



Contrasting organic carbon respiration pathways in coastal wetlands undergoing accelerated sea level changes

P. Owen Clower^a, Kanchan Maiti^{a,*}, Marshall Bowles^b

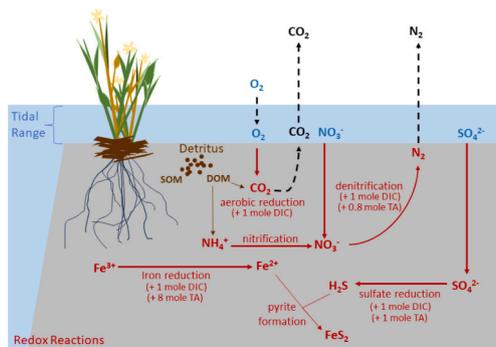
^a Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA, USA

^b Louisiana Universities Marine Consortium, Chauvin, LA, USA

HIGHLIGHTS

- First study to document the relative importance of major soil respiration pathways in the Mississippi River Delta Plain.
- Iron reduction contributed most to soil carbon respiration in the brackish marsh.
- Sulfate reduction contributed most to soil carbon respiration in the salt marsh.
- Both iron and sulfate reduction were more prominent than denitrification.
- Salt marshes and brackish marshes operate under different microbial pathways.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Wei Shi

Keywords:

Sulfate reduction
Iron reduction
Dissolved inorganic carbon
Seasonal change
Salinity change
Coastal Louisiana

ABSTRACT

Carbon cycling in coastal wetland soil is controlled by a complex interplay between microbial processes and porewater chemistry that are often influenced by various external forcings like wind, river discharge, and sea-level changes, where most of the organic carbon is mineralized to its inorganic form by various aerobic and anaerobic respiration pathways. The export of this inorganic carbon (DIC) from coastal wetlands has long been recognized as a significant component of the global carbon cycle. The major objective of this work is to determine the relative contribution of various respiration pathways to seasonal DIC production in two contrasting marshes (brackish and salt). The DIC fluxes estimates for the brackish and salt marshes were found to range between 36.52 ± 5.81 and 33.98 ± 2.21 $\text{mmol m}^{-2} \text{d}^{-1}$ in winter and 133.10 ± 102.60 and 82.37 ± 30.87 $\text{mmol m}^{-2} \text{d}^{-1}$ during summer of 2020. For the brackish marsh, aerobic respiration and iron reduction were found to be the primary contributors to DIC production representing 17.91–35.21 % and 61.13–81.97 % of total measured organic matter (OM) respiration respectively. On the other hand, aerobic respiration and sulfate reduction were the primary contributors to DIC production in the salt marsh, accounting for 37.91–83.93 % and 15.87–62.04 % of the total measured OM respiration respectively. The Mississippi River Deltaic Plain experiences high relative sea level rise and expected to undergo rapid change in salinity regime in near future from additional changes in river discharge, proposed sediment diversion plans, and storm surge intensities. The current study represents the first attempt to concurrently estimate various respiration pathways in this region and more studies are needed to understand the trajectories of soil OM respiration pathways and its impact on coastal carbon cycling.

* Corresponding author.

E-mail address: kmaiti@lsu.edu (K. Maiti).

<https://doi.org/10.1016/j.scitotenv.2024.174898>

Received 17 December 2023; Received in revised form 20 June 2024; Accepted 17 July 2024

Available online 25 July 2024

0048-9697/© 2024 Elsevier B.V. All rights reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Coastal wetlands support some of the highest primary productivity rates on the planet and play a vital role in the global carbon cycle. The water saturated soil conditions in these ecosystems limit the availability of O_2 and slows down the soil carbon decomposition through various anaerobic microbial processes. This results in substantial carbon sequestration in wetland soils, with total C burial rate estimates of 5 to 112 Tg C yr^{-1} (Duarte and Cebrián, 1996; Duarte et al., 2005; Nellemann and Corcoran, 2009; Mcleod et al., 2011). There is a large variability in C burial rates in wetland soils partly due to high spatial variability in the various mineralization pathways and associated environmental controls, which limits the ability to better constrain the carbon budget (Breithaupt et al., 2012; Quintana et al., 2015; Reddy and DeLaune, 2008; Alongi, 2014; Alongi et al., 2001). In most sediments, organic matter decomposition follows a diagenetic reaction sequence, whereby surface aerobic processes (oxygen as the electron acceptor) are followed by anoxic processes (e.g., electron acceptors: nitrate, manganese, iron, and sulfate), in deeper sediment (Burdige, 2011; Hu and Cai, 2011). The different microbial respiration processes in soil produce different amounts of dissolved inorganic carbon for every mole of terminal electron acceptor (Table S1), which results in carbon loss either through exchange with atmosphere (as CO_2) or transport to adjacent water bodies. However, the role of various anaerobic microbial processes in mineralizing soil carbon is highly variable with microbial sulfate reduction (MSR) being a predominant pathway for organic matter oxidation during early diagenesis in coastal wetland sediments (Howarth, 1984; Alongi et al., 2000; Ferreira et al., 2007; Moeslund et al., 1994). Sulfate reduction can account for up to 90 % of organic matter decomposition in salt marsh sediments (Howarth, 1984; Kristensen et al., 1995; Rickard, 2012). This is of particular relevance in current climate change scenarios where sea-level rise is expected to impact the salinity regime of many coastal wetlands.

The average sea level is expected to increase by 3.2 mm yr^{-1} with recent studies showing that sea level rise is accelerating and projected to rise 30 cm by 2050 (Sweet et al., 2022). Such an increase in sea level will cause changes in the salinity regime which will alter the physicochemical nature of the soil-water environment by altering chemical equilibria and mineral solubility. Increased concentrations of solutes, especially sulfate, alter the biogeochemical cycling of major elements including carbon, nitrogen, phosphorus, sulfur, iron, and silica. The effects on wetland biogeochemistry include decreased inorganic nitrogen removal, decreased carbon storage and increased generation of toxic sulfides which can induce physiological stress in wetland biota and ultimately can result in large shifts in wetland communities and their associated ecosystem functions (Herbert et al., 2015). Studies suggest that intrusion of low salinity seawater to freshwater wetlands can accelerate organic carbon mineralization through the short-term increase in SO_4^{2-} induced respiration (Chambers et al., 2011). Elevated salinity has also been shown to accelerate carbon loss through shifts in microbial respiration processes, as well as DOC leaching, despite a reduction in microbial biomass and enzyme activities (Servais et al., 2019). These impacts can be profound in areas with relatively high sea level changes, such as coastal Louisiana.

Coastal Louisiana is currently undergoing some of the highest relative sea level increase in the world due to a combination of global sea level rise (3 mm yr^{-1}) and land subsidence rates between 2 and 7 mm yr^{-1} (Byrnes et al., 2019), which has resulted in coastal land loss of ~5000 km² between 1932 and 2010 (Couvillion et al., 2011). These factors have led to increased vulnerability of Louisiana wetlands to changes in salinity and associated impact of altered soil carbon mineralization pathways. Salt intrusion has been linked to tissue death and photosynthesis decline in Louisiana freshwater plants (Pezeshki et al., 1989; DeLaune and Pezeshki, 1994). This could lead to a reduction in carbon fixation and organic matter accumulation, thereby becoming another factor that prevents marsh accretion from keeping up with sea-

level rise.

Louisiana coastal wetlands are current facing the impacts of salinity changes due to accelerated sea-level changes that regions around the globe will be facing in near future, which makes it an important study area to understand the current contribution of sulfate reduction to carbon mineralization pathways with respect to other microbially mediated respiration pathways. Louisiana coastal marshes are also highly productive leading to organic carbon accumulations of 2.7–3.3 Tg C yr^{-1} (Baustian et al., 2017) which makes it even more important to understand current and future contribution of various carbon mineralization pathways in this region. Thus, the major objective of this study is to investigate two contrasting marshes under different salinity regimes, to understand the relative contributions of various organic matter mineralization pathways in the soil. Currently, there exists little to no data on sulfate reduction rates from this region as the major emphasis is on denitrification, due to the high nitrate loading of the region, which leads to formation of largest coastal hypoxia zone in Louisiana shelf every year (Yu et al., 2006; VanZomerem et al., 2013; Turner et al., 2019; Vaccare et al., 2019; Upreti et al., 2021). We hypothesize that sulfate reduction will be a significant driver of organic carbon remineralization in the salt marsh compared to the brackish marsh despite high denitrification rates reported from this region.

2. Materials & methods

2.1. Sample location descriptions

This study was carried out in the Barataria Basin, Louisiana, USA, located just west of the Mississippi River in the northern Gulf of Mexico (Fig. 1). The northern half of this basin consists of a series of semi-enclosed marsh basins while the southern half of the basin consists of tidally influenced marshes which connect to a large bay system bound by barrier islands. This basin encompasses approximately 6000 km² of wetlands and water bodies but has experienced land loss at a rate of 23 km² y^{-1} from 1974 to 1990 (Louisiana Coastal Wetlands Conservation and Restoration Task Force, 1993; Barras et al., 1994). Two contrasting marsh types (brackish and salt) with different salinity regimes were sampled during the winter and summer of 2020. The brackish marsh was located just outside Lafitte, LA (29.67202°; -90.13549°) in the northern half of the Barataria Basin, south of Lake Salvador (Fig. 1). The salt marsh was located west of Port Sulpher, LA (29.4978237°; -89.91673°) in the southern half of the Barataria Basin (Fig. 1).

These two sites were selected due to their proximity to long-term monitoring stations, which are a part of Louisiana's Coastwide Reference Monitoring System (CRMS). The brackish marsh is located near CRMS site 4245 that has been monitored since 2008 while the salt marsh is near CRMS site 0224, which has been monitored since 2006. The monitoring stations are located approximately 10–30 m from our sampling sites. The sampling sites had elevations of <0.2 m, making them susceptible to flooding for a large portion of the year both during our study period (Fig. 2) and prior (He et al., 2022).

For the purpose of this study the site closest to the Gulf of Mexico was identified as a salt marsh with a seasonal salinity regime between 3.5 and 20.16, while the site located furthest away from the Gulf of Mexico was identified as a brackish marsh with a seasonal salinity regime between 0.14 and 9.35 for 2020 (Fig. 2). Their long-term salinity trend of the previous 5 years shows a similar salinity regime, of 0.12–16.58 and 2.59–23.43, respectively. During winter sampling (February 2020) the brackish marsh had a salinity of 0.22 while the salt marsh had a salinity of 10.81, and both marsh sites had water temperatures of approximately 22 °C (Fig. 2). During summer sampling (July/August 2020) the brackish and salt marshes had a salinity of 0.24 and 4.5 and water temperatures of 30 °C and 31.39 °C, respectively (Fig. 2). These salinity ranges are common in the Barataria Basin as they range from near zero in the upper reaches of the estuary to about 25 in the southernmost section of the estuary (Das et al., 2012).

2.2. Sample Collection

Samples were collected during two seasonal trips to each of the two marshes. The brackish and salt marshes were visited within a week of each other during the same season. During each trip, adjacent water quality parameters from the closest water source (a nearby creek), such as temperature, salinity, specific conductance, dissolved oxygen (DO) concentration were measured in field using a YSI handheld meter (YSI professional plus).

Porewater samples were collected approximately 10 m from the marsh edge in proximity of where the core samples were collected. Porewater samples were collected at 4 cm intervals 2 to 30 cm below the marsh surface with a syringe attached to a specially designed porewater sampler. These samplers were made of a 90 cm-long clear acrylic rigid tubes with 2.5 mm internal diameter and a luer-lock attachment at one end. The bottom 2 cm of the other end was sealed with epoxy, and 10 holes with diameter of ~1.5 mm were drilled above the bottom seal to allow porewater to seep into the tubes (McKee et al., 1988; He et al., 2022). Porewater samples were collected after discarding dead volume and rinsing the syringe with porewater. DIC, TA, nutrient, sulfate, and iron porewater samples were then collected directly using a syringe connected to a tube. Those samples were passed through a 0.45 mm glass fiber syringe filter and collected without headspace into air-tight vials, by filling from the bottom and allowing overflow to minimize atmospheric contamination (Anderson et al., 2020). Samples were preserved with 20 μ L of a saturated mercuric chloride (HgCl_2) solution. Porewater samples for dissolved iron were acidified by drawing in 0.5 mL concentrated nitric acid into the syringes and then stored capped and inside air-tight Mylar bags. We were unable to collect porewater from the 2 cm depth on several occasions due to dry conditions. Water samples were taken from the field to the laboratory on ice and stored at 5 °C until analysis.

Intact sediment cores were collected at each site. Six cores were collected to carry out intact incubation experiments to determine DIC, DO, and nutrients fluxes. Another core was collected for analysis of total

organic carbon content. At the salt marsh site, an additional core was collected to determine sulfate reduction rates. All cores were collected within 2 m of each other and at approximately 10 m from the nearest creek. We were careful to collect cores free from any protruding plants in order to insure similar conditions across all cores and seasons at each marsh. Coring was done using an acrylic tube (diameter of 10 cm) with a specially designed metal-teeth head to cut through roots. The core tube was slowly hand pressed into the soil while twisting to easily cut through any roots and simultaneously limit compaction. Upon reaching the desired depth of 25 cm the core retrieved from the soil, filled with 2 in. of field water from the adjacent creek to prevent drying out, and then placed on ice until it could be returned to the laboratory to be stored at 5 °C. Twenty liters of water were collected and filtered using a pump from the nearest creek for use during sediment core incubations.

2.3. Laboratory incubation experiments

The core incubation experiment was started within 18 h of sample collection. A temperature-controlled water bath was adjusted to the ambient water temperature recorded in the field; the winter incubation was performed at 22 °C while the summer incubation was performed at 30 °C. The overlying water column of each core was replaced with site specific water that had been bubbled to oxygen-saturation. This experiment setup assumed a flooded marsh in order to get results that are comparable across sites and seasons. Each core was then capped without any headspace using custom PVC caps fitted with two O-rings (to keep the core airtight) and stirrers and then submerged into the temperature-controlled water bath (Upreti et al., 2019). Each core tube was attached to an elevated water reservoir, such that when a sampling port was opened for sampling, the volume removed was simultaneously replaced with reservoir water via gravity. The water bath with sediment cores was covered to prevent primary production and left to sit for an hour to allow the sediment cores to acclimate before the first samples were collected.

Thereafter samples were collected every 4 h until oxygen levels



Fig. 1. Location of the brackish and salt marsh. The brackish marsh was located just outside Lafitte, LA. The Salt marsh site was located west of Port Sulphur, LA. Both sites were located south of New Orleans, LA and north of Barataria Bay.

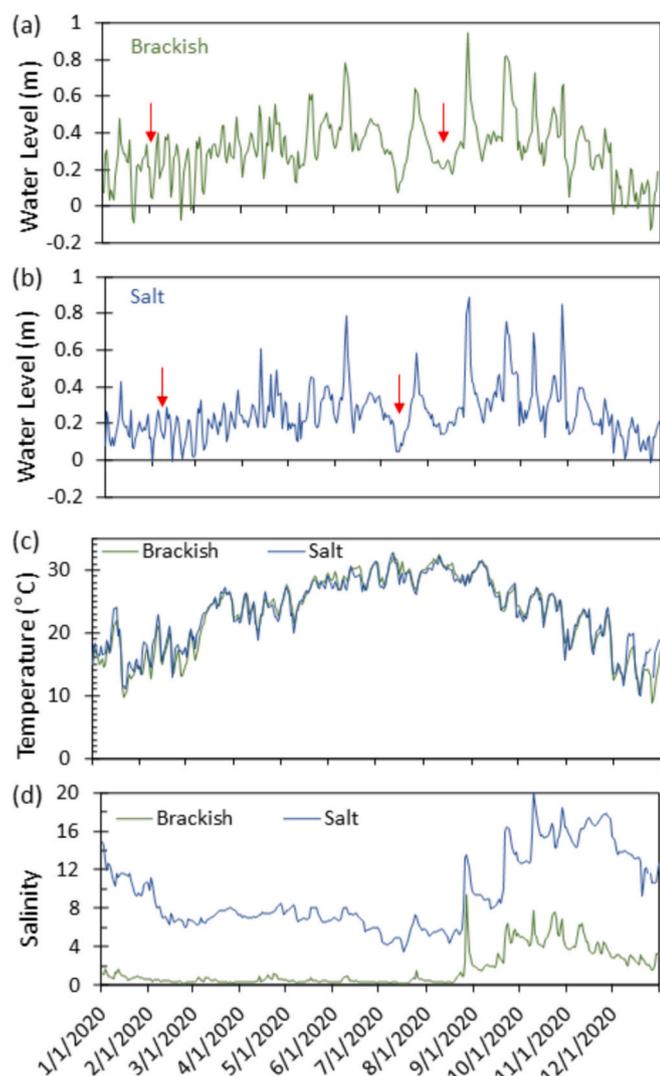


Fig. 2. Surface water level (a, b), temperature (c) and salinity (d) of the brackish and salt marsh sites. Sampling dates are marked with red arrows. Data source: Retrieved from Coastal Information Management System (CIMS) database. <http://cims.coastal.louisiana.gov>. Accessed 11 November 2023.

became depleted ($\sim 0 \mu\text{M}$), or 24 h were reached. Water samples were collected at each sampling time only after discarding the first ~ 10 mL of dead volume in the tube. Water samples were collected by filling sampling vials from the bottom and allowing water to overflow. DIC and N_2/Ar samples were collected in Labco vials, spiked with $10 \mu\text{L}$ of HgCl_2 and placed in a refrigerator. DIC samples were filtered through a $0.45 \mu\text{m}$ GF filter prior to collection. Filtered nutrient samples (NO_x) were also collected and preserved frozen. Dissolved oxygen (DO) concentrations inside the cores were recorded every sampling period using a Presens Microx 4 O_2 sensor. DIC, nutrient, and DO analysis was carried out on samples from each time point and utilized to calculate fluxes (Ghaisas et al., 2019). The aerobic respiration rates were calculated from triplicate sediment cores. The rates are calculated for each individual core by assuming a linear drop in O_2 concentration over time and reported as an average of the three cores with an uncertainty equal to its standard deviation. The dissolved inorganic carbon production rates were calculated in a similar manner from triplicate sediment core incubations concurrent with O_2 measurements. A linear increase in DIC concentration over time is assumed and reported as an average of the three cores with an uncertainty equal to its standard deviation.

2.4. Post-incubation porewater measurements

Porewater samples were collected at the end of sediment core incubation experiments following the same procedure as in the field. The porewater sampler was used in the same way as in the field.

2.5. DIC & TA measurements

Dissolved inorganic carbon samples were measured using the standard protocol for the semi-automated Apollo SciTech AS-C5 Dissolved Inorganic Carbon Analyzer (Newark, DE, USA). A 0.5 to 1 mL sample was acidified by phosphoric acid, and the extracted CO_2 gas was quantified with a built-in infrared CO_2 detector with a precision $< 1\%$ (Cai and Wang, 1998). Certified reference material (CRM batch 187; DIC = $2002.85 \pm 0.40 \mu\text{mol/kg}$; Dickson, 2010) was used to make the standard curves for calculation.

TA samples were analyzed by Gran titration (Gran, 1952) using the semi-automated Apollo SciTech AS-ALK2 Total Alkalinity Titrator (Newark, DE, USA). The precision of this method is $< 1\%$ and the titration was conducted at a controlled temperature of 25°C . Certified reference material (CRM batch 187; TA = $2204.98 \pm 0.37 \mu\text{mol/kg}$; Dickson, 2010) was used to calibrate the machine.

2.6. Nutrient and iron measurements

Dissolved $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ were analyzed using a Seal Analytical Auto Analyzer via methods from (Zhang et al., 1997) and (U. S. EPA, 1993 Method 350.1) respectively. Sulfate and Chloride were measured using Dionex ICS-1000 Ion Chromatograph (Bowles et al., 2011). Total dissolved iron was measured using a Varian Vista-MPX ICP-OES following USEPA method 200.6, 1986). The measured porewater dissolved iron was assumed to reduced Fe^{+2} and independently confirmed through ferrozine method for select porewater samples. The iron reduction rates were indirectly calculated by measuring the change in porewater iron concentration over time using Eq. 1 below.

$$\text{Fe}_{\text{red}} = \frac{1}{t} \sum n [C_{\text{post}} - C_{\text{pre}}] \phi h \quad (1)$$

where Fe_{red} is the iron reduction rate, C_{post} and C_{pre} are pre- and post-incubation Fe^{+2} concentrations at each depth, ϕ is the corresponding porosity, h is the thickness for each depth layer and t is the incubation time period. This estimate of potential iron reduction rate should be considered a lower limit as it does not consider any dissolved Fe that may have diffused into the overlying water column or removed by iron sulfide precipitation.

2.7. Sulfate reduction rates

Sulfate reduction rates were determined on one core from the salt marsh during each sampling period. Briefly the core was sectioned at 4 cm intervals and 2 cm^3 subsamples were taken from each section using a cut off 5 mL syringe with a butyl rubber stopper. For each depth, four replicate subsamples were collected. The samples were injected with a $^{35}\text{SO}_4^{2-}$ tracer solution, with a radioactivity corresponding to 25 kBq, through the rubber stopper and only three were incubated for 24 h at temperatures recorded in field. The fourth subsample was used as a control sample. The entire sampling and tracer injection was carried out in a N_2 filled glove box. To halt microbial activity samples were ejected into a 50 mL centrifuge tube containing 10 mL of 20% (w/v) zinc acetate, with the control sample immediately ejected into zinc acetate after injection. After ejection the samples were shaken vigorously. To retrieve the radioactive sulfide produced, samples were rinsed of sulfate by centrifuging to separate it and then distilled via a one-step wet-acid reduction. The sulfide was trapped in 5% (w/v) zinc acetate (Roy et al., 2014). The radioactivity of the sulfide and sulfate samples were measured using Scintiverse BD (Fisher) and Scintisafe Gel (Fisher)

scintillation cocktails, respectively in a TRI-Carb 3100TR Perkin-Elmer scintillation counter.

Sulfate reduction rates (SRR) were only calculated for the salt marsh using Eq. 2 below:

$$SRR = F \times SO_4^{2-} \times 1.06 \times \phi / t \tag{2}$$

where F is the fraction of $^{35}S^-$ tracer reduced during incubation, $[SO_4^{2-}]$ is the sulfate concentration in the porewater, ϕ is porosity, and t the incubation time. The factor 1.06 (Bowles et al., 2011) is an estimated isotope fractionation factor between $^{32}SO_4^{2-}$ and $^{35}SO_4^{2-}$ during bacterial sulfate reduction, which corrects for the slightly slower turnover of the heavy $^{35}SO_4^{2-}$. Unfortunately, due to ongoing pandemic, we were unable to procure sufficient $^{35}SO_4^{2-}$ in a timely fashion to carry out sulfate reduction at both sites which resulted in our decision to not perform sulfate reduction experiment at brackish sites. The sulfate reductions rates appear to be low at brackish site given the low porewater sulfate concentrations and high porewater Fe^{+2} concentrations compared to the salt marsh site.

2.8. TOC & TN measurements

Total organic carbon was determined using one core from each site during each sampling period. This core was sliced into 4 cm intervals,

subsampled, weighed, and then dried at $\sim 60^\circ C$. Dried subsamples were then ground using a mortar and pestle and homogenized through a 125- μm filter. Approximately 20 mg of each sample was placed into open Costech silver capsules and placed in a vacuum glass desiccator to fumigate with 12 N hydrochloric acid (HCl) for 12 h to remove inorganic carbon (Hedges and Stern, 1984). Upon completion samples were then repacked into tin capsules to ensure no loss of sample and analyzed in a Costech 1040 CHNOS Elemental Combustion system following the standard EPA method 440.0 (Zimmerman et al., 1997).

3. Results

3.1. Total organic carbon (TOC) percentage

The brackish marsh had a higher TOC percentage than the salt marsh. In winter, the brackish marsh had an average TOC percentage of $13.5\% \pm 3.74\%$ versus $9.3\% \pm 2.63\%$ for the salt marsh (Fig. S1). The same was true for summer as the brackish marsh had a TOC percentage of $13.5\% \pm 3.79\%$ versus $9.1\% \pm 2.63\%$ for the salt marsh site (Fig. S1). Thus, the brackish marsh had a greater TOC percentage than salt marsh across seasons while no seasonal difference in OC was observed within the two marshes.

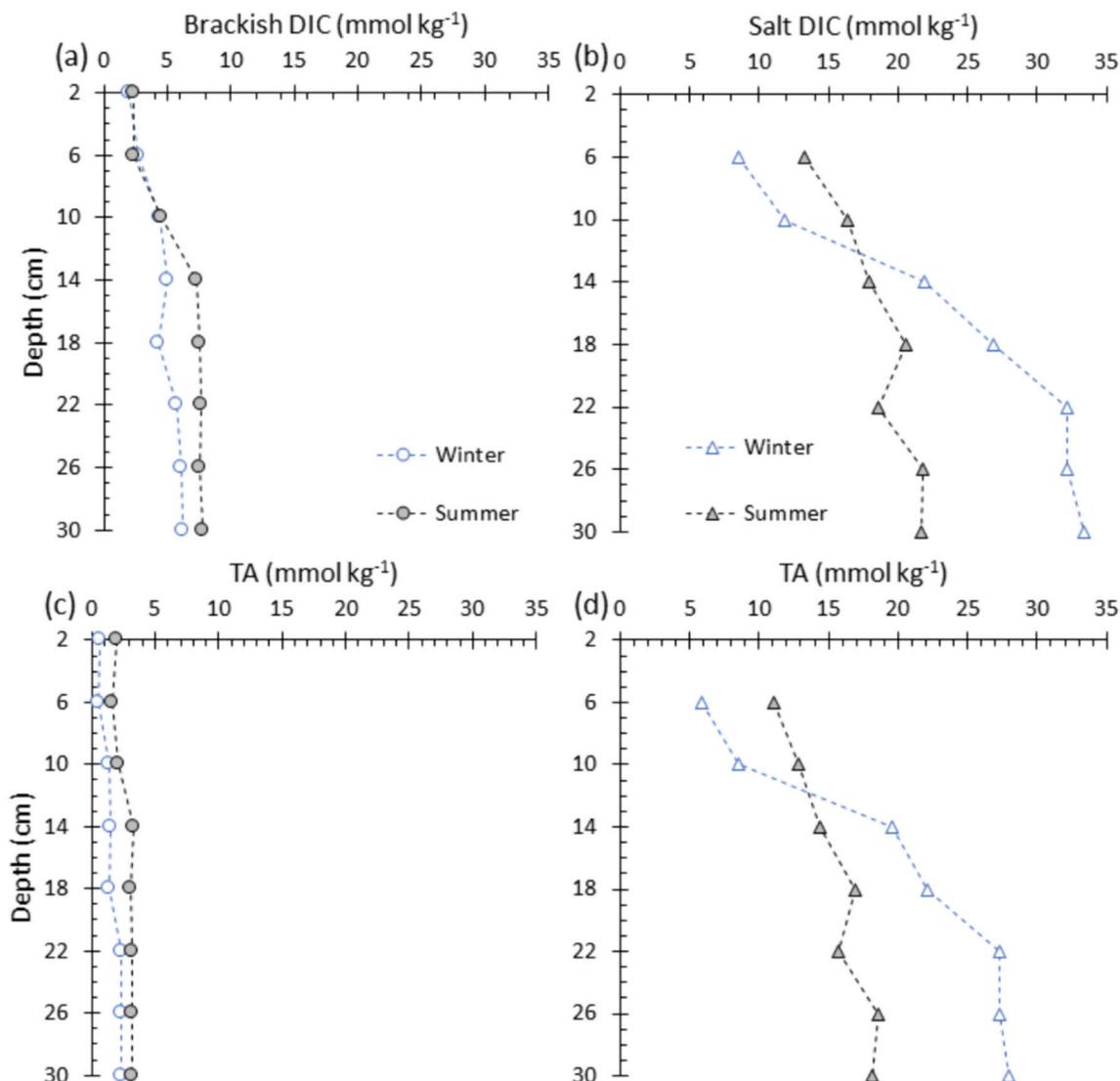


Fig. 3. Infield porewater DIC (a & b) and TA (c & d) concentrations by depth at the brackish marsh (a & c) and salt marsh (b & d).

3.2. Porewater chemistry

3.2.1. Dissolved inorganic carbon

Porewater data showed a general increase in DIC with soil depth. During the winter, the brackish marsh DIC ranged from 2.04 mmol kg⁻¹ at 2 cm to 6.17 mmol kg⁻¹ at 30 cm and for the summer the range was similar with 2.36 mmol kg⁻¹ at 2 cm to 7.73 mmol kg⁻¹ at 30 cm. For the salt marsh during the winter the DIC range was 8.58 mmol kg⁻¹ at 4 cm to 33.42 mmol kg⁻¹ at 30 cm and the summer DIC ranged from 13.23 mmol kg⁻¹ to 21.65 mmol kg⁻¹ (Fig. 3). The salt marsh had greater porewater DIC than the brackish marsh across both sampling periods.

3.2.2. Total alkalinity (TA)

Porewater data showed a general increase in TA with soil depth. During the winter, the brackish marsh TA ranged from 0.61 mmol kg⁻¹ at 2 cm to 2.39 mmol kg⁻¹ at 30 cm and for the summer the range was similar with 1.95 mmol kg⁻¹ at 2 cm to 3.21 mmol kg⁻¹ at 30 cm. For the salt marsh during the winter the TA range was 5.83 mmol kg⁻¹ at 4 cm to 28.02 mmol kg⁻¹ at 30 cm and the summer TA ranged from 11.13 mmol kg⁻¹ to 18.18 mmol kg⁻¹ (Fig. 3). The salt marsh had greater porewater TA than the brackish marsh across both sampling periods.

3.2.3. Nutrients

The salt marsh had low nitrate and nitrite (N + N) ranging from 0.41 μM at 6 cm to 0.66 μM at 30 cm and 1.28 μM at 2 cm to 0.37 μM at 30 cm in winter and summer respectively. The brackish marsh during the winter ranged between 15.32 μM at 6 cm to 0.58 μM at 30 cm, and during the summer ranged from 6.54 μM at 2 cm to 2.18 μM at 30 cm. The brackish marsh had greater N + N concentrations than the salt marsh site across both seasons (Fig. S2).

For the brackish marsh, the range of ammonium in winter was 15.64 μM at 2 cm to 4.29 μM at 30 cm, while the range during the summer was 33.94 μM at 2 cm to 5.48 μM at 30 cm. During the winter the salt marsh had a range of 75.34 μM to 699.25 μM and during the summer the range was 217.70 μM to 500.92 μM. Thus, NH₄ concentrations were lower in the brackish marsh when compared to the salt marsh in both sampling periods (Fig. S2).

3.3. Incubation chemistry

3.3.1. Aerobic respiration

During the winter sampling the brackish marsh was found to have an aerobic respiration rate of 24.37 ± 2.15 mmol m⁻² d⁻¹. There was not a substantial difference from the salt marsh which had an aerobic respiration rate of 27.0 ± 5.13 mmol m⁻² d⁻¹ (Fig. 4). During the summer the brackish marsh had an aerobic respiration rate of 42.58 ± 5.29 mmol m⁻² d⁻¹ and the salt marsh had an aerobic respiration rate of 45.45 ± 16.63 mmol m⁻² d⁻¹ (Fig. 4). A substantial difference in aerobic

respiration rates were observed between the seasons at both marshes.

3.3.2. Sediment core DIC production rates

During winter sampling the brackish marsh was found to have a DIC production rate of 36.52 ± 5.81 mmol m⁻² d⁻¹. This did not significantly differ from the salt marsh which had a DIC production rate of 33.98 ± 2.21 mmol m⁻² d⁻¹ (Fig. 4). During the summer the brackish marsh had a DIC production rate of 133.10 ± 102.60 mmol m⁻² d⁻¹ and the salt marsh had an DIC production rate of 82.37 ± 30.87 mmol m⁻² d⁻¹ (Fig. 4).

3.3.3. Nitrates and ammonium

The change in net nitrate (N + N) concentration was the greatest in the brackish marsh during both sampling periods. During the winter the rate was -2.03 ± 0.10 mmol m⁻² d⁻¹ while during the summer the rate was -0.23 ± 0.04 mmol m⁻² d⁻¹ (Fig. S3). The N + N removal rates were extremely small at the salt marsh with winter sampling having a rate of 0.04 ± 0.01 mmol m⁻² d⁻¹ and the summer having a rate of 0.05 ± 0.30 mmol m⁻² d⁻¹. The change in net ammonium concentration was greatest in the salt marsh during the summer with -3.24 ± 2.80 mmol m⁻² d⁻¹ this is likely due to higher aerobic respiration rates observed during this period. In the brackish marsh the ammonium drawdown was much smaller: during the winter it was -0.23 ± 0.03 mmol m⁻² d⁻¹ and during the summer it was -0.17 ± 0.09 mmol m⁻² d⁻¹ (Fig. S3).

In this study the change in nitrate concentration over time is utilized as an estimate of potential denitrification rate. Previous study from this region has shown direct denitrification to be the dominant pathway for NO₃⁻ removal, with potential denitrification rates calculated from nitrate uptake overestimating total denitrification rates, especially under high nitrate concentrations in summer (Upreti et al., 2019). The nitrate concentration during our study was much lower than the above-mentioned study but nevertheless this potential denitrification rate calculated using nitrate uptake should be considered the lower limit of the denitrification rate.

3.4. Potential iron reduction rates

In the brackish marsh the in situ porewater iron concentration varies between 15.74 μM at the surface to up to 264.73 μM at 14 cm during winter. This pattern of increased porewater Fe with depth was observed in summer as well with concentrations varying between 4.70 μM at the surface and 442.80 μM at 14 cm. Thus, field porewater samples showed the greatest presence of iron at 14 cm for both winter and summer. This pattern continued when looking at the post incubation porewater samples with the greatest iron concentration between 10 and 14 cm for both winter and summer being 457.96 μM and 728.21 μM respectively. In the salt marsh the field porewater iron concentrations were significantly lower varying between 3.48 μM at the surface and 6.506 μM at 14 cm

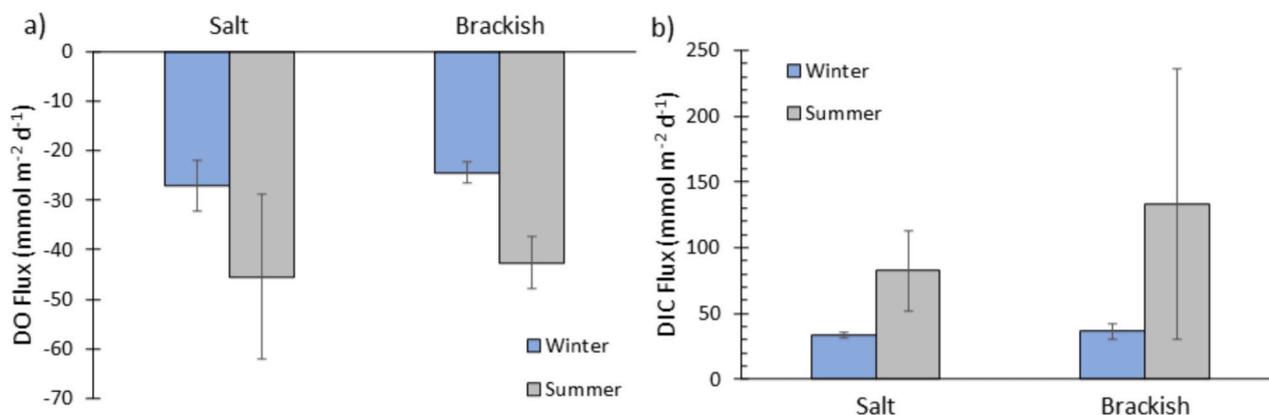


Fig. 4. (a) Aerobic respiration for intact sediment core incubations. (b) Dissolved inorganic carbon production rate for sediment core incubations.

during the winter and 1.77 μM at the surface to 12.03 μM at 10 cm during the summer. The post incubation porewater samples for the salt marsh, during the winter did not contain any detectable iron in the top 14 cm and during the summer they ranged from 0 μM at the surface to 0.605 μM at 14 cm. These levels were negligible compared to the brackish marsh. No iron reduction rate was calculated for the salt marsh site due to a low concentration of iron. The cumulative rate of iron reduction in the top 14 cm was 169.23 $\text{mmol m}^{-2} \text{d}^{-1}$ in winter and 779.66 $\text{mmol m}^{-2} \text{d}^{-1}$ in summer (Fig. 5). It should be noted that because iron reduction was not measured directly then these rates should be considered the lower range of iron reduction in the brackish marsh as some reduced iron could potentially be removed through iron sulfide precipitation.

3.5. Potential sulfate reduction (SO_4^{2-})

Field porewater samples showed sulfate present at both sites. The brackish marsh had a range of 0.75–1.75 mM during the winter compared to 0.09–0.53 mM during the summer. The salt marsh had a range of 1.02–6.76 mM during the winter and 0.17–0.66 mM during the summer. For both sites, porewater sulfate was greater in winter than in summer, with the salt marsh having greater sulfate concentrations overall (Fig. 6). For the salt marsh the cumulative SRR for the top 30 cm core was $2.55 \pm 2.06 \text{ mmol m}^{-2} \text{d}^{-1}$ during winter compared to significantly higher rates of $37.20 \pm 14.90 \text{ mmol m}^{-2} \text{d}^{-1}$ during summer (Fig. 6). Sulfate reduction was not calculated for the brackish marsh due to the observed combination of low sulfate and high iron concentrations in the porewater.

4. Discussion

Tidal wetlands represent one of the most important global carbon pools due to their efficient carbon sequestration capacity (0.0426 Gt y^{-1}) (Chmura et al., 2003). Salt and brackish marsh sediments are rich in organic matter with oxygen being utilized rapidly in surface sediments and most organic matter remineralization occurring under anoxic conditions (Howarth, 1993; Alongi, 1998). Anaerobic organic carbon mineralization reactions are mediated by various types of heterotrophic microbes (Meronigal and Neubauer, 2009), together with a series of electron acceptors, that includes nitrate (NO_3^-), manganese oxides (Mn(IV)), ferric iron oxides (Fe(III)), sulfate (SO_4^{2-}), and CO_2 (Keller and Bridgman, 2007). Because of the abundance of sulfate in seawater, anaerobic microbial respiration coupled to the terminal decomposition of organic matter in salt marsh sediments is thought to be dominated by sulfate reduction while brackish and freshwater marshes are dominated

by denitrification, iron reduction and methanogenesis (Howarth, 1993; Alongi, 1998). Typically, these electron acceptors follow a predictable and thermodynamically favorable sequence that results in production of variable amount of DIC as a function of their metabolic pathway (Table S1). However, the pathway for organic matter remineralization under anaerobic respiration can diverge based on multitude of factors such as organic matter content, salinity, nutrient input, inundation, etc.

For the Louisiana marsh system, the relative importance for different organic matter respiration pathways is not well constrained, especially along salinity gradients. Salinity influences the quantity and quality of organic carbon which act as electron donors during organic carbon mineralization processes. In this study we clearly see a difference in soil organic carbon content between the two sites with the brackish marsh having higher OC content ($13.5 \pm 3.74\%$ in winter and $13.5 \pm 3.79\%$ in summer) compared to the salt marsh ($9.3 \pm 2.63\%$ in winter and $9.1 \pm 2.63\%$ in summer) (Fig. S1). Previous studies of marshes influenced by freshwater discharge e.g. from Mississippi River and Georgia coast, USA (Nyman et al., 1990; Craft, 2007; Więski et al., 2010) found such negative relationship of OC content with salinity and attributed it to plant productivity and rapid organic matter mineralization.

4.1. Pathways for C remineralization in Louisiana marshes

Globally, wetland soils store approximately one third of the terrestrial soil carbon (Bridgman et al., 2006). Wetland ecosystems and the global carbon cycle are intricately related in large part to anaerobic soil conditions resulting from flooded or saturated soils in wetland environments. Under these oxygen-limited conditions, mineralization of organic matter in wetland soils relies on a complex microbial processes that ultimately mineralizes organic compounds to carbon dioxide (CO_2) and/or CH_4 (Meronigal et al., 2004). The cumulative rates of microbial mineralization are controlled by organic matter quality and climatic variables such as temperature, but it is generally assumed that the outcome of dominant mineralization pathway is dependent on the energetic favorability of the terminal electron acceptors (TEAs) used by competing microbes (Meronigal et al., 2004). In order of decreasing energetic yield, and thus decreasing competitiveness, the primary inorganic TEAs used in the absence of oxygen are: NO_3^- (denitrification), Mn(III, IV) (manganese reduction), Fe(III) (iron reduction), and SO_4^{2-} (sulfate reduction). These processes release CO_2 as a respiratory end product.

The different soil respiration pathways quantified in this study are summarized in Table 1. To the best of our knowledge this study represents the only work from Louisiana salt marshes where all the different respiration pathways except methanogenesis were quantified

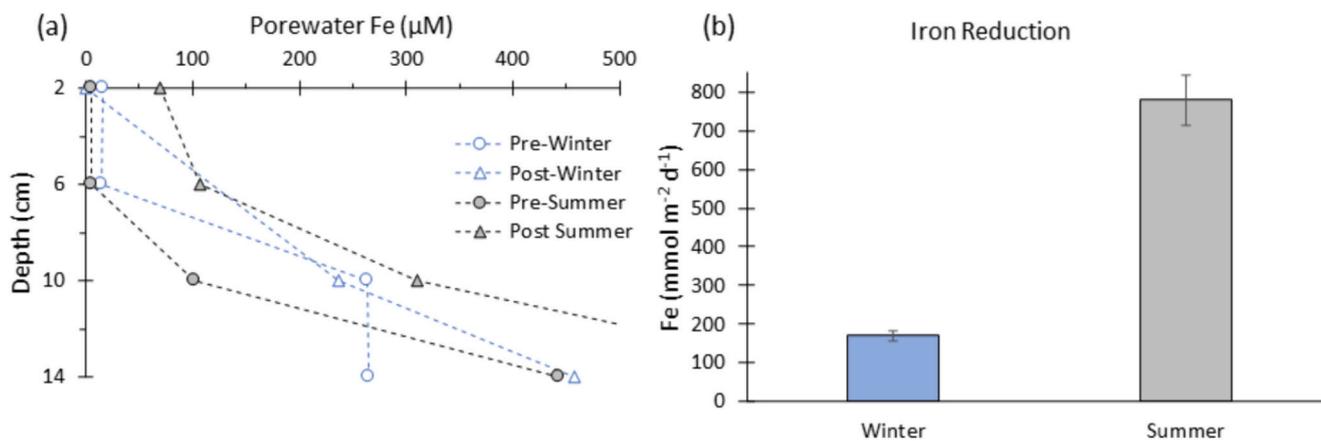


Fig. 5. Iron data for brackish marsh. Porewater iron concentrations for the salt marsh are not shown due to being so small. (a) Porewater concentrations of Fe^{+2} is shown from pre-incubation samples and post-incubation samples between both seasons. Note 6 cm data is missing in post-winter due sample being container breaking. (b) Iron reduction between seasons at the brackish marsh.

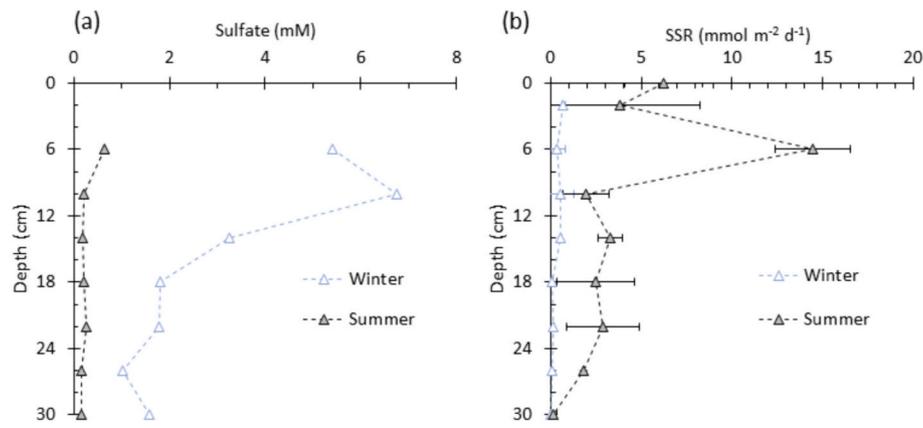


Fig. 6. Water sulfate concentrations (a) and sulfate reduction rates (b) are shown from winter and summer sampling of the salt marsh. Brackish marsh sulfate concentrations were not displayed for clarity between both panels. Note sulfate reducing rates are converted to an areal extent for every 2 cm of the soil core to keep units comparable with other measurements.

concurrently. Methane production was not quantified in this study for three primary reasons (i) previously studies have demonstrated negative correlation between CH₄ flux and salinity, with potential methane production rates in the range of 6.0–15.58 mmol m⁻² d⁻¹ for brackish to saltwater marshes (Crozier and DeLaune, 1996; Krauss et al., 2016); (ii) potential methane fluxes from whole core incubation in freshwater marshes of upper Barataria region are also reported to be <1.87 mmol m⁻² d⁻¹ (He et al., 2023) and (iii) anaerobic methane oxidation—with sulfate as the electron acceptor—will reduce methane fluxes and is likely incorporated via sulfate reduction rates (Segarra et al., 2013).

In these tidal wetlands, the changes in soil water levels and chemistry over intertidal elevation gradient creates a complex vertical and geochemical environment. This is overlain by spatial zonation in flooding duration and extent, evapotranspiration and salinity all of which influence the OM decomposition rates and pathways. Since these marshes are rich in organic matter, with OC content up to 18 % (Fig. 3), and contain relatively impermeable clay minerals, oxygen is utilized rapidly in surface sediments and a large fraction of freshly accumulated organic matter can be remineralised under oxic conditions with limited flooding. In our study, water level data (Fig. 2) show flooding throughout the year with only a few times during the year not being flooded. During those few times when these sites are not flooded there would likely be an increase in oxic conditions and thus greater aerobic respiration.

Not all oxygen uptake is aerobic respiration, however in general aerobic respiration results in mole equivalent production of DIC (Table S1) and represents a significant fraction of total OC consumption or DIC production irrespective of season (Table 2). Thus, aerobic

Table 1

Different soil respiration pathways quantified in this study. Values represent the mmol of each electron receptor taken up in this study ± STD.

Respiration pathways	mmol m ⁻² d ⁻¹			
	Brackish winter	Salt winter	Brackish summer	Salt summer
Aerobic respiration (O ₂ mmol m ⁻² d ⁻¹)	24.37 ± 2.15	27.0 ± 5.13	42.58 ± 5.29	45.45 ± 16.63
Potential denitrification (NO ₃ mmol m ⁻² d ⁻¹)	2.03 ± 0.10	0.05 ± 0.01	0.23 ± 0.04	0.05 ± 0.30
Potential iron reduction (Fe mmol m ⁻² d ⁻¹)	169.23 ± 14.22	N/A	779.66 ± 65.49	N/A
Sulfate reduction (SO ₄ mmol m ⁻² d ⁻¹)	N/A	2.55 ± 2.06	N/A	37.20 ± 14.90

respiration was found to be significant pathway for OM remineralization across season and site. At the brackish marsh during the winter aerobic respiration contributed 24.37 mmol m⁻² d⁻¹ of DIC and during the summer contributed 42.58 mmol m⁻² d⁻¹ of DIC (Table 2). This reveals that aerobic respiration leads to greater DIC production during the summer than in the winter. The difference in DIC contribution between seasons is attributed to lower aerobic respiration in winter (24.37 ± 2.15 mmol m⁻² d⁻¹) than when compared to the summer (42.58 ± 5.29 mmol m⁻² d⁻¹) (Table 1). However, despite aerobic respiration being lower during the winter, percentage wise aerobic respiration was more important for the brackish marsh during the winter then summer, contributing 35.21 % of DIC production versus 17.91 % during the summer (Table 2).

This same pattern was true for the salt marsh. Winter sampling showed lower DIC production from aerobic respiration of 27 mmol m⁻² d⁻¹ while contributing 83.93 % of our total measured DIC. And during the summer more DIC was produced from aerobic respiration at 45 mmol m⁻² d⁻¹ while contributing only 37.91 % of our total measured DIC (Table 2). Thus, salt marsh also had lower aerobic respiration during the winter (27 ± 5.13 mmol m⁻² d⁻¹) than when compared to the summer (45.45 ± 16.63 mmol m⁻² d⁻¹) (Table 1). This reveals that despite varying salinities and microbial regimes, the two marshes had the same aerobic respiration across seasons, which led to similar DIC contributions. The most obvious reason for this disparity is likely linked with temperature. The core incubations for each of these sites were conducted with 8 °C differences between winter and summer, 22 °C and 30 °C respectively. Temperature plays an important role in determining individual respiration rates, potentially more than salinity, which is definitely important in determining which microbial process contribute

Table 2

Bold values represent relative contribution of various respiration pathways to the sum of DIC production. Italicized values represent the percentage each pathway contributed relative to the sum for a given site and season.

Respiration pathways	DIC production (mmol C m ⁻² d ⁻¹)			
	Brackish winter	Salt winter	Brackish summer	Salt summer
Aerobic respiration	24.37	27.0	42.58	45.45
Potential denitrification	<i>2.54 (3.67 %)</i>	<i>0.06 (0.19 %)</i>	<i>0.29 (0.12 %)</i>	<i>0.06 (0.05 %)</i>
Potential iron reduction	42.31	N/A	194.91	N/A
Sulfate reduction	N/A	<i>5.11 (15.87 %)</i>	N/A	74.39
Sum	69.22	32.17	237.78	119.9

to those rates, as we see with iron and sulfate reduction. Another factor may be the flooding differences throughout the year (Fig. 2). During the winter, there is less rain, leading to less waterlogged soil conditions, and thus less anaerobic respiration due to greater oxygen levels in the soil, this combined with temperature, leads to lower DIC production but increases the proportion of DIC production attributed to aerobic respiration.

The potential denitrification rates in our study were lower than many previous studies from the Mississippi River Delta plain. It is important to note that our rates are based on nitrate loss and thus should be treated as potential denitrification rates. A previous study from the marsh in Barataria Bay has shown direct denitrification to be the dominant pathway for NO_3^- removal over coupled nitrification-denitrification (by Upreti et al., 2019). DNRA rates are also reported to be <10 % of the total NO_3^- consumption from this region (Upreti et al., 2022). In the same study the nitrate removal rates were found to be similar to total denitrification rates in winter and about half of total denitrification rates in summer when the nitrate concentration were >40 μM . This suggests that nitrate removal rates when used as a proxy for denitrification rates will likely be an overestimate in summer for our study sites. In general, high nitrate loading in Louisiana estuaries favors higher denitrification rates. A recent denitrification study from Barataria Basin observed nitrate levels as high as 82 μM in the upper parts of the basin (Upreti et al., 2021). Other studies have reported denitrification rates from 0.51 to 21.6 $\text{mmol N m}^{-2} \text{d}^{-1}$ (Yu et al., 2006; VanZomerem et al., 2013; Turner et al., 2019; Vaccare et al., 2019; Upreti et al., 2021). However, most of these studies are situated further north of our study sites in fresher water. Thus, during our study, it is possible that nitrate levels had already undergone significant removal in the upper wetlands, leading to lower levels of nitrate at our sites, contributing to lower denitrification levels. The other possibility could be influence of saltwater inflow from Gulf of Mexico which with its slower nitrate level could have a diluting effect. For our salt marsh it is also possible that sulfate reduction can inhibit nitrate reduction due to competition for electron donor resources but also due to the production of H_2S which is toxic and can thus decrease nitrogen removal efficiency. The potential denitrification rates measured in this study were $-2.03 \pm 0.10 \text{ mmol m}^{-2} \text{d}^{-1}$ and $-0.23 \pm 0.04 \text{ mmol m}^{-2} \text{d}^{-1}$ for the brackish marsh along with $-0.05 \pm 0.01 \text{ mmol m}^{-2} \text{d}^{-1}$ and $-0.05 \pm 0.30 \text{ mmol m}^{-2} \text{d}^{-1}$ for the salt marsh (winter and summer respectively). These rates coincide with low nitrate concentrations (0.23–15.32 μM). Thus, denitrification did not contribute significantly to OC remineralization and was only found to be responsible for 2.54 $\text{mmol C m}^{-2} \text{d}^{-1}$ and 0.29 $\text{mmol C m}^{-2} \text{d}^{-1}$ for our brackish marsh in winter and summer respectively, and 0.06 $\text{mmol C m}^{-2} \text{d}^{-1}$ for both winter and summer at the salt marsh site (Table 2). Though our study reflects low denitrification rates it is likely that under different conditions, i.e., flooding, temperature, nitrate availability, etc. that we could expect greater denitrification rates.

Microbial-mediated iron reduction or dissimilatory iron reduction (DIR) is strongly associated with organic matter decomposition, and it is being increasingly recognized as an important part of the carbon cycle (Pan et al., 2016). It is clear in our study from changes in porewater Fe concentration that iron reduction plays an important role in this region (Fig. 5). Our potential iron reduction rates of 169.23 $\text{mmol m}^{-2} \text{d}^{-1}$ and 779.66 $\text{mmol m}^{-2} \text{d}^{-1}$ represent a significant fraction of the organic matter remineralization pathway in brackish marsh (Table 1). However, the iron reduction pathway was not prominent for salt marshes with porewater iron concentration being extremely low, although Fe^{+2} removal by sulfide cannot be completely ruled out iron reduction is generally not considered a significant reaction pathway in saltmarsh sediments (Jacobson, 1994; Alongi, 1998). This is due to high levels of sulfate in the salt marsh environment favoring sulfate reduction and sulfide, one of the primary byproducts of sulfate reduction, leading to the production of pyrite and other iron oxides thereby removing bioavailable iron from being able to be used in microbial respiration (Koretsky et al., 2003; Rickard, 2006; Burton et al., 2011).

There is no prior study from coastal Louisiana quantifying iron remineralization pathway, but other studies have shown that iron reduction can be the main way of mineralization of organic matter in many types of wetlands. Lipson et al. (2013) estimated that DIR contributed 40–63 % of ecosystem respiration in a lake basin. Dubinsky et al. (2010) found that DIR accounted for 44 % of anaerobic respiration in a tropical forest soil. The concentration and availability of soluble organic carbon are important factors that control the metabolic pathways and reduction rate of Fe(III). Jia et al. (2018) demonstrated that glucose-modified biochar increased DIR by 13–35 % compared with unmodified biochar in paddy soils. The concentration and phase of Fe oxides can affect DIR. Amorphous Fe(III) oxides such as goethite, hematite, ferrihydrite which are also operationally defined as reactive iron (rFe) are considered to be the predominant form that takes part in DIR due to the low availability of Fe in crystalline Fe(III) oxides (Lovley, 1991). Previous studies from the region have reported soil/sediment rFe content of 8.5–1.5 $\text{mg g}_{\text{dw}}^{-1}$ and 11.9–6.5 $\text{mg g}_{\text{dw}}^{-1}$ from coastal Louisiana marshes and adjacent shelf respectively (Shields et al., 2016; Ghaisas et al., 2021) suggested that is abundant rFe available to carryout DIR in these marsh soil.

Based on an iron reduction rate of 169.23 $\text{mmol m}^{-2} \text{d}^{-1}$, iron reduction accounted for 42.31 mol of C remineralization (Table 2) representing ~61.13 % of the total measured OM respiration in the winter (Table 2). During the summer, iron reduction accounted for an even higher percentage with an iron reduction rate of 779.66 $\text{mmol m}^{-2} \text{d}^{-1}$ accounting for ~81.97 % of the total measured respiration of 237.78 $\text{mmol m}^{-2} \text{d}^{-1}$. Thus, iron reduction in the brackish marsh was the most important pathway in both seasons, regardless of aerobic respiration.

A number of studies in the past have reported that sulfate is the major terminal electron acceptor in salt marshes dominated by *Spartina alterniflora* and that respiration via sulfate reduction accounts for 50 % to 90 % of the primary production (Howarth and Teal, 1979; Howarth and Giblin, 1983; Howes et al., 1984). A similar study of salt marsh dominated by *Juncus roemerianus* in Alabama reported that equivalent to 16 % to 90 % of the annual belowground production may be remineralized through sulfate reduction (Miley and Kiene, 2004). These studies all concluded that sulfate reduction plays an important role in terms of relative importance to total respiration. Howarth and Giblin (1983) concluded based on other studies that the SRR in Sapelo Island constituted the mineralization of one to two orders of magnitude more organic matter than other microbial pathways. Howarth and Teal (1979) reach a similar conclusion as sulfate reduction was found to be the most important respiration pathway during a two-year study of a New England salt marsh in Cape Cod, MA. Howarth (1984) estimates that sulfate reduction accounts for perhaps 70 % and 90 % of the total microbial respiration. Further, these studies support these conclusions and find that in salt marshes, sulfate reduction is commonly responsible for as much as 90 % of the organic matter remineralization, with iron and manganese reduction playing relatively minor roles when compared to sulfate reduction (Gaillard et al., 1989; Burdige, 1993; Carey and Taillefert, 2005).

In our current study sulfate reduction still accounted for the greatest anaerobic respiration pathway for DIC during both winter and summer, and the greatest pathway during the summer, with rates of 2.55 $\text{mmol m}^{-2} \text{d}^{-1}$ and 37.20 $\text{mmol m}^{-2} \text{d}^{-1}$ respectively. The winter rate was lower than the summer which follows what has been shown in the area (DeLaune et al., 2002). This was likely attributable to tidal patterns and lower sulfate in the soil during the winter, this would be expected because mean tides are in general lower during the winter in the area of this study (Chabreck and Hoffpauir, 1962). Thus, if true, the salt marshes during the winter would have lower sulfate levels and higher tides in the spring would need to replenish sulfate concentrations to increase sulfate reduction. Another reason possibly would be the reduction in microbial population size/activity during the cooler winter months. These rates are lower than the rates reported by the only study

of Louisiana salt marshes of $91.5\text{--}109.59\text{ mmol m}^{-2}\text{ d}^{-1}$ (DeLaune et al., 2002). Based on a sulfate reduction rate of $2.55\text{ mmol m}^{-2}\text{ d}^{-1}$, sulfate reduction accounted for 5.11 mol of C remineralization (Table 2) representing $\sim 15.87\%$ of the total measured OM respiration in the winter (Table 2). During the summer, sulfate reduction accounted for an even higher percentage with a SRR of $37.20\text{ mmol m}^{-2}\text{ d}^{-1}$ accounting for $\sim 62.04\%$ of the total measured OM respiration of $119.9\text{ mmol m}^{-2}\text{ d}^{-1}$. Thus, sulfate reduction is the dominant anaerobic pathway in the salt marsh with it being the most important pathway during the summer, and second only to aerobic respiration during the winter but with rates lower than previous observations (Howarth and Teal, 1979; Howarth and Giblin, 1983; DeLaune et al., 2002).

This can be attributed to several factors. Much like the reasons for winter having lower sulfate reduction, our salt marsh site is likely located further inland than most in these other studies. This can be gleaned via the salinity of the salt marsh throughout the year; it never exceeds 20 ppt and for most of the year is around 10 ppt (Fig. 2). Lower salinity means these marshes are receiving less sulfate from the ocean leading to lower sulfate concentrations in the soil needed for sulfate reduction. Thus, we should expect higher sulfate reduction rates from a salt marsh located close to the ocean, such as reported in DeLaune et al. (2002) with the salt marsh site having a sulfate reduction rate of $91.5\text{ mmol m}^{-2}\text{ d}^{-1}$.

4.2. Significance of soil carbon remineralization to coastal carbon budget

Our study shows the importance of aerobic and various anaerobic respiration pathways leading to carbon remineralization in marsh soil, with salinity playing a key role in governing some of these anaerobic respiration pathways. The DIC fluxes estimated using whole core incubations for the brackish and salt marsh were found to range between 36.52 ± 5.81 and $33.98 \pm 2.21\text{ mmol m}^{-2}\text{ d}^{-1}$ in winter and 133.10 ± 102.60 and $82.37 \pm 30.87\text{ mmol m}^{-2}\text{ d}^{-1}$ in summer (Fig. 4), suggesting a large fraction of the DIC produced can be transferred to overlying water during high tide or adjacent tidal channels during falling tide. Several studies have shown that respiration processes in marsh sediments result in the increase of dissolved inorganic carbon (DIC) concentration and partial pressure of CO_2 ($p\text{CO}_2$) in tidal water (Cai and Wang, 1998; Raymond and Hopkinson, 2003; Wang and Cai, 2004). Tidal water, after exchange with salt marshes, have also been shown to contain higher TA, indicating that marshes also export TA to adjacent coastal waters (Wang and Cai, 2004). Anaerobic respiration in marsh sediments generates most of the exported alkalinity. Our study shows the importance of both sulfate and iron remineralization pathways in these marshes indicating potential contribution of alkalinity from these wetlands to coastal ocean. Porewater DIC and TA depth profiles from both the marshes show progressive increase with depth to as high as 30 mmol kg^{-1} for DIC and 28 mmol kg^{-1} for TA from 22 to 30 cm in the salt marsh (Fig. 3). Even at our brackish marsh DIC was $>5\text{ mmol kg}^{-1}$ deeper than 14 cm with the TA surpassing 3 mmol kg^{-1} . A previous study from this region has also reported high DIC and TA in porewaters (He et al., 2022). Thus, TA export from marshes could also be an important term in the Louisiana coastal ocean alkalinity budget (Hu and Cai, 2011). Thus, marshes can act as source of both DIC and TA which can greatly influence the buffering capacity of the coastal ocean. This is particularly important for this region which is undergoing subsidence and wetland loss leading to accelerated relative sea level changes.

5. Conclusion

With this understanding of the current state of microbial driven organic remineralization, the future of this system under sea-level rise scenarios and resulting salinity intrusion are uncertain. This study shows that salt marshes and brackish marshes operate under different microbial pathways. The decrease of iron reduction across the system and increase in sulfate reduction over a wider area due to saltwater intrusion

leading to an increase in sulfate concentrations is likely. Increasing SO_4 concentrations are generally associated with rapid increases in SO_4 reduction rates and the acceleration of overall organic matter mineralization in freshwater wetland soils (Lamers et al., 1998; Weston et al., 2006). Sulfate reduction also results in the formation of sulfide (H_2S , HS^- , S^{2-}), which is toxic to many organisms (Lamers et al., 2013; Herbert et al., 2015). Thus, saline waters have the potential to shift microbial communities, though the precise response of these communities to saltwater intrusion can vary (Herbert et al., 2015). Thereby an increasing salinity regime due to sea level rise would affect the future carbon cycle through the use of different microbial processes with different efficiencies. However, some studies show that salinization will result in altered community composition without major changes in microbial function as freshwater organisms are replaced by their brackish/saline analogues (Hobbie, 1988; Hart et al., 1991; Nielsen et al., 2003).

This is the first study from coastal Louisiana marshes that simultaneously documented the relative importance of major soil respiration pathways in salt and brackish marshes. Despite the focus on denitrification in this region, our study shows that sulfate respiration and iron reduction are the predominant microbial pathways to soil organic carbon remineralization in salt marshes and brackish marshes respectively. Thus, future studies need to focus on detailed biochemical processes and microbial communities that influence these processes. Such study is needed to provide a holistic understanding of the future soil carbon preservation and loss in coastal wetlands across the salinity gradient that are currently undergoing both “pulsed and pressed” climatic change. Future research into brackish and salt marshes is needed to understand how a potential shift in microbial process away from iron reduction and towards sulfate reduction due to saltwater encroachment could affect the local and global delta carbon cycle.

CRedit authorship contribution statement

P. Owen Clower: Writing – review & editing, Writing – original draft, Visualization, Supervision, Investigation, Formal analysis. **Kanchan Maiti:** Writing – review & editing, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Marshall Bowles:** Writing – review & editing, Resources, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work is partly supported by NSF Chemical Oceanography Program OCE 1756788. Special thanks to Chris Swarzenski and Gina Groseclose for helping with field sampling. As well as Dr. Songjie He for help with field sampling and proofreading this article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.174898>.

References

- Alongi, D.M., 1998. Coastal Ecosystem Processes. CRC Press.
- Alongi, D.M., 2014. Carbon cycling and storage in mangrove forests. *Ann. Rev. Mar. Sci.* 6, 195–219.

- Alongi, D.M., Tirendi, F., Clough, B.F., 2000. Below-ground decomposition of organic matter in forests of the mangroves *Rhizophora stylosa* and *Avicennia marina* along the arid coast of Western Australia. *Aquat. Bot.* 68 (2), 97–122.
- Alongi, D.M., Wattayakorn, G., Pfitzner, J., Tirendi, F., Zagorskis, I., Brunskill, G.J., Clough, B.F., 2001. Organic carbon accumulation and metabolic pathways in sediments of mangrove forests in southern Thailand. *Mar. Geol.* 179 (1–2), 85–103.
- Anderson, M.M., Maiti, K., Xue, Z.G., Ou, Y., 2020. Dissolved inorganic carbon transport in the surface-mixed layer of the Louisiana Shelf in northern Gulf of Mexico. *J. Geophys. Res. Oceans* 125 (11) e2020JC016605.
- Barras, J.A., Bourgeois, P.E., Handley, L.R., 1994. Land loss in coastal Louisiana 1956–90. In: National Biological Survey, National Wetlands Research Center Open File Report 94-01, 4 pp. 10 color plates.
- Baustian, M.M., Stagg, C.L., Perry, C.L., Moss, L.C., Carruthers, T.J., Allison, M., 2017. Relationships between salinity and short-term soil carbon accumulation rates from marsh types across a landscape in the Mississippi River Delta. *Wetlands* 37, 313–324.
- Bowles, M.W., Samarkin, V.A., Bowles, K.M., Joye, S.B., 2011. Weak coupling between sulfate reduction and the anaerobic oxidation of methane in methane-rich seafloor sediments during ex situ incubation. *Geochim. Cosmochim. Acta* 75, 500–519.
- Breithaupt, J.L., Smoak, J.M., Smith III, T.J., Sanders, C.J., Hoare, A., 2012. Organic carbon burial rates in mangrove sediments: strengthening the global budget. *Global Biogeochem. Cycles* 26 (3).
- Bridgman, S.D., Megonigal, J.P., Keller, J.K., Bliss, N.B., Trettin, C., 2006. The carbon balance of North American wetlands. *Wetlands* 26 (4), 889–916.
- Burdige, D.J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. *Earth Sci. Rev.* 35 (3), 249–284.
- Burdige, D.J., 2011. 5.09 Estuarine and coastal sediments–coupled biogeochemical cycling. *Treat. Estuar. Coast. Sci.* 5, 279–308.
- Burton, E.D., Bush, R.T., Johnson, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochim. Cosmochim. Acta* 75 (12), 3434–3451.
- Byrnes, M.R., Britsch, L.D., Berlinghoff, J.L., Johnson, R., Khalil, S., 2019. Recent subsidence rates for Barataria Basin, Louisiana. *Geo-Mar. Lett.* 39 (4), 265–278.
- Cai, W.J., Wang, Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnol. Oceanogr.* 43 (4), 657–668.
- Carey, E., Taillefert, M., 2005. The role of soluble Fe (III) in the cycling of iron and sulfur in coastal marine sediments. *Limnol. Oceanogr.* 50 (4), 1129–1141.
- Chabreck, R.H., Hoffpauir, C.M., 1962. The use of weirs in coastal marsh management in Louisiana. In: Proceedings of the Annual Conference Southeastern Association of Game Fish Commissioners, Vol. 16, pp. 103–112.
- Chambers, L.G., Reddy, K.R., Osborne, T.Z., 2011. Short-term response of carbon cycling to salinity pulses in a freshwater wetland. *Soil Sci. Soc. Am. J.* 75 (5), 2000–2007.
- Chmura, G.L., Anisfeld, S.C., Cahoon, D.R., Lynch, J.C., 2003. Global carbon sequestration in tidal, saline wetland soils. *Global Biogeochem. Cycles* 17.
- Couvillion, B.R., Barras, J.A., Steyer, G.D., Sleavin, W., Fischer, M., Beck, H., Heckman, D., 2011. Land Area Change in Coastal Louisiana from 1932 to 2010.
- Craft, C., 2007. Freshwater input structures soil properties, vertical accretion, and nutrient accumulation of Georgia and US tidal marshes. *Limnol. Oceanogr.* 52 (3), 1220–1230.
- Crozier, C.R., DeLaune, R.D., 1996. Methane production by soils from different Louisiana marsh vegetation types. *Wetlands* 16, 121–126.
- Das, A., Justic, D., Inoue, M., Hoda, A., Huang, H., Park, D., 2012. Impacts of Mississippi River diversions on salinity gradients in a deltaic Louisiana estuary: ecological and management implications. *Estuar. Coast. Shelf Sci.* 111, 17–26.
- DeLaune, R.D., Pezeshki, S.R., 1994. The influence of subsidence and saltwater intrusion on coastal marsh stability: Louisiana Gulf coast, USA. *J. Coast. Res.* 77–89.
- DeLaune, R.D., Devai, I., Crozier, C.R., Kelle, P., 2002. Sulfate reduction in Louisiana marsh soils of varying salinities. *Commun. Soil Sci. Plant Anal.* 33 (1–2), 79–94.
- Dickson, A.G., 2010. Standards for ocean measurements. *Oceanography* 23 (3), 34–47.
- Duarte, C.M., Cebrian, J., 1996. The fate of marine autotrophic production. *Limnol. Oceanogr.* 41 (8), 1758–1766.
- Duarte, C.M., Middelburg, J.J., Caraco, N., 2005. Major role of marine vegetation on the oceanic carbon cycle. *Biogeochemistry* 2 (1), 1–8.
- Dubinsky, E.A., Silver, W.L., Firestone, M.K., 2010. Tropical forest soil microbial communities couple iron and carbon biogeochemistry. *Ecology* 91 (9), 2604–2612.
- Ferreira, T.O., Otero, X.L., Vidal-Torrado, P., Macías, F., 2007. Effects of bioturbation by root and crab activity on iron and sulfur biogeochemistry in mangrove substrate. *Geoderma* 142 (1–2), 36–46.
- Gaillard, J.F., Pauwels, H., Michard, G., 1989. Chemical diagenesis in coastal marine sediments. *Oceanol. Acta* 12 (3), 175–187.
- Ghaisas, N.A., Maiti, K., White, J.R., 2019. Coupled iron and phosphorus release from seasonally hypoxic Louisiana shelf sediment. *Estuar. Coast. Shelf Sci.* 219, 81–89.
- Ghaisas, N.A., Maiti, K., Roy, A., 2021. Iron-mediated organic matter preservation in the Mississippi River-influenced shelf sediments. *J. Geophys. Res. Biogeosci.* 126 (4) e2020JG006089.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* 77 (920), 661–671.
- Hart, B.T., Bailey, P., Edwards, R., Hortle, K., James, K., McMahon, A., Swadling, K., 1991. A review of the salt sensitivity of the Australian freshwater biota. *Hydrobiologia* 210 (1–2), 105–144.
- He, S., Maiti, K., Swarzenski, C.M., Eusey-Quirk, T., Groseclose, G.N., Justic, D., 2022. Porewater chemistry of Louisiana marshes with contrasting salinities and its implications for coastal acidification. *Estuar. Coast. Shelf Sci.* 268, 107801.
- He, S., Maiti, K., Ghaisas, N., Uprethi, K., Rivera-Monroy, V.H., 2023. Potential methane production in oligohaline wetlands undergoing erosion and accretion in the Mississippi River Delta Plain, Louisiana, USA. *Sci. Total Environ.* 875, 162685.
- Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnol. Oceanogr.* 29 (3), 657–663.
- Herbert, E.R., Boon, P., Burgin, A.J., Neubauer, S.C., Franklin, R.B., Ardón, M., Gell, P., 2015. A global perspective on wetland salinization: ecological consequences of a growing threat to freshwater wetlands. *Ecosphere* 6 (10), 1–43.
- Hobbie, J.E., 1988. A comparison of the ecology of planktonic bacteria in fresh and salt water. *Limnol. Oceanogr.* 33 (4 part 2), 750–764.
- Howarth, R.W., 1984. The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments. *Biogeochemistry* 5–27.
- Howarth, R.W., 1993. Microbial processes in salt-marsh sediments. In: Ford, T.E. (Ed.), *Aquatic Microbiology: An Ecological Approach*. Blackwell, Oxford, pp. 239–259.
- Howarth, R.W., Giblin, A., 1983. Sulfate reduction in the salt marshes at Sapelo Island, Georgia. *Limnol. Oceanogr.* 28 (1), 70–82.
- Howarth, R.W., Teal, J.M., 1979. Sulfate reduction in a New England salt marsh. *Limnol. Oceanogr.* 24 (6), 999–1013.
- Howes, B.L., Dacey, J.W., King, G.M., 1984. Carbon flow through oxygen and sulfate reduction pathways in salt marsh sediments. *Limnol. Oceanogr.* 29 (5), 1037–1051.
- Hu, X., Cai, W.J., 2011. An assessment of ocean margin anaerobic processes on oceanic alkalinity budget. *Global Biogeochem. Cycles* 25 (3).
- Jacobson, M.E., 1994. Chemical and biological mobilization of Fe (III) in marsh sediments. *Biogeochemistry* 25, 41–60.
- Jia, R., Li, L., Qu, D., Mi, N., 2018. Enhanced iron (III) reduction following amendment of paddy soils with biochar and glucose modified biochar. *Environ. Sci. Pollut. Res.* 25, 91–103.
- Keller, J.K., Bridgman, S.D., 2007. Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient. *Limnol. Oceanogr.* 52 (1), 96–107.
- Koretsky, C.M., Moore, C.M., Lowe, K.L., Meile, C., DiChristina, T.J., Van Cappellen, P., 2003. Seasonal oscillation of microbial iron and sulfate reduction in saltmarsh sediments (Sapelo Island, GA, USA). *Biogeochemistry* 64 (2), 179–203.
- Kraus, K.W., Holm Jr., G.O., Perez, B.C., McWhorter, D.E., Cormier, N., Moss, R.F., Raynie, R.C., 2016. Component greenhouse gas fluxes and radiative balance from two deltaic marshes in Louisiana: pairing chamber techniques and eddy covariance. *J. Geophys. Res. Bioge.* 121 (6), 1503–1521.
- Kristensen, E., Ahmed, S.I., Devol, A.H., 1995. Aerobic and anaerobic decomposition of organic matter in marine sediment: which is fastest? *Limnol. Oceanogr.* 40 (8), 1430–1437.
- Lamers, L.P., Tomassen, H.B., Roelofs, J.G., 1998. Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.* 32 (2), 199–205.
- Lamers, L.P., Govers, L.L., Janssen, I.C., Geurts, J.J., Van der Wel, M.E., Van Katwijk, M.M., Smolders, A.J., 2013. Sulfide as a soil phytotoxin—a review. *Front. Plant Sci.* 4, 268.
- Lipson, D.A., Raab, T.K., Gorla, D., Zlamal, J., 2013. The contribution of Fe (III) and humic acid reduction to ecosystem respiration in drained thaw lake basins of the Arctic Coastal Plain. *Global Biogeochem. Cycles* 27 (2), 399–409.
- Louisiana Coastal Wetlands Conservation and Restoration Task Force, 1993. Louisiana Coastal Wetlands Restoration Plan. Task Force.
- Lovley, D.R., 1991. Dissimilatory Fe (III) and Mn (IV) reduction. *Microbiol. Rev.* 55 (2), 259–287.
- McKee, K.L., Mendelssohn, I.A., Hester, M.W., 1988. Reexamination of pore water sulfide concentrations and redox potentials near the aerial roots of *Rhizophora mangle* and *Avicennia germinans*. *Am. J. Bot.* 75 (9), 1352–1359.
- McLeod, E., Chmura, G.L., Bouillon, S., Salm, R., Björk, M., Duarte, C.M., Silliman, B.R., 2011. A blueprint for blue carbon: toward an improved understanding of the role of vegetated coastal habitats in sequestering CO₂. *Front. Ecol. Environ.* 9 (10), 552–560.
- Megonigal, J.P., Neubauer, S.C., 2009. Chapter 19: biogeochemistry of tidal freshwater wetlands. In: GME, Perillo, Wolanski, E., Cahoon, D.R., Brinson, M.M. (Eds.), *Coastal Wetlands: An Integrated Ecosystem Approach*.
- Megonigal, J.P., Hines, M.E., Visscher, P.T., 2004. Anaerobic metabolism: linkages to trace gases and aerobic processes. In: Schlesinger, W.H. (Ed.), *Biogeochemistry*. Elsevier-Pergamon, Oxford, UK, pp. 317–424.
- Miley, G.A., Kiene, R.P., 2004. Sulfate reduction and porewater chemistry in a gulf coast *Juncus roemerianus* (Needlerush) marsh. *Estuaries* 27, 472–481.
- Moeslund, L., Thamdru, B., Barker Jørgensen, B., 1994. Sulfur and iron cycling in a coastal sediment: radiotracer studies and seasonal dynamics. *Biogeochemistry* 27, 129–152.
- Blue carbon: the role of healthy oceans in binding carbon: a rapid response assessment. In: Nellemann, C., Corcoran, E. (Eds.), 2009. UNEP/Earthprint.
- Nielsen, D.L., Brock, M.A., Rees, G.N., Baldwin, D.S., 2003. Effects of increasing salinity on freshwater ecosystems in Australia. *Aust. J. Bot.* 51 (6), 655–665.
- Nyman, J.A.A., DeLaune, R.D., Patrick Jr., W.H., 1990. Wetland soil formation in the rapidly subsiding Mississippi River deltaic plain: mineral and organic matter relationships. *Estuar. Coast. Shelf Sci.* 31 (1), 57–69.
- Pan, W., Kan, J., Inamdar, S., Chen, C., Sparks, D., 2016. Dissimilatory microbial iron reduction release DOC (dissolved organic carbon) from carbon-ferrihydrite association. *Soil Biol. Biochem.* 103, 232–240.
- Pezeshki, S.R., DeLaune, R.D., Patrick, W.H., 1989. Assessment of saltwater intrusion impact on gas exchange behavior of Louisiana Gulf Coast wetland species. *Wetl. Ecol. Manag.* 1, 21–30.
- Quintana, C.O., Shimabukuro, M., Pereira, C.O., Alves, B.G., Moraes, P.C., Valdemarsen, T., Sumida, P.Y., 2015. Carbon mineralization pathways and bioturbation in coastal Brazilian sediments. *Sci. Rep.* 5 (1), 1–13.
- Raymond, P.A., Hopkinson, C.S., 2003. Ecosystem modulation of dissolved carbon age in a temperate marsh-dominated estuary. *Ecosystems* 6, 694–705.
- Reddy, K.R., DeLaune, R.D., 2008. *Biogeochemistry of Wetlands: Science and Applications*. CRC Press.

- Rickard, D., 2006. The solubility of FeS. *Geochim. Cosmochim. Acta* 70 (23), 5779–5789.
- Rickard, D., 2012. Microbial sulfate reduction in sediments. In: *Developments in sedimentology*, Vol. 65. Elsevier, pp. 319–351.
- Røy, H., Weber, H.S., Tarpgaard, I.H., Ferdelman, T.G., Jørgensen, B.B., 2014. Determination of dissimilatory sulfate reduction rates in marine sediment via radioactive ³⁵S tracer. *Limnol. Oceanogr. Methods* 12 (4), 196–211.
- Segarra, K.E., Comerford, C., Slaughter, J., Joye, S.B., 2013. Impact of electron acceptor availability on the anaerobic oxidation of methane in coastal freshwater and brackish wetland sediments. *Geochim. Cosmochim. Acta* 115, 15–30.
- Servais, S., Kominoski, J.S., Charles, S.P., Gaiser, E.E., Mazzei, V., Troxler, T.G., Wilson, B.J., 2019. Saltwater intrusion and soil carbon loss: testing effects of salinity and phosphorus loading on microbial functions in experimental freshwater wetlands. *Geoderma* 337, 1291–1300.
- Shields, M.R., Bianchi, T.S., Gélinais, Y., Allison, M.A., Twilley, R.R., 2016. Enhanced terrestrial carbon preservation promoted by reactive iron in deltaic sediments. *Geophys. Res. Lett.* 43 (3), 1149–1157.
- Sweet, W.V., Hamlington, B.D., Kopp, R.E., Weaver, C.P., Barnard, P.L., Beakaert, D., Zuzak, C., 2022. Global and Regional Sea Level Rise Scenarios for the United States: Updated Mean Projections and Extreme Water Level Probabilities Along US Coastlines. National Oceanic and Atmospheric Administration.
- Turner, R.E., Swenson, E.M., Milan, C.S., Lee, J.M., 2019. Spatial variations in Chlorophyll a, C, N, and P in a Louisiana estuary from 1994 to 2016. *Hydrobiologia* 834, 131–144. <https://doi.org/10.1007/s10750-019-3918-7>.
- U.S. EPA, 1993. Method 350.1: Nitrogen, Ammonia (Colorimetric, Automated Phenate), Revision 2.0. Cincinnati, OH.
- Upreti, K., Maiti, K., Rivera-Monroy, V.H., 2019. Microbial mediated sedimentary phosphorus mobilization in emerging and eroding wetlands of coastal Louisiana. *Sci. Total Environ.* 651, 122–133.
- Upreti, K., Rivera-Monroy, V.H., Maiti, K., Giblin, A., Geaghan, J.P., 2021. Emerging wetlands from river diversions can sustain high denitrification rates in a coastal delta. *J. Geophys. Res. Biogeosci.* 126, e2020JG006217 <https://doi.org/10.1029/2020JG006217>.
- Upreti, K., Rivera-Monroy, V.H., Maiti, K., Giblin, A.E., Castañeda-Moya, E., 2022. Dissimilatory nitrate reduction to ammonium (DNRA) is marginal relative to denitrification in emerging-eroding wetlands in a subtropical oligohaline and eutrophic coastal delta. *Sci. Total Environ.* 819, 152942.
- Vaccare, J., Meselhe, E., White, J.R., 2019. The denitrification potential of eroding wetlands in Barataria Bay, LA, USA: implications for river reconnection. *Sci. Total Environ.* 686, 529–537.
- VanZomerem, C.M., White, J.R., DeLaune, R.D., 2013. Ammonification and denitrification rates in coastal Louisiana bayou sediment and marsh soil: implications for Mississippi river diversion management. *Ecol. Eng.* 54, 77–81.
- Wang, Z.A., Cai, W.J., 2004. Carbon dioxide degassing and inorganic carbon export from a marsh-dominated estuary (the Duplin River): a marsh CO₂ pump. *Limnol. Oceanogr.* 49 (2), 341–354.
- Weston, N.B., Dixon, R.E., Joye, S.B., 2006. Ramifications of increased salinity in tidal freshwater sediments: geochemistry and microbial pathways of organic matter mineralization. *J. Geophys. Res. Biogeosci.* 111 (G1).
- Więski, K., Guo, H., Craft, C.B., Pennings, S.C., 2010. Ecosystem functions of tidal fresh, brackish, and salt marshes on the Georgia coast. *Estuar. Coasts* 33, 161–169.
- Yu, K., DeLaune, R.D., Boeckx, P., 2006. Direct measurement of denitrification activity in a Gulf coast freshwater marsh receiving diverted Mississippi River water. *Chemosphere* 65, 2449–2455.
- Zhang, J., Ortner, P.B., Fischer, C.J., 1997. Method 353.4 Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis. U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-15/012.
- Zimmerman, C.F., Keefe, C.W., Bashe, J., 1997. Method 440.0 Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis. U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-15/009.