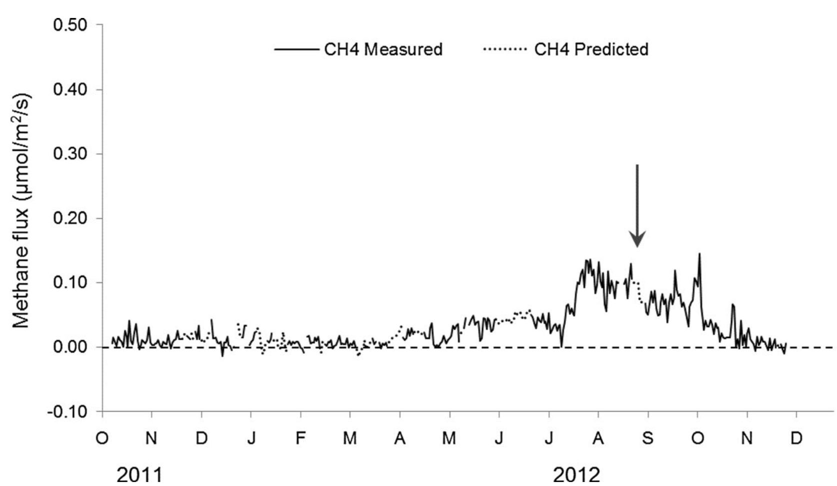

Fig. 5 Mean daily methane flux from the brackish study site. The arrow indicates the passage of Hurricane Isaac which flooded (>1.0 m) the marsh surface

Table 4 Monthly mean methane flux (observed and predicted) with corresponding environmental data for the brackish site. The reduced multiple regression model for predicting monthly methane flux contained the covariates of water temperature and salinity (see SEM, Appendix B for predictive equations). Environmental data source: Coastwide Reference Monitoring System (CRMS-*Wetlands*)

Year	Month	Water Temperature	Salinity	Water Level	Observed Methane Flux	Predicted Methane Flux
		(°C)	(psu)	(m NAVD88)	(g CH_4/m^2/mo)	(g CH_4/m^2/mo)
2011	Oct	22.9	6.7	0.30	0.54	0.90
	Nov	19.2	11.4	0.31	0.50	0.21
	Dec	15.7	9.5	0.28	0.60	0.28
2012	Jan	16.7	7.4	0.23	0.37	0.35
	Feb	17.5	6.3	0.24	0.24	0.23
	Mar	23.0	6.6	0.36	0.22	0.23
	Apr	24.6	5.5	0.41	0.75	0.59
	May	27.9	5.2	0.36	1.27	1.24
	Jun	29.3	8.9	0.45	1.84	1.48
	Jul	29.4	6.2	0.44	2.59	1.95
	Aug	27.6	3.7	0.56	4.31	4.24
	Sep	28.5	4.3	0.51	2.89	3.15
	Oct	23.9	5.8	0.37	1.93	1.19
	Nov	18.2	10.8	0.30	0.32	0.47
	Dec	19.5	11.7	0.35	0.06	0.20

These sites can be used to create robust monthly means of the two most critical variables (salinity and water temperature) to inform methane emission factors for baseline (reference area) conditions, at least when salinity is less than 18 psu as we document here.

Freshwater River Diversion and Environmental Variables Affecting Methane Emissions

The freshwater site exhibited remarkable stability with respect to methane emissions among years despite a more than two-fold difference in river volume discharged into the wetland. The low discharge in the first year corresponded with a drought on the Mississippi River, while river diversion discharge during the second year was similar to typical annual diversion operations. Our working hypothesis was that methane emissions would be suppressed by increased river discharge, given the potential for increased loading of river-borne alternate electron acceptors, such as nitrate (Reddy and DeLaune 2008), sulfate (Swarzenski et al. 2008), and iron-oxides. Although the effect of river discharge on wetland methane emissions contributed significantly to the multiple regression, from a practical standpoint a meaningful relationship cannot be developed that couples the response of methane flux to river discharge. Thus, we must conclude that the magnitude of ionic loading was insufficient with respect to location of our study site or a discharge response threshold was not observed. The location of our site, which is outside of the dominant flow paths and within an interior wetland setting, may explain to some degree why differences in methane emissions were negligible between years. This would suggest that methane regulation by river water constituents (ionic loading) is constrained to near-field, localized areas and/or higher discharge conditions would be required to have a detectable effect on methane efflux.

Methane emissions from freshwater wetlands in Louisiana using chamber based methods have reported rates more than two times greater than our annual estimates (DeLaune et al. 1983). However, freshwater tidal wetlands in Virginia emitted methane at rates (96 g CH_4/m^2/yr; Neubauer 2013) more comparable to our study (63 g CH_4/m^2/yr). In addition, based on a summary of methane emissions from temperate, rich-fen wetlands, Turetsky et al. (2014) showed that emissions (66 g CH_4/m^2/yr; largely derived from chamber studies) were also comparable to our estimates from the freshwater site.

While water depth relative to the soil surface is commonly recognized as a primary factor controlling methane emissions (Whalen 2005), the lack of a strong statistical relationship in the case of both of the sites studied here may suggest that persistent soil saturation or inundation, which is typical of micro-tidal delta wetlands in Louisiana, sustains anaerobic conditions near the soil surface, which is optimal for methane production. In a 3-yr study of methane efflux rates across a range of tidal wetlands in Louisiana's Delta Plain, Alford et al. (1997) found that water level depth was also insignificant in describing methane emissions. Combining the results of both Alford et al. (1997) and Crozier and DeLaune (1996), the most important factors for predicting methane emissions in these micro-tidal systems were temperature, labile carbon

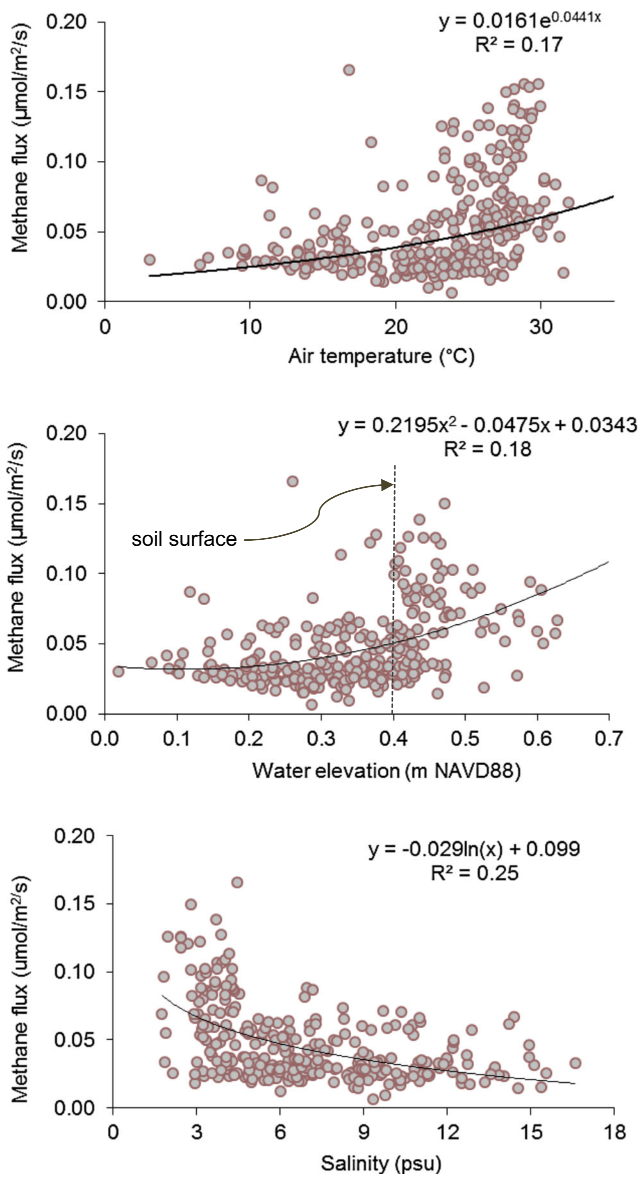

Fig. 6 Mean daily methane flux trends with air temperature, water elevation, and salinity from the brackish study site over one year. For these relationships, methane flux was adjusted by +0.02 μmol/m^2/s to accommodate negative values

availability, and sulfate concentration, which largely correspond to the sensitive variables from our analyses.

Implications to Climate Regulation with Large-Scale Wetland Restoration

Our study confirms that natural Louisiana tidal freshwater marshes, on an annual basis, produce enough methane to offset annual soil carbon sequestration estimates, if long-term rates of $^{137}Cs/^{210}Pb$ measured deposition are assumed appropriate for carbon balance accounting purposes. The conservative approach of using long-term or multiple year integrated (feldspar accretion) soil carbon accumulation is recognized under wetland carbon offset monitoring protocols (ACR and VCS). When we account for annual net ecosystem exchange (using quasi-continuous measurements of both CH_4 and CO_2 fluxes with EC), the conclusion of the freshwater marsh as a net radiative source changes, as opposed to using average soil carbon accumulation as the basis of comparison. For instance, based on a complete accounting of the annual carbon fluxes (CO_2 + CH_4) from our freshwater site, we found that net CO_2 uptake was substantially greater than CH_4 emissions for both years, enough to determine that this site is a net radiative sink using GWPs, or will become a net radiative sink using sustained flux global warming and cooling potentials in combination (sensu Neubauer and Megonigal 2015). While EC is acceptable for determining carbon project benefits, the effect of nonlocal emissions of CO_2 and CH_4 exported elsewhere in the estuary would still need to be resolved. Moreover, the cost of EC monitoring may be cost prohibitive for most carbon projects. Using soil carbon accumulation for determining project benefits (for herbaceous temperate wetlands, at least) appears to be a conservative approach from a market perspective, despite some uncertainty differentiating allochthonous and autochthonous contributions to the soil record (Poffenbarger et al. 2011).

From a climate forcing perspective, the results from this study demonstrate that methane release from the brackish marsh generally can offset one-half or more of the annual soil carbon sequestration, when long-term rates of soil carbon sequestration from healthy coastal marshes are assumed (~200 g C/m^2/yr). A caveat is that our brackish marsh site experienced a rapid transition from an initially healthy to deteriorated state, and there was a net carbon loss when net ecosystem exchange of both CO_2 and CH_4 were considered in tandem (data not shown). At the present time, the benefits of restoring wetlands in the Mississippi River Delta for climate regulation will hinge not as much on annual sequestration benefits as also preventing the loss of existing wetland area and the subsequent emissions of organic-rich soils after erosion and transport into the marine environment. As delta wetlands deteriorate to open water, it has been demonstrated that often 1.5 m of wetland soil is eroded (Wilson and Allison 2008), which is equivalent to the loss of appreciably more than one century of wetland carbon burial.

Wetland restoration schemes in the Mississippi River delta are being planned and implemented to reintroduce sediments to the estuary and rebuild wetlands in the form of dredged sediment placement and sediment diversions from the river. The current coast-wide plan (CPRA 2012) calls for investment of >20 billion (USD) to sustain and/or rebuild 130,000 ha of wetland

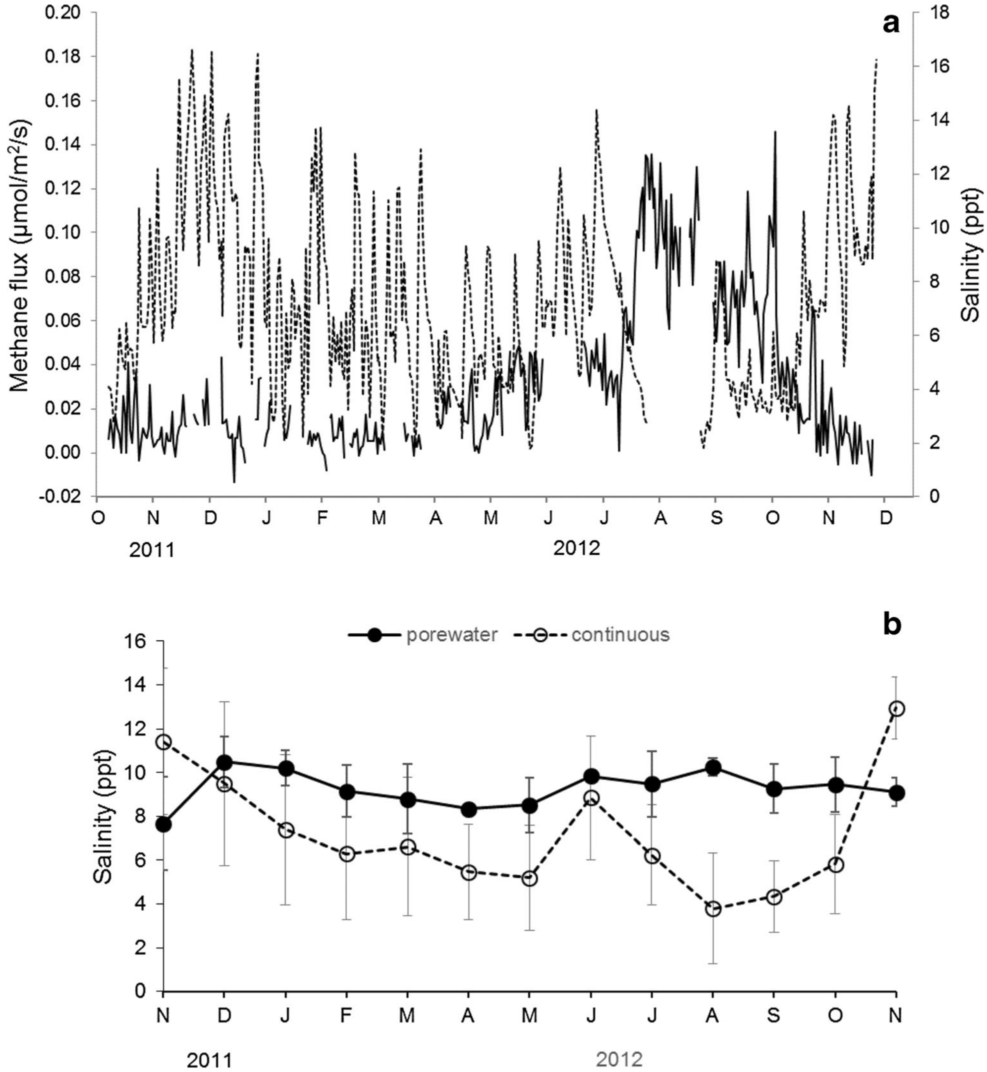

Fig. 7 Mean daily methane flux (solid line) and continuous salinity (A) and monthly mean porewater and continuous salinity (B) from the brackish study site

over 50 years. As the coastal restoration master plan is implemented, there will be substantial freshening of some estuarine areas, which will have implications for increasing methane emissions, while concomitantly preventing losses of existing soil carbon. Even though increasing freshwater delivery to the estuary will

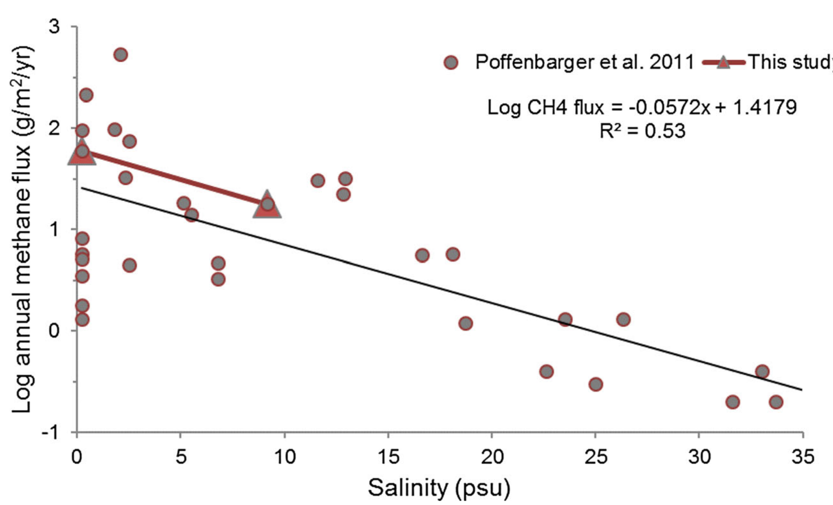

Fig. 8 Comparison of annual methane emissions and salinity developed by Poffenbarger et al. 2011(chamber-based from various tidal wetlands) and the ecosystem-level annual fluxes from this study

increase future methane emissions, the combined effects of barrier island restoration, wetland creation, and river diversions could have considerable climate regulation benefits by reducing emissions of vast reservoirs of wetland soil carbon, in addition to enhancing future carbon sequestration. In general, regardless of salinity, projects that restore or enhance annual carbon sequestration, while further reducing the loss of soil carbon will be most advantageous in the context of providing carbon offset benefits.

Conclusions

Despite the heterogeneity of temperate estuaries summarized in the Poffenbarger et al. (2011) meta-analysis and the perceived shortcomings of chamber based studies, taken in light of the supporting results of this study, salinity remains a robust predictor of annual methane emissions. From a climate perspective, the combined results of our study with the Poffenbarger salinity-methane model can be useful for quantifying and refining the expected contribution of methane from mature tidal marsh landscapes to climate forcing.

From an applied standpoint, practitioners of wetland carbon offset projects could use the salinity-methane relationship to establish default annual methane emission factors. The relationships developed by this study also provide the ability to predict annual methane emissions on a greater temporal frequency (monthly) for fresh and brackish coastal marshes in the Mississippi River Delta. With respect to carbon offset project scenarios, given the diverse types of tidal wetland restoration strategies applied at regional scales, annual methane emission factors could potentially be used with justification from project developers as data become available.

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