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ARTICLE

Salinity Influence on Methane Emissions from Tidal Marshes

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Abstract The relationship between methane emissions and salinity is not well understood in tidal marshes, leading to uncertainty about the net effect of marsh conservation and restoration on greenhouse gas balance. We used published and unpublished field data to investigate the relationships between tidal marsh methane emissions, salinity, and porewater concentrations of methane and sulfate, then used these relationships to consider the balance between methane emissions and soil carbon sequestration. Polyhaline tidal marshes (salinity >18) had significantly lower methane emissions (mean ± sd=1±2 $g m^{-2} yr^{-1}$) than other marshes, and can be expected to decrease radiative forcing when created or restored. There was no significant difference in methane emissions from fresh (salinity=0–0.5) and mesohaline (5–18) marshes (42±76 and 16±11 $g m^{-2} yr^{-1}$, respectively), while oligohaline (0.5–5) marshes had the highest and most variable methane emissions (150±221 $g m^{-2} yr^{-1}$). Annual methane emissions were modeled using a linear fit of salinity against log-transformed methane flux ($\log(CH_4) = -0.056 \times \text{salinity} + 1.38$; $r^2 = 0.52$; $p < 0.0001$). Managers interested in using marshes as greenhouse gas sinks can assume negligible methane emissions in polyhaline systems, but need to estimate or monitor methane emissions in lower-salinity marshes.

Keywords Carbon sequestration · Sulfate reduction · Methane flux · Porewater

Introduction

Concern about global climate change has sparked interest in developing effective ways to remove greenhouse gases from the atmosphere. Wetland ecosystems can act as greenhouse gas sinks through the photosynthetic uptake of carbon dioxide and subsequent storage in long-lived biomass (e.g., wood) or burial in soils, and as sources through the release of methane and nitrous oxide produced during anaerobic organic matter decomposition. North American wetlands sequester approximately 49 million tons of carbon per year (Bridgham et al. 2006), yet freshwater wetlands are also an important natural source of atmospheric methane (Schlesinger 1997). Policymakers striving to expand carbon sinks have considered the conservation and restoration of wetlands as a carbon offset activity in the context of climate change policy (Wylynko 1999, Watson et al. 2000); however, further assessment of the greenhouse gas balance of wetlands is needed in order to develop policies that effectively decrease radiative forcing.

It is generally understood that wetlands exposed to high concentrations of sulfate (an anion present in seawater) emit methane at relatively low rates. The presence of sulfate in tidal marsh soils allows sulfate-reducing bacteria to

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outcompete methanogens for energy sources, consequently inhibiting methane production (DeLaune et al. 1983, Bartlett et al. 1987, Wang et al. 1996). This relationship can be complicated by site-specific conditions that may allow methane production in saline marshes to persist despite the inhibitory effects of sulfate (Megonigal et al. 2004, Weston et al. 2011). For example, methanogenesis can occur in saline marshes if sulfate availability is limited by resupply through diffusion or sulfide oxidation (King and Wiebe 1978). The relationship between sulfate concentrations and methane emissions is further complicated by variability in rates of methane oxidation, which can consume a large fraction of the methane produced in soils before it is emitted to the atmosphere (Megonigal and Schlesinger 2002, Whalen 2005). Because methane production and oxidation are regulated by temperature and plant activity, significant temporal and spatial variation in the sources and sinks of both sulfate and methane can create conditions where the two processes coexist.

While the general relationship between sulfate concentration and methane emissions is well-supported, it is not known if there is a specific salinity ratio or sulfate concentration above which tidal marsh methane emissions are negligible in the context of carbon sequestration and greenhouse gas emissions. It is also unclear to what extent methane emissions in tidal marshes are offset by carbon sequestration (or vice versa) in various salinity regimes.

Here we report an analysis of literature-derived and new field data on methane emissions from tidal marshes. Our objectives were to: (1) quantify the relationship between methane emissions and salinity in tidal marshes and (2) interpret tidal marsh methane emissions in the context of carbon sequestration rates and the radiative balance of tidal marshes.

Methods

Data were gathered from published in situ studies of herbaceous tidal marshes ranging in salinity from tidal freshwater to polyhaline, and from two original field studies (Table 1); two of the tidal freshwater sites had a tree canopy overtopping herbaceous vegetation. We did not include mangroves. We chose studies that included data on methane emissions and salinity, conductivity, or chlorinity (these units are interconvertable); porewater methane and sulfate; or porewater methane and salinity (as calculated from conductivity or chlorinity) (Table 1, Online Appendix 1). We only used porewater data if the sample depth of porewater methane could be matched with either salinity or sulfate. Individual sample locations within a site were eliminated if they did not match these criteria, as were sites where methane fluxes could not be matched to a salinity regime. The ideal methane emissions study would have reported porewater salinity measured at the same time emissions were measured, but given the scarcity of data, we accepted studies if they reported the salinity of an adjacent tidal creek or an annual average salinity during the same growing season. Descriptions of the different methods used to measure the variables included in our analysis are found in Online Appendix 2.

In analyzing methane flux data from the selected studies, we used average annual methane emissions when it was reported. If methane emissions had been measured over all seasons of the year but the annual rate was not reported (i.e., Kelley et al. 1995, Megonigal and Schlesinger 2002), we calculated it by extracting emission rates from tables and figures, then interpolated between time points. For short term studies lasting a few days to months over the growing season, we calculated average daily methane emission and converted it to annual emission using the rate conversion factors determined by Bridgham et al. (2006) (annual:daily ratio of 0.36 for tidal freshwater wetlands and 0.34 for wetlands with salinity >0.5). These factors were based on 30 studies that reported both annual and daily rates, and they represent the ratio of average annual flux in units of g m^{-2} yr^{-1} to average daily flux in units of mg m^{-2} d^{-1} (Bridgham et al. 2006). We averaged annual fluxes when more than one year was reported for a given site.

Several of the studies in this review used either transparent or opaque flux chambers, with just three studies that used both. The presence of light can have either large effects (Van der Nat and Middelburg 2000) or negligible effects (Bartlett et al. 1987) on methane emission rates, depending on plant community composition. Most studies in this analysis did not account for possible differences in methane emissions in light and dark conditions. In three of the studies, both light and dark measurements were made, allowing a day length-integrated rate to be calculated for a 24-h period. We used the day length-integrated rate reported by Van der Nat and Middelburg (2000) in our analysis, and calculated such a rate from data reported by Hirota et al. (2007) and Wang et al. (2009) (Table 1).

In the studies included in this analysis, methane emissions were either measured at low tide when the soil surface was exposed (e.g., Van der Nat and Middelburg 2000, Megonigal and Schlesinger, 2002), or under both flooded and exposed conditions (e.g., DeLaune et al. 1983, Tong et al. 2010). Bartlett et al. (1985, 1987) found no effect of water level on methane emissions over full tidal cycles. Kelley et al. (1995) reported a large spike in emissions when the water table was nearest the soil surface, and Tong et al. (2010) reported that methane emissions when the soil surface was exposed were 55% of emissions under flooded conditions. Tong et al. (2010) explicitly

Table 1 Summary of data extracted from references and one original study on annual methane emissions from tidal marsh ecosystems

Site name	Dominant plant species	Chamber[a]	Sample frequency[b]	Salinity[c]	Soil surface flooding[d]	Daily flux reported (mg $CH_4/m^2/d$)	Annual flux reported[e] (g CH_4/m2/yr)	Annual flux estimated[f]	Annual flux used	Ref[g]
Fresh	*Panisum hemitomon*	dark	13 (17 mo)	0.4	not systematic		213.3		213.3	1
Brackish	*Spartina patens*	dark	13 (17 mo)	1.8	not systematic		97.3		97.3	1
Salt	*Spartina alterniflora*	dark	13 (17 mo)	18.1	not systematic		5.7		5.7	1
Creek bank	*S. alterniflora*	dark	16 (20 mo)	18.7	exposed		1.2		1.2	2
High marsh	*S. patens, Distichlis spicata*	dark	13 (13 mo)	22.6	exposed		0.4		0.4	2
Short *Spartina*	*S. alterniflora*	dark	21 (24 mo)	26.3	exposed		1.3		1.3	2
Site 1	*Spartina cynosuroides*	dark	11 (12 mo)	5.1	not reported		18.2		18.2	3
Site 2	*S.alterniflora, S. cynosuroides*	dark	11 (12 mo)	12.8	not reported		22.4		22.4	3
Site 3	*S.alterniflora*	dark	11 (12 mo)	16.6	not reported		5.6		5.6	3
GI Near Bank	*Acer rubrum, Peltandra virginica*	dark	8 (13 mo)	0.25	exposed		8.2		8.2	4
GI Far Bank	*A. rubrum, P. virginica*	dark	8 (13 mo)	0.25	exposed		5.7		5.7	4
UF Near Bank	*A. rubrum, P. virginica*	dark	8 (13 mo)	0.25	exposed		5.1		5.1	4
UF Far Bank	*A. rubrum, P. virginica*	dark	8 (13 mo)	0.25	exposed		3.5		3.5	4
Upland edge	*Carex spp., Juncus gerardii*	dark	6 (1.5 mo)	23.5	not systematic	3.7		1.3	1.3	5
High marsh	*S. patens*	dark	6 (1.5 mo)	31.6	not systematic	0.5		0.2	0.2	5
Middle marsh	*Plantago maritima*	dark	6 (1.5 mo)	33.7	not systematic	0.6		0.2	0.2	5
Low marsh	*S. alterniflora*	dark	6 (1.5 mo)	35.1	not systematic	0.6		0.2	0.2	5
Scirpus Close	*Scirpus lacustris*	light + dark	68 (24 mo)	2.5	exposed		4.5		4.5	6
Phragmites Far	*Phragmites australis*	light + dark	68 (24 mo)	2.5	exposed		75.4		75.4	6
Sweet Hall	*P. virginica*	light	8 (15 mo)	0.25	exposed		96.0		96.0	7
Lower site	*Nyssa sylvatica, P. virginica*	dark	17 (20 mo)	0.25	exposed		1.3		1.3	8
Upper site	*Fraxinus spp., P. virginica*	dark	16 (20 mo)	0.25	exposed		1.8		1.8	8
Alresford Creek	*not reported*	light	12 (12 mo)	25.0	not reported		0.3		0.3	9
Colne Point	*not reported*	light	12 (12 mo)	33.0	not reported		0.4		0.4	9
C_3 Ambient CO_2	*Schenoplectus americanus*	light	14 (24 mo)	6.8	exposed	13.9		4.7	4.7	10
C_4 Ambient CO_2	*S. patens, D. spicata*	light	7 (24 mo)	6.8	exposed	9.6		3.3	3.3	10
Salt marsh	*Carex rugulosa, P. australis*	dark			flooded	600.0		204.0		11
Salt marsh	*Carex rugulosa, P. australis*	light			flooded	2365.7		804.3		11
24-h Day		light + dark	7 (3d)	2.1		1585.8		539.2	539.2	11
CD Marsh	*Scirpus mariqueter*	light			exposed		14.4			12
CD Marsh	*S. mariqueter*	dark			exposed		13.8			12
24-h Day		light + dark	9 (12 mo)	5.5			14.1		14.1	12
Wildlife	*S. patens, S. americanus*	dark	6 (6 mo)	11.6	exposed	90.0		30.6	30.6	13
Barbados	*S. patens, S. americanus*	dark	6 (6 mo)	12.9	exposed	94.0		32.0	32.0	13

Table 1 (continued)

Site name	Dominant plant species	Chamber[a]	Sample frequency[b]	Salinity[c]	Soil surface flooding[d]	Daily flux reported (mg $CH_4/m^2/d$)	Annual flux reported[e] (g CH_4/m2/yr)	Annual flux estimated[f]	Annual flux used	Ref[g]
Shanyutan wetland	*P. australis*	dark		2.3	exposed	122.4		41.9		14
Shanyutan wetland	*P. australis*	dark		4.2	flooded	48.0		16.3		14
Shanyutan wetland	*P. australis*	dark		2.3	exposed	112.8		38.7		14
All flood stages		dark	10 (12 mo)	2.3	Flooded + exposed		32.6		32.6	14

[a] "light" and "dark" indicate whether or not the chambers were transparent; "light + dark" indicates that both transparent and opaque chambers were used and the authors integrated the two rates in calculating emissions. In cases where the authors did not perform this calculation (references 11, 12), their light and dark emissions were used to calculate a day length-weighted sum for a 24 h period

[b] Number of sampling events (total length of study)

[c] Porewater salinity was reported when available (references 3, 5 and 14). Salinity in references 5 and 14 were from surface water when the site was flooded. In most cases the salinity of a nearby creek or water body is reported. The salinity of tidal freshwater wetlands was assigned a value of 0.25, the mid-point of their salinity range (0–0.5) by definition. Salinity for reference 10 was taken from Fig. 1 of Erickson et al. (2007)

[d] Indicates whether the soil surface was exposed or flooded during emission measurements. In cases deemed "not systematic", fluxes were measured under both flooded and exposed conditions but flooding was either determined to have no effect on emissions (reference 1), or the effects were not determined (reference 5). Reference 14 was the only study to systematically account for the effects of flooding

[e] Emissions for reference 4 were based on Table 2 and accounted for the length of time between sample dates. They differ for this reason from the values reported in Bridgham et al. (2006) that were based on Table 1 of reference 4. Emissions for reference 8 taken from the 20-month period reported in Fig. 3; the last four months of the two-yr period were estimated from mean flux rates during the same months in the previous years

[f] Estimated from daily flux rates by multiplying freshwater sites by 0.36 and saline sites by 0.34 (see Bridgham et al. 2006)

[g] 1 = DeLaune et al. 1983 (fig 4), 2 = Bartlett et al. 1985 (pg. 5714), 3 = Bartlett et al. 1987 (pg. 190), 4 = Kelley et al. 1995 (table 2), 5 = Magenheimer et al. 1996 (table 2), 6 = Van der Nat and Middelburg 2000 (table 1), 7 = Neubauer et al. 2000 (pg. 22), 8 = Megonigal and Schlesinger 2002 (fig. 3, mean values), 9 = Nedwell et al. 2004 (table 2), 10 = Marsh et al. 2005 (fig. 3), 11 = Hirota et al. 2007 (fig. 2), 12 = Wang et al. (fig. 4) 2009, 13 = this paper, 14 = Tong et al. 2010 (pg. 510)

accounted for variation across the tidal cycle in their estimate of daily methane emission rate. Several studies did not specify the flooding conditions during methane flux measurements. Given the limited size of this data set, we did not attempt to analyze the data for methodological biases related to light, water table depth, or other factors.

Porewater data were drawn from studies that reported at least two of three variables—[CH_4], a salinity metric (salinity, [Cl^-] or conductivity) and [SO_4^{2-}]—at each depth or sample point. This dataset was limited to three studies because most studies reported just one of the three variables, usually [CH_4]. Data were extracted from two of the studies (Bartlett et al. 1987, Tong et al. 2010) by visual interpretation of graphs, while 3108 observations from a third study were obtained from the authors (Keller et al. 2009). The methane flux and porewater data were compiled into three subsets: methane emissions versus salinity (31 observations), porewater methane versus salinity (3136 observations), and porewater methane versus sulfate concentration (3139 observations). We did not relate porewater sulfate concentration to methane emissions because either the two variables were not reported, or the reported values could not be paired with one another at a given location or time.

We supplemented literature data on methane emissions with original data from two marshes in the Blackwater National Wildlife Refuge, Maryland, USA. We made monthly measurements of methane emissions and porewater concentrations of methane, sulfide, and salinity. One marsh had been created in 2003 using locally dredged organic and mineral materials and the other was natural. We collected data from May through October 2008 at three interior-marsh locations distributed across the full area of the marsh. Methane emissions were measured with opaque static chambers, withdrawing five headspace samples by plastic syringe over a 1-hr period. Samples were stored in the same syringes used to take them until analysis. In order to quantify leakage rates, replicate syringes were filled with methane standard gases in the field and analyzed as samples (Megonigal and Schlesinger 2002). A correction factor was applied to samples based on the average difference in methane concentration between fresh and stored standards. Methane concentration was quantified, typically within 48 hr of collection, by flame ionization chromatography on a Shimadzu GC-14A gas chromatograph (Shimadzu Corporation, Kyoto, Japan).

We added additional sites to our porewater analysis with a synoptic sample of tidal marshes located along a salinity gradient on the Nanticoke River, Maryland and Delaware, USA. The samples were taken over approximately one week in late July of 2008. Measurements included salinity and porewater methane, taken at three locations in each of five marsh sites (Table 1). Porewater was sampled using a sipper (Online Appendix 2) and the analytical methods described by Keller et al. (2009). Dissolved methane concentration was quantified with flame ionization gas chromatography after equilibration with an equal volume of ambient air. An aliquot of the sample was 0.45 μm filtered, then analyzed on a Dionex DX 500 ion chromatography system (Dionex Corporation, Sunnyvale, California, USA) for chloride concentrations.

Many of the studies reporting methane emissions did not provide measurements of porewater salinity, so we often used salinity reported for a nearby tidal creek. In converting porewater conductivity to salinity for this analysis, pressure was calculated based on the depth at which the measurement was taken, with the pressure at 1 m depth of water equal to roughly 1 dbar. If temperature was not reported, we assumed 20°C for our calculations. Salinity was calculated from chloride concentration using the equation: salinity= 1.80655 × chlorinity (Lyman 1969).

There were too few studies of nitrous oxide emissions from tidal wetlands to detect patterns across salinity gradients, and we did not attempt to do so. We did not consider studies of carbon dioxide emissions because only the net flux (uptake minus emissions) is meaningful for greenhouse gas budgets in the context of radiative forcing. The most common way of estimating net carbon dioxide flux is the indirect approach of measuring changes in the pools of soil organic matter or wood, which increase as carbon is sequestered and often decrease with perturbation. We discuss some issues to be considered when using pools to estimate changes in carbon storage in tidal wetland ecosystems.

Statistical Analyses

Regression and correlation analyses were performed in Microsoft Excel and S-Plus (Insightful Corporation, 2001). Normality of the distribution of methane emissions within salinity regimes was tested with Statistical Analysis Software (SAS Institute, 1987) using Proc Univariate. Because two of the distributions were not normally distributed, methane emissions was log transformed before being tested with ANOVA and a least significant difference (LSD) means comparison test in SAS. Quantile curves of the relationships among the [CH_4], [SO_4^{2-}] and salinity data from Keller et al. (2009) were calculated by dividing the x-axis (i.e., [SO_4^{2-}] or salinity) into 13 (approximately 1 mM) bins, calculating quantiles separately for each bin using SAS Proc Univariate, then fitting a curve to the quantiles versus the mid-point of each bin with a second-order polynomial in Microsoft Excel. Quantiles of the Chmura et al. (2003) marsh (not mangrove) data were calculated with S-Plus, which uses linear interpolation between ordered data.

Results

Methane Emissions Versus Salinity

Consistent with prior work, we found a negative relationship between porewater salinity and methane flux (Fig. 1). This trend was only partly supported when the data were grouped by salinity class. Mean methane emissions were significantly lower for polyhaline (>18) systems than the other salinity classes (Table 2). Methane emissions were generally lower in mesohaline (5–18) systems than in freshwater (<0.5) systems, but this difference was not statistically significant. Oligohaline systems (0.5–5) had significantly higher emissions than the other classes, including tidal freshwater wetlands. However, the sample size of the oligohaline class was also the smallest at five replicates. Removing one oligohaline site with very high emissions, measured over just three days in August (Hirota et al. 2007), changed the result of the analysis such that the only significant difference overall was between polyhaline and non-polyhaline systems. The highest variability coincided with the highest emissions in the salinity range of 0–5 (Table 2). Polyhaline marshes had a mean methane emission rate of 1.1 g CH_4 m^{-2} yr^{-1}, which is equivalent to emitting 0.3 Mg CO_2 ha^{-1} yr^{-1} based on a 100-year global warming potential. We modeled the influence of salinity on methane emissions with a curvilinear relationship based on the linear fit of salinity against log-transformed methane emissions (r^2=0.52; $p<$ 0.0001; $\log(CH_4) = -0.056 \times \text{salinity} + 1.38$) (Fig. 1).

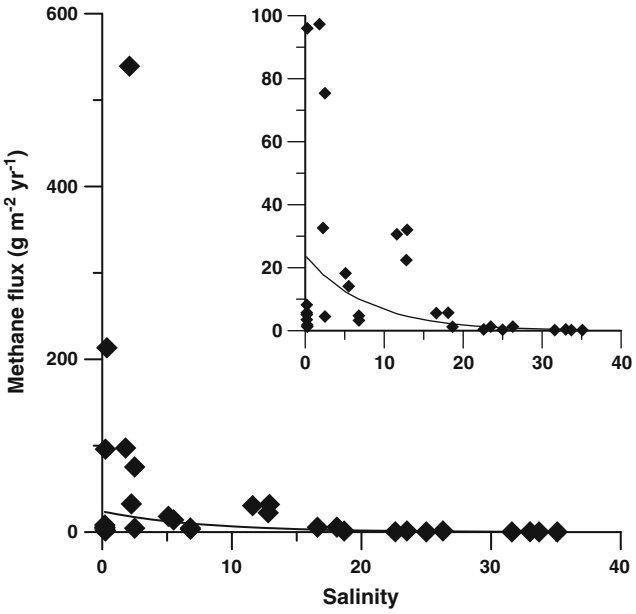

Fig. 1 Tidal marsh methane emissions versus salinity from published sources and field sites in Maryland, USA (Table 1). The black-line curve is the linear fit of the salinity data against the log-transformed methane flux data. The inset presents the same data and curve, but does not show points with emissions above 100 g CH_4 m^{-2} yr^{-1}

Porewater Methane, Sulfate and Salinity Relationships

The data available for evaluating the relationship between salinity and porewater methane concentration included a series of sites on the Nanticoke River that ranged in salinity from 0 to 5.5, a large dataset collected from a single marsh with an average salinity of 6.8 (Keller et al. 2009), and a third dataset collected from a single marsh with average salinity of 2.3 (Tong et al. 2010) (Fig. 2a). These data indicated a negative relationship between the two factors within this limited salinity range. As with methane emissions, both concentration and variability of porewater methane concentrations decreased with increasing salinity. It seems that salinity places an upper limit on methanogenesis, but the lower limit is governed by factors other than salinity.

The datasets available for evaluating the relationship of porewater sulfate and methane concentrations, other than that of Keller et al. (2009), covered a salinity range of 5–17. These data suggest that there may be a threshold at about 4 mM sulfate, above which [CH_4] was generally <25 μM (with one outlying point) and below which values ranged widely from 0 to 520 μM (Fig. 2b). There were no data other than Keller et al. (2009) to evaluate the relationship of salinity and sulfate. The Keller data indicates a positive relationship between the two variables, but with considerable variability (Fig. 2c).

Discussion

The goal of our literature synthesis was to analyze methane emissions in the context of the common notion that created or restored tidal wetlands are effective ecosystems for mitigating radiative forcing and consequent climate change (Chmura et al. 2003, Bridgham et al. 2006, Nellemann et al. 2009). To our knowledge, the last attempt to relate tidal wetland methane emissions to salinity and related factors was based on a single tidal creek (Bartlett et al. 1987), and methane emissions were not interpreted in the context of soil carbon sinks. Although the studies we reviewed varied widely with respect to methods (Online Appendix 2), data analysis, and specific sources of temporal and spatial variability, we found clear relationships between methane emissions and salinity. These data are sufficient for an initial approximation of the ranges of methane emissions that may be expected across salinity classes and to interpret methane emissions in the context of carbon sequestration rates and the radiative balance of tidal marshes.

Table 2 Statistical summary and carbon dioxide equivalents of methane emissions by salinity class from tidal marshes based on published and new field data

Salinity Class	Salinity range		Methane emissions (g m^{-2} yr^{-1})					Carbon dioxide equivalent of methane emissions (Mg CO_2 ha^{-1} yr^{-1}) [a]			
	ppt	N	Mean	Median	Min	Max	Standard deviation	Mean	Median	Min	Max
Fresh	<0.5	8	41.9[a]	5.4	1.3	213	76	10.5	1.4	0.33	53
Oligohaline	0.5–5	5	150[b]	75.4	4.5	539	221	37.5	18.9	1.1	135
Mesohaline	5–18	8	16.4[a]	16.2	3.3	32.0	11	4.1	4.0	0.83	8.0
Polyhaline	>18	10	1.12[c]	0.40	0.2	5.7	2	0.3	0.10	0.10	1.4

[a] Calculated based on a methane global warming potential of 25 (100-yr time horizon)

Factors Regulating Methane Emissions

We observed a significant log-linear relationship between salinity and methane emissions among 31 tidal marshes (Fig. 3). Our analysis confirms the results of Bartlett et al. (1987), who reported a log-linear relationship between annual methane emissions and salinity across three study sites. The present analysis extends this relationship to a wider range of salinity conditions, particularly to low salinity levels, and suggests that it is generally applicable to tidal marshes. The relationship should be useful for informing wetland creation, management, or research decisions in the absence of site-specific information, but it must be recognized that log transformation obscured a great deal of the variation in methane emissions. The magnitude and causes of this variation are important to consider before initiating projects.

High variation in methane emissions was found at low salinity (<5); similarly the variation in porewater methane increased dramatically at sulfate concentrations <4 mM. At low sulfate concentrations, it is likely that spatial and temporal variation in carbon and sulfate availability creates zones or microsites where sulfate reduction exceeds sulfate supply, causing sulfate reduction to become substrate-limited. Methanogens are the least competitive group of heterotrophic microorganisms in wetland soils, which

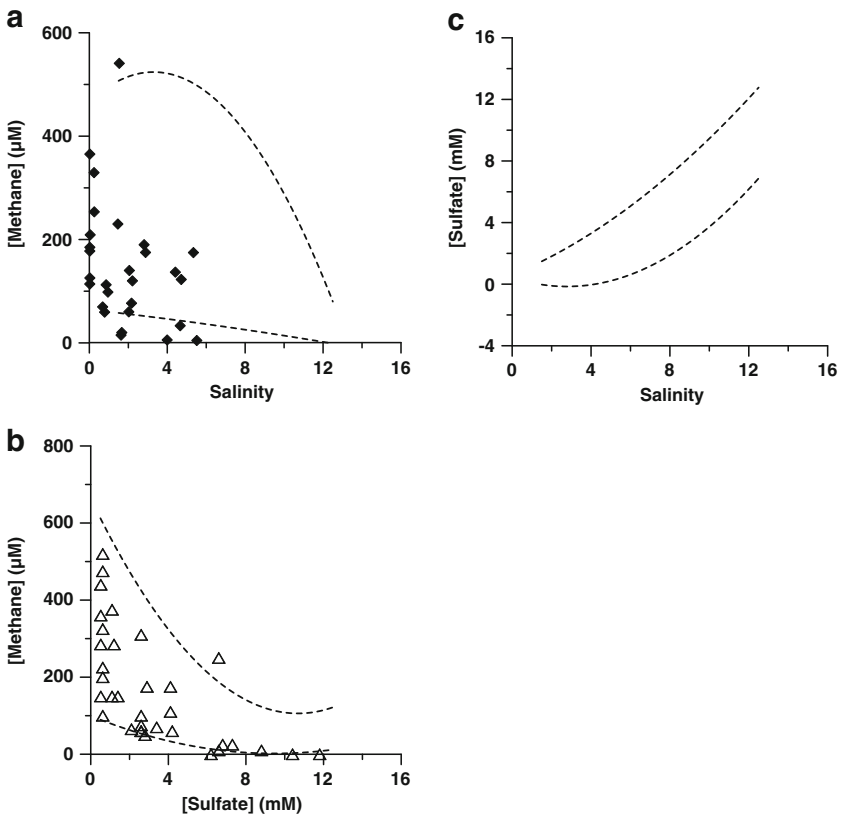

Fig. 2 Relationships among porewater solutes from published and new field data (Online Appendix 1). The dashed-line curves are polynomial fits of the 5% and 95% quantiles of porewater methane data collected by Keller et al. (2009). The panels show: **a** methane concentration versus salinity, **b** methane concentration versus sulfate concentration, and **c** salinity versus porewater sulfate concentration

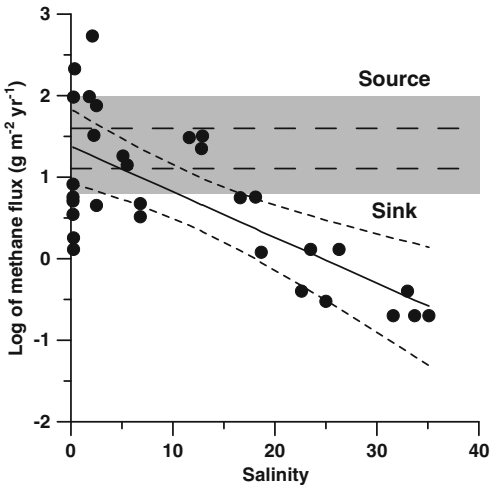

Fig. 3 Tidal marsh methane emissions versus salinity from published and new field data. The curve is a linear fit of salinity against log-transformed methane flux data with 95% confidence intervals (pointwise). The horizontal gray band represents the methane emission equivalents of the 5 and 95% quantiles of tidal marsh carbon sequestration rates reported by Chmura et al. (2003); the horizontal dashed lines are the 25 and 75% quantiles of this data set (methane equivalence based on a global warming potential of 25)

makes them sensitive to spatiotemporal variation in the availability of the major electron acceptors O_2, NO_3^-, Fe^{3+}, and SO_4^{2-}. Because none of these electron acceptors generally dominate freshwater wetland soils, microsite-level variation forms readily in response to imbalances in supply and consumption. As sources of both organic carbon and certain electron donors, plants are a major source of variation in methane emissions and the high diversity of plant species in freshwater wetlands, compared to saline wetlands, may contribute to the relatively high variation in methane emissions at low salinity levels (Sutton-Grier and Megonigal 2011). Because few methane studies have been done in tidal marshes in the salinity range of 5–15 (Figs. 1 and 2a), it is possible that our limited dataset did not capture high variability that also exists in the mid-salinity range.

Our analysis suggests that porewater methane concentrations are negligible at sulfate concentrations >4 mM (Fig. 2b). This estimate is somewhat higher than thresholds estimated in marine sediments, where methane production was found to be negligible at sulfate concentrations >1 mM (Senior et al. 1982, Winfrey and Ward 1983). The higher threshold in marsh soils versus marine sediments may reflect the relatively high supply of labile organic carbon (electron donor compounds) in marshes. At higher rates of organic carbon inputs, sulfate-depletion is rapid and higher sulfate concentrations may be needed to drive diffusion into microsites.

Salinity and sulfate data from Keller et al. (2009) plotted in Fig. 2c indicate considerable variability in sulfate concentration at a given salinity level. Sulfate concentrations can change independently of salinity due to local sulfate depletion, yielding high porewater methane concentrations despite high salinity levels. Sulfate depletion occurs because of diffusion limitation from tidal floodwater into soils, or perhaps slow sulfide oxidation. Similarly, low-salinity marsh soils on gypsum ($CaSO_4$) substrate can have low rates of methane production (Rejmankova and Post 1996). Thus, sulfate concentration should be a more accurate correlate of porewater methane than salinity.

The Influence of Salinity on Radiative Forcing

The competing effects of carbon dioxide uptake and storage versus methane emissions on radiative forcing can be compared by applying the global warming potential (GWP) of methane. GWPs are estimated as the average radiative forcing caused by an instantaneous release of a mass of greenhouse gas over a given period of time (time horizon) versus the average forcing caused by releasing the same mass of carbon dioxide. In this analysis, we used a time horizon of 100 years, consistent with the United Nations Framework Convention on Climate Change (UNFCCC) and the U.S. Environmental Protection Agency in their annual greenhouse gas inventory (EPA 2009). At the 100-yr time horizon, methane has a GWP of 25 on a mass basis, indicating that emitting one gram of methane causes 25 times the radiative forcing of emitting one gram of carbon dioxide over the following 100 years (IPCC 2007). The GWP of methane decreases over longer time horizons because methane is removed from the atmosphere at a faster rate than carbon dioxide (Whiting and Chanton 2001). Therefore, if a time horizon longer than 100 years were used, the relative effects of methane release would be less, in which case smaller soil carbon sequestration rates would offset the methane emissions from a given marsh. A longer-term (>100 yr) perspective may be appropriate for some created wetland and restoration investments, but it may not be viable in carbon trading markets.

We calculated the carbon dioxide equivalent (CO_2eq) of methane emissions over a 100-yr time horizon for each of our salinity classes (Table 2). Because of highly variable methane emissions, the CO_2eq of fresh and oligohaline marshes ranged from 0.3 to 135 Mg CO_2 ha^{-1} yr^{-1}. The central tendencies (mean and median) and high variance in methane emissions among fresh and oligohaline sites make it difficult to generalize about whether classes with mean salinity <5 are neutral, net sources, or net sinks with respect to greenhouse gas balance (Fig. 3). Because of such variation, the suitability of creation, restoration, or conservation projects in fresh and oligohaline sites for the purpose of carbon crediting programs will require site-specific, and possibly in situ, data. The CO_2eq of methane emissions

from mesohaline marshes were generally lower than those from fresh and oligohaline marshes, but substantial relative to typical carbon sequestration rates. For example, the mean carbon sequestration rate reported by Chmura et al. (2003) of 2.1 Mg C ha^{-1} yr^{-1} equates to 7.7 Mg CO_2 ha^{-1} yr^{-1}. Judging from the mean methane emission rate (converted to CO_2eq) for the mesohaline class, 52% of carbon sequestration is offset by methane emissions. This mean carbon sequestration rate is close to the maximum CO_2eq methane emission rate we observed in the mesohaline class (Table 2). Nonetheless, there were some mesohaline sites with negligible CO_2eq rates of methane emissions. In order to use mesohaline marshes in carbon crediting programs, a portion of the carbon sequestration benefit will need to be subtracted to account for methane emissions unless it can be demonstrated that the site has low methane emissions. Polyhaline marshes had consistently low CO_2eq methane emissions, indicating that it may be feasible to assign carbon credits in these systems without accounting for methane emissions.

The total carbon sequestered by an ecosystem can be estimated through intensive monitoring of net carbon dioxide exchange (e.g., Neubauer et al. 2000, Cornell et al. 2007), or by measuring changes in the size of the major carbon pools. The latter approach is most common because it is less data intensive, particularly in marshes where there is relatively little carbon accumulation in long-lived (100 year) woody biomass. Thus, rates of carbon sequestration in tidal marshes are well approximated by estimating changes in the size of the soil organic matter carbon pool. Using this approach, Chmura et al. (2003) performed a comprehensive review of 154 sites and estimated the mean sequestration rate of saline tidal wetlands globally (2.1 Mg C ha^{-1} yr^{-1}). However, the dramatic variation in carbon sequestration rates across wetlands make using the mean value indefensible for identifying a threshold above which a created or restored tidal marsh can be considered a net carbon sink. We addressed variation in soil carbon sequestration rates by calculating quantiles for the 107 marsh (not mangrove) studies in Chmura et al. (2003). These data have a lognormal distribution with a median of 1.4 Mg C ha^{-1} yr^{-1}, which is considerably lower than the mean. The 5, 25, 75, and 95% quantiles of this dataset are 0.4, 0.9, 2.7, and 6.5 Mg C ha^{-1} yr^{-1}, respectively; the methane emission equivalents of these quantiles are plotted in Fig. 3. Recognizing the variation in both soil carbon sequestration and methane emissions in the two datasets, we propose that the salinity regime required to assure a net reduction in radiative forcing is >18. Above 18, one can be 95% confident that the methane emitted by a tidal marsh will be less (in CO_2eq units) than the carbon dioxide sequestered as soil carbon in most (95%) tidal marshes (Fig. 3). Thus, we propose that created or restored tidal marshes in polyhaline environments will reliably act as net sinks with respect to radiative forcing (Fig. 3).

Based on the datasets we used, it is reasonably conservative to propose that created or restored marshes in a polyhaline salinity regime will decrease radiative forcing. However, there are a number of important qualifications. It must be noted that rates of soil carbon sequestration reported in Chmura et al. (2003) overestimate of the amount of soil carbon that remains stored for a period of 100 yr, the time frame most relevant to carbon crediting programs. Studies of soil carbon sequestration rates in marshes integrate over depth intervals that include the soil surface where most of the carbon is initially deposited and carbon concentrations are typically highest (Craft et al. 1993). Because a portion of freshly deposited soil carbon is labile and will decay over a 100 yr time frame, the long-term sequestration rate will be less than surface carbon concentrations suggest. A second assumption is that all soil carbon sequestration represents recently fixed carbon dioxide (i.e., additional sequestration) as opposed to sediment-associated organic carbon that might have been equally stable without being deposited in a marsh. For the purpose of carbon sequestration protocols, the term *additional* is defined as carbon that would not have been sequestered without the actions taken in the protocol. Studies are needed to determine the proportion of the soil carbon pool that is additional sequestration and remains stable for a period of 100 yr or more.

Efforts to develop a carbon credit protocol for tidal wetlands would benefit from a more thorough understanding of the factors that contribute variation to soil carbon sequestration rates. Chmura et al. (2003) found no significant differences in sequestration rate as a function of climatic regime or ecosystem type (mangrove swamp or salt marsh). In a comprehensive review of 41 tidal freshwater (salinity <0.5), brackish (salinity=0.5–15) and salt marshes (salinity >15) in the coterminous United States, Craft (2007) did not find a significant correlation between salinity and soil carbon accumulation. However, other data in the Craft (2007) review suggested that carbon sequestration may vary with salinity at the basin or regional scale. Soil carbon sequestration was negatively correlated to salinity in three estuaries in Georgia, USA, and sequestration rates were 2–3 times higher in the freshwater-dominated estuary than the other two saltwater-dominated estuaries (Craft 2007). In a subsequent review that incorporated many additional tidal freshwater wetland sites, Neubauer (2008) reported higher mean soil surface accretion rates in tidal freshwater marshes (0.76 cm yr^{-1}) than the brackish and salt marshes reviewed by Craft (0.60 and 0.50 cm yr^{-1}, respectively). The direction and magnitude of these relationships suggest that soil carbon sequestration and methane emissions may both increase with decreasing

salinity. If so, creating or restoring tidal marshes for the purpose of carbon sequestration may be feasible at lower salinity regimes than Figure 3 suggests. Finally, it is noteworthy that tidal freshwater wetlands can be forested (e.g., Megonigal and Schlesinger 2002), providing the potential for an additional carbon sink in long-lived woody biomass (Whigham 2009).

In addition to the qualifications associated with carbon sequestration estimates, there are a number of other caveats that should be considered when applying the results of this literature review to specific sites. We considered only salinity-dependent methane emissions in evaluating the greenhouse gas contributions of tidal marshes. In practice, there are a number of other factors beyond methane emissions and carbon sequestration that influence the status of a wetland as a greenhouse gas source or sink. Although it is likely that most of the carbon buried in tidal marsh soils is derived from in situ primary production, it is possible that some of the carbon was imported from an off-site location. Such imported carbon does not represent true sequestration at the larger landscape scale unless it would have decomposed more rapidly if not intercepted by the marsh (Bridgham et al. 2006). Similarly, some fraction of the methane produced in a marsh is transported in water flowing downstream and may be emitted to the atmosphere elsewhere. In this case, methane emissions from the marsh itself do not reflect the total amount of methane the wetland contributes to the atmosphere (Kelley et al. 1995, Neubauer et al. 2000). This analysis did not consider emissions of nitrous oxide which has a GWP an order of magnitude greater than methane (EPA 2009). Nitrous oxide is an end-product of denitrification that tends to be minor in highly reduced wetland soils (Megonigal et al. 2004). Although there are very few data from tidal wetland soils on nitrous oxide emissions, it is not likely to significantly change an analysis based solely on methane emissions unless there is a significant external source of nitrate to the system, such as from agricultural or municipal runoff. Finally, the relationship between methane emissions and salinity (Figs. 1 and 3) reflect the fact that the sites in this review are regularly flooded. In tidal wetlands that are infrequently flooded, salinity may not be a good predictor of the sulfate pool, which is likely to be highly depleted. In such cases, a salinity >20 may or may not indicate low rates of methane emissions depending on factors such as hydrology, methane oxidation rates and sulfide oxidation.

Conclusions

There are several references in the literature to the notion that created or restored tidal marshes have the potential to mitigate radiative climate forcing by simultaneously burying soil carbon at high rates and emitting methane at low rates (Chmura et al. 2003, Bridgham et al. 2006, Nellemann et al. 2009). We evaluated this idea by reviewing the tidal marsh literature on methane emissions and related pore-water chemistry. Across 31 observations at sites ranging in salinity from <0.5 to >18, methane emissions decreased with increasing salinity, confirming and extending the work of Bartlett et al. (1987) who found a log-linear relationship between these parameters across three sites. This result suggests that the expected range of methane emissions from saline marshes can be predicted by salinity, which should prove useful in efforts to model the process. Our model represents the current empirical knowledge on methane emissions from temperate tidal marshes, but the model should be considered preliminary and undergo further testing prior to widespread application. In particular, more research is needed on methane emissions from wetlands in the intermediate salinity range, particularly mesohaline wetlands, and on nitrous oxide emissions from tidal wetlands generally.

Because polyhaline marshes emitted very low amounts of methane (Table 1, Fig. 3), we suggest that creating or restoring tidal marshes at salinity >18 should reliably decrease radiative forcing of climate. An important caveat to this statement is that the wetland may need to be regularly inundated for this rule to apply; more research is needed to establish whether the rule applies to infrequently flooded tidal sites where limited sulfate availability may enhance methane emissions, or persistently exposed soil surfaces may diminish methane emissions due to methane oxidation. The efficacy of creating or restoring tidal marshes to mitigate radiative forcing is less certain in mesohaline environments, and highly uncertain in oligohaline and freshwater tidal marshes, which emit methane at rates more variable than other salinity classes. The variation in methane emissions at low salinity and documented variation in soil carbon storage rates across salinity gradients (Craft 2007, Neubauer 2008) suggest that site-specific information may be necessary when planning projects at salinities <18. Further research should be invested in developing easily measured, site-specific parameters that further constrain methane emission and soil carbon storage estimates. Even so, in some cases detailed field investigations and possibly direct methane monitoring may be required to verify the radiative forcing effects of created or restored tidal fresh, oligohaline and mesohaline wetlands.

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