THE BIOGEOCHEMICAL EFFECTS OF SEA LEVEL RISE ON COASTAL WETLAND SOIL CARBON

By

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To my husband and my mom

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
C	Carbon
CA	Control (water level) ambient (salinity)
CE	Control (water level) elevated (salinity)
DDI	Distilled de-ionized
DI	De-ionized
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EC	Electrical conductivity
FID	Flame ionization detector
GWP	Global warming potential
HT	High tide
IA	Inundated (water level) ambient (salinity)
IE	Inundated (water level) elevated (salinity)
IPCC	Intergovernmental panel on climate change
LOC	Labile organic carbon
LOI	Loss on ignition
LOI	Loss on ignition
LSM	Least squares means
LT	Low tide
MBC	Microbial biomass carbon
MUF	Methylumbelliferone
N	Nitrogen
NEP	Net ecosystem productivity

NS	Not significant
OC	Organic carbon
OM	Organic matter
P	Phosphorus
PLFA	Phospholipid fatty acid
Ppt	Part per thousand
PVC	Polyvinyl chloride
SLR	Sea level rise
SOC	Soil organic carbon
SRB	Sulfate reducing bacteria
SRP	Soluble reactive phosphorus
SRS	Shark River Slough
TFM	Tidal freshwater marsh
TKN	Total kjeldahl nitrogen
TLOC	Total labile organic carbon
TOC	Total organic carbon
TPF	1,3,5-triphenylformazan
TTC	Triphenyltetrazoliym chloride

Abstract of Dissertation Presented to the Graduate School
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Coastal wetlands are among the most productive ecosystems in the world, sequestering and storing a significant portion of global carbon (C). Sea level rise (SLR) and extreme sea level events (storm surges, astronomical tides) threaten the sustainability of coastal wetlands and the C stored within them. Three studies were conducted in Florida (USA) with the common goal of improving the mechanistic understanding of how increased salinity and increased inundation affect bigeochemical C cycling in coastal wetland soils. All three studies emphasized the impacts of saltwater intrusion and inundation on soil respiration, methanogenesis, and dissolved organic C (DOC), but differed in location, scale (i.e., the degree of experimental control), and focus.

The two mechanisms by which salinity influences C biogeochemistry- the sulfate effect (additional electron acceptors) and the osmotic effect (high ionic strength) where separated. Sulfate causes a short-term stimulation of CO_2 production in proportion to the concentration added, and a continuous suppression of CH_4 production. Ionic strength does not affect CO_2 production and causes only minor suppression of CH_4. Changes in salinity from fresh to ~14 ppt appear to cause the greatest shift in

biogeochemical pathways for C mineralization. However, the availability of other parameters (C lability, nutrients, and microbial community) ultimately determines the persistence of the observed salinity effects. Short-term pulses of higher (or lower) salinity may have a greater impact on C cycling than gradual changes in salinity. Freshwater wetlands pulsed with brackish seawater experience significant increases in the rate of C loss, as do salt marshes pulsed with freshwater. However, all studies indicate microbial communities adapt quickly (1-2 weeks) to changes in salinity.

Increased inundation poses a more long-term threat to coastal wetland sustainability, causing disintegration of soil structure, decreased in soil respiration, and increased in DOC export. Meanwhile, the simultaneous increase of both salinity and inundation causes a synergistic decline in the rate of C loss. The overall affect of SLR on coastal wetland C storage depends on wetland type, with freshwater tidal wetlands generally having enhanced rates of C loss and brackish and salt marshes demonstrating decreased rates of C loss.

CHAPTER 1
INTRODUCTION

Sea Level Rise and Coastal Wetlands

Changes in global sea level are a natural part of the geologic history of the earth. Since the end of the last glacial maximum (~21,000 years before present), isostatic adjustment of the crust and exchange between ocean and land water reservoirs (glaciers, ice caps, etc.) have increased mean sea level about 120 m. In the 2,000 years prior to 1850, sea level was relatively stable, changing only about 0.0 to +0.2 mm y^{-1}. However, from 1850 to 1950 sea level rose at a rate of ~1.7 mm y^{-1}, and since 1993, this rate has increased to between 2.8 and 3.1 (± 0.7) mm y^{-1}. This rate of sea level rise (SLR) translates into a ~60 cm increase by 2100 under a business-as-usual scenario (IPCC 2007).

A major concern of SLR is the impact to human populations and infrastructure. Approximately 23% of the world's population lives within 100 m of sea level, and 10% within 10 m of sea level (IPCC 2007; McGranahan et al. 2007). Threats to livelihoods, public health, and social and economic stability are receiving increasing attention in the scientific literature, as well as a global debate over coping strategies (Dasgupta et al. 2011; Nicholls and Cazenave 2010; McGranahan et al. 2007). Nevertheless, a significant portion of coastal land remains sparsely populated or undeveloped, providing important environmental services, such as storm abatement, flood control, wildlife habitat, nutrient cycling, and carbon storage (Barbier et al. 2011). Many of these natural coastal lands are coastal wetlands. Defined by the presence of hydrophytic vegetation and waterlogged hydric soils, coastal wetlands also have a tidally influenced hydroperiod. Coastal wetlands occupy the land fringe, tolerating full or even

hypersaline conditions ($\geq$ 35 ppt), but also extend inland along the entire salinity gradient. The landward end-member, tidal freshwater marshes (TFM), have ocean-influenced hydrology but remain fresh (<0.5 ppt; Figure 2-1).

Coastal wetlands are considered among the most productive ecosystems in the world,providing more ecosystem services than any other coastal environment (Gedan et al. 2009). Some of the more tangible ecosystem services include: wildlife habitat, nursery grounds for shellfish and commercial fisheries, coastline stabilization, storm surge abatement, livestock fodder, and building material. However, arguably the most important functions of coastal wetlands are less tangible- nutrient cycling, pollution removal, and carbon (C) storage (Barbier et al. 2011; Gedan et al. 2009). The storage and burial of C in coastal wetlands is of global importance due to the link between atmospheric CO_2 and climate change (IPCC 2007).

Globally, salt marshes are estimated to cover up to 400,000 km^2, and mangroves 138,000 - 152,000 km^2 (McLeod et al. 2011). Despite their small areal coverage relative to terrestrial and ocean ecosystems, salt marshes and mangroves sequester large amounts of CO_2, approximately 210 g CO_2 m^{-2} yr^{-1} (Chmura et al. 2003). The large C sequestration capacity is a function of high primary productivity, slow decomposition, and the ability to trap and bury significant amounts of allochthonus C from terrestrial run-off and tidal deposition (Armentano and Menges 1986).

Coastal wetlands have persisted during centuries of fluctuations in sea level through natural feedback mechanisms of vertical soil accretion and landward migration (e.g., Kirwan and Temmerman, 2009; Alongi 2008; Donnelly and Bertness 2001). However, there is growing concern over the ability of coastal wetlands to adapt to

accelerations in the rate of SLR, especially in systems already disturbed by adjacent development, dredging and filling, changes in sediment loads, invasive species, etc. (Day et al. 2008; Nicholls et al. 1999). Predictions of global coastal wetland loss associated with SLR are between 20 and 30% by 2100 (IPCC 2007; Nicholls et al. 1999). The impacts of SLR on coastal wetlands are already evident in many areas of the world. For example, there is a growing area of research that utilizes historical data, remote sensing, and biological indicators to document and assess landscape-scale changes in coastal wetlands caused by SLR (e.g., Hussein 2009; Smith 2009; Gaiser et al. 2006; William et al. 1999). Despite increasing documentation of ecosystem changes, there are still significant gaps in understanding of the *mechanisms* prompting these landscape-scale changes. There is also uncertainty regarding the perpetuation of coastal wetland ecosystem services during these observed transformations.

Coastal Wetland Carbon Biogeochemistry

From a systems approach, SLR exerts two major driving forces on coastal wetlands- increases in salinity and inundation. The best way to understand these drivers is to observe the most elementary response. In wetlands, soil microorganisms are usually the first to respond to environmental changes due to their sensitivity (large surface to volume ratio) and rapid turn-over rate. Microbes play a critical role in wetlands by controlling everything from the rate at which nutrients become available to plants and animals, to the storage and burial of soil C. The size, structure, and activity of the soil microbial community is manifested in biogeochemical cycles, the transformation and exchange of energy and matter between biotic and abiotic components of the environment (Reddy and DeLaune 2008). Carbon plays a central role in nearly all biogeochemical cycles as a substrate and electron donor during

heterotrophic respiration (Figure 1-2). Primary production (CO_2 fixation) and lateral inflows (overland run-off and deposition) introduce C-containing organic matter to a wetland. The organic matter then undergoes a degradation process that includes leaching, enzyme hydrolysis, and microbial respiration. These processes break-down complex C polymers into monomers, and then further mineralize the C into CO_2 and CH_4, which are released to the atmosphere (Figure 1-2). The efficiency with which microbes mineralize C is crucial to determining a wetland's C balance: how much of the C fixed and imported into the system becomes stored or buried, and how much is mineralized, exported, or released as CO_2 and CH_4. Most coastal wetlands function as net C sinks (Bridgham et al. 2006).

Dissertation Overview

Sea level rise could impact the ability of coastal wetlands to function as global C sinks by altering the rate and nature of biogeochemical C cycling (Morris et al. 2002). A comprehensive review of current literature regarding the impacts of SLR on C cycling reveals significant gaps in the understanding of how the main drivers associated with SLR (salinity and inundation) affect C cycling in coastal wetlands, especially the final stage of the C cycle- microbial respiration. The overarching goals of this dissertation are to (1) improve the mechanistic understanding of how salinity and inundation affect biogeochemical carbon cycling, (2) vary scale (i.e., degree of experimental control) to translate biogeochemical processes into real-world observations, and (3) provide insight into the broader question of how coastal wetland C storage might be affected by SLR. Figure 1-3 provides a conceptual diagram outlining how the system drivers (salinity and inundation) are related to other biogeochemically important processes that I predicted will impact the rate of wetland C loss (e.g., changes in water chemistry, saltwater

intrusion, water level, and tidal cycle). This diagram also indicates in which chapter of the dissertation the topic is addressed.

Objectives and Hypotheses

The first objective of this dissertation was to review the current literature and identify knowledge gaps in the understanding of how SLR impacts coastal wetland C cycling, which is presented in Chapter 2 of this dissertation. Objective 2 was to determine the process-level impacts of salinity on microbially-mediated C cycling in a wetland soil (Chapter 3). I hypothesized the high ionic strength of saltwater would decrease the activity of all soil microbes, but the presence of sulfate (SO_4^{2-}), an alternative electron acceptor used during anaerobic respiration, will stimulate CO_2 production by promoting sulfate reduction. Assessing the importance of time-scale (pulsing events vs. gradual changes) on the biogeochemical response of C cycling to changes in salinity was the third objective, and is covered in Chapters 3-5. I expected that short-term, dynamic changes in salinity would have a greater effect on the rate of C cycling than gradual changes, a consequence of the high capacity of soil microbial population to adapt to environmental change. Objective 4, addressed in Chapters 4 and 5, was to determine the importance of tidal cycle on C cycling, and how the magnitude of tidal effect differs along the coastal wetland continuum from TFMs to salt marshes and mangroves. The hypothesis for this objective was that production of CO_2 would be higher under low tide conditions and will be directly related to the height of the water table, regardless of wetland type. The fifth objective involved the quantification of the effect of increased inundation (reduced soil exposure during low tide) on the rate and biogeochemical pathways of C cycling. I expected increased inundation would reduce the overall rate of C cycling, but would increase the contribution of methanogenesis to C

loss, relative to respiration. This objective is included in Chapters 4 and 5. In objective 6, the interactive effects of simultaneous increases in both salinity and inundation on the rate of C cycling were determined (Chapter 5) under the hypothesis that increases in salinity would accelerate C loss, while increases in inundation would decrease the rate of C cycling. Both processes occurring simultaneously would effectively cancel-out the other, resulting in a minimal or no effect on overall C cycling. The final objective was to assess the importance of other physical and biological variables within the wetlands studied on the rate of C cycling as possible covariants. The hypothesis for objective 7 was that inherent differences in soil properties (organic matter, C, and nitrogen (N) content), nutrient availability (N and phosphorus (P)), and microbial community size would co-vary with coastal wetland type, salinity, and inundation, and influencing the response of C cycling to SLR; this topic is covered in Chapters 4 and 5.

Dissertation Organization

This dissertation is organized into 6 Chapters. Chapter 1 (this Chapter) introduces the concept of sea level rise, the importance of C storage in coastal wetlands, and provides an overview of the objectives and format of the dissertation. This is followed by Chapter 2, which involves a comprehensive literature review of current knowledge pertaining to the effects of SLR on the three major regulators of C biogeochemistry: C quality, electron acceptor availability, and microbial community. Chapters 3-5 focus on individual research studies presented in order of increasing scale and complexity. Chapter 3 focuses on a microcosm study disentangling the impacts of salt (ionic strength) and seawater (containing sulfate) on potential respiration and methanogenesis in an organic freshwater wetland soil. An intact soil core study investigating the impacts of salinity pulsing events and tidal cycle on C loss along a coastal wetland salinity

gradient is the subject of Chapter 4, and Chapter 5 presents a mesocosm study on the effects of increased salinity, inundation, and the combination thereof, on C loss and porewater nutrients in an Everglades peat soil. Finally, Chapter 6 provides a synthesis of conclusions drawn from all the dissertation studies and a theoretical discussion on the fate of coastal wetlands as C sinks during SLR.

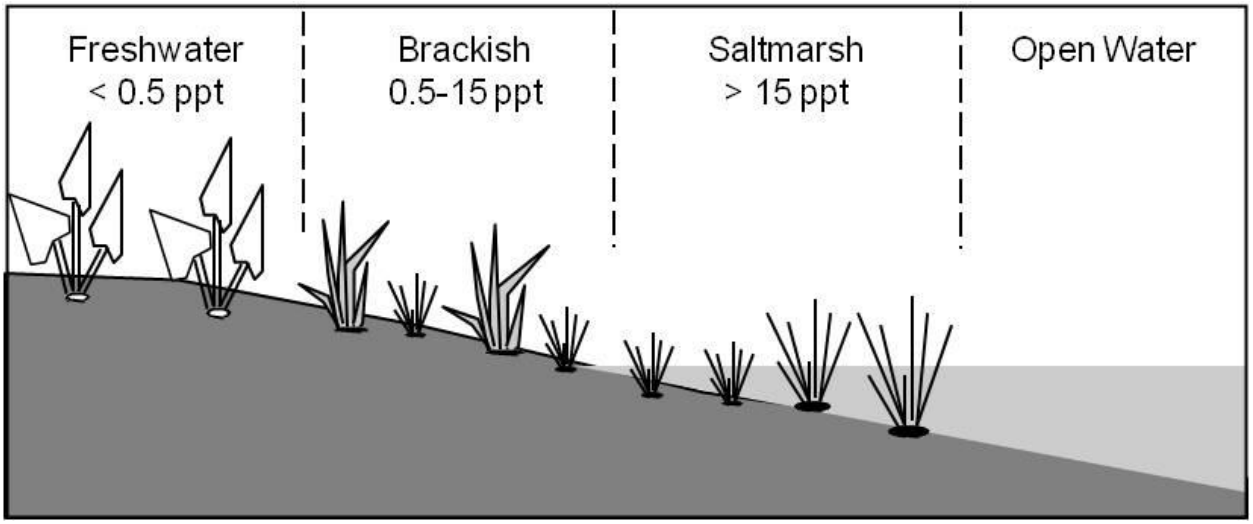

Figure 1-1. Conceptual diagram of a coastal wetland salinity gradient. Coastal wetlands can have salinities ranging from freshwater to hypersaline, but all have a tidally-influenced hydroperiod.

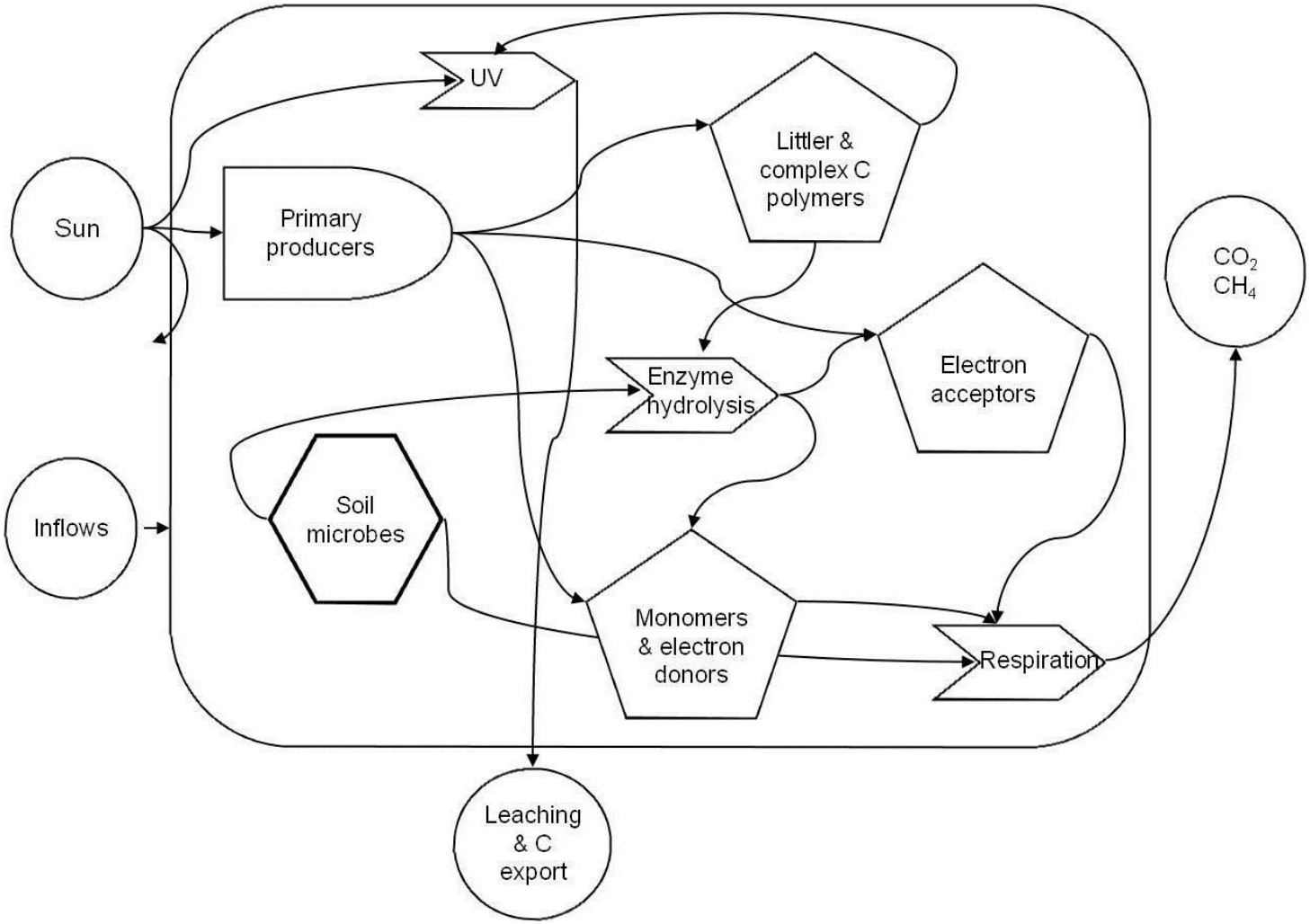

Figure 1-2. Simplified systems diagram of a wetland soil organic carbon cycle. Carbon enters a wetland through photosynthesis and external inflow. It is then degraded through processes of leaching, hydrolosis, and microbial respiration to be exported or released as carbon dioxide or methane. The remaining carbon is stored in wetland soils.

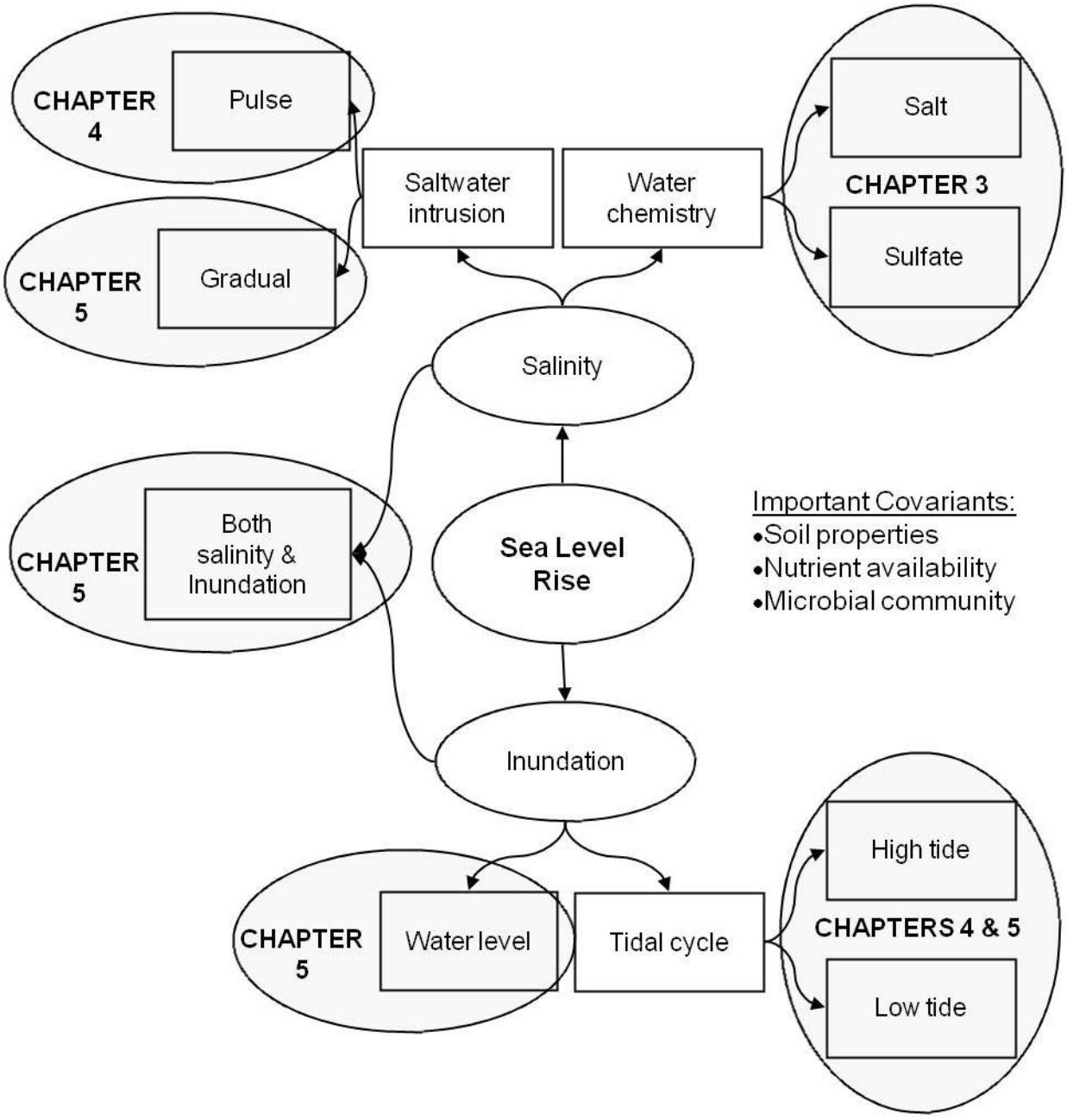

Figure 1-3. Flow diagram of research objectives and dissertation organization. The dissertation's central focus is on the two main drivers accompanying sea level rise: salinity and inundation, and the associated impacts of other ecosystem characteristics.

CHAPTER 2
SEA LEVEL RISE IMPACTS ON BIOGEOCHEMICAL CARBON CYCLING IN COASTAL WETLANDS

Background

Biogeochemistry is the scientific study of the interactions between biological, chemical, and physical processes in nature; it includes aspects of biology, soil science, chemistry, and geology. Specifically, biogeochemistry focuses on the cycling, or transformation, of elements between various phases (e.g., solid, liquid, gas) and states (e.g., organic or inorganic; oxidized or reduced) with an emphasis on the exchange of energy and matter between biotic and abiotic components of the environment through oxidation-reduction reactions (Reddy and DeLaune 2008).

Sea level rise can impact C biogeochemistry in coastal wetlands by three main mechanisms: (1) the complete loss of wetland area, (2) an increase in inundation, and/or, (3) an increase in salinity. While the first is fairly straightforward (a decrease in wetland area means a reduction in C cycling and storage), the latter two mechanisms involve more subtle changes in the chemistry, biology, and geomorphology of coastal wetlands. This includes multi-directional changes in the C balance, variations in the end-products of C cycling, and numerous feedback loops.

The goal of this review is to present the current state of knowledge regarding how C biogeochemistry in coastal wetlands is impacted by SLR, with special emphasis on the role of inundation and salinity on C cycling and storage. The impacts of SLR on coastal wetlands are seen over a range of time scales, which eventually lead to the modification of the chemical, biological, and geological environment of coastal wetlands (Figure 2-1). The challenge in discussing SLR impacts on any particular system or process is that ecosystem drivers never occur in isolation. That is, disentangling the

response of C biogeochemistry to alterations in inundation and salinity due to SLR, from the response to the many other environmental variables (e.g., temperature, nutrient availability, human disturbance, etc.) is nearly impossible. Laboratory and mesocosms studies increase the control researchers have over extraneous variables, but reduce the applicability of results to real-world conditions. Both manipulative and observational studies are included in this review, and a discussion of the influence of additional/extraneous variables is included when warranted.

On the most basic level, biogeochemical C cycling requires an electron donor (C substrate), an electron acceptor (O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}, or CO_2), and soil microbes to mediate the energy exchange. As a result of this energy exchange, some C is released to the atmosphere as CO_2 or CH_4, while the remaining C is stored, buried, or exported from the system (Figure 2-2). This review is organized according to the 3 major regulators of C biogeochemistry: (1) C quantity and quality (primary production, soil properties, and organic matter quality), (2) electron acceptor availability, and (3) microbial community (bacteria, fungi, and enzyme activity). The review concludes with a discussion of the overall C balance (decomposition rates, C emissions, C storage and accretion). Brief summaries are included at the end of each sub-section and predictions of the overall response of the variable in question are presented when there is ample evidence to support it.

Coastal Wetland Responses to Sea Level Rise

The most basic way C bioegeochemistry is disrupted by SLR is through direct loss of wetland area. In recent history, humans have been to blame for the majority of coastal wetland loss; at least 35% of global mangrove habitat has been lost since 1980 due to activities such as resource harvesting, filling for development, and mariculture

(Valiela et al. 2001). However, the loss of coastal wetland area to SLR is increasing. According to IPCC estimates, SLR of 18 to 59 cm before the end of this century will result in the loss of 30% of the world's coastal wetlands (2007). Coastal wetland loss as a consequence of SLR is a non-linear process, but it somewhat predictable with the current knowledge of salt marsh ecomorphological processes (Fagherazzi et al. 2012). Still, the human response to SRL remains a wild card. Nicholls et al. (1999) estimates that a 38 cm increase in sea level will result in a 22% loss of aerial coastal wetland coverage, but up to 70% of that loss will be the result of human intervention, such as the construction of sea walls. Humans also disrupt natural wetland dynamics with coastal development and the construction of hard shoreline structures (e.g., dikes, walls, armorment) that alter sediment delivery patterns. In Louisiana, it is estimated that for every 1 m^{-2} of coastal wetland lost, 30 kg of stored C are also lost (DeLaune and White 2011).

Coastal wetland loss not directly attributed to human activity is often traced back to increased salinity. Wetland plant species have different degrees of salinity tolerance, with freshwater species being most sensitive to salinity changes. Salt can negatively impact plant productivity by: (1) osmotic stress (Batzer and Shartiz 2006), (2) the accumulation of hydrogen sulfide (Koch et al. 1990), and (3) the inhibition of nutrient uptake (Bradley and Morris 1991). If more salt-tolerant species are not able to colonize a wetland impacted by increased salinity rapidly, plant mortality can lead to peat collapse and significant elevation loss (DeLaune et al. 1994); creating a feedback loop that eventually ends in the conversion of coastal marshes to open water (Nyman et al. 1990). The physical mechanisms underpinning the conversion of vegetated marshes to

open-water mud flats has been successfully simulated with numeric models, whereby aboveground biomass disturbance reduces soil stability and sediment trapping, local shear stress increases, the elevation of the marsh platform decreases, and the systems shifts to a non-vegetated equilibrium state (Fagherazzi et al. 2012). The vulnerability of marshes to submergence during SLR can be estimated with knowledge of the tidal range and sediment availability in the local coastal zone (Reed 1995).

Increased inundation, on the other hand, appears to be something most coastal wetlands are adept at naturally compensating for and is less likely to lead to significant submergence. Coastal wetlands occupy a specific elevation niche relative to sea level and marsh vegetation thrives when the marsh platform is between mean sea level and mean high tide (Morris et al. 2002). The natural responses of coastal wetlands to increased inundation are: (1) keeping pace with sea level through vertical accretion, or (2) migrating landward to maintain optimal elevation relative to sea level. Understanding the physical setting of a wetland can often assist in determining the most probable response to SLR (Figure 2-3).

Keeping pace with sea-level rise occurs through a natural feedback loop that has allowed coastal wetlands to persist since the last ice age: increased inundation depth enhances sedimentation, inorganic sediments accelerate primary production and organic matter accumulation, and the marsh accretes to a new equilibrium with sea level (Fagherazzi et al. 2012). Inorganic sediment promotes plant growth by providing nutrients (Ca, K, and P), increasing the availability of cation adsorption sites on the soil, and diminishing nutrient leaching (Patrick and Khalid 1974). Inorganic sediments also contain appreciable amounts of iron (III) that can precipitate S^{2-}, thereby removing this

toxin from the system (Nyman and DeLaune 1999). Enhanced plant productivity strengthens the soil matrix with additional root production, promotes organic matter accumulation, and contributes to vertical accretion (Mudd et al. 2009). In the coastal wetlands of the Mississippi River delta, organic soil formation accounts for 70-80% of vertical accretion and sediment deposition the remaining 20-30% (Day et al. 2000). Despite this natural feedback, some researchers question the ability of coastal wetlands to keep pace with the current rate of SLR, citing concerns over the human alteration of the volume of sediment presently delivered to the coastal zone (Day et al. 2008).

Landward marsh migration is a process observed in coastal wetlands with low relief and minimal impediment from human development. The seaward edge of an existing wetland may submerge with SLR, while simultaneously expanding landward to maintain the optimal level of tidal inundation (Gaiser et al. 2006; Adam 2002; Donnelly and Bertness 2001). Certain wetland types fare better during the process of marsh migration due to factors such as coastal morphology, tidal range, soil type, and human infrastructure (Moorhead and Brinson 1995). In coastal Georgia, models predict a 20% decline in salt marsh area, a 24% decline in tidal freshwater swamp area, and a 10% increase in brackish marshes area; salt marshes are at greater risk of submersion and freshwater wetlands at a greater risk of infrastructure impediment (Craft et al. 2009). Landward marsh migration has been extensively documented using historic aerial photographs and biological indicators as proxies of past salinity. In the Chesapeake Bay region, soil profiles reveal a current landward marsh migration rates of 3.5 to 6.8 m y^{-1}, up from a rate of 0.2 to 1.3 m y^{-1} prior to 1850, suggesting a capacity to adjust to changing rates of SLR (Hussein 2009). Marsh migration has also been recorded in

Florida (Gaiser et al. 2006; Ross et al. 2000; Williams et al. 1999) Cape Cod (Smith 2009), Rhode Island (Donnelly and Bertness 2001), and North Carolina (Moorhead and Brinson 1995; Hackney and Cleary 1987).

Carbon Quantity and Quality

Carbon functions as an electron donor during aerobic and anaerobic microbial respiration and is subsequently broken-down (decomposed) and/or released into the atmosphere (as CO_2 or CH_4) during the process. Importantly, C not utilized by microbes can remain stored in the soil for days to centuries, effectively reducing wetland greenhouse gas emissions. The source, amount, and quality of C are critical to predicting the balance between C emissions and C storage under SLR. This section is divided into primary production, soil properties, and organic matter quality; 3 regulators of coastal wetland C biogeochemistry that can be impacted by changes in salinity and inundation.

Primary Production

Primary producers (macrophytes, mangroves, and algae) represent the major autochthonous input of organic C to coastal wetlands. The diversity, density, and life history of primary producers differ with salinity and region, but two general patterns are evident: (1) species richness is negatively correlated with salinity, and (2) biomass production decreases with increasing distance from the equator. Macrophyte species richness in Georgia declined by half between the tidal freshwater marsh (TFM) plant community and the brackish plant community, and > 50% again, from brackish marsh to salt marsh plant community (Wieski et al. 2010). Even within a specific wetland, primary production varies spatially with generally decreasing biomass as distance from a tidal creek increases (Gonzalez Trilla et al. 2010; Neubauer et al. 2000).

Tidal freshwater marshes are typically the most spatially and temporally heterogeneous of all coastal wetlands. Displaying no clear pattern of species distribution, TFM's contain large, diverse seed banks and support 50-60 species of macrophytes that vary seasonally (Odum 1988). In a Virginia TFM, net primary productivity was 94% macrophytes (536 to 715 g C m^{-2} y^{-1}) and 6% macroalgae (59 g C m^{-2} y^{-1}; Neubauer et al. 2000). Salt marshes exhibit a similar biomass allocation between macrophytes and algae, but often with lower overall productivity (Miller et al., 2001). As salinity increases, plant diversity decreases and zonation patterns based on inundation and salinity tolerance become evident (Odum 1988). An abbreviated summary of aboveground biomass data by locations and salinity is presented in Table 2-1.

Belowground biomass also varies with salinity. Brackish marsh macrophytes tend to have shallower roots (0-8 cm deep) than TFM macrophytes (13-20 cm deep), possibly because TFM species translocate more C and nutrients belowground just prior to the dormant season (Neubauer et al. 2005). Nevertheless, salt marshes have the greatest proportion of biomass stored belowground. Approximately 60% of *Spartina alterniflora* biomass, for example, is contained within the soil (Good et al. 1982). A study of a *S. alterniflora* marsh in Louisiana found an annual belowground production rate of 11,676 g m^{-2}, compared to only 1,821 g m^{-2} produced aboveground (Darby and Turner 2008). The accumulation of belowground biomass is an important energy reserve tightly coupled to overall marsh and estuarine productivity; this energy is transferred during oxidation-reduction reactions, leaching, diffusion, bioturbation, and erosion (Roman and Daiber 1984).

In tropical locations, mangroves replace herbaceous vegetation in saline wetlands. Over 70% of mangrove-dominated wetlands occur between 0 and 10° latitude (Twilley et al. 1992). Generally, mangrove biomass production decreases from an average of 2.8 Mg km^{-2} nearest the equator, to 0.96 Mg km^{-2} between 30 and 40° (Twilley et al. 1992) where solar radiation and temperatures are lower. In addition to location, mangrove productivity may also be regulated by salinity. A mesocosm study in China where *Aegiceras corniculatum* was exposed to wastewater of varying salinities revealed the highest aboveground biomass in the 15 ppt treatment, with decreases of 33 and 44% in the comparable 0 ppt and 30 ppt treatments, respectively (Wu et al. 2008). Similar to salt marshes, mangroves maintain high belowground biomass. Estimates from south Florida range from 2,317 to 4,674 g m^{-2} for belowground biomass (Castañeda-Moya et al. 2011). The ratio of aboveground:belowground biomass in mangroves is highly sensitive to nutrient availability and inundation frequency. Where resources are high and inundation low, belowground biomass was 17-33% of aboveground biomass; limitations in resources and high inundation resulted in root production 2-10 x greater than aboveground production (Castañeda 2010).

While salinity tolerance is an important determinant of vegetation zonation patterns in coastal wetlands, inundation can also affect C assimilation rates. In a temperate salt marsh, tidal inundation (fully or partially submerging marsh vegetation) decreased the rate of C fixation approximately 46% compared to the control condition (Kathilankal et al. 2008). A study in Argentina also indicated higher aboveground productivity in the high marsh (less frequently inundated), compared to the low marsh (Table 2-1;Gonzalez Trilla et al. 2010).

A crude meta-analysis (ignoring latitude and other physical factors) of the effects of salinity on aboveground biomass in herbaceous coastal wetlands revealed no significant differences between fresh (1151 ± 455 g C m^{-2} y^{-1}), brackish (1441± 766 g C m^{-2} y^{-1}) and salt marshes (1177 ± 370 g C m^{-2} y^{-1}). The high variability confirms that salinity is not the only (or possibly, even the major) factor controlling primary production in coastal wetlands. Several studies indicate the importance of inundation/elevation (Gonzalez Trilla et al. 2010; Roman and Daiber 1984), nutrient and sediment delivery (Wieski et al. 2010), litter quality (Craft et al. 2009), and temperature (Gonzalez Trilla et al. 2010) in regulating coastal wetland aboveground productivity.

Soil Properties

Soils can be short-term and long-term reservoirs of C in coastal wetlands, as well as the habitat for most of the microbes involved in C cycling. Therefore, the chemistry, texture, structure, and organic matter content of the soil greatly influences C biogeochemsity. The general properties of soils found in saltwater and freshwater wetlands differ substantially: TFMs have more autochthonous organic C and receive allocthonous C from terrestrial sources (high in clays, silts, and recalcitrant organic matter), whereas saline wetlands have less authothonous C and higher inorganic C inputs from marine sources (including fine sands and phytoplankton; Wieski et al. 2010; Paludan and Morris 1999; Odum 1988; Hatton et al. 1983). Differences in the amount of sediment deposition are the primary reason that soil bulk density increases with salinity and proximity to the sea (Craft 2007). A comparative study of soils in fresh, brackish, and salt marshes of the Mississippi River delta revealed percent pore space (by volume) decreased from 96% in the TFM to 88% in the salt marsh, and percent organic C (by weight) decreased from 17% in the TFM to 12% in the salt marsh (Nyman

et al. 1990). Differences in pore space volume has consequences for accretion rate; 1 cm of soil requires 656 g m^{-2} of organic matter in a TFM, 565 g m^{-2} in a brackish marsh, and 758 g m^{-2} in a salt marsh in Louisiana (Nyman et al. 2006).

Given that freshwater and brackish soils tend to have lower bulk density and higher pore space volume, these soils are more vulnerability to compaction and structural collapse. Peat collapse can be caused by vegetation death, erosion, and excessive soil bioturbation. Vegetation death may result from salinity stress (Williams et al. 1999), drought (DeLaune et al. 1994), herbivory (Smith 2009), or human disturbance (Kirwan et al. 2008). When vegetation dies, the structural support provided by the live roots is lost, and lacunae (gas-filled structures encompassing up to 29% of root space) are also lost (DeLaune et al. 1994). The extremely low bulk density that results means the soil can no longer support itself and the solid material compacts to fill the void. Understanding the risk factors for peat collapse may help prevent wetland loss and C release. Root death likely occurs prior to any noticeable decline in aboveground biomass and may be a warning of impending peat collapse (Turner et al. 2004). Other factors, such as eutrophication, reduce soil stability (Turner 2011). In a South Carolina salt marsh, fiddler crab (*Uca Pugnax*) burrows near tidal creek heads reached > 800 m^2 and was negatively correlated with plant stem density and positively correlated with infiltration rates (Hughes et al. 2009). It was hypothesized that the crabs destabilized the soil by consuming and damaging root structures causing peat collapse. When wetlands submerge, the organic C stored in the soil is released into the adjacent estuary or continental shelf where it is either buried or decomposed by marine microbes (Li et al. 2011; White et al. 2009).

Increased tidal inundation raises the ratio of inorganic C to organic C. For example, tidally-dominated marshes have 50% less soil organic C and accrete organic C three times slower than river-dominated marshes. The higher concentration of organic C in river-dominated marshes is due to higher primary productivity, slower decomposition, and lower sedimentation rates (Craft 2007). However, the relationship between C accumulation and distance from the coast is sometimes non-linear. The turbidity maximum of an estuary may coincide with the location of a brackish marsh, creating an area of significantly higher soil C at an intermediate location along the salinity gradient (Wieski et al. 2010). Intermediate marshes (2 to 10 ppt) have been shown to contain 32% more C than comparable freshwater marsh soils in the Mississippi River delta (Nyman et al. 1990). In general, freshwater wetlands tend to have a higher organic C content and lower bulk density (Figure 2-4).

Overall, the physical soil properties of TFMs make them larger reservoirs of organic C, but they are also more susceptible to peat collapse and submergence than saline wetlands. Sea level encroachment in TFMs will simultaneously increase soil stability and decrease the density of soil organic C.

Organic Matter Quality

Carbon is contained within the matrix of organic matter (OM) and the ability of microbes to break-down OM depends on the quality of the material, including the complexity of the C bonds and the availability of essential nutrients. The quality of autochthonous OM can vary along salinity gradients. Saltwater wetland plants generally produce lower quality litter than freshwater wetland plants and tend to be more rigid in order to withstand tides and turbulence. The salt marsh plant, *S. alterniflora,* is composed of 80% lignocellulose (Benner et al. 1986). Only a small group of organisms

can decompose lignin (actinomycetes, some fungi and eukaryotes) making lignin content a good predictor of decomposition rate (Penton and Newman 2008; Gennari et al. 2007; Enriquez et al. 1993; Benner et al. 1986). Other intrinsic characteristics of organic matter that are influenced by salinity include fiber content, plant morphology, and the presence of inhibitors (waxes, cutins, tannins, etc.; Webster and Benfield 1986).

Concentrations of sulfide, an end product of sulfate reduction, increase with salinity and have been shown to inhibit plant uptake of N (Bradley and Morris 1991). Therefore, increases in salinity can increase the C:N ratio of OM (Mendelssohn and Morris 2000). The ratio of C:N in OM is inversely related to rate of microbial respiration and is a good predictor of the balance between C decomposition and C storage. One study in Georgia found biomass quality (leaf C:N) was greater in the TFM (34.5 ± 2.8), compared to the brackish (40.9 ± 1.3) and salt marsh (36.4 ± 1.8; Craft et al. 2009). Other studies have found even lower C:N in TFM soils, with values of 11.6 to 12.1 in Virginia (Neubauer et al. 2000). All of this information provides a clear picture of a decline in autochthonous organic matter quality as salinity increases, which reduces the lability of C substrates for microbial decomposition, and possibly increase soil C storage.

Electron Acceptor Availability

Both salinity and inundation exert strong control over the abundance of different electron acceptors used during oxidation-reduction reactions. Redox potential, a measure of the magnitude of electron pressure in the soil (indicated by Eh), is high when the water table is low, allowing for greater O_2 diffusion and faster, more efficient aerobic C cycling. When inundation increases, redox potential drops and anaerobic microbes capable of using alternative electron acceptors are favored. Alternative

electron acceptors are used in a specific sequence depending on their availability and energy yield; energy yield decreases from O_2, NO_3, Fe^{3+}, Mn^{4+}, SO_4^{2-}, and CO_2 (Patrick and DeLaune 1977). In general, increased salinity raises the soil redox potential of anaerobic wetland soils by providing additional SO_4^{2-}electron acceptors (Mendelssohn et al. 1999). The subsequent sections discuss specific electron acceptors, in turn, focusing on how SLR (salinity and inundation) may impact availability.

Oxygen

The solubility of oxygen in water decreases ~30% as salinity increases from freshwater to marine systems (Capone and Kiene 1988) potentially leading to lower dissolved O_2 in the water column of encroaching seawater in coastal wetlands. Oxygen availability in the soil is inversely related to the height of the water table and the level of inundation (Yu et al. 2006). While frequency and duration of inundation will certainly increase in many coastal wetlands due to SLR, the turbid, well mixed nature of seawater and daily tidal dynamics may actually enhance soil oxygenation in certain cases by creating a more dynamic hydroperiod (Capone and Kiene 1988). Soil microbes are particularly active during low tide when respiration rates are 50 to 300% greater than at high tide due to increased aerobic respiration (Chapter 4; Gribsholt and Kristensen 2003).

Soil oxygen availability is also strongly linked to plant productivity since many wetland plants can translocate O_2 from the atmosphere to their root zone to alleviate stress from waterlogging. Salt marsh plants generally allocate more biomass belowground than fresh and brackish marsh species and may subsequently increase oxygen availability in the soil rhizosphere. Organisms such as crabs, which cause extensive bioturbation and oxygenation of the soil, are also more common in saline

wetlands. Recent research indicates soil hydraulic conductivity, a function of both the composition of organic matter and the aggregative/dispersive forces of salt, may be critical in determining how quickly O_2 can diffuse into the soil following the ebb tide. Along a gradient of TFM, brackish, and salt marsh habitats in north Florida, saline soils drained an average of 5 times faster than TFM soils, leading to higher low tide respiration rates in the brackish and salt marsh soils (2226 ± 230 mg CO_2-C m^{-2} d^{-1}) compared to the freshwater soil (1578 ± 229 mg CO_2-C m^{-2} d^{-1}; Chapter 4). Overall, it is conceivable that SLR could increase O_2 availability in coastal wetlands, as long as the marsh is able to adapt to increased inundation by maintaining an optimal elevation relative to the tidal cycle.

Nitrate

Several aspects of the nitrogen cycle are affected by increased salinity. One study indicated ammonification (organic N → NH_4^+) is stimulated by salinities up to 45 ppt (Pathak and Rao 1998). Although attributed to enhanced N mineralization, the increase in NH_4^+ observed by Pathak and Rao is more likely a result of the abiotic displacement of NH_4^+ from the soil cation exchange complex by the influx of sea salts, especially Na^{2+} and K^+. Edmonds et al. (2009) observed a pulse of porewater NH_4^+ when 10 ppt saltwater was added to a freshwater sediment, but the increase was transient, lasting only12 days following saltwater addition. Similarly, the reintroduction of seawater to a diked salt marsh in Cape Cod produced a 50-fold increase in porewater NH_4^+ within 1 month, but concentrations returned to baseline after 5 months (Portnoy and Giblin 1997). Concentrations of 10 ppt saltwater are believed to completely efflux all the exchangeable NH_4^+ from the sediment surface, replacing it primarily with Na^{2+} (Baldwin

et al. 2006; Weston et al. 2006a); salinities >10 ppt do not contribute to any additional NH_4^+ exchange (Rysgaard et al. 1999).

Nitrification, the transformation of NH_4^+ to NO_2/NO_3^-, appears to be stimulated by dilute salinity (10 ppt), but reduced by salinities >17 ppt in soils (Pathak and Rao 1998). The mechanism of this inhibition is not well understood, but it is thought to be a combination of osmotic stress and the inhibition of nitrifying bacteria enzymes by the abundant chloride (Cl^-) in saltwater (Seo et al. 2008; Gennari et al. 2007). The inhibition of nitrification by Cl^- has been demonstrated in agricultural soils treated with Cl^- containing fertilizers (Roseberg et al. 1986), but has not received any attention in the coastal wetland literature.

Denitrification ($NO_3^- \rightarrow N_2/N_2O$) is more consistently suppressed by increased soil salinities (Wu et al. 2008). Coastal wetland studies indicate that denitrification potential is 2-3 times greater in freshwater and brackish marshes, compared to salt marshes (Craft 2007) with the highest variability in denitrification rates occurring in salt marshes (Nielsen et al. 2003). Similar to nitrification, chloride toxicity has also been suggested as possible a cause of reduced denitrification in coastal wetlands (Seo et al. 2008). Interestingly, denitrifiers may have the capacity to adapt to high Cl^- concentrations. In inland watersheds, denitrification enzyme activity is only reduced by Cl^- if the system is not already acclimated to low-levels of Cl^- exposure (Hale and Groffman 2006).

The overall impact of salinity on the N cycle appears to be driven by both abiotic (the release of NH_4^+ from the soil surface) and biotic (the suppression of nitrification and denitrification) processes. In general, we can expect SLR to cause a short-term pulse of NH_4^+, which will likely accumulate in the soil since nitrifying and denitrifying bacteria

are physiologically reduced by salinity. According to current knowledge, the availability of NO_3^- as an electron acceptor is likely to decrease as a result of SLR, but additional work on the applicability of Cl^- toxicity to coastal systems and the mechanism for Cl^- inhibition is greatly needed.

Iron and Manganese

Iron and manganese reduction occurs at redox potentials between -100 and 300 mV. While manganese is usually found at low concentration in soils, Fe is the fourth most abundant element on earth, comprising ~4% (by weight) of the average soil (Reddy and DeLaune 2008). Ferric iron (Fe^{3+}) can be a significant source of electrons during C metabolism in certain anaerobic soils (Lovley and Phillips 1986). Along a coastal wetland salinity gradient, iron availability is tightly coupled with S and P cycling. In freshwater, Fe is commonly associated with dissolved organic C (Paludan and Morris 1999), metal complexes (Reddy and DeLaune 2008), and inorganic P (Harris 1999). In fact, Fe has such a high affinity for P that it causes the latter to be immobilized, making P the major limiting nutrient in most freshwater systems (Blomqvist et al. 2004). Increasing salinity overwhelms the soil with sulfide (S^{2-}) produced during sulfate reduction, triggering the release of P and allowing Fe to precipitate with S^{2-} to form pyrite and other minerals (Blomqvist et al. 2004). The precipitation of S with Fe is critical to maintaining low porewater sulfide, a known stressor to wetland plant productivity (King et al. 1982).

Iron is unique from the other electron acceptors because it reacts abiotically over half of the time in many wetland soils, and thus does not always function in C cycling (Neubauer et al. 2005; Kostka et al. 2002). Nevertheless, the biogeochemical reduction of iron can be high in TFMs, especially during peak biomass production when the soils

have lower electron pressure (Neubauer et al. 2005). Freshwater sediments with an abundance of iron oxides occluded to the soil surface may experience a rapid release of Fe when saltwater is introduced. A laboratory study showed a spike in soluble Fe^{2+} (+148%) following seawater addition to a freshwater soil (Weston et al. 2006a). In brackish marshes, Fe has limited availability, making sulfate reduction the dominant form of anaerobic respiration (Neubauer et al. 2005). Generally, the role of Fe^{3+} as an electron acceptor during C cycling is expected to decrease with SLR due to the precipitation of Fe with S and the reduction in terrestrial sediment inputs, which tend to be high in iron.

Sulfate

Sulfate concentrations in seawater are normally between 20 and 30 mM, as compared to concentrations of 0.1 to 0.2 mM observed in freshwater (Capone and Kiene 1988). The high concentration of SO_4^{-2} in seawater can 'buffer' the redox potential of a wetland to a level suitable for sulfate reduction, between -175 mV and -350 mV (Jakobsen et al. 1981). Salt marsh studies consistently indicate that sulfate reduction accounts for the majority of C mineralization (70% to 90%), and sometimes up to 100% of respiration in surface soils (0-5 cm; Kostka et al. 2002; Howarth 1984). The availability of SO_4^{2-} in the soil of coastal wetlands decreases with distance from the sea because it is rapidly reduced prior to diffusing into the soil profile. In salt marshes, SO_4^{2-} is abundant throughout the top 50 cm of the soil profile (~20 µg SO_4^{2-} cm^{-3}), while only trace amounts are observed in brackish and freshwater wetland soils (<1 µg SO_4^{2-} cm^{-3}; DeLaune et al. 1983). A laboratory study manipulating the abundance of SO_4^{2-} in a freshwater wetland soil indicated an acceleration of anaerobic soil respiration in direct proportion to the amount of SO_4^{2-} added (Chambers et al. 2011). Similar studies have

shown that the addition of 10 ppt seawater to freshwater sediments will cause sulfate reduction to replace methanogenesis as the dominate pathway of C mineralization in just 12 days, and can be responsible for up to 95% of C loss after 35 days (Weston et al. 2006b). It is clear that SLR will increase the availability of SO_4^{2-} and sulfate reduction will become the major pathway for C decomposition with increasing salinity.

Carbon Dioxide

Used as an electron acceptor by hydrogenotrophic methanogens, CO_2 can be an important component of C decomposition in highly reduced wetland soils. Methanogenesis still releases C into the atmosphere, but as methane (CH_4), a greenhouse gas with 25 times greater heat-trapping capacity than CO_2 over a 100 year time horizon (IPCC 2007) Methanogens are archea, can only respire specific monomer substrates, and have a lower energy yield than all other electron acceptors (Reddy and DeLaune 2008). Nonetheless, CH_4 production is considerable in soils and sediments with extreme electron pressure, indicated by a redox potential <-250 mV. The "last resort" nature of methanogenesis was illustrated in a bottle incubation where saturating concentrations of NO_3^- and SO_4^{2-} were added to a highly anaerobic soil. This quickly caused CH_4 production to decrease by 99% and 78-90%, respectively, in favor of denitrification and sulfate reduction (Dodla et al. 2009).

Initially, sulfate reduction and methanogenesis were believed to be mutually exclusive, and some studies suggested that SO_4^{2-} or S^{2-} exerted a direct toxic effect on methanogens (Zehnder et al. 1982). It is now understood that both sulfate reducing bacteria (SRB) and methanogens can be active simultaneously, but normally occur at different zones or soil depths. In freshwater lake sediments, SRB are most abundant at 0-2 cm soil depths (-100 to -150 mV), while methanogens dominate at 3-6 cm soil

depths (-250 to -300 mV; Cappenberg 1974). Sulfate reduction may become limited by the rate of SO_4^{2-} diffusion into the soil profile, causing CH_4 concentrations to increase with depth while SO_4^{2-} concentrations decrease with depth (Lee et al. 2008). In addition to soil depth, methanogens also have an advantage in salt marsh sediments with low flushing rates; CH_4 evolution of up to 8 µg CH_4 cm^{-3} have been reported in soils with minimal water exchange (King and Wiebe 1980).

The difference in energy yield between SO_4^{2-} and CO_2 is a major factor controlling the balance between SRB and methanogens (Jackobsen et al. 1981), but the nature and abundance of various substrates (electron donors) are also important. A substrate may be either non-competitive (utilized only by SRB or methanogens) or competitive (utilized by both SRB and methanogens). While the presence of H_2, a competitive substrate, will allow SRB to 'inhibit' methanogenesis by out-competing it with higher use efficiencies (Winfrey and Zeikus 1977), the existence of certain substrates will support methanogens and not SRB. For example, only methanogens are capable of using methanol and methylated amines as their electron donors. Conversely, H_2, acetate, and formate function as competitive substrates (Oremland and Polcin 1982; Oremland et al. 1982). It is also important to note that CH_4 can be produced without using CO_2 as an electron acceptor by acetoclastic methanogens (Wang et al. 1996). Some research suggests the prevalence of organic acids, especially acetate, can predict up to 92% of the variability in CH_4 emissions from wetlands (Christensen et al. 2003). In TFM soils, acetoclastic methanogens dominated over hydrogenotrophic methanogens, a relationship that was strongly depth-dependent, but remain unchanged with slight (5 ppt) increases in salinity (Weston et al. 2011).

Generally, the use of CO_2 as an electron acceptors is expected to decrease greatly due to salinity (sulfate) increases associated with SLR.

Microbial Community

Soil and shallow sediments contain an estimated 10^8 microbial cells per g of soil (Reddy and DeLaune 2008). The microbial community is mainly comprised of bacteria, but also includes fungi, archea, and eukaryotes. The soil microbial community is considered the 'key hole' of C biogeochemistry because it often represents the rate-limiting step in C cycling. Estimates of total ecosystem metabolism in salt marshes indicate 10-20% of all metabolism is from soil microbial activity (Miller et al. 2001), an impressive statistic considering the scale difference between bacteria and macrophtyes.

Organisms capable of survival in saline conditions occur in all major domains of life (bacteria, archea, and eukarya) and rely on two main strategies for osmoregulation—the accumulation of KCl in the cytoplasm, or the biosynthesis and/or accumulation of compatible solutes (Oren 2008). The accumulation of salts requires significant cellular adaptation, therefore, the accumulation of organic osmotic solutes is more common (Welsh 2000). All soil microbes require the appropriate C substrates and electron acceptors in order to respire and decompose C, but the identity, diversity, and activity of the microbes ultimately determines the rate of C cycling. The impact of inundation on the soil microbial community is fairly straight-forward: as water level increases, the population shifts toward anaerobes, favoring bacteria over fungi, as discussed below. However, the response to salinity, tidal cycle, and the complex interactions between microbes and other biogeochemical factors affected by SLR requires more in-depth attention.

Soil Bacteria

While the density and diversity of bacteria in freshwater and marine soils are comparable, the heterotrophic communities themselves are believed to be distinct (Capone and Kiene 1988). In the coastal Everglades (Florida), bacterial species diversity remained high (Shannon-Weiner index of 3.7 to 4.0) along a salinity gradient between 0 to 49 ppt, but the bacterial community structure diverged significantly. The divergence was based primarily on soil salinity, and secondarily on the availability of the limiting nutrient, phosphorus (Ikenaga et al. 2010). Conversely, a laboratory study found a significant increase in bacterial diversity (using RNA) when a Louisiana freshwater swamp soil was exposed to 3.5 ppt salinity (Jackson and Vallaire 2009). Locations where salinity fluctuations are more commonplace may maintain a larger diversity of bacterial species that can thrive under a broader suite of conditions. A study conducted in a Baltic bay found that estuarine bacterial communities were able to adapt faster to artificial salinity manipulations than riverine bacterial communities (Langenheder et al. 2003). Local and regional characteristics also have a strong influence on bacterial composition. In ten salt marshes between Maine and Florida, soil bacterial abundance increased with decreasing latitude, which also correlated strongly with soil organic matter content (Blum et al. 2004). Similar correlations between soil bacterial abundance and dissolved organic C have been observed in western salt marshes (USA; Cao et al. 2008).

Microbial biomass carbon (MBC) is a common index for estimating the size of the soil microbial community by measuring the amount of C contained within cell walls (Vance et al. 1987). Most studies concerning the effect of salinity on MBC have been conducted in agricultural or upland systems where saline soils are produced by the

evapoconcentration of salts. These studies have produced dramatically inconsistent results (Gennari et al. 2007; Yuan et al. 2007; Muhammad et al. 2006; Rasul et al. 2006; Pattnaik et al. 2000). Little additional insight is provided by the coastal wetland literature because no studies have measure *in-situ* MBC along a coastal salinity gradient. In the laboratory, freshwater wetland soils incubated with varying concentration of artificial seawater (3 to 35 ppt) did not produce any differences in MBC (Chambers et al. 2011). Similarly, a more in-depth look at microbial community structure (using DNA and RNA) following the exposure of freshwater river sediments to 10 ppt salinity revealed no difference in bacterial or archeal community composition after 5 weeks (Edmonds et al. 2009).

The metabolic quotient (qCO_2) is an index of the efficiency of the microbial community (Wong et al. 2008). High salinity typically causes microbial communities to have an elevated qCO_2 because stressful environments cause organisms to produce more CO_2 per individual (Saviozzi et al. 2011; Tripathi et al. 2006). However, some studies have found an inverse relationship between qCO_2 and salinity; this could be an artifact of shifting microbial populations (Chapter 4; Wong et al. 2008).

The limited data on coastal wetland soil bacterial communities appears to suggest that although metabolic pathways may shift following changes in salinity, the microbial communities themselves are highly adaptive to salt (Chambers et al. 2011; Edmonds et al. 2009) and SLR is not likely to cause a significant change in bacterial community size or diversity. However, additional *in-situ* studies of MBC, phospholipid fatty acid biomarkers, and genetic information in a variety of coastal areas is necessary to tease-out salinity effects from other environmental variables.

Fungal Decomposers

Historically, fungi were thought to play a minor role in decomposition in wetlands because nearly all are strict aerobes. However, a growing number of studies contradict this, showing significant fungal biomass and fungal respiration associated with decaying wetland plants, up to 70% in some wetlands (Hackney et al. 2000). High concentrations of lignocelluloses, long periods of 'standing-dead,' and low quality litter favors fungal decomposers, which have a lower N requirement (C:N of 10:1) than bacteria (C:N of 4:1; Sterner and Elser 2002). Given that salt marsh plants possess all the above mentioned characteristics, it follows that fungi must be critical to the decomposition process in salt marshes. However, published literature suggests that fungi are highly sensitive to salinity and are found in lower abundance in saline soils, compared to freshwater soils (Yuan et al. 2007; Rasul et al. 2006). This may be because high salinity can disrupt spore germination and sexual reproduction in fungi (Van Ryckegem and Verneken 2005). A significant shift in the fungi:bacteria ratio, from 9:1 to 1:4, was observed when a floodplain soil experienced only slight increases in electrical conductivity (EC; Sardinha et al. 2003). Similar to bacterial communities, fungal communities ordinate along salinity gradients, with some species adapted only to freshwater environments, some only to saltwater environments, and some distributed ubiquitously (Van Ryckegem and Verneken 2005). Fungal species are also somewhat plant specific, colonizing only one or more species of vegetation. In salt marshes, standing-dead *Spartina* species have some of the highest fungal diversity and density, with fungal cells exceeding bacterial cells 165:1 (Torzilli et al. 2006).

Inundation also drives fungal abundance and diversity. In salt marshes, even slight elevation changes between high marsh and low marsh areas yield considerable

differences in fungal abundance (Cordova-Kreylos et al. 2006). When the redox potential of a wetland soil was artificially manipulated in the laboratory, fungal activity exceeded bacterial activity in the aerobic range (Eh >+250 mV), while the reverse was true when Eh dropped below 0 mV (Seo and DeLaune 2010). Understanding the role of fungi in coastal wetland decomposition and its' sensitivity to salinity is necessary for predicting how the C balance of coastal systems will be impacted during SLR. Current literature suggests that a decrease in fungal decomposers is likely to result from both increased salinity and increased inundation in coastal wetlands.

Enzyme Activity

Soil enzymes consist of amino acids synthesized by bacteria and other cells to catalyze reactions. Enzymes are critical to C mineralization because they hydrolyze complex C-polymers (cellulose, proteins, lipids, lignin) to form monomers (sugars, amino acids, fatty acids) that bacteria can utilize for respiration (Reddy and DeLaune 2008). The rapidity with which enzymes respond to environmental conditions and the relative ease of quantifying their activity makes them ideal indicators of soil metabolic activity (Makoi and Ndakidemi 2008).

Several enzymes involved in the hydrolysis of C polymers (dehydrogenase, β-glucosidase, and cellulase) have been studied under different ionic conditions to determine the impact of osmotic stress on synthesis and activity. Dehydrogenase is an intercellular enzyme involved in basic metabolism and is commonly found in anaerobic microbes (Tripathi et al. 2007). Considered a strong indicator of overall soil biological activity, dehydrogenase activity increased exponentially when seawater concentrations increased from 0 to 30 ppt in a mangrove mesocosm (Wu et al. 2008; Frankenberger

and Dick 1983). This was directly contrary to the findings of Tripathi et al. (2007), who found a linear decrease in *in-situ* dehydrogenase activity when EC was raised from 0 to 30 mS cm^{-1} in a coastal rice paddy soil. An additional study investigating the effect of NaCl on dehydrogenase enzymes indicated a slight decrease in activity when EC was increased from 2 to 8 mS cm^{-1}, but the effect was transient and disappeared after 40 days of incubation (Saviozzi et al. 2011).

The enzyme responsible for glucose production, *β*-glucosidase, decreased slightly in response to the addition of 3.5 ppt artificial seawater to a freshwater wetland soil, though not significantly (Jackson and Vallaire 2009). In a Korean coastal bay, *in-situ β*-glucosidase activity decreased by 42% as salinity increased from 1 to 45 mS cm^{-1} (Siddikee et al. 2011). Cellulase is responsible for the depolymerization of cellulose and was suppressed in 5 species of fungi exposed to EC increases of 0 to 3 mS cm^{-1} (Malik et al. 1979).

The only study to test the impact of salinity on enzymes involved in N and P cycling (important nutrients in C biogeochemistry) was conducted by Jackson and Vallaire (2009). They found both phosphatase and NAGase enzyme activities decreased approximately 20% following the addition of 3.5 ppt seawater. Differences in enzyme activities may be due to osmotic stress, which is known to interfere with enzyme and membrane activities (Van Ryckegem and Verneken 2005). Changes in nutrient or C availability that accompany SLR may indirectly alter enzyme synthesis and activity (Baldwin et al. 2006). For the most part, enzyme activity appears to be negatively impacted by salinity, which would decrease the rate of microbial C cycling. Studies targeting the impact of seawater (rather than just EC) on enzymes and *in-situ*

measurements of enzymes along coastal wetland gradients would greatly improve our understanding of the relationship between SLR and soil enzymes.

Carbon Balance

Although a mechanistic understanding of how each regulator of C cycling is individually impacted by increased salinity and inundation is necessary, the overall purpose of this review is to provide insight on how the balance of C in coastal wetlands will be affected by SLR. In large part, the future of coastal wetlands as a global C sink depends on whether an area of wetland submerges, accretes vertically, or migrates landward in response to SLR. Basic environmental factors can be used to predict which trajectory a wetland ecosystem will take (Figure 2-3). In general, submergence will lead to the loss of existing C stores and the loss of the ability to sequester C in the future. Vertical accretion is expected to add to the C sink potential of a wetland because the size and distribution of wetland types remains unchanged, while additional organic and inorganic C is added to the system. Finally, the most difficult scenario for predicting future C balance is landward marsh migration. Models and observations note that when coastal wetlands migrate, some types (e.g., TFM, brackish, salt marshes) tend to lose area, while others gain area (Craft et al. 2009). It is during marsh migration that the mechanistic analysis of C cycling regulators presented in this review becomes most valuable. For example, if the proportion of brackish marsh to salt marsh increases, as predicted for part of Georgia (Craft et al. 2009), we could expect to see the following responses in the larger wetland ecosystem: (1) a slight increase in productivity, diversity, and quality of above ground biomass and OM, (2) an increase in the availability of Fe^{3+}, NO_3^-, and O_2 as electron acceptors (though SRB will likely still dominate respiration), and (3) greater fungal biomass and enzyme activity contributing

to decomposition. The magnitude of each of these responses will determine the effect on the overall C balance. The final section in this chapter provides a review of current research related to the rate of decomposition, greenhouse gas emissions, C export, accretion rates, and C storage capacity in coastal wetlands.

Decomposition

A growing number of studies have investigated the overall rate of decomposition (C loss through mineralization) along a coastal wetland salinity gradient, but results have been contradictory (Figure 2-5). The decomposition of *in-situ* litter material placed in mesh bags and distributed along a coastal salinity gradient resulted in the loss of 41-49% of the initial mass in a salt marsh, compared to 29-30% loss in a brackish marsh, and 30-36% loss in a TFM (Craft 2007). The difference in decomposition rate was well correlated with salinity and showed no relationship to litter quality (Craft 2007). These findings are in contrast to a similar study in a coastal wetland in Denmark using cotton strips. Cotton tensile strength loss was used as a proxy for the rate of cellulose decomposition and indicated a general decrease in decomposition rate as salinity increased (Mendelssohn et al. 1999). In this study, decomposition rate was not influenced by salinity, but was positively correlated with soil N and P. Salinity does not seem to impact the rate of decomposition during the initial leaching stage (first 3 days), but after 7 days, decay rates were significantly faster in freshwater sites in a litter bag study in a Portuguese estuary (Quintino et al. 2009). Two additional studies, one in arid streams (Reice and Herbst 1982) and one in transitional wetlands (Sangiorgio et al. 2008) corroborate the results of Mendelssohn et al. (1999) and Quintino et al. (2009), indicating decomposition rates are faster in freshwater than in saltwater systems. A definitive conclusion regarding how salinity impacts the amount and rate of C loss

through decomposition cannot be made with the existing literature, but it appears that inherent site characteristics (e.g., nutrient availability and litter quality) play a significant role.

Greenhouse Gas Emissions

Carbon dioxide is the end product of aerobic and anaerobic microbial respiration and is typically the major greenhouse gas emitted from all types coastal wetlands, representing 94-99% of all C emissions (Chapter 4). Even *in-situ* measurements from a TFM (which have the lowest salinity and, typically, the highest rates of methanogenesis) indicted only 6% of C loss through CH_4 flux (Neubauer et al. 2000). The rate of CO_2 production in wetland soils is a product of the size, activity, and metabolic efficiency of the microbial community (the topic of the previous section). Since microbial ecology studies can be time consuming, the rate of CO_2 and CH_4 flux is often used as a general proxy for their activity.

The majority of studies investigating CO_2 flux from natural systems of differing salinities have been conducted in upland soils exposed to evaporative salinity. Work by Gennari et al. (2007), Malik et al. (1979), Muhammad et al. (2006), and Pathak and Rao (1998) in arid and semi-arid agricultural soils all found significant declines in CO_2 flux with increasing salt and EC. This research suggests differential salt tolerances among microbes (Malik et al. 1979) and that increasing salinity is not necessarily fatal to the soil microbes, but just reduces metabolic efficiency (Gennari et al. 2007). Unfortunately, the applicability of these studies to coastal systems is limited. Seawater exposes microbes to not only increased EC and ionic stress, but also excess SO_4^{2-}. One study attempted to disentangle the 'ionic effect' from the 'sulfate effect' in the laboratory by incubating freshwater wetland soils with varying concentrations of artificial seawater or

salt (NaCl). Results indicated the ionic effect of NaCl on CO_2 flux was insignificant, while the SO_4^{2-} containing seawater cause a short-term (~2 weeks) acceleration in CO_2 flux in direct proportion to the amount of SO_4^{2-} added (Chambers et al. 2011). In a similar study, 10 ppt seawater added to a freshwater wetland soil doubled the rate of C mineralization and was attributed to increased sulfate reduction and nutrient availability (Weston et al. 2006b).

Two studies have looked at differences in soil respiration along the existing salinity gradient in Barataria Bay, Louisiana. Both found that the TFM had the highest rate of CO_2 emissions (618 g CO_2-C m^{-2} y^{-1}), followed by the salt marsh (418 g CO_2-C m^{-2} y^{-1}), and the brackish marsh (180 g CO_2-C m^{-2} y^{-1}; Nyman and DeLaune 1991; Smith et al. 1983). Differences in organic matter quality and hydrology were cited as important regulators of CO_2 flux in this system (Nyman and DeLaune 1991). There is a need for additional long-term studies of *in-situ* CO_2 production along coastal wetland salinity gradients and an investigation of this non-linear response of CO_2 flux to salinity.

It has long been recognized that CH_4 production is significantly higher in freshwater systems than saline systems (DeLaune et al. 1983; Whelan 1974). Measurements of methane emissions along a coastal wetland salinity gradient in Louisiana were 4.3, 73, and 160 g CH_4-C m^{-2} for saltwater, brackish, and freshwater marshes, respectively (DeLaune et al. 1983). Laboratory studies indicate a salinity of ~14 ppt is sufficient for near-complete suppression of CH_4 emissions (Chambers et al. 2011). In some cases, low salinities (5 ppt) may actually stimulate CH_4 production in TFM soils (Weston et al. 2011). Field studies indicate the relationship between salinity and CH_4 production is complicated by heterogeneity in soil, vegetation, sulfate

availability, and methane oxidation (King and Wiebe 1980). High rates of CH_4 emissions (1.0 to 6.7 x 10^3 kg y^{-1}) have been documented in some fully saline estuarine and mangrove wetlands (Purvaja and Ramesh 2001).

A recent meta-analysis of *in-situ* CH_4 flux rates from numerous coastal marshes revealed significantly lower CH_4 flux rates in marshes with salinities >18 ppt (1.1 ± 2 g m^{-2} y^{-1}), and generally lower rates with salinities of 5-18 ppt (16.4 ± 11 g m^{-2} y^{-1}), compared to freshwater (<0.5 ppt) marshes (41.9 ± 76 g m^{-2} y^{-1}). However, oligohaline (0.5 to 5 ppt) marshes had the highest emission rates (150 ± 221 g m^{-2} y^{-1}; Poffenbarger et al. 2011). This log-linear relationship between salinity and CH_4 flux has been observed in 2 separate studies (Poffenbarger et al. 2011; Bartlett et al. 1987), but the reasons for it remain unclear.

In sum, although our understanding of how inundation and salinity impact CO_2 and CH_4 emissions is growing, there is still a great deal of uncertainty. Specifically, there is evidence of a dip in CO_2 flux and increase in CH_4 flux in brackish wetlands. How wide-spread this phenomenon is, and what factors are contributing to it, remains unknown.

Carbon Export

Of the coastal wetland C that is not mineralized by microbes, some portion is exported. The greater the tidal range, the greater the proportion of C exported from the wetland to the marine food web (Twilley et al. 1992). Mangroves are thought to lose more litterfall to tidal export (10 to 50%) than TFMs, which are estimated to lose only 5-10%, mainly to leaching (Neubauer et al. 2000). One study estimated that only 1 to 5% of autochthonous C actually remains in a salt marsh, and the remaining 95-99% is

exported to the ocean (Middelburg et al. 1997). In general, C export decreases with distance from the coast and tidal amplitude.

Carbon Accretion and Storage

A significant amount of both organic and inorganic C is stored long-term in coastal wetland soils. It is estimated that globally, mangroves and salt marshes store 44.6 Tg C y^{-1} (Chmura et al. 2003). In North America alone, estuarine wetlands store 10.2 Tg C y^{-1}, approximately ~31% of the total wetland C accumulated annually (Bridgham et al. 2006). A recent review of the potential C sequestration capacity of global "blue carbon" ecosystems estimated salt marshes and mangroves bury 218 ± 24 and 226 ± 39 g C km^{-2} y^{-1}, respectively (McLeod et al. 2011).

Annual C sequestration can be calculated as the vertical accretion rate, multiplied by the soil bulk density and soil C content (Armentano and Menges 1986). Generally, soil accretion rates are greatest in wetlands in warm climates with high moisture and nutrient availability to fuel primary production (Armentano and Menges 1986). Vertical accretion is one way wetlands can cope with SLR and is likely to increases the overall C sequestration rate (Figure 2-3). Vertical accretion rates, however, do not directly mimic SLR rates. There is a lag period between the onset of increased inundation and the establishment of a new elevation equilibrium. In a step-wise sea level increase, marshes can lose 10+ cm of elevation before they equilibrate; sometimes requiring several decades to reach equilibrium, depending on the sediment supply (Kirwan and Temmerman 2009). Under continuous SLR, the marsh platform is always moving toward equilibrium, but never quite reaches it (Fagherazzi et al. 2012).

Coastal wetlands located in regions with larger tidal amplitudes are expected to be more resilient to SLR because of the constant influx of nutrient and sediment-rich

tidal water (Nicholls et al. 1999). The high rate of sediment deposition and higher than average allocation of C to belowground biomass by salt marsh plants can significantly enhance salt marsh accretion rates (Chmura et al. 2003). A review of coastal wetland accretion rates across the globe ranged from 0 to 43 mm y^{-1} (DeLaune and White 2011). Sediment accumulation has high spatial variability (due to differences in vegetation density and distance from tidal creeks) and temporal variability (based on storm frequency and sea level variations). The temporal variability was exemplified in a study of sedimentation rates in a New England salt marsh where over a 3 year period rates ranged from <5 mm y^{-1} to 24 mm y^{-1}, depending on local storm activity (Roman et al. 1997).

Accretion rates and C accumulation rates are generally thought to decrease from TFMs to salt marshes, possibly due to higher organic matter export in saline wetlands (Craft 2007). A review of data on soil accretion rates in TFM along the US Atlantic and Gulf coasts found a range of 0.11 to 2.19 cm y^{-1} (Neubauer 2008). In mangroves, accretion rates differ according to geomorphology. Twilley et al. (1992) estimated that reef mangrove accretion is less than 1 mm y^{-1}, while basin mangroves and riverine mangrove communities accrete 1-2 mm y^{-1} and >2 mm y^{-1}, respectively. Spatial variability of accretion rates are also observed in salt marshes, especially between low marsh areas (117 g C m^{-2} y^{-1}) and high marsh areas (65 g C m^{-2} y^{-1}; Choi and Wang 2004).

It is clear that there are a great many site-specific, spatial, and temporal factors to consider when estimating C accumulation in coastal wetlands. Despite the patterns described above, a study along a coastal salinity gradient in Louisiana revealed no

significant difference in annual C accumulation between TFM, brackish, and salt marsh sites, with rates ranging from 183 to 296 g C m^{-2} y^{-1} (Smith et al. 1983).

Summary and Research Gaps

Coastal wetlands represent a significant reservoir of global C, sequestering an estimated 210 g CO_2 m^{-2} yr^{-1}, an order of magnitude greater than peatlands, while also providing such important ecosystem services as nutrient cycling, erosion control, storm abatement, and wildlife habitat (Choi and Wang 2004; Chmura et al. 2003). With global sea level rising at a rate of ~3 mm y^{-1}, the fate of intertidal wetlands depends upon their ability to accrete vertically or migrate laterally. If neither of these options is achievable, the wetland will submerge. Close to 5,000 km^{-2} of coastal marsh in Louisiana has converted to open water since 1930 and predictions for global coastal wetland loss due to SLR range from 22 to 30% by 2100 (DeLaune and White 2011; IPCC 2007; Nicholls et al. 1999). Our ability to understand the fate of the large quantity of soil organic C stored in coastal wetlands hinges upon our knowledge of how biogeochemical C cycling will be impacted by seawater encroachment into previously fresh, intermediate, and brackish marshes.

Saltwater intrusion produces a few predictable changes to the physical wetland environment, such as increased mineral sediment deposition, increased soil bulk density, a shift to less diverse salt-tolerant vegetation, and a widening and incising of tidal channels. Chemically, the electrical conductivity will increase, causing many of the cations previously held to the soil exchange complex, such as NH_4^+ and Fe^{3+}, to be released into solution. Phosphorus availability increases as Fe precipitates with the plentiful S^{2-}, possibly causing the limiting nutrient to shift from P to N. But the principal chemical change brought about by seawater is an increase in the abundance of SO_4^{2-},

which decreases the electron pressure and causes sulfate-reducing bacteria to proliferate at the expense of methanogens and fermenting bacteria. There is also evidence that increasing salinity can cause saprophytic fungi populations to decline, decreasing the ability to breakdown recalcitrant C compounds.

Soil microbes appear to be very resilient to ionic stress, with community composition shifting quickly toward more salt tolerant species without a detectable decrease in overall community size. Available data suggest that after the initial stress response passes and soil microbes adapt to a higher salinity regime, they produce less CO_2, synthesize fewer enzymes, and decompose organic matter at a slower rate. However, the slower rate of microbial C cycling in saline wetlands does not necessarily translate into greater C storage under SLR. On the contrary, saline wetlands assimilate less C than freshwater wetlands to begin with, have a higher rate of C export, and are the most vulnerable to submergence.

This review illuminates many aspects of the biogeochemical response of C cycling to SLR that need additional research. A more detailed study of soil bacterial abundance, microbial biomass C, and enzyme activity along existing salinity gradients is needed to sort-out the current contradictions in the literature. Also, the idea that nitrifiers and denitrifiers experience physiological stress in saline conditions, thus reducing the rate of N cycling, needs to be validated with field data, and the physiological mechanism needs to be discerned. Finally, much of the current literature suggests an underlying question—how important is the time scale to this discussion? Several of the chemical and biological responses discussed herein are the result of short-term studies involving laboratory manipulations, such as the impact of increasing

salinity on a freshwater wetland soil. The results of these studies can be dramatic: a 50-fold increase in porewater NH_4^+ within 1 month of saltwater re-introduction (Portnoy and Giblin 1997); a tripling of soluble Fe^{2+} following a 10 ppt seawater addition to a freshwater soil (Weston et al. 2006b); and a 20% increase in microbial respiration with 3.5 ppt seawater (Chambers et al. 2011). But we do not know how persistent these responses are in nature. Will they lessen as a system becomes adapted to a new salinity regime? In tidal freshwater marshes specifically, where abundant high-quality organic C tends to accumulate due to a dearth of alternative electron acceptors, what percent of that labile C will be mineralized once an influx of SO_4^{2-} occurs, and will the mineralization rate slow once a new equilibrium is established? While there have been recent many advances recently in our understanding of the ecomorphological processes that led to wetland submergence at the saltwater end (Fagherazzi et al. 2012), the biogeochemical controls on C balance during the processes of marsh migration and vertical accretion are critical to enhancing our ability to model and predict how SLR will impact the C storage capacity of coastal wetlands.

Table 2-1. Aboveground biomass estimates for coastal wetlands. Aboveground biomass data from published literature according to salinity regime (fresh (<0.5 ppt), brackish (5-15 ppt), and salt (>15 ppt).

Salinity	Dominant Plant Species	Location	Biomass ($g\ m^{-2}\ y^{-1}$)	Reference
Fresh	*Peltandra virginica*	Virginia, USA	626 ± 127	Neubauer et al., 2000
Fresh	*Zizaniopsis miliacea*	Georgia, USA	1400 ± 200	Craft et al., 2008
Fresh	*Zizaniopsis miliacea, Spartina cynosuroides*	Georgia, USA	1424 ± 91	Wieski et al., 2010
Brackish	*Juncus roemerianus*	Georgia, USA	1712 ± 112	Craft et al., 2008
Brackish	*Juncus roemerianus*	North Carolina, USA	812 ± 145	Christian et. al., 1990
Brackish	*Juncus roemerianus, Spartina alterniflora*	Georgia, USA	1715 ± 95	Wieski et al., 2010
Brackish	*Spartina densifolia* (High marsh)	Argentina	2599 ± 705	Gonzalez Trilla et al., 2010
Brackish	*Spartina densifolia* (Low marsh)	Argentina	1392 ± 790	Gonzalez Trilla et al., 2010
Brackish	*Spartina patens, Schoenoplectus americanus*	Maryland, USA	418 ± 44	Langley et al., 2009
Salt	*Spartina alterniflora*	Georgia, USA	996 ± 152	Craft et al., 2008
Salt	*Spartina alterniflora*	South Carolina, USA	780 ± 50	Morris et al., 2002
Salt	*Spartina alterniflora*	Georgia, USA	994 ± 93	Wieski et al., 2010
Salt	*Spartina alterniflora*	Louisiana, USA	1821	Darby and Turner, 2008
Salt	*Spartina alterniflora* (Short)	Delaware, USA	785 ± 251	Roman and Daiber, 1984
Salt	*Spartina alterniflora* (Tall)	Delaware, USA	1487 ± 74	Roman and Daiber, 1984
Salt	*Spartina anglica*	Netherlands	1435	Middelburg et al., 1997
Salt	*Spartina patens*	Delaware, USA	1118 ± 351	Roman and Daiber, 1984

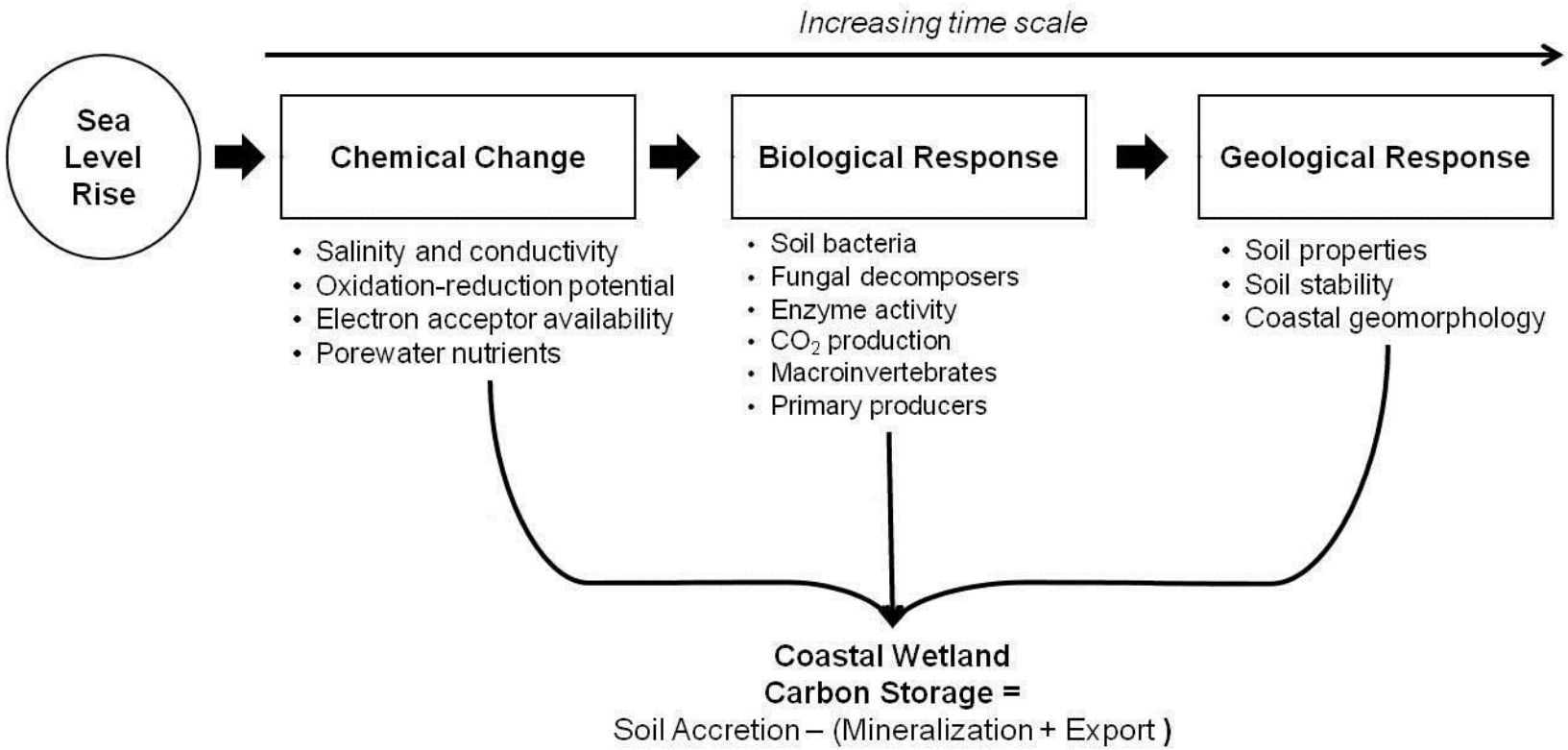

Figure 2-1. Sea level rise affects on coastal ecosystems over time. A conceptual flow chart of how sea level rise successively impacts the chemical, biological, and geological environment of a coastal wetland. The cumulative result is a potential change in the capacity of the soil to store soil organic carbon, a vital ecosystem service.

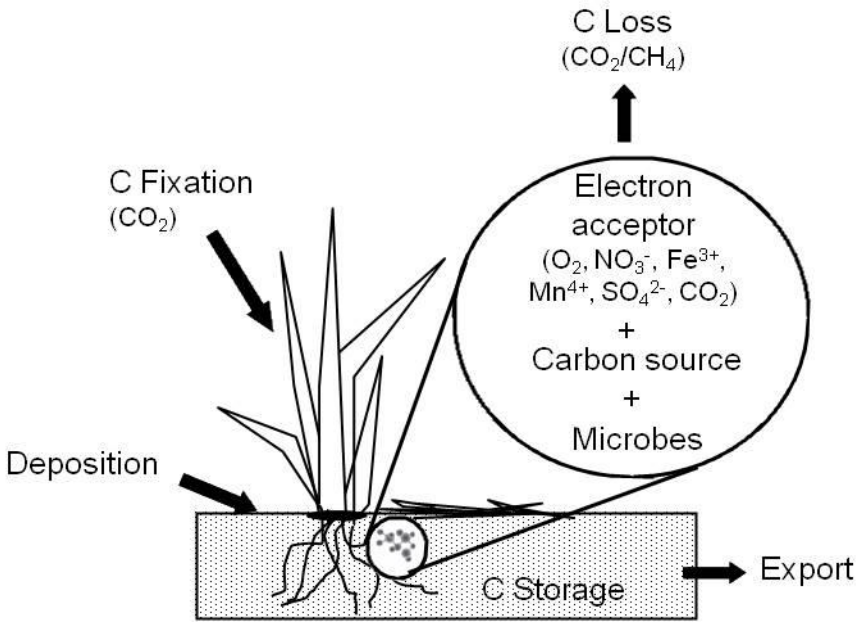

Figure 2-2. The generalized carbon cycle in coastal wetlands. Soil microbes play a key role in regulating how much carbon is sequestered in the soils, versus how much carbon is mineralized and released to the atmosphere as CO_2 or CH_4.

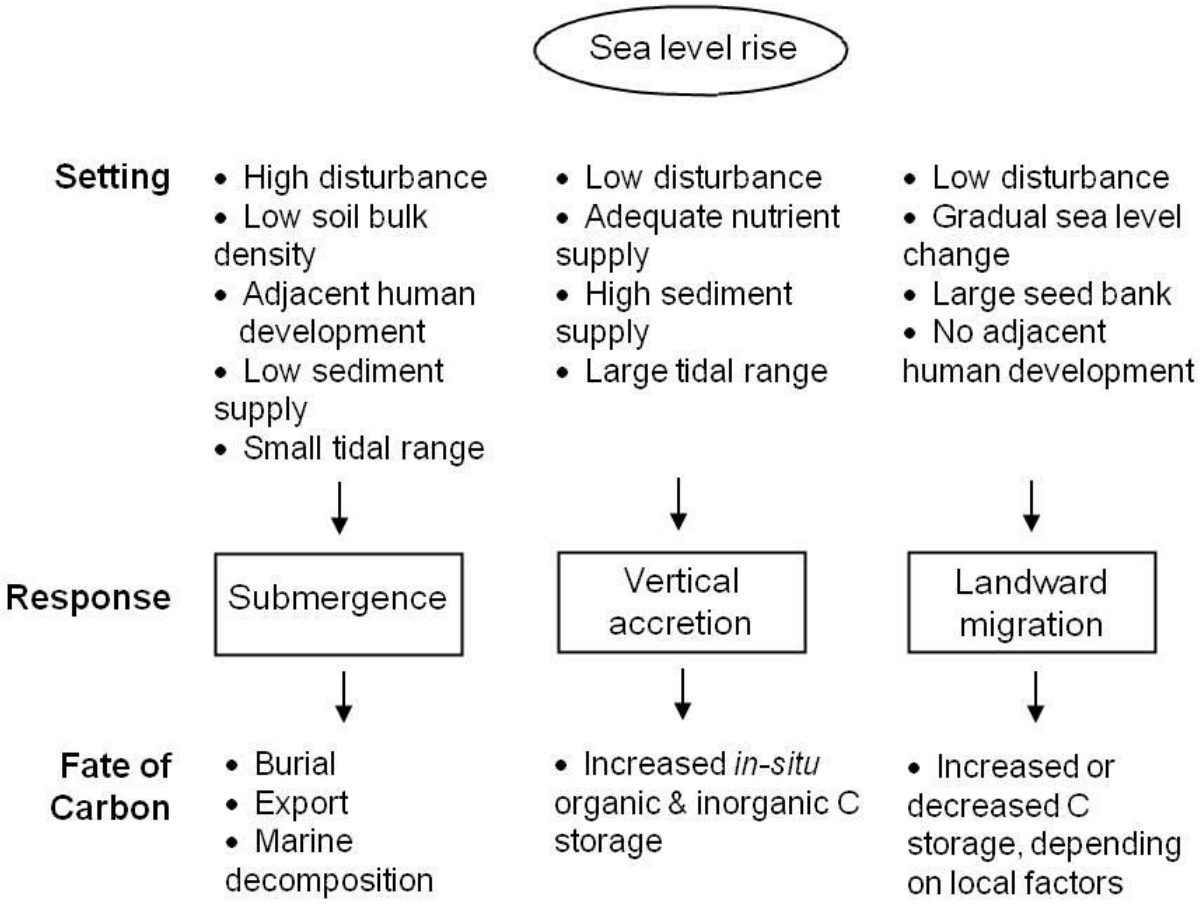

Figure 2-3. Coastal wetland responses to sea level rise. The three general responses of coastal wetlands to sea level rise, the physical setting that often leads to the response, and the fate of carbon under each scenario.

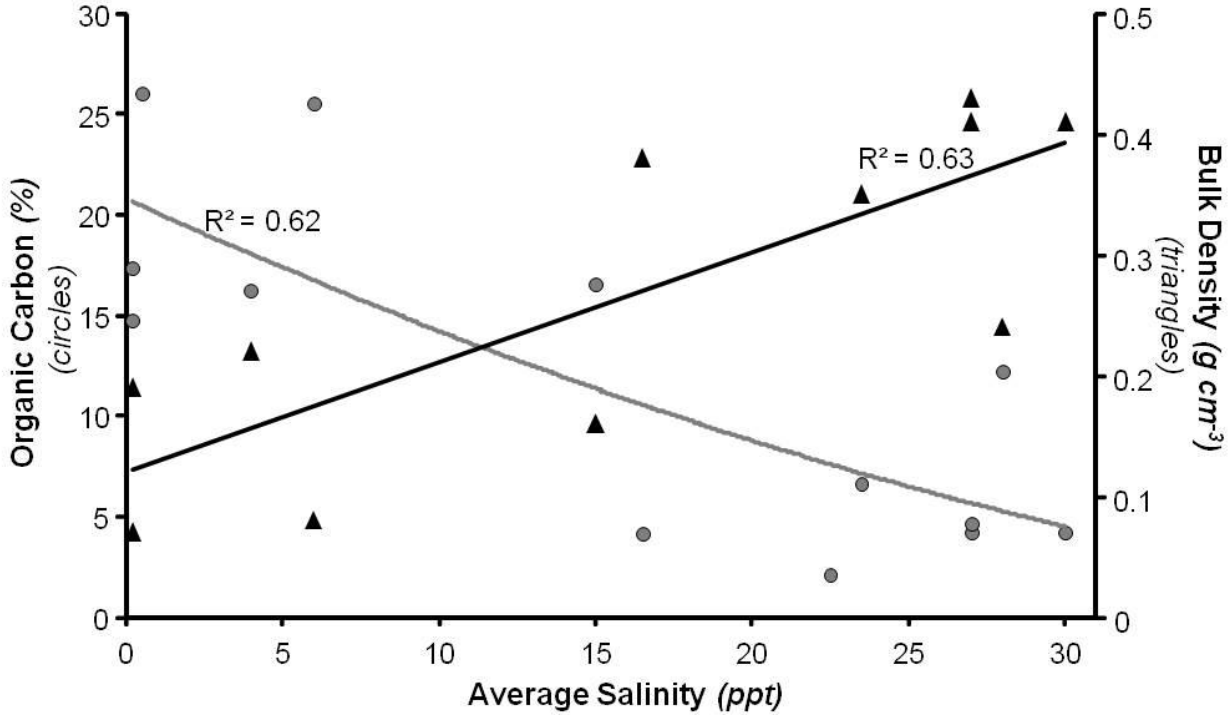

Figure 2-4. Soil carbon and bulk density as a function of salinity. Soil organic C content is represented by circles (left y-axis) and soil bulk density is represented by triangles (right y-axis). R-squared values represent the best-fit regression for each parameter. Data compiled from Neubauer (2008); Craft (2007); and Nyman et al. (1990).

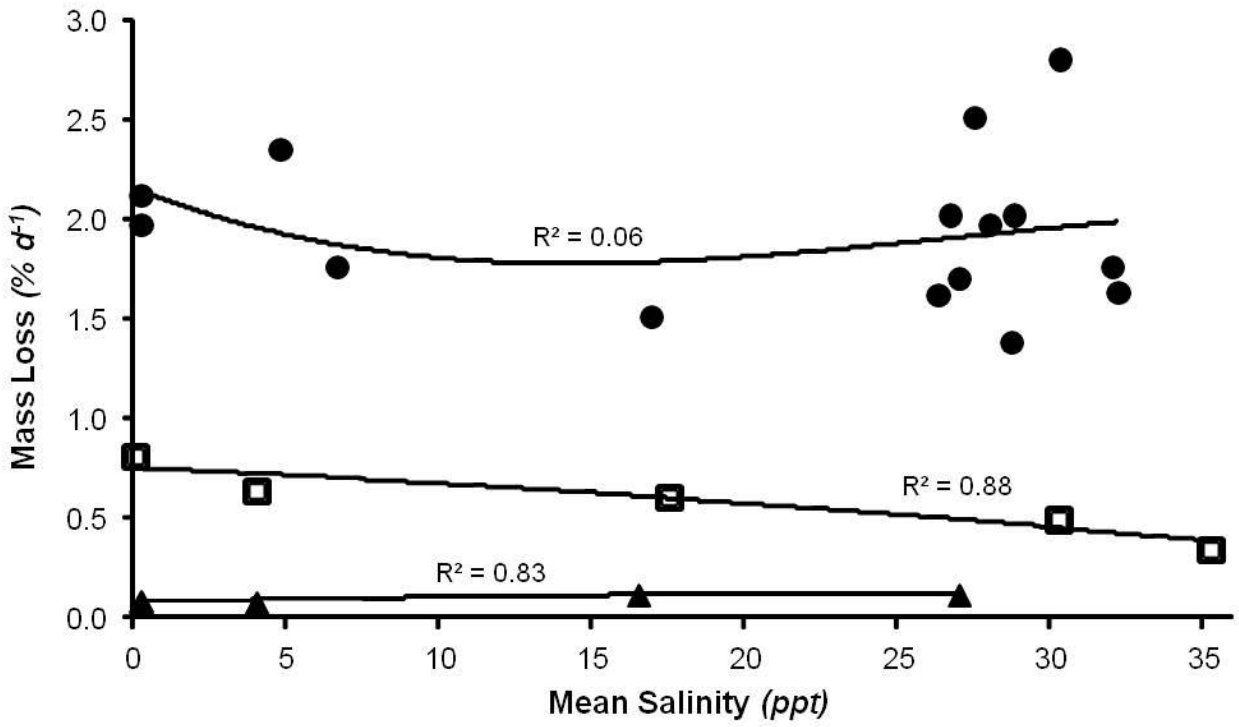

Figure 2-5. Decomposition as a function of salinity. Data represent the relationship between average water salinity (ppt) and decomposition rate, as determined using mesh litter bags placed on the soil surface. R-squared values represent best-fit regression from each study. Filled triangles (▲) represent data from Craft (2007), open squares (☐) are from Quintino et al. (2009), and filled circles (●) are from Sangiorgio et al. (2008).

CHAPTER 3
SHORT-TERM RESPNSE OF CARBON CYCLING TO SALINITY PULSES IN A FRESHWATER WETLAND

Background

The soil microbial pool is responsible for many ecosystem processes, including the transfer of C from the organic pool (e.g., biomass) to the inorganic pool (e.g., CO_2 and CH_4; Wetzel 2001). The rate at which microbes mineralize C is especially important in wetlands, where the high level of primary productivity means changes in the C source/sink potential of wetlands could have implications for the global C cycle. Salinity is a prevalent environmental stressor with the potential to alter the rate of C cycling in wetlands (Sangiorgio et al. 2008; Wong et al. 2008; Pattnaik et al. 2000). The impact of soil salinity in arid and semi-arid regions on crop productivity and nutrient cycling has been studied extensively. Findings indicate that high salt concentrations in upland and paddy soils can decrease the size of the soil microbial community (Muhammad et al. 2006; Pattnaik et al. 2000), decrease the rate of microbial respiration (Gennari et al. 2007; Muhammad et al. 2006; Pathak and Rao 1998), and decrease the rate of methanogenesis (Pattnaik et al. 2000). Such an overall decrease in the rate of C cycling in these systems is often attributed to osmotic/ionic stress inflicted on the microbial population by increased conductivity in the soil-water environment (Frankenberger and Bingham 1982; Gennari et al. 2007).

Rising sea level and increasing frequency of saltwater intrusion events also cause stress to microbial populations in freshwater wetlands near the coast. It is estimated that during the 20th century, sea level rose ~1.7 mm yr^{-1}. Since 1993, this rate has increased to 2.8 to 3.1 ± 0.7 mm yr^{-1} (IPPC 2007). Increasing sea level will amplify the impacts of storm surges and increase the area inundated by extreme tidal

events (Michener et al. 1997). In contrast to saline conditions caused by high evaporation rates in arid and semi-arid inland soils, seawater contains a relatively uniform mixture of several salts, macro, and micro-nutrients (Kester 1967). Of particular importance to wetland soils is the abundance of sulfate (SO_4^{2-}) in seawater, which can function as an alternative electron acceptor during anaerobic microbial respiration. Sulfate concentrations in seawater are normally between 20 and 30 mM, as compared to concentrations of 0.1 to 0.2 mM of SO_4^{2-} observed in freshwater (Capone and Kiene 1988).

Studies investigating the effect of seawater on C cycling have historically been performed along existing salinity gradients in estuaries and coastal zones, or using intact soil cores to measure long-term fluxes. In Louisiana coastal wetlands, microbial respiration rates are highest in freshwater wetlands, followed by salt marshes, and lowest in brackish wetlands (Nyman and DeLaune 1991; Smith et al. 1983). Methane production rates are significantly lower in salt marshes, compared to freshwater wetlands, because the abundant SO_4^{2-} is more energetically favorable for anaerobic respiration than methanogenesis (Magenheimer et al. 1996; Bartlett et al. 1987; King and Wiebe 1980). It has been found that within 12 days of 10 ppt seawater addition to a freshwater tidal marsh soil in Georgia, USA, the dominant microbial pathway switched from methanogenesis to sulfate reduction (Weston et al. 2006b). Despite the extensive knowledge regarding competition between methanogens and sulfate reducing bacteria, few studies have directly addressed the mechanistic process by which salinity exposure influences microbial mineralization pathways and rates. Specifically, no studies have attempt to distinguish between the importance of ionic stress (increased conductivity),

compared to the addition of the sulfate electron acceptor, in altering C mineralization rates following a saltwater pulse. This is important for evaluating the relevance of the trends observed for C cycling in agricultural saline soils (i.e., the documented decrease the size, activity, and composition of the microbial population) to coastal soils subjected to saltwater pulses.

This study sought to determine the process by which salinity affects C cycling in a freshwater wetland soil. Specifically, is the microbial community inhibited by ionic stress and/or the addition of sulfate, and what effect does this have on the overall rate of C cycling? This was done by comparing how microbial respiration, methanogenesis, and microbial population size respond to different concentrations of seawater (containing SO_4^{2-}) and salt (strictly NaCl) additions. I hypothesized that potential respiration rates would be reduced by additions of both seawater and NaCl due to increased ionic stress to the microbial community, but potential methanogenesis would be reduced to a much greater extent in the seawater treatments due to competition with sulfate reducers. I also anticipated a reduction in the size of the microbial population with increasing concentrations of both seawater and NaCl.

Methods

Experimental Design

A bulk field-composite peat soil sample (0-10 cm) was collected from St John's Marsh Conservation Area (27.91833 N, -80.77389 W), a freshwater wetland dominated by an even mix of *Typha spp*. and *Salix spp.* (Figure 3-1). Upon return to the lab, the soil was homogenized and approximately 15-g wet weight soil was added to 70-mL glass serum bottles. Seven treatment types were evaluated. They consisted of seawater at concentrations of 35 ppt, 14 ppt, and 3.5 ppt, NaCl at concentrations of 35

ppt, 14 ppt, and 3.5 ppt, and a de-ionized (DI) water treatment to serve as the freshwater control. The seawater and NaCl treatments functioned as discrete analogues of ionic stress (measured in ppt) while allowing for the isolation of the sulfate reduction effect on C mineralization. All treatments were prepared in triplicate. Fifteen-mL of randomly assigned treatment solution was added to each bottle to form a soil slurry.

Three concentrations of seawater treatments were made using Neomarine Reef Salt mix (Brightwell Aquatics, Elysburg, PA). Thirty-five grams of salt mix was diluted in 1 L of DI water to create 35 ppt seawater. The solution was purged with ambient air for several hours to establish the CO_2/HCO_3 equilibrium, and then pH and specific conductivity (mS cm^{-1}) were measured. The seawater solution was further diluted with DI water to 14 ppt and 3.5 ppt seawater treatments and pH and specific conductivity were again noted. The ionic content of the artificial seawater mimicked that of natural seawater without any additional nutrients or C. Sulfate was the only available electron acceptor in the seawater treatments.

Three levels of NaCl treatments were made by diluting 35-g crystalline NaCl in 1 L DI water. The solution was purged with ambient air for several hours to establish the CO_2/HCO_3 equilibrium, and then pH and specific conductivity were measured. The NaCl solution was further diluted with DI water to 14 ppt and 3.5 ppt NaCl treatments and pH and specific conductivity were noted.

Bottles were capped with butyl stoppers and aluminum crimp-caps, evacuated to -75 kpa, and flushed with O_2-free N_2 gas for 1 minute to create anaerobic conditions. Incubation bottles were then placed in the dark on a circulating shaker at 30°C.

Headspace was extracted and measured on a gas chromatograph (Shimadzu Scientific Instruments GC 8A, Columbia, MD) fitted with a TCD detector and FID detector to determine the concentrations of CO_2 and CH_4, respectively. Headspace samples were measured after 1, 2, 4, and 6 days to produce a rate of production per g soil, per day. All bottles were then purged with O_2-free N_2 gas for 1 minute to prevent CO_2 accumulation in the headspace, and the sampling cycle repeated again. The sampling and purging sequence was repeated for three weeks and the rates of potential CO_2-C and CH_4-C production were calculated over time.

Soil Properties

Bulk density was determined after oven drying a known volume of subsample at 70 °C until constant weight. Percent organic matter (% OM) was determined using the loss-on-ignition (LOI) method (Nelson and Sommers 1996). Three grams of triplicate ground, dried soils were placed in a muffle furnace at 550°C for 4 hours, cooled, and re-weighed. Percent weight LOI was calculated as the difference between the soil weight before and after ashing, multiplied by 100.

Soil pH and specific conductivity were measured on all samples after completion of the three-week incubation period. A 2:1 (water:soil) suspension was created and allowed to equilibrate for 30 min before measurement (Thomas 1996; US EPA 1983). pH was measured using an Accument Research pH meter AR50 (Fisher Scientific, Waltham, MA) and specific conductivity was measured on a Markson EC Meter model 1054.

Total extractable organic C (TOC), extractable organic C (OC), and microbial biomass C (MBC) were determined for all samples following the three-week incubation period using the fumigation-extraction method after Vance et al. (1987). TOC was

defined as the extractable organic carbon extracted from the fumigated samples and OC was defined as the extractable organic C extracted from of the non-fumigated samples. Microbial biomass C (MBC) was determined by subtracting the extractable C of the non-fumigate from the corresponding fumigate sample. Duplicate 5-g wet weight samples were prepared in 25 mL centrifuge tubes. One set was fumigated with chloroform for 24 h and the other set served as the non-fumigated control. Following the chloroform treatment, both fumigates and non-fumigates were extracted with 25 mL of 0.5 *M* K_2SO_4, agitated for 30 min on a circulating shaker, and centrifuged at 5000 rpm for 10 min. The supernatant was vacuum-filtered through a Whatman # 42 filter paper and stored at 4 °C until analyzed for total organic carbon (Shimadzu Scientific Instrument TOC 5050A, Columbia, MD). An extraction efficiency coefficient of k_{EC} = 0.37 was applied to all samples (Sparling et al. 1990).

Data Analysis

Statistical analysis was performed using SAS 9.1 software (SAS Institute Inc., Cary, NC). All data sets were first tested to determine if the assumptions of homogeneity and normality were met using the Levene's Test and Shapiro-Wilk Test, respectively. Where these assumptions were not met, the raw data was log transformed and further statistical analysis was conducted using the dataset that fulfilled the assumptions of homogeneity and normality. A two-way repeated measures ANOVA model ($\alpha = 0.05$) was used to determine the interaction between CO_2/CH_4 production, treatment, and time. Significance differences were identified using the Least Squares Means (LSM) post-hoc test. One-way ANOVA models ($\alpha = 0.05$) were also used to identify significant differences between pH, conductivity, sulfate concentration, NaCl concentration, extractable C indicators, and microbial biomass. Pearson's Product

correlations were performed to determine if correlations exist between CO_2/CH_4 production and sulfate concentration, NaCl concentration, pH, conductivity, extractable C indicators, and microbial population indicators.

Results

Soil Properties

The soil consisted of a flocculant peat and had a bulk density of 0.097 ± 0.01 g cm^{-3}, and an organic matter content of 55 ± 0.6%. Initial soil pH was 6.82 ± 0.02; at the conclusion of the experiment, soil pH was highest for the 35 ppt seawater treatment (7.15 ± 0.03) and lowest for the 35 ppt NaCl treatment (6.41 ± 0.04). The pH of the 3.5 ppt seawater, 3.5 ppt NaCl, and freshwater control treatments did not differ from the intial pH (Table 3-1). Specific conductivity ranged from 28.5 ± 0.4 mS cm^{-1} to below the detection limit (0.3 mS cm^{-1}), for the 35 ppt NaCl and the freshwater control, respectively (Table 3-1). Specific conductivity was significantly different for all treatments ($p < 0.01$) except the 3.5 ppt seawater and 3.5 ppt NaCl treatments. Sulfate and NaCl concentrations were significantly different between all treatments (Table 3-1).

Potential Microbial Respiration

The rate of potential CO_2 production was significantly higher in the 35 and 14 ppt seawater treatments, compared to the freshwater control and the NaCl treatments, during week 1 ($p < 0.01$), but did not differ significantly during weeks 2 and 3 (Figure 3-2). There were no significant differences in CO_2 production rate between the NaCl treatments throughout the entire study. Considering all the treatments, time was a significant factor for CO_2 production ($p < 0.001$), as well as the interaction between time and treatment ($p < 0.001$). Significantly greater rates of microbial respiration occurred during week 1 for all treatments, compared to weeks 2 and 3 (Figure 3-2). However,

the contribution of sulfate reduction to respiration decreased over time, as seen by the difference in CO_2 production between the seawater treatments and the freshwater control. During week 1, it can be estimated that 44% of anaerobic respiration was mediated by sulfate reduction, while sulfate reduction accounted for 21% and 15% of respiration during weeks 2 and 3, respectively.

The total amount of CO_2 produced over the three-week incubation period was significantly greater ($p < 0.01$) for all the seawater treatments, compared to the freshwater control (Figure 3-3). Total CO_2 production was 32% higher in the 35 ppt seawater treatment, compared to the freshwater control, 29% higher in the 14 ppt seawater treatment, and 20% higher in the 3.5 ppt seawater treatment. Total CO_2 produced by the NaCl treatments did not differ from the freshwater control (Figure 3-3).

The variables that correlated with CO_2 production differed between the seawater and NaCl treatments. Seawater respiration rates were positively correlated ($p < 0.01$) with indicators of extractable C (TOC and OC; Table 3-2). Respiration in NaCl treatments was positively correlated with pH and negatively correlated with conductivity and organic C ($p < 0.01$; Table 3-2).

Potential Methanogenesis

The rate of potential CH_4 production was significantly lower ($p < 0.001$) for the 35 ppt and 14 ppt seawater treatments, compared to the 3.5 ppt seawater and freshwater control for all three weeks (Figure 3-4). The 35 and 14 ppt NaCl treatments also had a significantly lower rate of CH_4 production during weeks 1 and 2, compared to the 3.5 ppt NaCl and freshwater control, but did not differ significantly during week 3 (Figure 3-4). Time was not a significant factor for CH_4 production rate.

The total amount of CH_4 produced over the three-week incubation period was significantly less for the 35 and 14 ppt seawater and NaCl treatments, compared to the freshwater control (Figure 3-5). Total methane production was 94% and 79% lower in the 35 and 14 ppt seawater treatments, respectively, compared to the freshwater control. Total methane production was reduced by 55% and 23% in the 35 and 14 ppt NaCl treatment, respectively, compared to the freshwater control (Figure 3-5). Neither the seawater nor NaCl 3.5 ppt treatments differed from the freshwater control in methane production.

In contrast to respiration, methane production in the seawater treatments was not correlated with indicators of extractable C, but did show a significant negative correlation with pH and conductivity (Table 3-2). NaCl treatments showed a significant positive correlation with pH and negative correlation with conductivity ($p < 0.01$; Table 3-2). The negative correlation between NaCl and organic C suggests methanogens were not C limited (Table 3-2).

Sulfate Versus NaCl

Sulfate (i.e., seawater treatments) and NaCl additions had significantly different effects on potential respiration, potential methanogenesis, and other variables of interest. Sulfate in high concentrations produced a short-term increase in microbial respiration (Figure 3-2). This relationship between sulfate and CO_2 was also observed as a significant positive correlation between these variables ($r = 0.64$; $p < 0.01$; Table 3-3-3). In contrast, methanogenesis decreased as sulfate concentration increased (Figure 3-4). A significant negative correlation existed between CH_4 and sulfate concentration ($r = -0.80$; $p < 0.01$; Table 3-3). Sulfate also showed a strong ($p < 0.01$) positive correlation with the ratio of CO_2:CH_4 production and pH (Table 3-3). The ratio

of CO_2:CH_4 was similar for all NaCl treatments, the 3.5 ppt seawater treatment, and the freshwater control (2.0 ± 0.5), but significantly higher for the 14 ppt seawater (11.2 ± 1.4) and 35 ppt seawater (43.3 ± 4.0).

The NaCl addition had no effect on potential respiration (Figure 3-2), nor was there a correlation between NaCl concentration and respiration (Table 3-3). The affect of the NaCl addition on methanogenesis was slightly greater than for respiration, with the 35 and 14 ppt NaCl treatments reducing CH_4 production for 2 weeks (Figure 3-4). Sodium chloride concentrations > 13 mg L^{-1} may negatively impact methanogenesis, but concentrations below this (as seen in the 3.5 ppt seawater and NaCl treatments) were not correlated with methanogenesis (Table 3-3). The main affect of NaCl was a significant increase in conductivity, total extractable organic C, extractable organic C, and pH (Tables 3-1 and 3-3)

Discussion

High concentrations of seawater (14 and 35 ppt) caused a significant increase in pH, while high concentrations of NaCl (14 and 35 ppt) decreased pH (Table 3-1). The increase in pH caused by seawater is likely a result of the high $CaCO_3$ content of the seawater mix and a product of sulfate reduction, while strictly NaCl additions may have displaced H^+ ions from the cation exchange complex and caused the pH to decrease. A similar displacement of ammonium ions from sediments by NaCl has been observed (Baldwin et al. 2006) and is further supported by the strong negative correlation between pH and NaCl concentration in this study (Table 3-3). While it is unlikely that this near-neutral range in pH between treatments (6.4 to 7.2) could cause microbial inhibition, it is an interesting side effect of salinization that could select for specific microbial species in the long-term. Specific conductivity significantly increased in all 14

and 35 ppt treatments (Table 3-1), but did not mirror the conductivity of the added solution due to a dilution effect by the soil pore water. Conductivity was most strongly correlated with NaCl concentration (Table 3-3).

Potential Microbial Respiration

In general, seawater additions had a stimulatory effect on potential CO_2 production rate (Figure 3-2) and the total amount of CO_2 produced was directly related to the concentration of seawater added (Figure 3-3). Over the three-week incubation, total CO_2 production was 32% higher in the 35 ppt seawater treatment, 29% higher in the 14 ppt seawater treatment, and 20% higher in the 3.5 ppt seawater treatment, as compared to the freshwater control. However, the stimulation of respiration rate was short-lived; all seawater treatments returned to a CO_2 production rate similar to the freshwater control by week 3 (Figure 3-2). The difference in the magnitude of the increase in CO_2 production by the seawater treatments can be attributed to the increased availability of sulfate to serve as a terminal electron acceptor in anaerobic microbial respiration. Using the theoretical relationship of 1 mole SO_4^{2-}:2 moles CO_2 (Equation 3-1) indicates only ~20% of the sulfate added was reduced. Therefore, sulfate depletion was also not responsible for the decline in activity over time in the seawater treatments.

$$C_6H_{12}O_6 + 3SO_4^{2-} + 6H^+ = 3H_2S + 6CO_2 + 6H_2O \quad (3\text{-}1)$$

All of the treatments produced significantly more CO_2 the first week, compared to weeks 2 and 3 (Figure 3-2). This could be a limitation of the experimental design. Since CO_2 measurements were taken from a closed system with a finite supply of bioavailable C, over time the substrate limitation surpassed the alternative electron acceptor availability in regulating the rate of microbial activity. The agitation of the soil

slurry may have exaggerated the initial pulse of available electron donors by releasing C compounds previously protected with soil aggregates. Regardless, since all incubations were composed of replicate soils substrate, the difference in response between treatments can be attributed to the concentration of sulfate electron acceptors. The positive correlation between CO_2 production and indicators of extractable C ($p < 0.05$) support the hypothesis of a C limitation. A significant decrease in C flux rate over time has also been observed in studies of intact soil cores, with the decline in CO_2 and CH_4 production attributed to progressive C limitation (Weston et al. 2011).

Previous work has indicated that the percent of microbial respiration mediated by sulfate reduction increases as total respiration increases (Howarth 1984). The present study also found a logarithmic increase in the percent of respiration attributed to sulfate reduction as respiration rate increased. When respiration rates were highest (week 1), 44% of respiration was mediated by sulfate reducers, and when respiration was low (week 3), only 15% of respiration was mediated by sulfate reducers. This is owed to the assumption that SO_4^{2-} is the only alternative electron acceptor present in seawater that is not present in the freshwater control or NaCl treatments, and the fact that the soils were maintained under anaerobic conditions from the time of collection to the conclusion of the study.

In contrast to seawater, the NaCl addition had no effect on CO_2 production (Figure 3-2). Since NaCl does not function as an electron carrier as sulfate does, we can conclude that ionic stress alone does not affect microbial community respiration. However, these findings do not address whether microbial community structure or diversity was altered by the NaCl addition. Baldwin et al. (2006) performed a detailed

analysis of microbial community structure using phospholipid fatty acid (PLFA) biomarkers and discovered that NaCl > 5 mS cm^{-1} decreased microbial diversity, but did not alter microbial biomass. No significant differences in microbial biomass C between NaCl treatments were identified in the present study either (Table 3-1). Our findings suggest the tolerance of anaerobic microbes to ionic stress may be higher than initially anticipated, and the microbial community may have the ability to adapt to increased ionic stress within the period of 1 week (Figure 3-2). The high species richness of freshwater sediments is believed to allow the community to switch biochemical pathways in a matter of days (Edmonds et al. 2009).

Potential Methanogenesis

Sulfate reduction is thermodynamically preferred over methanogenesis because of the higher net energy yield for obligate anaerobes (Capone and Kiene 1988). The higher concentrations of sulfate in seawater led to the hypothesis that methane production would be lower in seawater wetlands, as compared to freshwater wetlands. This has been confirmed by numerous studies (e.g., Abril and Iversen 2002; Purvaja and Ramesh 2001; Reeburgh and Heggie 1977). However, some research has found maximum methane emissions occur at intermediate salinities (Sotomayor et al. 1994; Bartlett et al. 1987) and may still be substantial in saltwater wetlands with high carbon inputs (Biswas et al. 2007; Purvaja and Ramesh 2001).

By comparing the repression of CH_4 in seawater and NaCl treatments, this study was able to differentiate between the effect of sulfate competition and ionic stress on methanogenic microbes. Low concentration (3.5 ppt) of seawater and NaCl did not affect methane production (Figure 3-4). Seawater additions of 14 ppt and above did significantly, and persistently, reduce methanogenesis (Figure 3-4). Other work has

proposed a salinity of $\geq$13 ppt is required to alter CH_4 flux (Bartlett et al. 1987). Total methane production in this study was 94% and 79% lower in the 35 ppt and 14 ppt seawater treatments, respectively, compared to the freshwater control. A strong negative correlation ($p < 0.01$) between sulfate concentration and CH_4 production (Table 3-3) suggests sulfate reduction replaced methanogenesis as the main form of anaerobic respiration. However, the increase in CO_2 cannot be directly calculated from the decrease in CH_4 because of the use of competitive and non-competitive substrates between the two groups of anaerobes (Capone and Kiene 1988). An inverse correlation between conductivity and CH_4 production has been found previously by Magenheimer et al. (1996).

NaCl decreased CH_4 production, but to a lesser extent than the seawater did (Figure 3-4). Overall, the 35 ppt NaCl reduced CH_4 production by 55% and 14 ppt NaCl reduced CH_4 production by 23%, relative to the freshwater control. This repression of methanogenesis by NaCl is slightly less than found by Baldwin et al. (2006) where at little as 1 mS cm^{-1} decreased CH_4 production by 30% over 1 month.

Although the soil slurry design used herein limits the interpretation of the CH_4 flux rates to an estimation of *potential* methanogenesis, it does provide evidence for a differential sensitivity of methanogens to salt. The fact that the decline in CH_4 production was not directly correlated with the increase in CO_2 production suggests heterotrophic methanogens, rather than autotrophic (CO_2/H_2 using) methanogens, dominate in this soil and were most strongly affected by salt additions. Other work suggests high concentrations of NaCl will inhibit acetoclastic (heterotrophic)

methanogens (Baldwin et al. 2006), which may have been driven the short-term decrease in CH_4 production in the 35 and 14 ppt NaCl treatments (Figure 3-4).

Summary

This study used laboratory soil slurry incubations to assess the short-term effects of NaCl and seawater on anaerobic C cycling in a freshwater wetland soil. These idealized conditions (lack of diffusion barriers, constant redox conditions, and the exclusion of alternative electron acceptors) allowed for the isolation of the two opposing biogeochemical forces that act on coastal wetland soils subjected to a pulse of seawater: ionic stress and sulfate-induced respiration. Findings indicate the *concentration* (ppt) of the seawater being introduced to the freshwater soil is the critical factor in determining the impact on soil C cycling. Oligohaline seawater (3.5 ppt) accelerates overall C mineralization through the combined production of CO_2-C and CH_4-C (Figure 3-6), thus enhancing the rate of organic C decomposition. This occurs as a result of the short-term acceleration of sulfate reduction without the inhibition of methanogenesis. The overall C mineralization rate was 17% higher in the 3.5 ppt seawater treatment than the freshwater control (Figure 3-6). Mesohaline and haline concentrations of seawater (14 and 35 ppt) also produced a short-term stimulation of anaerobic respiration, but the effect was off-set by a decrease in methanogenesis (Figure 3-6). Although the effects on the C cycle observed in this study were temporary (1-2 weeks), the increased frequency of storm surges and extreme tidal events in coastal wetlands that are expected to accompany sea level rise, makes these findings significant. Additionally, the fact that the microbial response was temporary indicates that dynamic changes and “pulses” of seawater may be more influential to the C cycle in coastal wetland soils than gradual sea level rise.

The change in the CO_2:CH_4 ratio following seawater intrusion may have significant implications for global warming. Assuming a CO_2-equivalent radiative forcing of 25 for CH_4 (IPPC 2007), mid-salinity wetlands (14 ppt) have a 72% lower global warming potential (GWP) than freshwater wetlands, and high-salinity wetlands (35 ppt) have 86% lower GWP than freshwater wetlands.

Coastal wetlands in the contiguous United States are estimated to sequester 10.2 Tg C y^{-1}; equivalent to 31% of the total C sequestered in all contiguous U.S. wetlands (Bridgham et al. 2006). With sea level rise occurring at ~3 mm y^{-1} (IPPC 2007), the gently-sloping coastal zone of the Atlantic Ocean and Gulf of Mexico, USA, are already experiencing seawater encroachment into previously fresh and low-salinity wetlands (e.g., Hussein 2009; Donnelly and Bertness 2001; Williams et al. 1999). The results of this study suggest the biochemical effects of seawater intrusion, especially pulsing events, on organic C mineralization in coastal wetlands may require a re-evaluation of the carbon balance of coastal wetlands in light of predicted sea level rise.

Table 3-1. Soil and water properties according to treatment condition. Mean ± standard deviation of soil pH and specific conductivity measured following destructive sampling after the 3 week incubation. Sulfate and NaCl concentration in each treatment per g dry soil. Different letters indicate significant differences at $p < 0.01$.

Treatment	pH	Conductivity *(mS cm^{-1})*	Sulfate *(mg g^{-1})*	NaCl *(mg g^{-1})*	MBC *(µg g^{-1})*
Seawater 35ppt	7.15 ± 0.03^{a}	25.0 ± 1.2^{a}	30.4 ± 3.9^{a}	120.4 ± 15.5^{a}	371 ± 53
Seawater 14ppt	6.9 ± 0.06^{b}	11.3 ± 0.4^{b}	12.2 ± 0.6^{b}	48.1 ± 2.4^{b}	533 ± 84
Seawater 3.5ppt	6.78 ± 0.05^{c}	2.4 ± 0.5^{c}	3.5 ± 0.3^{c}	13.0 ± 1.0^{c}	415 ± 118
NaCl 35ppt	6.41 ± 0.04^{d}	28.5 ± 0.4^{d}	BD^{d}	421.7 ± 9.4^{d}	447 ± 97
NaCl 14ppt	6.54 ± 0.01^{e}	13.0 ± 0.5^{e}	BD^{d}	165.8 ± 14.2^{e}	596 ± 171
NaCl 3.5ppt	6.72 ± 0.01^{c}	3.64 ± 0.1^{c}	BD^{d}	4.2 ± 0.3^{f}	498 ±138
Freshwater Control	6.82 ± 0.01^{c}	BD^{f}	BD^{d}	BD^{f}	467 ± 32

BD = Below Detection; MBC = Microbial Biomass Carbon

Table 3-2. Correlations between soil parameters and C loss. Pearson's product correlation coefficients (r values). For all values, n = 9; df = 7; at r = 0.67, p = 0.05 (*); at r = 0.80, p = 0.01 (**); at r < 0.67, NS = Not Significant.

Soil Parameter	Treatment	CO_2 Production	CH_4 Production
pH	Seawater	NS	-0.75*
	NaCl	0.84**	0.94**
Conductivity	Seawater	NS	-0.81**
	NaCl	-0.90**	-0.96**
Total organic C	Seawater	0.76*	NS
	NaCl	NS	-0.72*
Organic C	Seawater	0.85**	NS
	NaCl	-0.82**	-0.93**
Microbial biomass C	Seawater	NS	NS
	NaCl	NS	NS

Table 3-3. Correlations between soil and water parameters. Pearson's product correlation coefficients (r values). For all values, n = 21; df = 19; at r = 0.44 p = 0.05 (*); at r = 0.55, p = 0.01 (**); at r < 0.44, NS = Not Significant.

Parameter	Sulfate *mg g^{-1}*	NaCl *mg g^{-1}*	Conductivity *mS cm^{-1}*	pH
CO_2	0.64**	NS	NS	0.71**
CH_4	-0.80**	NS	-0.61**	NS
CO_2:CH_4	0.97**	NS	0.54*	0.76**
Conductivity	0.48*	0.83**	-	NS
pH	0.82**	-0.59**	NS	-
Total organic C	NS	0.69**	0.54*	NS
Organic C	NS	0.84**	0.82**	NS

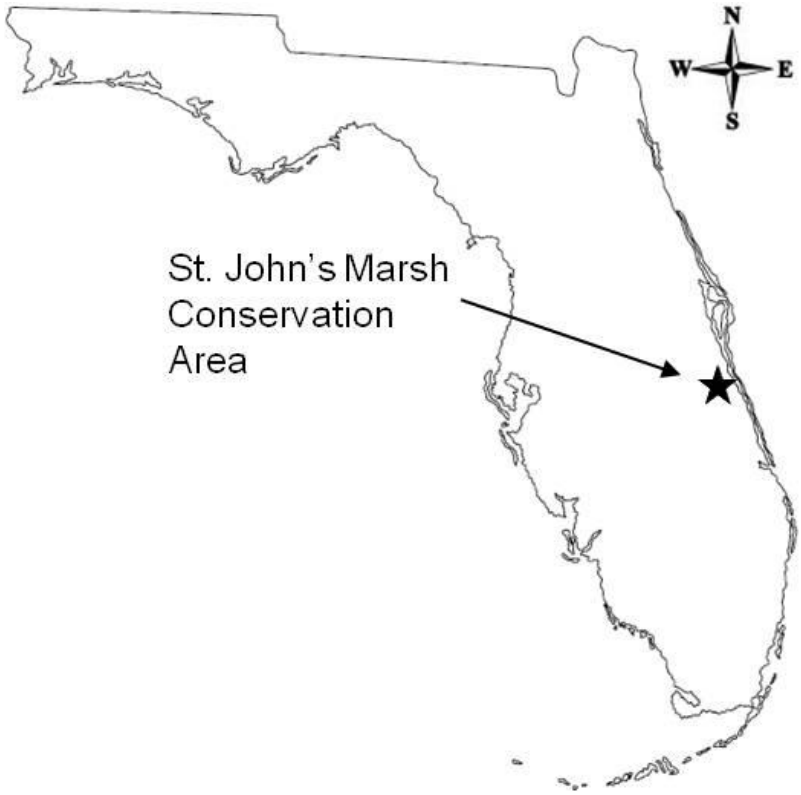

Figure 3-1. Site location map. The location of freshwater marsh soils collected for this manipulative laboratory experiment was in east central Florida, USA.

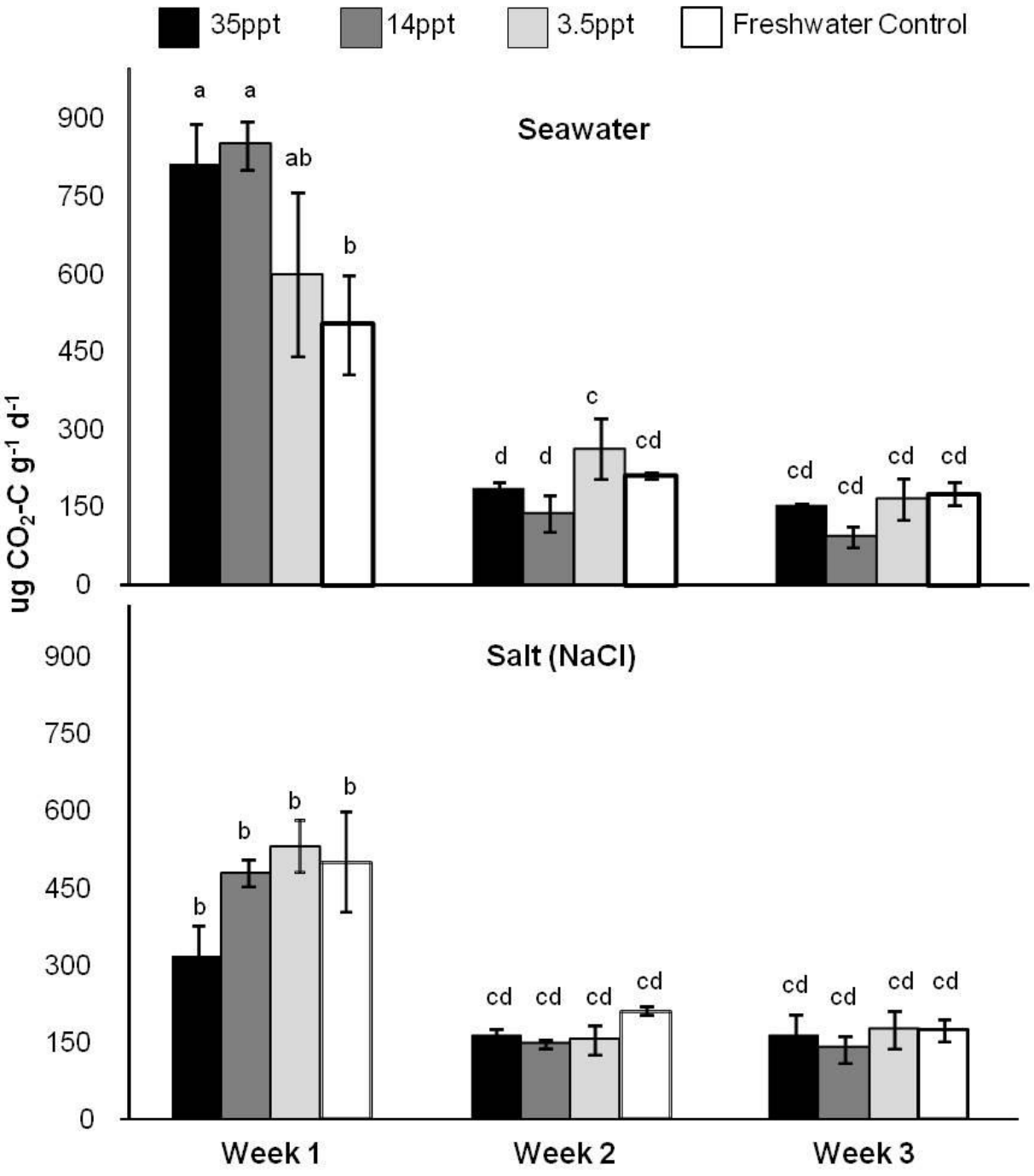

Figure 3-2. Potential soil respiration over time. Anaerobic microbial respiration rate by treatment over the 3 week incubation period. Error bars represent standard deviation; n = 3 for all treatments; different letters indicate significant differences at $p < 0.01$.

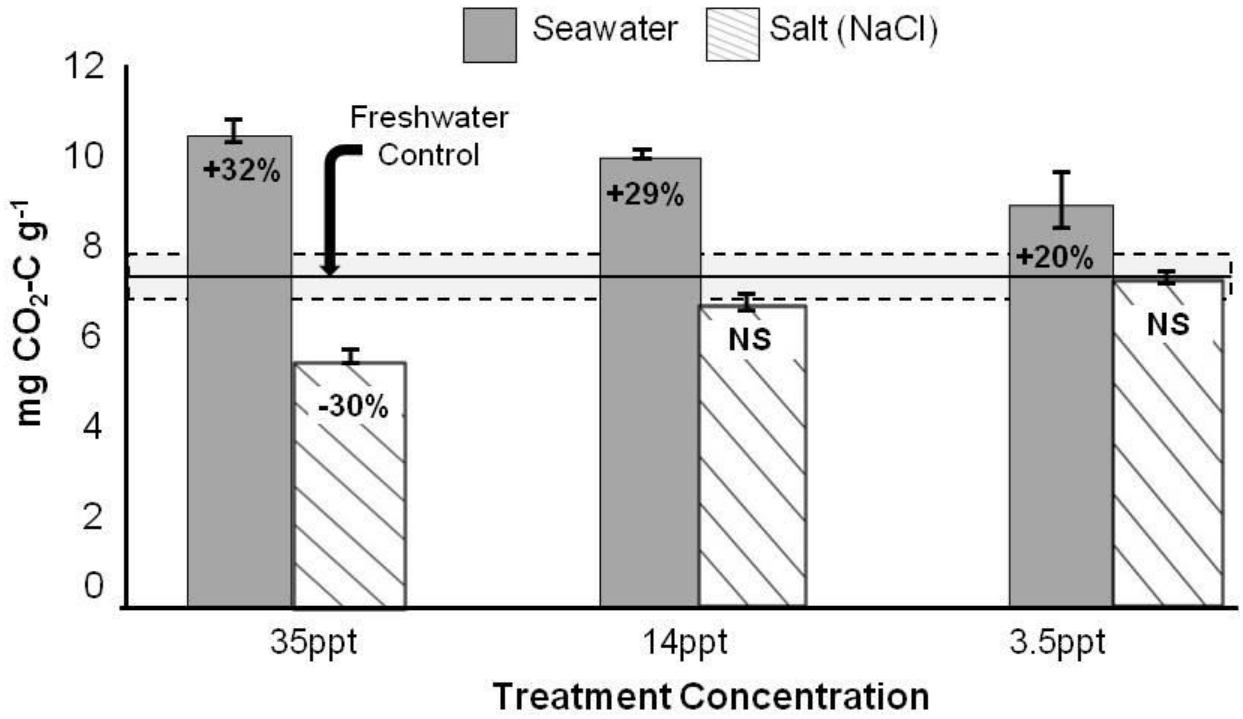

Figure 3-3. Total soil respiration. Mean total anaerobic CO_2 produced over the 3 week incubation period by treatment and concentration. Horizontal lines represent mean (solid line) and standard deviation (dotted line) of total production by the freshwater control. Percentages represent differences in mean total production compared to the freshwater control ($p < 0.05$). Error bars represent standard deviation; NS = not significant; n = 3 for all treatments.

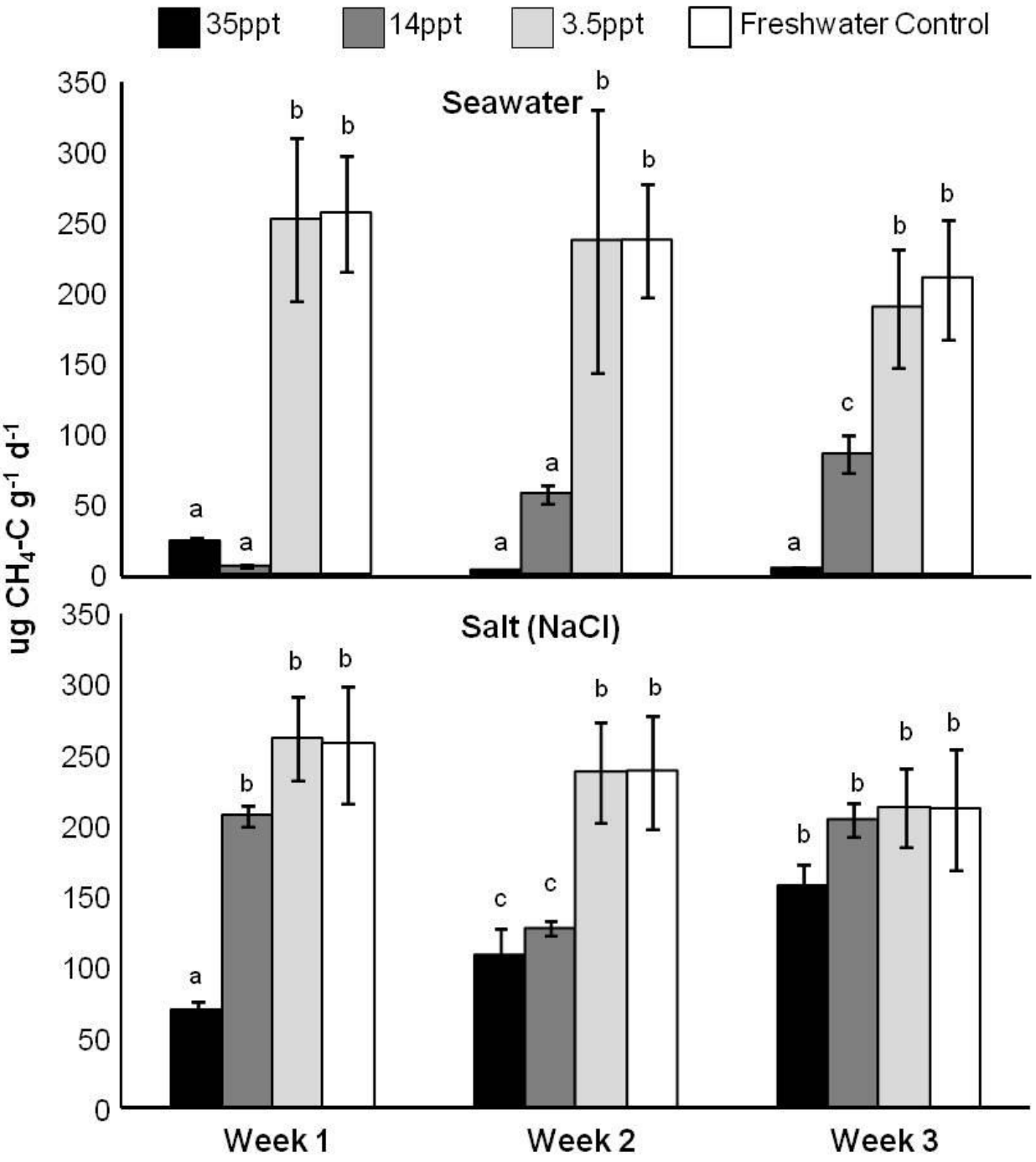

Figure 3-4. Potential methanogenesis over time. Methanogenesis rate by treatment over the 3 week incubation period. Error bars represent standard deviation; n = 3 for all treatments; different letters indicate significant differences at $p < 0.01$ for week 1, $p < 0.05$ for weeks 2 and 3.

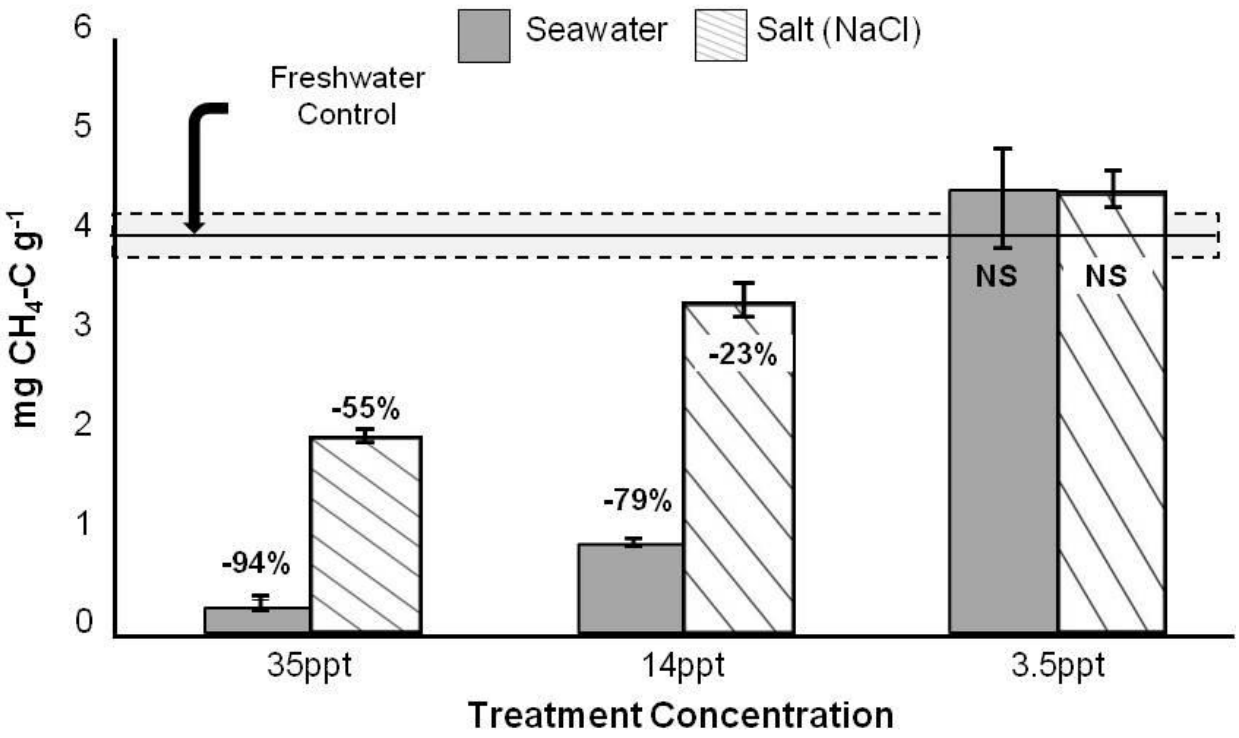

Figure 3-5. Total methanogenesis. Mean total CH_4 produced over the 3 week incubation period by treatment and concentration. Horizontal lines represent mean (solid line) and standard deviation (dotted line) of total production by the freshwater control. Percentages represent differences in mean total production compared to the freshwater control ($p < 0.05$). Error bars represent standard deviation; NS = not significant; n = 3 for all treatments.

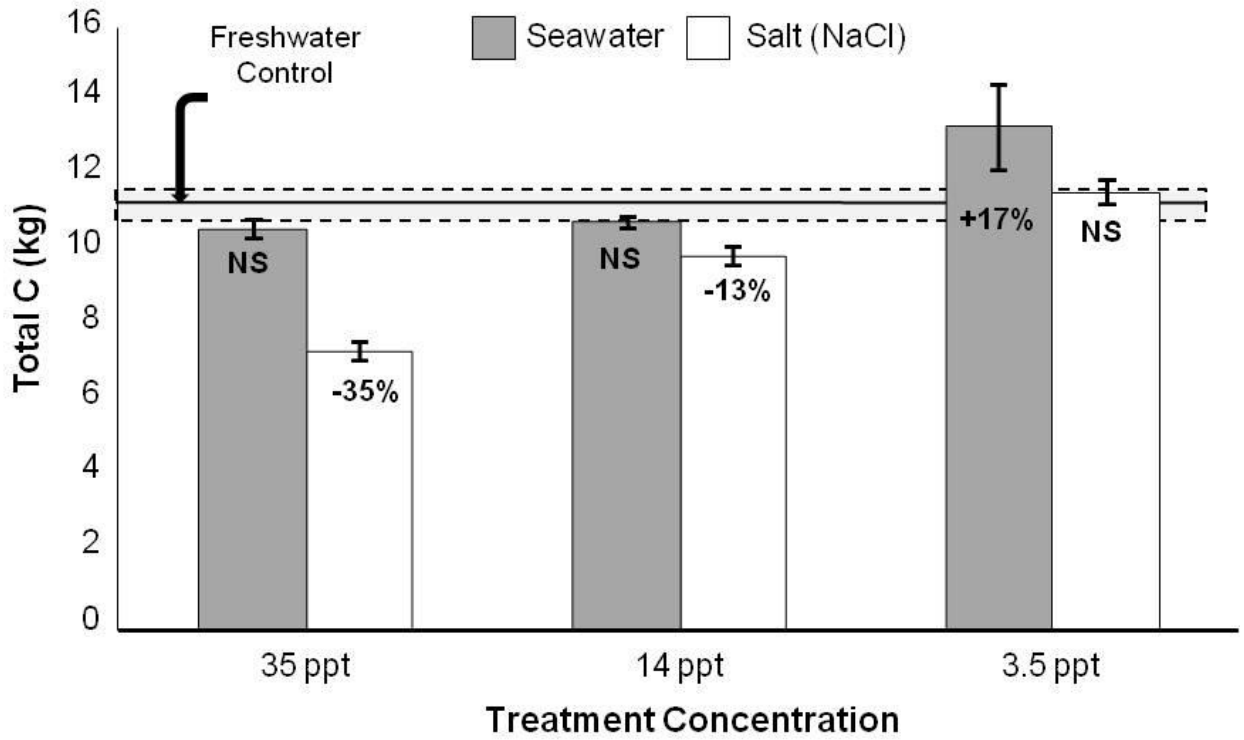

Figure 3-6. Total carbon loss. Total C (CH_4 and CO_2) produced over the 3 week incubation period by treatment and concentration. Horizontal lines represent mean (solid line) and standard deviation (dotted line) of total production by the freshwater control. Percentages represent differences in mean total production compared to the freshwater control ($p < 0.05$). Error bars represent standard deviation; NS = not significant; n = 3 for all treatments.

CHAPTER 4
EFFECT OF SALINITY PULSING EVENTS ON SOIL CARBON LOSS ALONG AN INTERTIDAL WETLAND GRADIENT: A LABORATORY EXPERIMENT

Background

Extreme sea level events (astronomical tides, frontal systems, tropical storms, and hurricanes) have a greater impact on the environment and society than mean sea level rise (SLR; Michener et al. 1997). With eustatic SLR occurring at a rate of 2.8 to 3.1 mm y^{-1}, storm surges are amplified and the area of land inundated during extreme coastal water levels is enlarged (Mousavi et al. 2011; IPCC 2007; Michener et al. 1997). Approximately 50% of SLR is ascribed to thermal expansion; global sea surface temperatures are predicted to increase an additional 1.1 to 6.4 ºC over than next century (IPCC 2007). Increasing sea surface temperatures are strongly correlated with longer duration and more intense tropical storms (IPCC 2007). In Florida (USA), there is evidence of increasing storm surge frequency (Park et al. 2011). It is predicted that the return period of a given coastal surge in Florida will *decrease* up to ten-fold by 2060 (from a 1-in-50 year return interval to a 1-in-5 year interval).

Most studies concerning coastal surges focus on the human and economic costs of flooding and infrastructure loss (Bloetscher et al. 2011; Park et al. 2011; Frazier et al. 2010), but natural coastal ecosystems are also impacted. Storm surges can introduce a pulse of saltwater to the coastal zone, temporarily inundating the carbon-rich soils of coastal wetlands. Coastal wetlands are a substantial sink for global C, accumulating 30 to 100 kg organic C m^{-2} in the same time the adjacent upland to accumulates 5 to 10 kg organic C m^{-2} (Coultas 1996). The rate of soil organic C (SOC) loss is highly sensitive to salinity due to the ability of sulfate (SO_4^{2-}), an abundant constituent of seawater, to function as an alternative electron acceptor during anaerobic respiration by microbes,

resulting in the accelerated mineralization of SOC (Chambers et al. 2011; Edmonds et al. 2009). The introduction of seawater to a freshwater wetland can induce a short-term increase (20-32%) in soil respiration from accelerated sulfate reduction under anaerobic conditions (Chambers et al. 2011). Evidence also suggests the high ionic strength of seawater and the presence of Cl^- ions can inhibit some soil microbial activity (Seo et al. 2008; Van Ryckegem and Verneken 2005). However, the inhibitory 'ionic effect' of seawater on soil microbes seems to be negligible in comparison to the stimulatory 'sulfate effect' (Chambers et al. 2011).

Freshwater pulses result from run-off during the heavy precipitation events that often accompany storms, or as point source stormwater discharges into coastal wetlands surrounded by urban development. According to Mulholland et al. (1997), regional climate models for the southeastern USA predict increasing precipitation in Florida, especially in conjunction with large, intense summer storms. The increase in precipitation is expected to exceed evapotranspiration and cause higher run-off volumes and more extreme hydrographs in Florida (Mulholland et al. 1997). In addition to climatic changes, extensive coastal urban development in Florida is continually increasing the coverage of impervious surfaces, further contributing to episodic freshwater discharges into coastal wetlands. The City of Jacksonville, Florida, has a 1-2% annual population growth and has lost 36% of their coastal wetlands since 1943 (US Census Bureau 2009; FDEP 2008). Much of the run-off from Jacksonville's impervious surfaces is discharged directly into the adjacent marsh, creating hot-spots of freshwater inputs to otherwise brackish or saline intertidal wetlands.

This study seeks to characterize and quantify the potential loss of ecosystem services (specifically, C storage) resulting from abrupt, short-term changes in surface water salinity in the coastal wetlands of Jacksonville, Florida. The goal was to answer three over-arching questions: (1) how do abrupt, short-term pulses of higher (or lower) salinity surface water affect the rate of SOC loss in coastal wetland soils, (2) does the impact of a salinity pulsing event differ between freshwater, brackish, and salt marshes, and (3) what nutrients, or other soil and water properties that co-vary with salinity, influence the response of SOC loss to salinity pulses? I hypothesized that freshwater marsh soils exposed to pulses of low salinities would have an overall higher rate of SOC mineralization due to combined effects of accelerated sulfate reduction and the maintenance of high *in-situ* rates of methanogenesis, as seen in a previous study (Chambers et al. 2011). I also predicted that salt marsh soils exposed to fresh or low-salinity pulses would have moderately accelerated rates of soil respiration due to the flushing of toxins (e.g., sulfide) and the alleviation of ionic stress for soil microbes.

To test these hypotheses, I conducted a laboratory study using intact soil cores collected from 3 intertidal wetlands along a natural salinity gradient and manipulated surface water salinity and tidal cycle to simulate salinity pulsing events. For the purpose of this study, SOC loss was defined as C loss through soil respiration, methanogenesis, and DOC release. Since coastal wetlands experience daily tidal fluctuations that alter the balance between aerobic and anaerobic soil respiration, I further specified CO_2 flux as occurring during low tide (LT) or high tide (HT).

Methods

Study Area

Thirty-six intact soil cores (12 from each of 3 sites) were collected along the natural salinity gradient of intertidal wetlands in the City of Jacksonville, Florida, USA. The sites were chosen based on accessibility and ambient surface water salinity. Soil cores were collected from the intertidal marsh platform adjacent to tributaries of the St. John's River (Figure 4-1). The freshwater tidal site was located along Cedar Creek (30°26'48.5"N, 81°40'17.1"W), the brackish site along Broward River (30°26'22.4"N, 81°37'33.1"W), and the salt marsh site along Pablo Creek (30°18'29.9"N, 81°25'9.8"W; Figure 4-1). Emergent marsh vegetation typical of a sub-tropical estuarine wetland dominated each site. The freshwater wetland had the highest species diversity with *Sagittaria lancifolia*, *Zizaniopsis miliacea*, and *Alternanthera philoxeroides* being the dominant species. *Juncus romerianus* and *Spartina patens* dominated the brackish marsh, and the salt marsh was a monoculture of *Spartina alterniflora*. All three sites were subject to diurnal micro-tidal fluctuations averaging 0.7 to 1.0 m in range (NOAA 2011).

Experimental Design

The experiment was designed and analyzed as a 3 x 3 x 3 mixed model treatment design (Table 4-1). Twelve intact soil cores were collected in each of the three wetland types (freshwater, brackish, and salt marsh) in 40-cm long x 10-cm diameter PVC tubes on April 15, 2011. All 12 soil cores from each site were collected within a 6 m^{-2} plot using care to minimize soil compaction and site heterogeneity. Aboveground vegetation was removed; the cores were capped on top and bottom, and then transported back to the laboratory. At the time of soil collection, 400 L of surface

water from the adjacent tidal creek was also collected, field-filtered through a 1-micron filter bag, and transported back to the lab. During sampling, all three sites were near low tide, with the freshwater and salt marsh sites on the ebb tide and the brackish site on the rising tide.

Once at the laboratory, the 12 field-replicate soil cores were randomly assigned to one of 4 conditions (freshwater, brackish, or saltwater salinity pulses, or immediate analysis; Table 4-1). Standard window screen mesh was affixed to the bottom of the cores and a 1-cm diameter drain hole was drilled exactly 10-cm above the soil surface (to maintain a 10-cm deep water column; Figure 4-2). The 10 cm deep water column was chosen to mimic the average tidal range of the St. John's River estuarine marshes where the soils were collected (NOAA 2011). The bottom of each core was plugged and flooded with ambient surface water (i.e., collected from the same site location) and allowed to acclimate for 1 week. Following acclimation, bottom plugs were removed, a leachate collection container was placed under each core, and surface water was allowed to drain through the soil profile and mesh screen for the first 24 hour dry-down period (Figure 4-2). After the first dry-down, the 9 cores selected for immediate analysis were destructively sampled by sectioning into 3 depth segments (0-5, 5-10, and 10-20 cm).

Following acclimation and initial dry-down, all remaining 27 cores underwent 3 cycles of 3 to 5-day salinity pulses, punctuated by 2 ambient surface water periods, each lasting ~12 days (Table 4-2). Between each cycle of surface water addition, all cores were unplugged, allowed to drain for 24 h, and leachate was collected. Once the

53 day manipulation experiment was complete, the remaining 27 cores were destructively sampled.

The goal of this design was to investigate both the short-term and cumulative impacts of pulsing events in each wetland type. Data from a hurricane storm surge in the Gulf of Mexico indicated that estuarine surface water salinities peak quickly to a maximum of ~25 ppt, and then receded slowly over the course of approximately 4 days (Li et al. 2009). Due to the abrupt, temporary, and dynamic nature of most saltwater (or freshwater) pulses that occur in coastal wetlands, the design included a return to ambient conditions following each salinity pulsing event (Table 4-2). This allowed for the identification of any possible legacy impacts from the surge on the rate of SOC loss after natural conditions resumed. Hydroperiod was designated as HT during periods of surface water flooding (10 cm water column), and LT during the dry-down periods. Soil cores were stored in the dark at 25° C and the top remained open to the atmosphere throughout the laboratory experiment.

Soil and Water Properties

Nine soil cores were destructively sampled on day 10 of the experiment (the baseline/initial soils), and the remaining 27 soil cores were destructively sampled on day 53 (Table 4-2). All soil cores were sectioned into 3 depth segments (0-5, 5-10, and 10-20 cm), stored at 4 ºC, and analyzed within 30 days. Soil property analysis included% moisture, bulk density,% organic matter (OM), total C, total N, and C fiber analysis (% fines (<0.025 mm), cellulose + hemicellulose, and lignin content). Moisture content and bulk density were determined after drying a subsample at 70° C to a constant weight. Percent OM was estimated by mass loss on ignition (LOI) where dry soils were combusted at 550° C for 5-h and final weight was subtracted from initial weight. Total C

and N content were determined using a Costech Model 4010 Elemental Analyzer (Costech 121 Analytical Industries, Inc., Valencia, CA). Dissolved OC was measured on a TOC Analyzer (Shimadzu Scientific Instrument TOC 5050A, Columbia, MD) following EPA method 415.1, which included filtering the water sample through a 0.45-µm membrane filter and acidifying the sample with H_2SO_4 until analysis (USEPA 1993). The fiber analysis was performed using a modified Ankom fiber fractionation method after Roberts and Rowland (1998). Fines (<0.025 mm) were defined as soil particles released from a 0.025 mm mesh bag placed in DI water, agitated, and rinsed. Cellulose + hemicellulose was the fraction solubilized in 24 N H_2SO_4, lignin content was the fraction combusted in a muffle furnace at 550 ºC and inorganic ash >0.025 mm was the material remaining following combustion.

During the laboratory experiment the surface water in each core was regularly monitored for salinity, conductivity, pH, dissolved oxygen (DO), and temperature using a hand-held YSI model 85 (YSI Inc., Yellow Springs, OH). Surface water (20-mL) was collected from each core 2-3 times during each event/condition to monitor sulfate (SO_4^{-2}) concentration and rate of loss. Sulfate samples were un-acidified, manually diluted, and analyzed on a Dionex DX 600 Ion Chromatograph (Thermo Scientific, Sunnyvale, CA) using standard method 4110B (Standard Methods 1997).

The surface water collected from each wetland type was analyzed for ammonium-N (NH_4^+-N) and soluble reactive P (SRP) on an AQ-2 Automated Discrete Analyzer (Seal Analytical, Mequon, WI) using EPA Methods 104-A Rev. 3, and 118-A Rev. 2, respectively (USEPA 1993). Depending on salinity, the sample matrix used was either de-ionized (DI) water or 13 ppt artificial seawater (Neomarine Reef Salt mix,

Brightwell Aquatics, Elysburg, PA) , with the 26 ppt salinity samples diluted by half. For total kjeldahl nitrogen (TKN) quantification, 10 mL of surface water was digested in glass tubes with a TKN salt catalyst and 0.5 mL of concentrated H_2SO_4. Samples were digested for 2 h at 160° C, and then at 360° C for 30 min. Tubes were cooled, 10-mL DI water added, vortexed, and the concentration was determined calorimetrically using a Technicon Autoanalyzer II (Seal Analytical, Mequon, WI), EPA Method 351.2 (USEPA 1993).

Soil Organic Carbon Loss

The rate of SOC loss was estimated by measuring the major pathways of organic C loss- CO_2 production (soil respiration, during both LT and HT), CH_4 production (methanogenesis), and DOC release. Soil respiration was determined using a portable infrared gas analyzer (Li-Cor 8100, Lincoln, NB) equipped with a 10-cm diameter chamber. The cores were plugged/sealed and CO_2 flux was measured (1-min) a total of 16 times during the 53 day study, including a minimum of one sampling during each dry-down, salinity pulse, and ambient surface water condition.

Methane was determined using soil slurry microcosms after Chambers et al. (2011). Approximately 5-g (wet weight) soil was prepared in triplicate and added to four 60-mL glass serum bottles. Bottles were capped with butyl stoppers and aluminum crimp-caps, evacuated to -75 kpa, and flushed with O_2-free N_2 gas for one minute to create anaerobic conditions. Eight mL of 0.5 ppt, 13 ppt, or 26 ppt seawater was added to create a slurry with duplicates every third. All incubations were maintained at a slight over-pressure and stored in the dark at 30° C. Headspace was extracted and measured on a gas chromatograph (Shimadzu Scientific Instruments GC 8A, Columbia,

MD) fitted with a flame ionization detector (FID) on days 3, 7, 12, and 17. Potential methanogenesis was calculated as CH_4–C production per g dry soil per day.

DOC release was quantified in the leachate collected during the soil core dry-down. Studies indicate that porewater seepage during ebb tide in salt marshes occurs primarily through the face of tidal creek banks (Gardner 2005). Therefore, I attempted to simulate a receding tide when surface water is drawn through the soil profile and then released to tidal creeks. Leachate was collected in 125-mL nalgene bottles, acidified, and stored at 4° C until analyzed. All DOC samples were filtered through a 0.45 µm membrane filter and analyzed using a TOC Analyzer (Shimadzu Scientific Instrument TOC 5050A, Columbia, MD) following EPA method 415.1 (USEPA 1993).

Nutrient Release

Nutrient release was determined by analyzing the leachate water collected during the dry-down periods for a total of 5 samplings during the study (Figure 4-2). Ammonium-N, SRP, and TKN were analyzed as described above for surface water properties. Organic-N was calculated as the difference between TKN and NH_4^+-N.

Microbial Indicators

Microbial biomass C (MBC) was determined by fumigation-extraction after Vance et al. (1987) and White and Reddy (2001). Duplicate 5-g (wet weight) samples were prepared in 25-mL centrifuge tubes. One set was fumigated with chloroform for 24 h and the other set served as the non-fumigated control. Following the chloroform treatment, both fumigates and non-fumigates were extracted with 25 mL of 0.5 *M* K_2SO_4, agitated for 30 min on a circulating shaker, and centrifuged at 5000 rpm for 10 min. The supernatant was vacuum-filtered through a Whatman # 42 filter paper and stored at 4 °C until analyzed for total organic carbon (Shimadzu Scientific Instrument

TOC 5050A, Columbia, MD). An extraction efficiency coefficient of k_{EC} = 0.37 was applied to all samples (Sparling et al. 1990). Total labile organic C (TLOC) was defined as the TOC for the fumigated samples and labile organic C (LOC) was defined as the TOC for the non-fumigated samples. The metabolic quotient (qCO_2) was calculated as the rate of soil respiration (mg CO_2-C kg soil^{-1} d^{-1}) divided by MBC (mg MBC kg soil^{-1}).

Beta-glucosidase enzyme activity was measured fluorometrically as described by Marx et al. (2001). Soil samples were homogenized, diluted by 100 with autoclaved distilled de-ionized (DDI) water, and sonicated for 10 seconds. Replicate soil slurry samples (150 µL) were added to each column of a 96 well plate. The top 4 rows were incubated with 100 µL (200 µ*M* final concentration) of fluorescently labeled substrate (methyl umbelliferone (MUF)-glucoside) for 4 hours. After 4 hours, labeled MUF-glucoside was added to the bottom 4 rows and 10 µL of 0.1 *M* NaOH was added to all wells. Formation of the fluorescent product MUF was measured at excitation/emission wavelength of 360/460 on a Synergy HT Multi-Mode Microplate Reader (BioTek, Winooski, VT). Quenching curves were prepared for each of the three wetland soils and coefficients were applied to the final values, expressed as mg MUF kg dry soil^{-1} h^{-1}.

Dehydrogenase enzymes activity was determined using the TTC (triphenyltetrazoliym chloride) method developed by Thalmann (1968) and modified by Alef (1995). Five-g wet weight soil was added to a 60 mL amber glass vial along with 5 mL TTC solution. Slurries were incubated in the dark for 24 hours, 40 mL acetone was added, the solutions were filtered through a Whatmann #2 filter paper, and the optical density of the solution was measured at 546 nm wavelength on a Spectrophotometer

(Shimadzu Scientific Instruments UV-160, Columbia, MD). Dehydrogenase activities were expressed as mg TPF kg dry soil^{-1} h^{-1}.

Data Analysis

Statistical analysis was performed using SAS 9.1 software (SAS Institute Inc., Cary, NC). All data sets were first tested to determine if the assumptions of homogeneity and normality were met using the Brown and Forsythe's Test and Shapiro-Wilk Test, respectively. Where these assumptions were not met, the raw data was $\log_{10}$ transformed and further statistical analysis was conducted using the dataset that fulfilled the assumptions. A three-way repeated measures ANOVA model ($\alpha = 0.05$) was used to determine the interaction between soil respiration rate, treatment condition, and time. A two-way repeated measures ANOVA model was used to determine significantly different means for complete data sets collected at common times for each soil core where time (t) was significant ($p < 0.05$, according to a treatment specific two-way ANOVA). This was determined to be true for DOC release and nutrient release. When t was deemed non-significant ($p > 0.05$; two-way ANOVA), the multivariate response was reduced to a univariate response and a one-way ANOVA model was used to determine significantly different means (Davis 2002). This method was determined to be appropriate for CO_2 flux. Non-repeated variables (soil and water properties, CH_4 flux, and microbial indicators) were measured using one and two-way ANOVA models ($\alpha = 0.05$). Pearson's Product correlations were calculated to determine correlations between SOC loss, soil and water properties, microbial indicators, and nutrient release. A Chi-Square test of independence was used to test if the percent of SOC lost to each pathway (respiration, methanogenesis, and DOC release) depended upon the treatment condition applied, and a Chi-Square of Goodness of Fit was used to test if the percent

of SOC lost to each pathway deviated significantly from that of the control condition (all at $\alpha = 0.05$). One intact core (a freshwater marsh soil pulsed with salt (26 ppt) water) was completely removed from the analysis as an outlier (>2.5 times the standard deviation). A simple theoretical model was developed to illustrate the effects of SLR on SOC loss using the results for the partitioning of C loss via the 4 pathways (HT CO_2, LT CO_2, CH_4, and DOC release) in each of the 3 wetland types. In this model, SLR is defined as an increase in time of HT and decreased time of LT. The linear model assumes current conditions are 50% HT and 50% LT and models an increase to 100% HT and 0% LT, with no real-time SLR scenario specified.

Results

Soil and Water Properties

The brackish marsh soil had a significantly ($p < 0.01$) higher bulk density than the freshwater and salt marsh soils; bulk density did not vary significantly with depth in any of the soils (Table 4-3). Soil organic matter content showed an inverse relationship with bulk density, with consistently higher OM in the freshwater and salt marsh soils (41-52%) compared to the brackish marsh soils (29-34%; Table 4-3). Similar to % OM, total C and total N were significantly higher in the freshwater and salt marsh soils compared to the brackish marsh soil ($p < 0.05$) and did not change significantly with depth (Table 4-3). The ratios of soil total C:N were 16.7 ± 1.4, 18.0 ± 1.7, and 17.9 ± 1.6 for the freshwater, brackish, and salt marshes, respectively. The C:N did not differ significantly with wetland type or depth. Carbon fiber analysis revealed the freshwater soil had significantly fewer fines (<0.025 mm; $p = 0.005$) than the brackish and salt marsh soils (Figure 4-3). Both the freshwater and salt marsh soil had higher lignin content ($p = 0.02$) and lower inorganic ash content (>0.025 mm; $p = 0.03$) than the brackish soil

(Figure 4-3). Cellulose + hemicelluloses content did not differ significantly with wetland type.

Surface water salinities were 0.56 ± 0.07, 13.5 ± 0.8, and 26.5 ± 1.8 ppt for the freshwater, brackish, and salt marsh surface water, respectively. Sulfate concentration and specific conductivity increased significantly with salinity, while DOC concentration in the surface water was inversely related with salinity (Table 4-4). Surface water pH was similar for all sites (averaging 7.7), and dissolved oxygen also did not vary significantly between sites (ranging from 6.4 to 6.9 mg L^{-1}; data not shown). Ammonium concentration was significantly higher ($p < 0.05$) in the freshwater, compared to the brackish site water, whereas TKN was not significantly different between wetland types (Table 4-4). SRP concentration was significantly greater ($p < 0.01$) in the freshwater compared to both the brackish and salt marsh surface water (Table 4-4).

Soil Organic Carbon Loss

Soil respiration was strongly affected by inundation level, with CO_2 flux significantly greater at LT (following a 24-h dry-down), compared to HT (10-cm water column), in the brackish and salt marsh soils (Figure 4-4). Using only the soil cores treated with the control condition, the average rate of CO_2 flux during HT was significantly greater ($p < 0.001$) in the freshwater marsh soil (1,033 ± 347 mg CO_2-C m^{-2} d^{-1}) than the salt marsh soil (500 ± 160 mg CO_2-C m^{-2} d^{-1}) and was negatively correlated with salinity ($p < 0.05$; Table 4-5). The rate of HT CO_2 flux was also positively correlated with DOC release, methanogenesis, qCO_2, SRP, and Organic-N (Table 4-5). During LT in the control condition soil cores, average CO_2 fluxes were greatest in the brackish and salt marsh soils (2450 ± 680 and 2052 ± 1031 mg CO_2-C m^{-2} d^{-1}, respectively), but were not statistically greater than the freshwater marsh soil at LT

(1578 ± 649 mg CO_2-C m^{-2} d^{-1}; Figure 4-4). Soil respiration rate at LT in the control condition cores was not correlated with any of the soil, water, or microbial indicators of interest (Table 4-5). Comparing average HT and LT CO_2 flux in each wetland type revealed significant differences in the magnitude of the tidal effect on soil respiration. Mean soil respiration rates were 53% greater at LT than at HT in the freshwater marsh soil, 230% greater at LT than HT in the brackish marsh soil, and 310 % greater at LT than HT in the salt marsh soil (Figure 4-4).

Time was not a significant factor in soil respiration rate over the course of the experiment ($p = 0.25$; three-way repeated measures ANOVA). Therefore, CO_2 flux measurements from the three salinity pulses were treated as replicates. Focusing on the effects of the salinity pulsing manipulation, results indicates that all of the freshwater marsh soil cores had significantly higher ($p < 0.01$) rates of CO_2 flux during HT (1056 ± 420 mg CO_2-C m^{-2} d^{-1}) than all of the other soil cores (Figure 4-5). Soil respiration rates in the brackish marsh soils were negatively affected by the pulse of freshwater (0.5 ppt), decreasing the average rate of CO_2 flux from 426 ± 85 mg CO_2-C m^{-2} d^{-1} in the control, to 286 ± 5 mg CO_2-C m^{-2} d^{-1} following the pulse ($p < 0.05$; Figure 4-5). Meanwhile, the pulse of salt (26 ppt) water had no significant impact on the brackish marsh soil CO_2 flux during HT (Figure 4-5). In the salt marsh soil, respiration rates during HT were not affected by the addition of either fresh (0.5 ppt) or brackish (13 ppt) water (Figure 4-5). Overall, the rate of CO_2 flux during the HT salinity pulsing events were positively correlated with DOC release, CH_4 flux, and SRP (all $p < 0.01$; Table 4-6).

Following each salinity pulse, some of the soil treatments experienced a legacy effect from the pulse, resulting in significantly different rates of CO_2 flux during the

subsequent LT (Figure 4-6). The freshwater marsh soil receiving a pulse of brackish (13 ppt) water had a CO_2 flux of 2587 ± 1230 mg CO_2-C m^{-2} d^{-1}, more than double the rate in the control treatment during the same period (1221 ± 426 mg CO_2-C m^{-2} d^{-1}; $p < 0.001$; Figure 4-6). In contrast, the freshwater marsh soil pulsed with salt (26 ppt) water showed no legacy effect. In the brackish marsh soil, respiration rate during LT was unaffected by either the freshwater or saltwater pulses, with an overall average flux rate of 1645 ± 291 mg CO_2-C m^{-2} d^{-1} (Figure 4-6). In the salt marsh soil, the pulse of fresh (0.5 ppt) water had a significant legacy effect, increasing CO_2 flux from 1578 ± 313 mg CO_2-C m^{-2} d^{-1} in the control treatment, to 2775 ± 710 mg CO_2-C m^{-2} d^{-1} following the pulse ($p < 0.05$). The pulse of brackish (13 ppt) water had no legacy effect on soil respiration in the salt marsh soil (Figure 4-6). The concentrations of NH_4^+ and MBC were positively correlated with CO_2 flux during the LT that followed the salinity pulsing events ($p < 0.05$; Table 4-6).

Between each salinity pulsing event, all soil cores were flooded with their original ambient site water for ~12 days to mimic a return to baseline, or natural field conditions (Table 4-2). During this ambient water phase, respiration rates for each salinity pulsing treatment condition were not significantly different than the control for that wetland type during both HT and LT measurements, suggesting a return to baseline conditions between each salinity pulse (data not shown).

The rate of methane production was an order of magnitude higher ($p < 0.001$) in the freshwater marsh control (0.5 ppt) treatment than in all other treatments (114 ± 9 mg CH_4-C m^{-2} d^{-1}; Figure 4-7). The addition of brackish (13 ppt) and salt (26 ppt) water to the freshwater marsh soil decreased methanogenesis by 98% and 97%, respectively.

In the brackish marsh soil, CH_4 flux ranged from below detection to 2.2 mg CH_4-C m^{-2} d^{-1} with no significant affect of surface water salinity changes. The salt marsh soil exposed to fresh (0.5 ppt) water had a higher CH_4 flux (8.0 ± 6.4 mg CH_4-C m^{-2} d^{-1}) than the control condition (0.12 ± 0.13 mg CH_4-C m^{-2} d^{-1}), but was not statistically significant ($p = 0.08$; Figure 4-7). Overall, CH_4 flux was positively correlated with DOC release, qCO_2, and SRP (Table 4-6). Methane flux had high within-treatment variability and can be interpreted as potential methanogenesis since it was measured in a slurry microcosm, rather than the intact soil cores.

DOC release from the control condition soil cores decreased significantly from freshwater, to brackish, to salt marsh wetland types ($p < 0.001$; Table 4-7). DOC release was inversely correlated with salinity and directly correlated with CH_4 flux, qCO_2, SRP, and organic-N (Table 4-5). The salinity pulsing events did have a significant impact of the rate of DOC release in both the freshwater and the salt marsh soils. The pulse of brackish (13 ppt) water in the freshwater marsh soil caused a significant decrease ($p < 0.01$) in DOC release from, from 18.3 ± 2.8 mg L^{-1} in the control, to 10.8 ± 2.2 mg L^{-1} following the pulse. Additionally, the pulse of fresh (0.5 ppt) water in the salt marsh soil caused a significant increase ($p < 0.01$) in DOC release, from 7.6 ± 0.7 mg L^{-1} in the control, to 11.4 ± 0.9 mg L^{-1} following the pulse. With the exception of the pulsing effects, the rate of DOC release was constant over time. Overall, DOC release following salinity pulsing events was positively correlated with CH_4 flux, qCO_2 and SRP, and negatively correlated with NH_4^+ and salinity (Table 4-6).

Over 98% of SOC loss in this study occurred through soil respiration, with the exception of the freshwater marsh control, which lost 94% of SOC to respiration. The

average total mass of SOC lost in the freshwater marsh control (0.5 ppt) treatment was significantly greater than in the brackish marsh salt (26 ppt) water treatment ($p = 0.009$), the salt marsh control (26 ppt) treatment ($p = 0.003$), and the salt marsh brackish (13 ppt) water treatment ($p = 0.05$; Figure 4-8). Since the total mass of SOC loss (Figure 4-8) was affected by the amount of time each conduction was measured during the experimental manipulation, a weighted average % SOC loss to each pathway was also calculated for the control condition (Figure 4-9). The freshwater marsh control lost the largest % of total SOC through HT CO_2 flux (55%), while the brackish and salt marsh controls lost the largest % SOC through LT CO_2 flux (62 and 70%, respectively). The freshwater marsh soil pulsed with brackish (13 ppt) water was the only treatment to deviate significantly from its' respective control in the % SOC lost to each of the 4 pathways. This treatment more closely resembled the SOC loss partitioning of the brackish marsh control (54% loss to LT CO_2 flux, 46% to HT CO_2 flux, and < 1% to methanogenesis) than the freshwater marsh control (Figure 4-9).

Nutrient Release

Among the soil cores receiving the control condition, the salt marsh soil released significantly more NH_4^+ than the freshwater and the brackish marsh soils ($p < 0.01$; Table 4-7). The salinity pulsing events had a significant effect on the freshwater marsh soil, more than doubling the concentration of NH_4^+ release when a pulse of brackish (13 ppt) water was added, from 0.02 ± 0.19 mg L^{-1} in the control, to 0.57 ± 0.79 mg L^{-1} following the pulse ($p = 0.02$). TKN release showed no significant difference between wetland type, salinity pulse, or time, averaging 1.2 ± 0.3 mg L^{-1}. Organic-N release differed significantly between wetland types and was greater in the freshwater and

brackish marsh soils than the salt marsh soil ($p < 0.05$; Table 4-7). Salinity pulsing events and time had no effect of organic-N release.

SRP release for the control condition was significant greater for the freshwater and brackish marsh soils than from the salt marsh soil, even when controlling for the concentration in the surface water ($p < 0.01$) (Table 4-7). Adding a pulse of fresh (0.5 ppt) water to both the brackish marsh and salt marsh soils caused a significant increase in SRP release ($p < 0.05$), but the effect was directly attributable to the increase in SRP from the added freshwater (i.e., the effect was no longer significant when surface water SRP concentration was controlled for).

Microbial Indicators

The concentration of MBC in the salt marsh soil control was more than twice that of the freshwater and brackish marsh soil controls ($p < 0.001$; Table 4-8). The salinity pulse of brackish water to the salt marsh soil caused a significant increase in MBC ($p < 0.01$) from 2105 ± 159 mg kg^{-1} in the control, to 2974 ± 365 mg kg^{-1} following the 13 ppt pulse. Time was not a significant factor for MBC; the amount of MBC was similar in both the baseline cores (sampled on day 10) and the final cores (sampled on day 53). MBC was positively correlated with soil organic matter content, TLOC, LOC, dehydrogenase activity, and NH_4^+ concentration ($p < 0.01$; data not shown). TLOC among the control condition cores was highest in the salt marsh soils ($p < 0.001$; Table 4-8). Similar to MBC, TLOC significantly increased in the salt marsh soil following the pulse of brackish (13 ppt) water, from 2345 ± 389 mg kg^{-1} in the control, to 3236 ± 389 mg kg^{-1} following the pulse ($p < 0.001$). LOC did not differ significantly between wetland types, nor was it affected by the salinity pulsing events. LOC was positively correlated with ß-glucosidase activity ($p < 0.05$; data not shown). The metabolic quotient (qCO_2)

was significantly lower in the salt marsh soil compared to the freshwater marsh soils ($p < 0.05$; Table 4-8) and was unaffected by the salinity pulsing events. The qCO_2 was positively correlated with LT CO_2 flux and DOC release in the control condition soils (Table 4-5), and positively correlated with CH_4 flux and DOC release following the salinity pulsing events (Table 4-6).

Beta-glucosidase activity was significantly lower in the brackish marsh soil compared to the freshwater marsh soil ($p < 0.05$; Table 4-8). The salinity pulsing events did not cause a significant change in ß-glucosidase activity. ß -glucosidase activity was positively correlated with soil moisture content, dehydrogenase activity ($p < 0.05$), and organic matter content ($p < 0.001$). Dehydrogenase activity showed a similar pattern to ß-glucosidase activity, but differences between wetland types were not significant (Table 4-8). Dehydrogenase activity was positively correlated with soil moisture ($p < 0.01$), organic matter content, and MBC ($p < 0.05$).

Discussion

Freshwater Tidal Marsh

The freshwater tidal marsh soil had higher soil moisture content (83 ± 2%) and a lower bulk density (0.18 ± 0.04 g cm^{-3}) than the brackish marsh, but both measurements were similar to the salt marsh soil (Table 4-3). Surface water concentrations of DOC, NH_4^+, TKN, and SRP were, on average, higher in the freshwater marsh than other wetland types (Table 4-4). Overall, the ecological characteristics of the freshwater tidal marsh concurred with observations from other US Atlantic coast freshwater tidal marshes, including high plant diversity, high spatial heterogeneity, high organic matter content, and measurable methanogensis (Neubauer et al. 2000; Odum 1988).

While the influence of inundation and water table on soil respiration rates in non-coastal wetlands and peatlands is well established (e.g., Wright and Reddy 2001; DeBusk and Reddy 1998; Clymo 1983), very few studies have investigated the impact of tides on coastal wetland soil respiration. I found the rate of CO_2 flux from the freshwater marsh soil during HT was significantly greater than the salt marsh soil, but LT CO_2 flux in the freshwater marsh was the lowest of the 3 intertidal wetland types (Figure 4-4). As a result, the magnitude of the tidal effect for the freshwater marsh was relatively small, averaging only a 53% increase in CO_2 flux between LT and HT. This tidal effect is similar to the 50% increase at LT found by Neubauer et al. (2000) in a temperate tidal freshwater marsh, but is substantially less than the tidal effects observed for the brackish marsh (230% increase at LT) and salt marsh (310% increase at LT) in this study. Differences in the magnitude of the tidal effect along the salinity gradient is likely attributable to difference in the hydraulic conductivity of the soils. The brackish marsh soil was observed to drain the quickest during the simulated ebb tide (> 1 to 2 h), followed by the salt marsh soil (2 to 6 h), and the freshwater marsh soil (up to 24 h); a pattern that mirrors the LT CO_2 flux rates in these soils (Figure 4-4). Soils with high water retention could allow anaerobic soil conditions to persist during LT, and subsequently decrease the rate and efficiency of microbial respiration (Freeman et al. 1993). Freshwater marsh soils in this study were classified as Maurepas muck and consisted of highly decomposed herbaceous histisols (USDA 1978). This particular peat composition has some of the lowest soil hydraulic conductivity and acts similar to a sponge in its ability to retain water against gravitational pull (Boelter 1965).

Methanogenesis was an order of magnitude greater in the freshwater marsh control (0.5 ppt) compared to all other treatments (Figure 4-7), as would be expected from previous literature indicating a higher energy yield for sulfate reducers, compared to methanogens (D'Angelo and Reddy 1999). However, the contribution of CH_4 flux to overall SOC loss was still minimal, representing only ~3% of the total SOC loss in the freshwater marsh (Figure 4-9). *In-situ* rates of methanogenesis in freshwater tidal marshes reported in other studies represent about 6% of C loss; my rates may be underestimated because 95% of CH_4 is normally released through macrophytes, which were not included in the present study (Neubauer et al. 2000).

Microbial indicators for the freshwater marsh showed intermediate concentrations of MBC, TLOC, and LOC, and the highest average value for qCO_2 (Table 4-8). Overall, the freshwater marsh control (0.5 ppt) lost the greatest total average mass of SOC (Figure 4-8), the majority of which was lost via HT soil respiration (55%), followed by LT soil respiration (41%), and methanogenesis (3%; Figure 4-9).

When the freshwater marsh soil was pulsed with brackish (13 ppt) water, HT CO_2 flux remained unchanged (Figure 4-5), but a significant legacy effect during LT from the brackish pulse was observed (Figure 4-6). The respiration rate of freshwater marsh soil pulsed with brackish (13 ppt) water increased 112% during the subsequent LT. This increase is at least partially explained by an influx of SO_4^{2-} to support sulfate reduction (Table 4-3), but the data also suggest a strong correlation (Table 4-6) between the acceleration of LT CO_2 flux and a tripling in the concentration of NH_4^+ release. The latter indicates a short-term disruption of N cycling following pulses of seawater, which could have significant ramification for coupled N and C cycling in coastal wetlands.

Chloride is the most abundant ion in seawater by weight, with approximately 7000 mg Cl^- L^{-1} in 13 ppt seawater (Kester et al. 1967). Chloride is known to inhibit both denitrification and nitrification in aquatic, wetland, and terrestrial ecosystems (Seo et al. 2008; Roseberg et al. 1986). Research indicates that aquatic systems that do not naturally contain significant Cl^- (i.e., inland forested watersheds) experience a complete inhibition of denitrification enzyme activity with Cl^-concentrations as low as 80 mg L^{-1} (Hale and Groffman 2006). Interestingly, urban steams commonly exposed to low-levels of Cl^- from the runoff of deicing salts do not experience any decline in denitrification when Cl^- concentrations increase, suggesting a capacity for microbial populations to adapt to long-term Cl^- exposure (Hale and Groffman 2006). I found no correlation between CO_2 flux and NH_4^+ under ambient (control) conditions (Table 4-5), but a significant correlation following the salinity pulsing events (Table 4-6).

The inhibition of nitrification by Cl^- has been demonstrated in agricultural soils treated with Cl-containting fertilizers and results in elevated NH_4^+ concentrations in the soil solution (Roseberg et al. 1986). Saltwater also disrupts N-cycling by replacing NH_4^+ ions on the soil cation exchange complex with other salts (e.g., Na^{2+}, K^+), and thus releases NH_4^+ in to solution (Baldwin et al. 2006; Weston et al. 2006; Portnoy and Giblin 1997). I hypothesize that during the HT 13 ppt pulse there was an increase in NH_4^+ availability, a precursor to coupled nitrification-denitrification, but microbes were not able to utilize the additional inorganic N until the stress caused by Cl^- ions was alleviated during the LT dry-down. To date, the mechanism of Cl^- inhibition of N-cycling is unknown and the relevance of the previous findings in inland systems to coastal systems warrants further investigation (Seo et al. 2008).

Methanogenesis decreased 98% when the freshwater soil was pulsed with brackish (13 ppt) water (Figure 4-7). Past laboratory studies have indicated that salinity concentrations of 14 ppt cause the near complete suppression of methanogenesis (Chambers et al. 2011) which agrees with the current study. *In-situ* methanogenesis along a coastal wetland salinity gradient in Louisiana revealed average annual CH_4 fluxes of 4.3, 73, and 160 g CH_4-C m^{-2} for fresh, brackish, and salt marshes, respectively (DeLaune et al. 1983). Higher measurements of CH_4 flux in the field, compared to laboratory, can be expected due to the presence of low-redox microzones within the natural soil structure (King and Wiebe 1980).

Microbial indicators were not altered as a result of the brackish pulse, but DOC release decreased significantly compared to the control condition following the pulse. In other laboratory studies, the addition of artificial seawater (no C source) to a freshwater wetland soils caused no change in DOC release (Weston et al. 2011). Since the ambient concentration of DOC in the brackish water is less than the freshwater (Table 4-4), the decrease in DOC release may have been due to DOC absorption to the peat matrix, or the utilization of DOC as a substrate for microbial respiration (Freeman et al. 1997).

Overall, the freshwater marsh soil pulsed with brackish water was the only treatment in the entire study that showed a significant deviation from the control condition in the partitioning of SOC loss via the 4 pathways measured in this study (Figure 4-9).

Adding a pulse of saltwater (26 ppt) to the freshwater marsh soil had no significant effect on soil respiration during HT (Figure 4-5) or the subsequent LT (Figure

4-6). Although the increase in SO_4^{2-} occurred (Table 4-4), the increase in NH_4^+ release (seen with the 13 ppt pulse) was not observed following the saltwater pulse, nor was the legacy effect of accelerated LT respiration. The reason for this is unclear, but it could be that the salinity was so high (26 ppt) the freshwater marsh microbial community was under too much osmotic stress to respond to the increased SO_4^{2-} abundance. High ionic conductivity is known to inhibit enzyme activity in the soil and cause the buildup of toxins associated with saltwater, such as sulfide (Frankenberger and Bingham 1982). Similar to the brackish pulse, the 26 ppt pulse did significantly suppress methanogenesis (Figure 4-7). No evidence was found of changes in microbial indicators, DOC release, or nutrient release as a result of the saltwater pulse in the freshwater marsh soil.

Brackish Marsh

The brackish marsh soil had significantly higher bulk density ($p < 0.0001$), lower organic matter, total C, and total N content (Table 4-3), and higher fines and inorganic ash (Figure 4-3) than the other wetland types, indicative of a system with greater tidal influence and higher inorganic sediment deposition. Although these characteristics are more commonly found in salt marshes (Craft 2007; DeLaune et al. 2002; Odum 1988), unique sedimentation patterns and/or the location of the estuary's turbidity maximum in relation to my sampling sites may have contributed to the brackish marsh site being the most inorganic of the three wetland types (Wieski et al. 2010; Nyman et al. 1990). Surface water from the brackish marsh had intermediate levels of DOC and SRP and the low concentrations of NH_4^+ and TKN (Table 4-4). Soil respiration rate in the brackish marsh control was moderate during HT, but had the highest average CO_2 flux rate at LT (Figure 4-4). As a consequence, the magnitude of the tidal effect in the

brackish marsh was large; a 230% increase in the rate of C loss via soil respiration between HT and LT. The brackish marsh soil was observed to have significantly higher hydraulic conductivity than the other wetland types, draining in a few hours when the bottom core plugs were removed, despite having the lowest overall porosity (Table 4-3). Salt can function as both a flocculating agent, causing hydrophilic colloids to aggregate, and as a dispersing agent, causing hydrophobic colloids to repel one another (Gregory 1989). Therefore, high concentrations of Na^{2+} can increase both the size of soil aggregates and the quantity of macropore spaces in the soil profile, allowing water to drain quickly and the soil to become aerobic faster during LT (Brady and Weil 2004). The acceleration of the soil respiration rate following a drop in the water table is well established in the literature and can create a mineralization rate up to 50 times faster than under flooded conditions (Clymo 1983). Methane production in the brackish marsh control was negligible (Figure 4-7). On average, the availability of labile C (MBC, TLOC, and LOC) was low in the brackish marsh (Table 4-8). ß-glucosidase, a soil enzyme involved in glucose production, is considered a good indicator of soil quality and general C mineralization rate (Makoi and Ndakidemi 2008). This study found ß-glucosidase to be significantly lower in the brackish marsh soil than the freshwater marsh soil (Table 4-8), but was no relationship was found between ß-glucosidase and salinity, as was also the case in a study by Jackson and Vallaire (2009). Dehydrogenase is produced during microbial respiration and was of interest in this study due to existing contradictions in the literature. Some research has found that dehydrogenase activity is strongly inhibited in saline soils (Saviozzi et al. 2011; Frankenberger and Bingham 1982), while others have found a positive relationship

between dehydrogenase activity and salinity (Wu et al. 2008). The current study found no significant differences in dehydrogenase activity with salinity or wetland type (Table 4-8).

Overall, the total mass of C lost from the brackish marsh was intermediate in comparison to the other wetlands types (Figure 4-8). Approximately 62% of SOC loss was to soil respiration during LT, 38% to soil respiration during HT, and >1% to DOC release (Figure 4-9).

When the brackish marsh soil was pulsed with fresh (0.5 ppt) water, there was a significant decline in HT soil respiration rate, with an average decrease of 33% (Figure 4-5). Sulfate reduction is the dominate pathway of soil respiration in brackish marshes (Weston et al. 2006b) and SO_4^{2-} tends to have a short residence time in the soil profile, being quickly utilized by microbes (DeLaune et al. 1983). The abrupt decline in SO_4^{2-} availability when freshwater was added (Table 4-3) would have diminished the rate of sulfate reduction and required non-sulfate reducing microbes to activate quickly to maintain the overall rate of soil respiration. The brackish marsh soil had low microbial biomass, relative to the other wetland types (Table 4-8). High microbial biomass often correlates with greater microbial diversity (Cordova-Kreylos et al. 2006), so the low biomass of the brackish marsh soil may have prevented the microbial community from adapting quickly to the decrease in SO_4^{2-} availability. Despite the negative influence of the freshwater pulse on HT CO_2 flux, no legacy effect of the pulse was seen during the subsequent LT (Figure 4-6). This supports the earlier hypothesis that LT respiration in the brackish marsh soil is dominated by aerobic microbes due to the high hydraulic conductivity of the soil, making SO_4^{2-} availability superfluous during LT. Methane

production, DOC release, microbial indicators, and nutrient release were not significantly affected by the freshwater pulse (Figure 4-7; Tables 4-7 and 4-8).

Adding a pulse of salt (26 ppt) water to the brackish marsh soil resulted in no change to the soil respiration rate during HT (Figure 4-5) or LT (Figure 4-6). Both brackish and salt marsh soil respiration is dominated by sulfate reduction (Weston et al. 2006b; Kostka et al. 2002; Howarth 1984), so the change in electron acceptor availability would be minimal. Similarly, the pulse of 26 ppt did not affect CH_4 flux, DOC release, microbial indicators, or nutrient release from the brackish marsh soil (Figure 4-7; Tables 4-7 and 4-8).

Salt Marsh

The physical properties of the salt marsh soil were similar to that of the freshwater marsh soil, having significantly lower bulk density than the brackish marsh soil and generally greater organic matter, total C, and total N content (Table 4-3). DOC and SRP in the salt marsh surface water were, on average, lower than the other wetland types, and the concentration of NH4+ and TKN were intermediate (Table 4-4). Under control conditions, the rate of soil respiration at HT was significantly lower in the salt marsh soil than in the freshwater marsh soil (Figure 4-4). The magnitude of the tidal effect was greatest in the salt marsh soil compared to the other wetland types; CO2 flux increased an average of 310% from HT or LT (Figure 4-3). The rate of drainage in salt marsh soil was about 2-6 hours, indicating a high hydraulic conductivity likely associated with the dispersive powers of high ionic strength saltwater (Brady and Weil, 2004). Similar to the brackish marsh soil, the salt marsh soil showed negligible methanogenesis (Figure 4-7). However, MBC and TLOC were highest in the salt marsh soil, and the metabolic quotient the lowest (Table 4-8). Most studies investigating the

affect of salinity on MBC have been performed in agricultural and upland systems and results have varied widely, from a positive relationship (Rasul et al. 2006), to a negative relationship (Muhammad et al. 2006), to no relationship at all (Gennari et al. 2007) between salinity and MBC. The qCO_2 is an index of the efficiency of the microbial community; stressed populations tend to produce more CO_2 per individual and have a higher qCO_2 (Wong et al. 2008). More saline environments are presumed to be more stressful to microbes and, as a result, typically exhibit a higher metabolic quotient (Saviozzi et al. 2011; Tripathi et al. 2006), but previous studies (Wong et al. 2008) have also found a decrease in qCO_2 with increasing salinity, as I did in the present study. The different finding could be a consequence of the *types* of microbial populations present in the soil. For example, fungi are known to produce less CO_2 per individual than bacteria and a commonly associated with the decomposition of *Spartina spp.*, the dominant macrophyte of this study' salt marsh site (Wong et al. 2008; Torzilli et al. 2006).

The salt marsh soil had significantly lower DOC, SRP, and organic-N release than the other wetland types (Table 4-7), and the highest concentration of NH_4^+ release. Overall, the salt marsh control had the lowest average total C loss of all treatments (Figure 4-8) and the largest percent of total C lost to soil respiration during LT (70%; Figure 4-9).

Adding a pulse of fresh (0.5 ppt) water to the salt marsh soil did not affect the rate of soil respiration during HT (Figure 4-5), but did cause a significant increase in CO_2 flux during the subsequent LT, an average increase of 76% in the rate of soil respiration (Figure 4-6). Past research has found that increasing tidal flushing can

enhance productivity in salt marshes through decreased osmotic stress and the removal deleterious compounds such as sulfide (King et al. 1982; King and Wiebe 1980). It follows that a flush of freshwater could accelerate microbial respiration in a salt marsh soil, as observed in this study.

The addition of freshwater to the salt marsh soil also increased methanogenesis from 0.12 ± 0.13 mg CH_4-C m^{-2} d^{-1} in the control, to 8.05 ± 6.14 mg CH_4-C m^{-2} d^{-1} following the pulse (Figure 4-7). Although this change was marginally significant ($p = 0.08$), the implications are still important considering CH_4 has a radiative forcing 25 times greater than CO_2 (IPCC 2007). This research suggests the discharge of precipitation run-off from urban development directly into salt marshes can accelerate both the production of CO_2 during LT and the release of CH_4 to the atmosphere, which may be an importance consideration for urban development adjacent to salt marshes.

The fresh (0.5 ppt) water pulse had no effect on soil microbial indicators (Table 4-8) or nutrient release (Table 4- 7), but did significantly increase the concentration of DOC release following the freshwater pulse. This could simply be a result of higher DOC concentration in the freshwater marsh surface water (Table 4-4).

The brackish (13 ppt) water pulse did not alter the rate of CO_2 flux in the salt marsh soil during either HT (Figure 4-5) or the subsequent LT (Figure 4-6), nor was there any change in CH_4 flux from the salt marsh soil (Figure 4-7). The brackish water pulse did, however, significantly increase the concentration of bioavailable C (MBC and TLOC) in the salt marsh soil. The activity of soil enzymes, DOC release, and nutrient release was not altered as a result of the 13 ppt pulse (Table 4-7 and 4-8).

Summary of Salinity Pulsing Effects

Pulses of brackish (13 ppt) water to freshwater tidal marshes cause the most significant effects on the overall rate of SOC loss (Table 4-9). This type of salinity pulsing event, which is likely a common occurrence in low relief coastal zones experiencing an increase in the frequency of storm surges and extreme tidal events, caused a substantial short-term increase in CO_2 flux during LT (Figure 4-6). Although this increase in CO_2 flux is somewhat off-set by a decrease in CH_4 flux and DOC release (Table 4-9), soil respiration is the major pathway of SOC loss in all coastal wetlands (Figure 4-9), and alterations in soil respiration rates are a primary concern for maintaining SOC storage. Pulses of higher salinity water (26 ppt) in freshwater tidal marshes, which may be seen in narrower, high relief coastal zones, do not appear to have consequences for SOC cycling that are as severe as the brackish pulses (Table 4-9). This could be because the intensity of the ionic strength increase prevents any significant microbial response to the pulsing event.

Brackish marshes are a dynamic intermediate environment that tend to be dominated by organisms functioning as generalists (Van Ryckegem and Verneken 2005). As a consequence, pulses of either fresh (0.5 ppt) or salt (26 ppt) water elicit minimal changes to the biotic environment of a brackish marsh and the overall rate of SOC loss (Table 4-9; Figure 4-8).

A pulse of lower-salinity surface water in a salt marsh often occurs as a consequence of heavy rain events, urban run-off, or stormwater discharge. Fresh (0.5 ppt) water pulses can significantly accelerate SOC loss in salt marshes through both higher LT CO_2 flux (Figure 4-6) and increased DOC release (Table 4-9). In comparison, brackish (13 ppt) water pulses are not manifested as changes to the overall rate of SOC

loss, but do appear to increase the availability of labile C, which could have significant consequences for microbial activity over a longer time span. Since many salt marshes respond to SLR through a natural feedback loop that promotes vertical marsh accretion (Fagherazzi et al. 2012), the accelerated SOC loss caused by high volumes of freshwater urban run-off could diminish the ability of salt marshes adjacent to urban development to keep pace with SLR through vertical soil accretion.

Sea Level Rise Implications

Aside from salinity pulsing effects, this study also identified noteworthy differences in the influence of tidal cycles (duration of inundation) on coastal wetland SOC loss, which could have far-reaching repercussions for wetland C storage capacity during eustatic SLR. Results reported here suggest that as coastal marshes become more saline, carbon loss during LT becomes increasingly important (Figure 4-9). Using a simple linear model to extrapolate these findings to future tidal inundation patterns suggests total SOC loss from freshwater tidal marsh soils may increase with greater tidal inundation (Figure 4-10). In contrast, increased tidal inundation may decrease SOC loss in brackish and salt marsh soils. A decrease in the rate of SOC loss could allow more C to remain stored in the soils of brackish and salt marshes, but it is important to consider that C *inputs* will likely also be altered by SLR (Kathilankal et al. 2008). For example, one study found that tidal inundation significantly reduced C assimilation in a temperate salt marsh. Fully or partially submerging marsh vegetation decreased the rate of C fixation by approximately 46% compared to the control condition. Predicting the overall effect of SLR on a wetland's C balance requires a complete C budget to be calculated (including aboveground and belowground biomass and sediment deposition rates). Possibly the only study that has attempted to establish

a complete C budget in a coastal wetland impacted by saltwater intrusion was performed by Neubauer (2011) in a tidal freshwater marsh. Neubauer (2011) found that a 10 ppt increase in salinity *decreased* net ecosystem productivity (NEP) by 55%, while greater inundation *increased* NEP by 75%, resulting in no overall change when these two parameters (salinity and inundation) where combined.

Summary

Coastal wetlands function as large storage reservoirs for global C in the form of SOC. In the contiguous USA only, 25,000 km^2 of coastal (estuarine) wetlands sequester over 10 Tg C y^{-1} (Bridgham et al. 2006). The combined effects of global SLR and coastal urban development are well documented threats to the health and sustainability of coastal wetlands, as well as the SOC stored within them (DeLaune and White 2012; Craft et al. 2009). However, limited attention has been given to the short-term, dynamic fluctuations in salinity that occur in coastal wetlands as a result of storm surges, extreme tidal events, and urban stormwater discharge. This study found that the impact of salinity pulsing events on the rate of SOC loss in coastal wetlands depends upon: (1) changes in SO_4^{2-} availability relative to the ambient condition, (2) the accumulation of NH_4^+ following seawater additions, (3) the ability of freshwater to flush toxins and reduce ionic stress from saline soils, and (4) the size of the microbial community available to respond to the chemical changes in the environment.

Freshwater tidal marshes are highly sensitive to pulses of 13 ppt surface water. Brackish water accelerates soil respiration by increasing SO_4^{2-} reduction and coupled nitrification-denitrification of NH_4^+. Ammonium accumulates in the soil solution as a result of both abiotic processes (desorption for NH_4^+ from the cation exchange complex) and biotic processes (inhibition of nitrifiers and denitrifiers by Cl^-) initiated by the

addition of seawater. While some negative impacts of brackish pulses are also observed in freshwater soils (a decrease in methanogenesis and DOC release), the overall effect is an increase in the SOC mineralization rate. Erratic environmental fluctuations are more commonplace in brackish marshes and likely minimize the consequences of salinity pulsing events in this type of intertidal wetland. However, decreases in CO_2 flux with pulses of freshwater were observed in the brackish soil and attributed to decreased SO_4^{2-} availability. Salt marshes respond to freshwater pulses with accelerated SOC loss due to the flushing of accumulated toxins, a reduction in osmotic stress, and the stimulation of low levels of methanogenesis. The salt marsh soil used in this study also benefited from a large soil microbial community, which presumably allowed for quicker adaptation to changing environmental conditions.

The ability of intertidal wetland soils to drain quickly during ebb tides proved crucial to the overall rate of CO_2 flux in this study. High soil hydraulic conductivity, a function of both organic matter composition and the aggregation/dispersive forces of salts, tends to magnify tidal effects in saline wetlands and allow for increased aerobic respiration in brackish in salt marshes during LT. The difference in soil properties along natural salinity gradients could have important implications for eustatic SLR. An increase in the duration of inundation due to SLR may decrease the overall rate of SOC loss in brackish and salt marshes, while increasing the rate of SOC loss in freshwater tidal marshes.

DOC concentration was inversely correlated with salinity and predicted 69-93% of the difference in HT soil respiration rate and CH_4 flux. In contrast, NH_4^+ concentration and MBC were better predictors of CO_2 flux during LT. Low microbial metabolic

efficiency (high qCO_2) correlated with higher DOC release and predicted 92% of the total rate of SOC loss in this study.

Table 4-1. Intact core experimental design. The experimental was a 3 (wetland types) x 3 (salinity levels) x 3 (triplicate intact soil cores) mixed model design. An additional 3 soil cores from each of the 3 sites were analyzed immediately to establish initial/baseline conditions.

Wetland Type	Salinity Pulse (ppt)			Immediate analysis	Total No. Intact Cores
	0.5	13	26		
Freshwater (0.5 ppt)	3	3	3	3	12
Brackish (13 ppt)	3	3	3	3	12
Salt Marsh (26 ppt)	3	3	3	3	12
					36

Table 4-2. Intact core experimental timeline. The experiment lasted a total of 53 days and included 3 periods of ambient site water conditions (HT) and 3 salinity pulsing events (HT), each punctuated by a 24-hour dry-down period (LT). A total of 36 intact soil cores were collected (12 from each wetland type); 9 cores (3 from each wetland type) were sacrificed after the acclimation period to establish baseline conditions, while the remaining 27 (9 from each wetland type) were exposed to 3 salinity pulsing events.

Day	Event/Condition	Tidal Phase
1	*--All 36 intact soil cores collected--*	
2-8	Ambient site water	HT
9 & 10	Dry-down	LT
10	*--Initial 9 cores destructively sampled--*	
11-14	Salinity pulse	HT
15 & 16	Dry-down	LT
17-26	Ambient site water	HT
27 & 28	Dry-down	LT
29-32	Salinity pulse	HT
33 & 34	Dry-down	LT
35-44	Ambient site water	HT
45 & 46	Dry-down	LT
47-50	Salinity pulse	HT
51 & 52	Dry-down	LT
53	*--Final 27 cores destructively sampled--*	

HT= high tide; LT= low tide

Table 4-3. Intact core soil properties. Soil properties (mean ± standard deviation; n = 3) by wetland type and soil depth for the control condition. Different letters represent significantly different means ($p < 0.05$) based on a two-way ANOVA.

	Depth (cm)	Bulk Density ($g\ cm^{-3}$)	Organic Matter (%)	Total C (%)	Total N (%)
Freshwater	0-5	0.17 ± 0.10^{a}	40.7 ± 7.9^{ab}	19.8 ± 1.1^{a}	1.25 ± 0.03^{a}
	5-10	0.18 ± 0.01^{a}	43.8 ± 1.1^{ad}	19.9 ± 1.0^{a}	1.23 ± 0.03^{a}
	10-20	0.19 ± 0.01^{a}	42.8 ± 4.7^{abd}	19.8 ± 2.8^{a}	1.10 ± 0.06^{b}
Brackish	0-5	0.26 ± 0.02^{b}	33.7 ± 1.9^{bc}	13.5 ± 1.0^{b}	0.72 ± 0.06^{c}
	5-10	0.28 ± 0.01^{b}	32.2 ± 1.5^{bc}	12.5 ± 1.0^{b}	0.70 ± 0.02^{c}
	10-20	0.28 ± 0.01^{b}	28.7 ± 0.8^{c}	11.5 ± 1.3^{b}	0.66 ± 0.03^{c}
Salt Marsh	0-5	0.18 ± 0.02^{a}	43.2 ± 1.1^{abd}	17.9 ± 1.0^{a}	1.10 ± 0.01^{b}
	5-10	0.16 ± 0.02^{a}	51.6 ± 2.8^{d}	21.9 ± 1.6^{a}	1.13 ± 0.03^{b}
	10-20	0.17 ± 0.01^{a}	46.2 ± 3.0^{abd}	19.4 ± 1.6^{a}	1.07 ± 0.12^{b}

Table 4-4. Intact core surface water properties. Surface water properties (mean ± standard deviation; n = 12) for the *control condition* by wetland type. Different letters represent significantly different means ($p < 0.05$) based on a two-way ANOVA.

Wetland Type	Sulfate ($mg\ L^{-1}$)	Conductivity ($mS\ cm^{-1}$)	DOC ($mg\ L^{-1}$)	NH_4^+ ($mg\ L^{-1}$)	TKN ($mg\ L^{-1}$)	SRP ($mg\ L^{-1}$)
Freshwater	43 ± 6^{a}	1.0 ± 0.1^{a}	11.5 ± 2.1	0.19 ± 0.01^{a}	0.91 ± 0.12	0.16 ± 0.01^{a}
Brackish	1485 ± 172^{b}	20.5 ± 1.2^{b}	9.6 ± 2.6	0.03 ± 0.04^{b}	0.69 ± 0.09	0.07 ± 0.02^{b}
Salt Marsh	3199 ± 842^{c}	39.3 ± 1.8^{c}	8.3 ± 2.1	0.13 ± 0.05^{ab}	0.78 ± 0.18	0.04 ± 0.02^{b}

Table 4-5. Correlations for the control condition. Pearson's product correlation coefficients for variables associated with SOC loss for the *control condition* of each wetland type (Figure 4-3). For each variable, n = 9 and df = 7; at p = 0.05, r = 0.67, and at p = 0.01, r = 0.79.

	DOC Release	CH_4 Flux	qCO_2	SRP	Org-N	Salinity
CO_2 Flux at HT	0.83	0.69	0.92	0.89	0.85	-0.71
CO_2 Flux at LT	NS	NS	NS	NS	NS	NS
CH_4 Flux	0.93	-	NS	NS	NS	NS
DOC Release	-	0.93	0.67	0.81	0.85	-0.87

NS = not significant; HT = high tide; LT = low tide; DOC = dissolved organic carbon; SRP = soluble reactive phosphorus

Table 4-6. Correlations for the salinity pulsing events. Pearson's product correlation coefficients for variables associated with SOC loss for the *salinity pulsing event* treatments (Figs. 4 and 5). For each variable, n = 26 and df = 24; at p = 0.05, r = 0.39, and at p = 0.01, r = 0.50.

	DOC Release	CH_4 Flux	NH_4^+	qCO_2	SRP	MBC
CO_2 Flux at HT	0.73	0.51	NS	NS	0.57	NS
CO_2 Flux at LT	NS	NS	0.41	NS	NS	0.39
CH_4 Flux	0.69	-	NS	0.40	0.47	NS
DOC Release	-	0.69	-0.57	0.53	0.76	-0.39

NS = not significant; HT = high tide; LT = low tide; DOC = dissolved organic carbon; SRP = soluble reactive phosphorus; MBC = microbial biomass carbon

Table 4-7. Nutrient release for the control condition. DOC and nutrient release (mean ± standard deviation; n = 3) for the *control condition* of each wetland type. Significantly different means ($p < 0.05$) represented by different letters and based on a repeated measures two-way ANOVA.

Wetland Type	DOC *(mg L^{-1})*	NH_4^+ *(mg L^{-1})*	TKN *(mg L^{-1})*	Org-N *(mg L^{-1})*	SRP *(mg L^{-1})*
Freshwater	18.3 ± 2.8^a	0.18 ± 0.15^a	1.18 ± 0.30	1.00 ± 0.34^a	0.68 ± 0.50^a
Brackish	10.6 ± 2.1^b	0.16 ± 0.21^a	1.07 ± 0.24	0.91 ± 0.47^a	0.30 ± 0.28^a
Salt Marsh	7.6 ± 0.7^c	0.71 ± 0.44^b	1.33 ± 0.40	0.63 ± 0.17^b	0.01 ± 0.01^b

DOC = dissolved organic carbon; TKN = total kjeldahl nitrogen; SRP = soluble reactive phosphorus

Table 4-8. Microbial indicators for the control condition. Microbial indicators (mean ± standard deviation; n = 3) for the control condition of each wetland type (0-5 cm). Significantly different means ($p < 0.05$) represented by different letters and based on a two-way ANOVA.

Wetland Type	MBC *(mg kg^{-1})*	TLOC *(mg kg^{-1})*	LOC *(mg kg^{-1})*	qCO_2 *(mg CO_2-C kg^{-1} d^{-1}/ mg kg^{-1})*	ß-gluco-sidase *(mg MUF kg^{-1} h^{-1})*	Dehydro-genase *(mg TPF kg^{-1} h^{-1})*
Freshwater	706 ± 157[a]	901 ± 214[a]	170 ± 30	0.26 ± 0.14[a]	318 ± 139[a]	148 ± 25
Brackish	606 ± 187[a]	755 ± 175[a]	163 ± 23	0.21 ± 0.17[ab]	90 ± 25[b]	31 ± 11
Salt Marsh	2105 ± 159[b]	2345 ± 133[b]	245 ± 29	0.06 ± 0.01[b]	250 ± 27[ab]	165 ± 89

MBC= microbial biomass carbon; TLOC= total labile organic carbon; LOC= labile organic carbon

Table 4-9. Summary of salinity pulsing effects. Summary of the observed *salinity pulsing event* treatment affects on SOC loss, nutrient release, and microbial indicators.

Wetland Type	Salinity Pulsing Event	Observed Effect *compared to control condition*
Freshwater	Brackish (13 ppt) water	Increase in LT CO_2 flux ($p = 0.004$) Decrease in CH_4 flux ($p < 0.001$) Decrease in DOC release ($p = 0.006$) Increase in NH_4^+ release ($p = 0.02$) Altered partitioning of SOC loss ($p = 0.05$)
Freshwater	Salt (26 ppt) water	Decrease in CH_4 flux ($p < 0.001$)
Brackish	Fresh (0.5 ppt) water	Decrease in HT CO_2 flux ($p = 0.02$)
Brackish	Salt (26 ppt) water	No effect
Salt marsh	Fresh (0.5 ppt) water	Increase in LT CO_2 flux ($p = 0.02$) Increase in DOC release ($p = 0.006$)
Salt marsh	Brackish (13 ppt) water	Increase in MBC ($p < 0.001$) Increase in TLOC ($p < 0.001$)

LT = low tide; HT = high tide; DOC = dissolved organic C; MBC = microbial biomass C; TLOC = total labile organic C

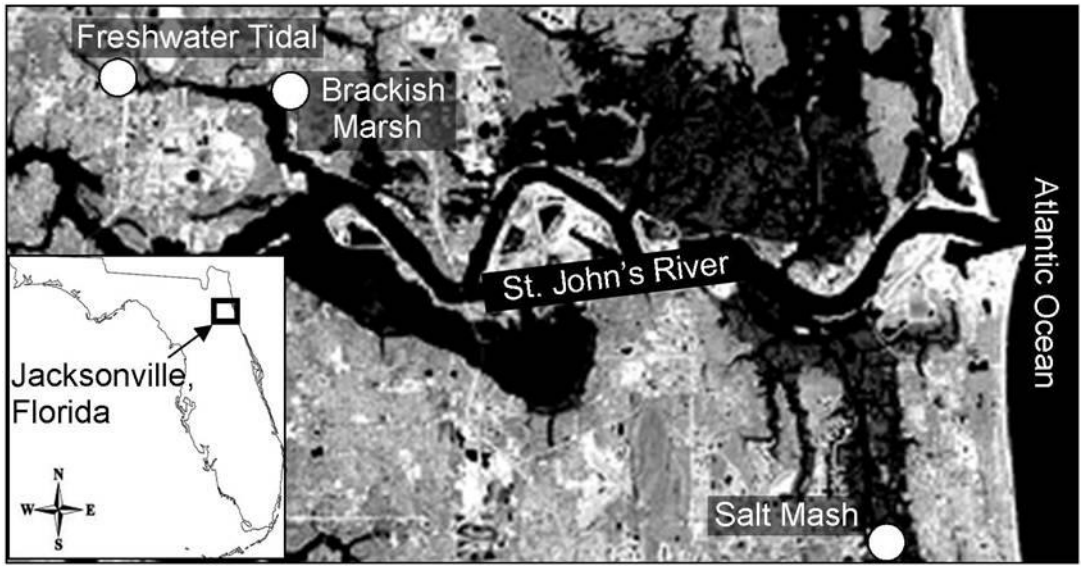

Figure 4-1. Site map. Aerial photograph indicating the approximate locations of each of the 3 wetland types in Jacksonville, FL, USA (see text for coordinates). All sites were associated with the St. John's River estuary.

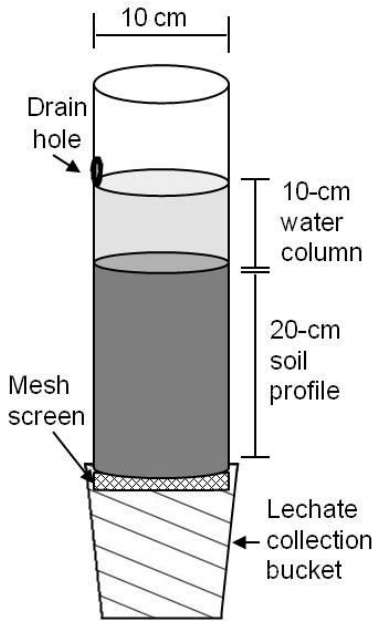

Figure 4-2. A schematic of the intact soil core design. The cores were stored in the dark at 25º C and remained open to the atmosphere. The bottom was sealed with a cap during high tide and all CO_2 flux measurements; the cap was removed and water allowed drainage to a leachate collection bucket during the ebb tide.

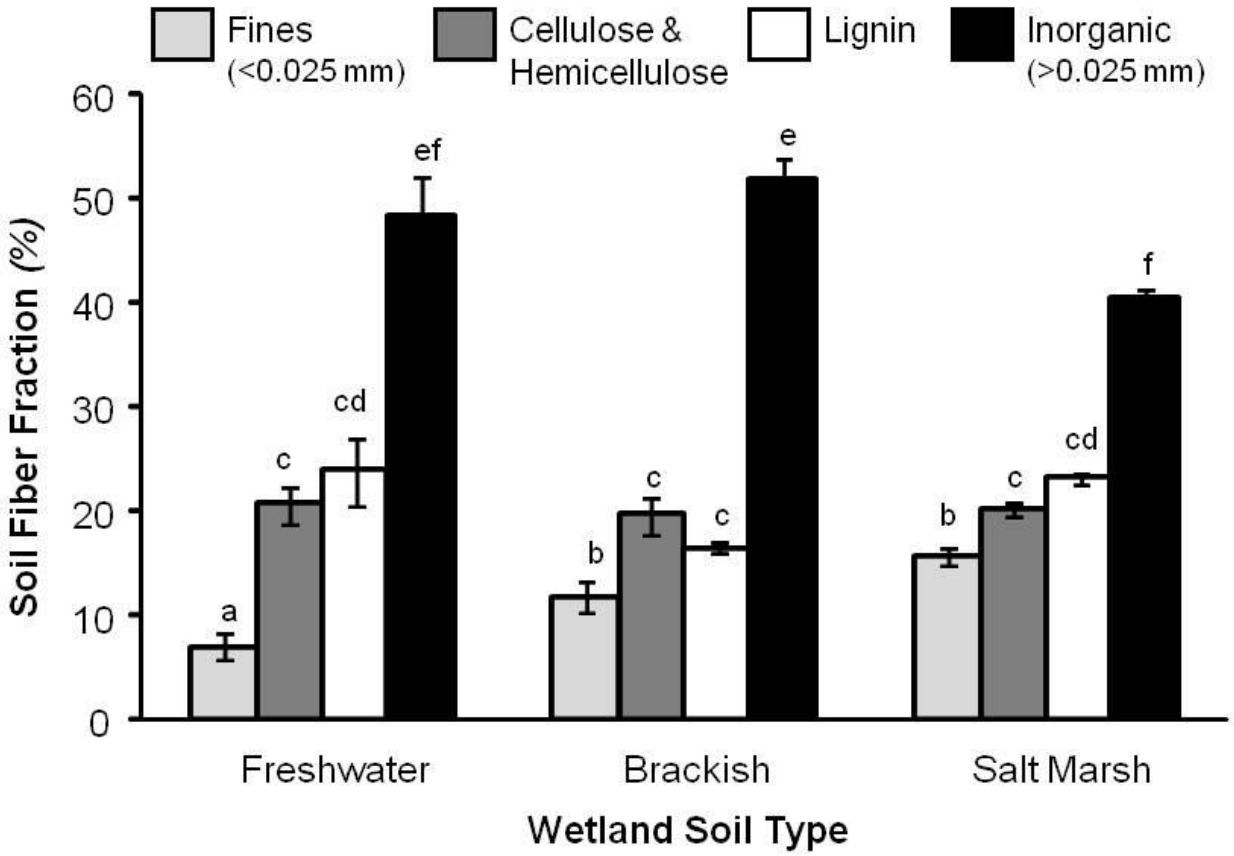

Figure 4-3. Soil fiber content. Percent fiber content in soils (0-10 cm) according to wetland type. Each bar represents mean percent of the *control condition* (n = 12); error bars represent standard error. Different letters represent significantly different means ($p < 0.05$) based on a one-way ANOVA.

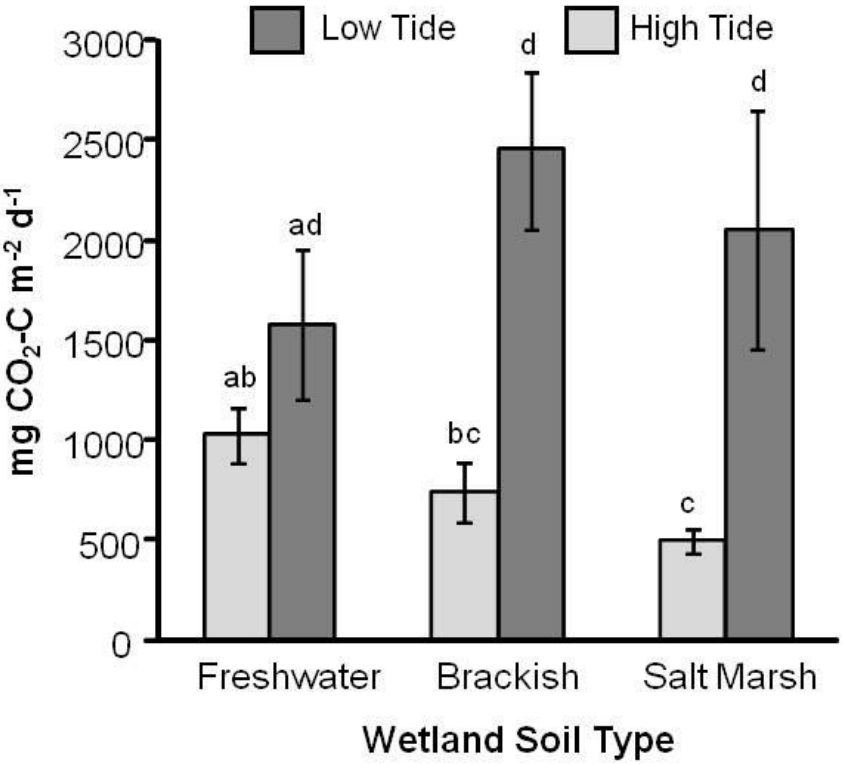

Figure 4-4. Tidal cycle effects on soil respiration. Effect of tidal cycle (low tide = post 24-h dry-down; high tide = 10 cm water column) on CO_2 flux rate according to wetland type. Each bar represents mean flux rate of the *control condition* (n = 9); error bars represent standard error. Different letters represent significantly different means ($p < 0.05$) based on a one-way ANOVA.

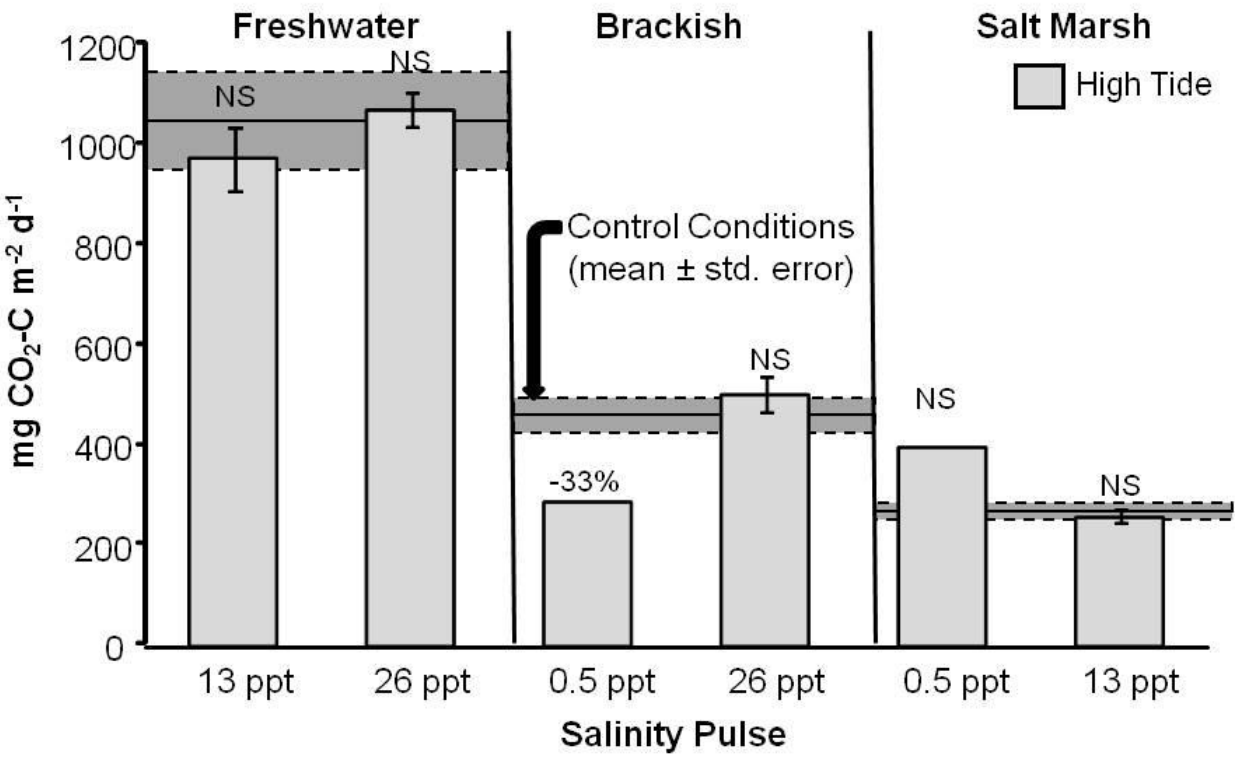

Figure 4-5. High tide salinity pulse effects on soil respiration. Effects of salinity pulse (high tide) on CO2 flux rate according to wetland type and surface water salinity. Horizontal bars represent mean (solid line) and standard error (dashed lines) of the control condition. Each bar represents mean flux rate (n = 18); error bars represent standard error; NS = not significantly different from the control condition; significantly different means ($p < 0.05$) represented by percentages and based on a two-way ANOVA.

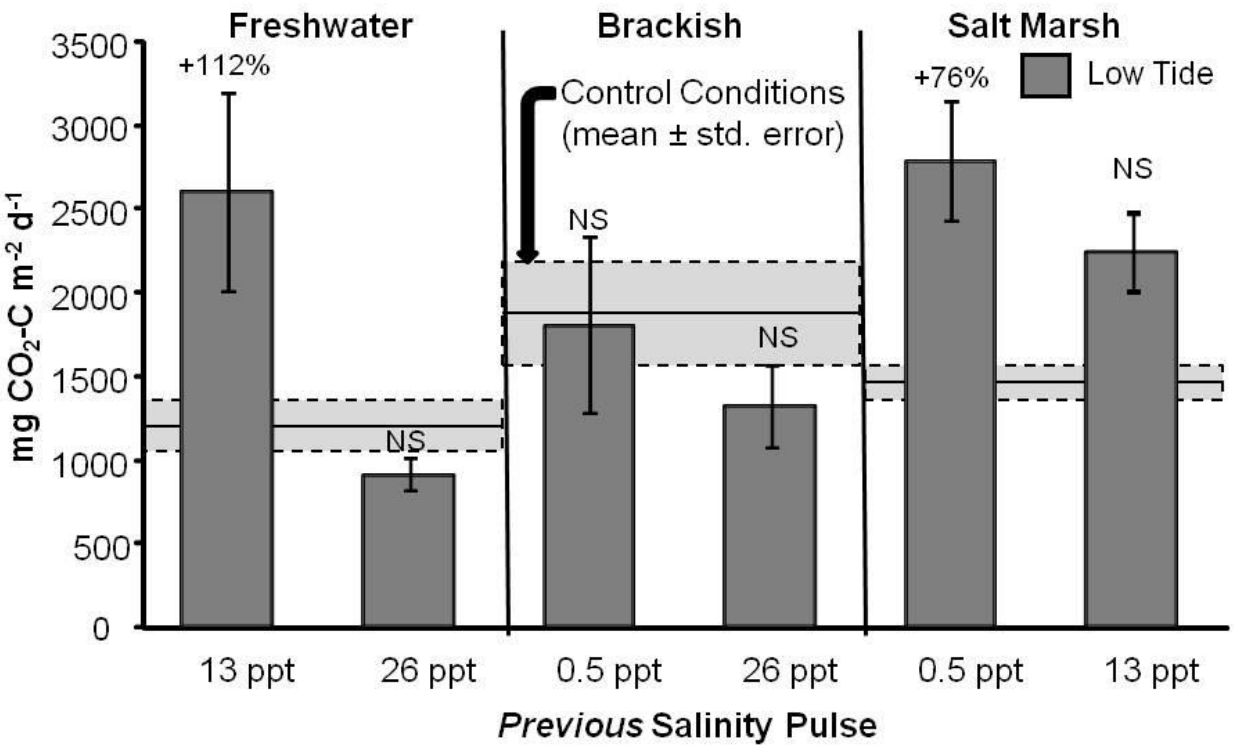

Figure 4-6. Low tide salinity pulse effects on soil respiration. Legacy effects of salinity pulse on subsequent low tide CO_2-C flux rate according to wetland soil type and pulse salinity. Horizontal bars represent mean (solid line) and standard error (dashed lines) of the control condition. Each bar represents mean flux rate (n = 18); error bars represent standard error; NS = not significantly different from the control condition; significantly different means ($p < 0.05$) represented by percentages and based on a two-way ANOVA.

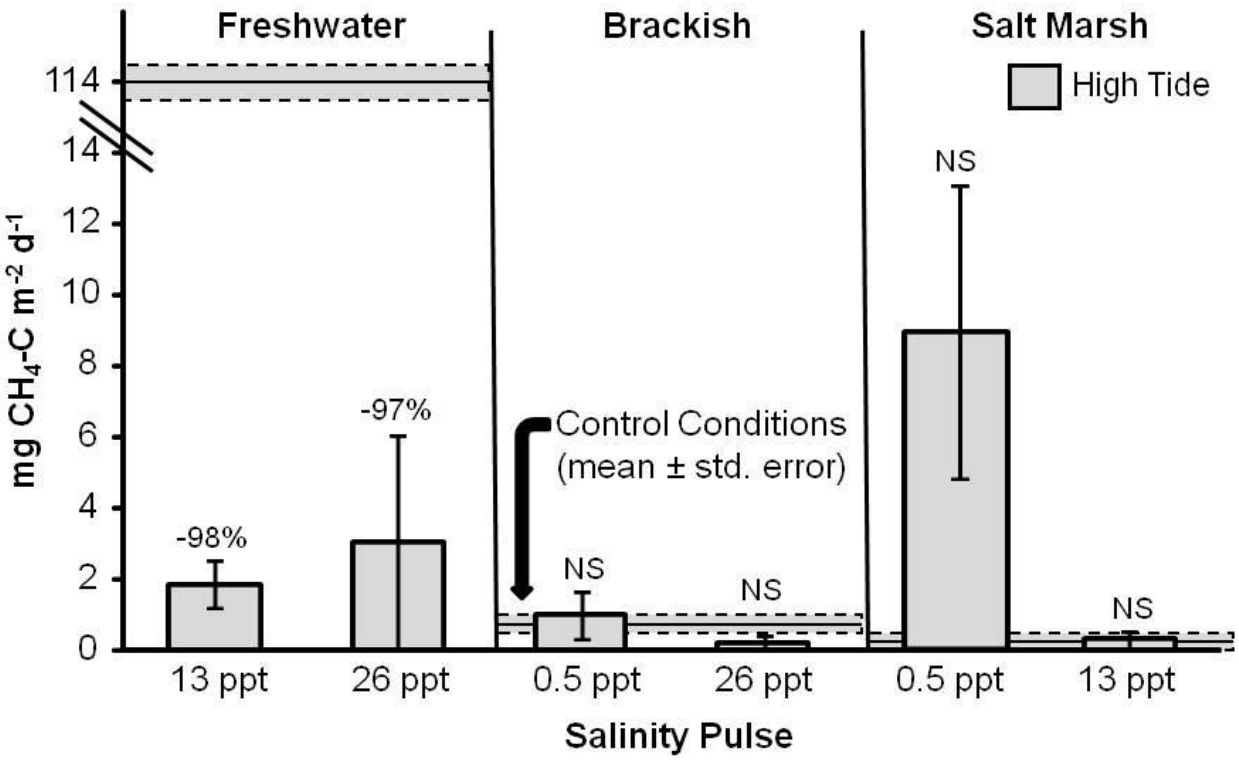

Figure 4-7. High tide salinity pulse effects on potential methanogenesis. Effects of salinity pulse (high tide) on CH_4-C flux rate according to wetland soil type and water salinity. Horizontal bars represent mean (solid line) and standard error (dashed lines) of the control condition. Each bar represents mean flux rate (n = 3); error bars represent standard error; NS = not significantly different from the control condition; significantly different means ($p < 0.05$) represented by percentages and based on a two-way ANOVA.

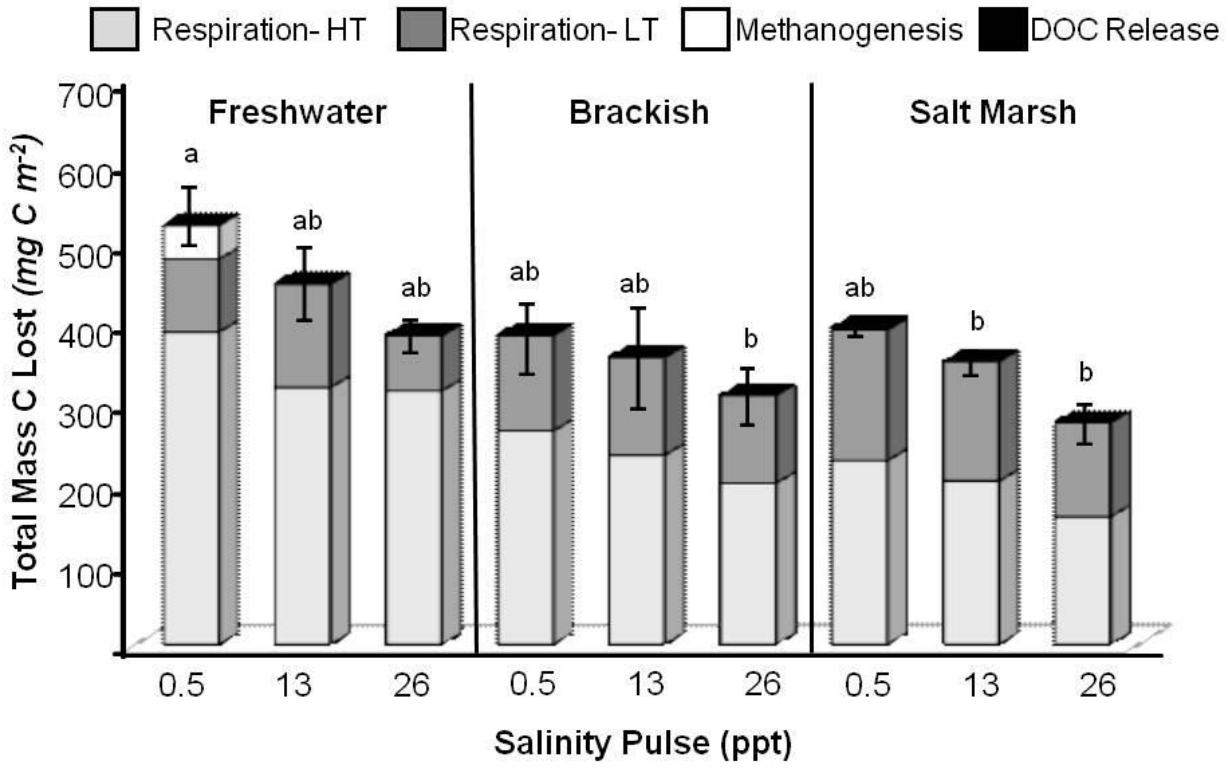

Figure 4-8. Total soil organic carbon loss. Mass of carbon lost (CO2-C + CH4-C, + DOC) during the 53 day laboratory experiment. Each bar represents mean mass C (n = 3); error bars represent standard error; significantly different means ($p < 0.05$) represented by different letters based on a two-way ANOVA.

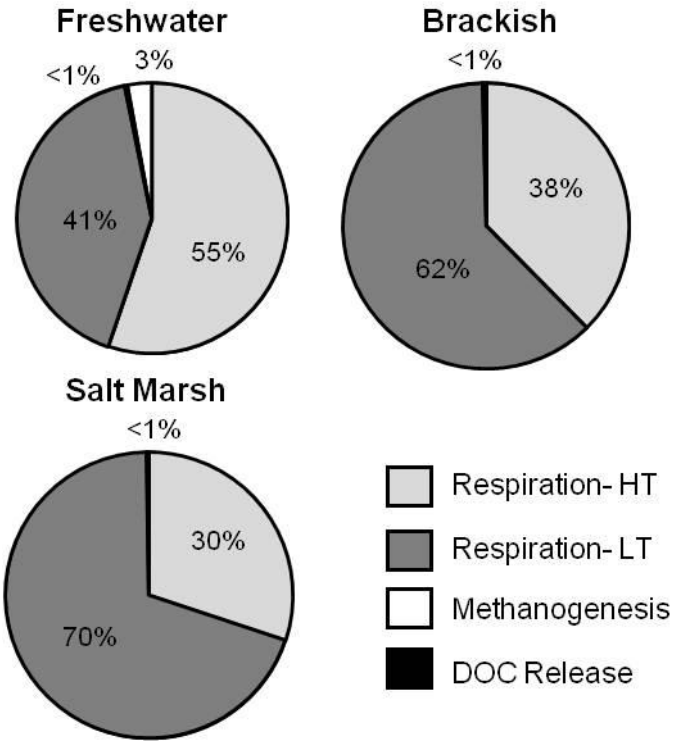

Figure 4-9. Soil organic carbon loss by pathway. Mean % of soil organic C lost by pathways (controlling for duration of measurement) according to soil type. Charts represent control condition (n = 3); the freshwater marsh soil treated with brackish (13 ppt) 'pulses' was the only treatment deviating significantly from its' respective control, according to a chi square goodness of fit ($p < 0.05$).

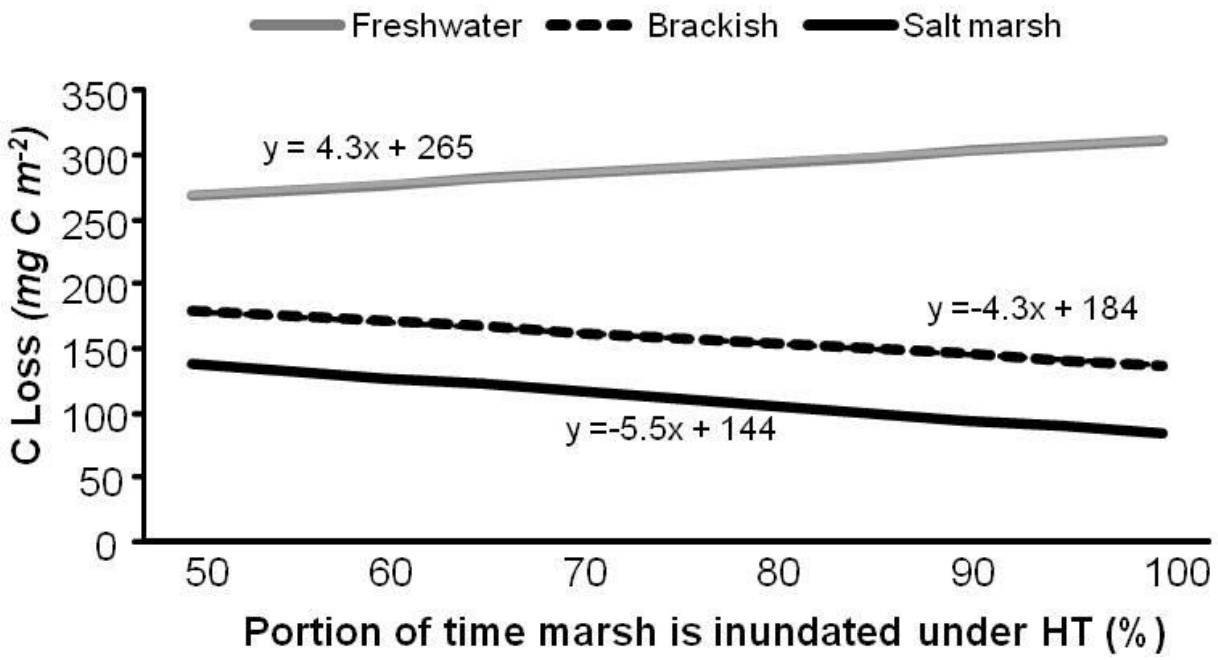

Figure 4-10. Modeled effects of increased inundation on soil carbon loss. A theoretical model indicating the effects of increased inundation (increased time of high tide (HT); decreased time of) on total soil organic C loss in 3 wetland types. Model projections assume current conditions are 50% HT, and 50% LT. The graph illustrates an increased to 100% of time under HT conditions and 0% under LT condition. Model assumes a linear response of soil respiration based on Figure 4-8 data.

CHAPTER 5
BIOGEOCHEMICAL EFFECTS OF SIMULATED SEA LEVEL RISE ON CARBON LOSS IN AN EVERGLADES PEAT SOIL

Background

Mangroves have higher rates of net primary productivity and carbon (C) sequestration than most forest ecosystems, with global estimates of 882,215 and 102,300 Mg C km^{-2} y^{-1}, respectively (Donato et al. 2011; Bouillon et al. 2008a). Despite the critical role of mangroves in global C cycling and storage, they are experiencing an areal loss of ~2% per year (Valiela et al. 2001). A substantial portion of this loss is due to human activities (e.g., development, wood harvest, mariculture), but environmental stressors also contribute. Being located on the land fringe means exposure to extreme environmental conditions, such as intense wave action, high winds, storm surges, and sea level rise (Alongi 2008).

The Everglades (south Florida) contains the largest mangrove forest in the contiguous USA (>1,400 km^{-2}) and overlies 5 to 6 m of peat soils (Welch et al. 1999; Spackman et al. 1966). Net ecosystem productivity in the mangroves of the Everglades is high, averaging about 1170 g C m^{-2} y^{-1}, but some characteristics of this expansive ecosystem are suggestive of a high vulnerability to submergence from sea level rise (e.g., low-relief carbonate geology and micro-tidal inundation; Barr et al. 2010 Alongi 2008; Nicholls et al. 1999). It is estimated that approximately half of Everglades National Park is currently within 0.3 and 0.6 m of sea level (Titus and Richman 2001). According to predictions by the Intergovernmental Panel on Climate Change (IPCC) for a “business as usual” scenario, eustatic sea level is expected to rise 0.2 to 0.6 m by 2100 (IPCC 2007).

All coastal wetlands, including mangrove forests, occupy a specific elevation niche relative to sea level and thrive when the marsh platform is between mean sea level and mean high tide (Morris et al. 2002). As sea level rises, coastal wetlands must maintain this ideal elevation by processes of vertical soil accretion or landward migration. Vertical accretion occurs through a natural feedback loop: increased tidal inundation enhances sedimentation, inorganic sediments accelerate primary production and organic matter accumulation, and the marsh platform accretes vertically to achieve a new equilibrium with sea level (Fagherazzi et al. 2012). This response of "keeping pace" with sea level rise (SLR) is most successful in coastal wetlands with low disturbance, adequate nutrient supply, sediment-rich coastal waters, and a moderate to large tidal amplitude (Nicholls et al. 1999). Landward migration is also a natural response to SLR observed in coastal wetlands with low relief, exposed to gradual changes in sea level, and with minimal adjacent development. During landward migration, the seaward edge of a wetland may submerge, but the wetland simultaneously expands landward to maintain the optimal degree of inundation and salinity with minimal loss of overall area (Adam 2002; Donnelly and Bertness 2001). If sea level rises too quickly and/or the local conditions do not support sufficient vertical accretion or landward migration, the wetland may experience decreased productivity, vegetation death, peat collapse, and eventual submergence (Nyman et al. 1990). Under current rates of SLR, it is predicted that between 20 and 30% of the world's coastal wetlands will be lost by the end of the century (IPCC 2007; Nicholls et al. 1999).

The ecological importance of the Everglades as a habitat for wildlife, epicenter of groundwater recharge, recreational haven, and provider of numerous other ecosystem

services (e.g., water quality improvement, nutrient cycling, and C storage) has generated a strong interest in the sustainability of the Everglades during SLR. Landward migration in response to SLR and freshwater inputs has been documented in the southeastern portion of the Everglades, near Taylor Slough. Here, vegetation zones have shifted as much as 3.3 km inland since 1940, as indicated by historic aerial photographs and biological indicators of past salinity regimes (Gaiser et al. 2006; Ross et al. 2000). Shark River Slough is a slow moving river that drains the majority of the Everglades, and tends to have higher nutrient availability, less groundwater influence, greater primary productivity, higher soil organic matter, and a larger tidal range than Taylor Slough (Rivera-Monroy et al., 2011; Ewe et al. 2006). This study sought to understand the fate of soil organic C in Shark River Slough under conditions of rising salinity, increased inundation, and the combination thereof.

Two possible fates of wetland soil organic C include: (1) decomposition and released back to the atmosphere as CO_2 and CH_4, or (2) loss via export within the water column as dissolved organic C (DOC) or dissolved inorganic C (DIC). The remaining C can remain stored in the soil for days to centuries.

Increasing surface water salinity from SLR introduces higher concentrations of sulfate (SO_4^{2-}) to the soil microbes of coastal wetlands. Sulfate is capable of functioning as an alternative electron acceptor during microbial respiration, resulting in the mineralization of soil organic C and the release of CO_2 to the atmosphere (Patrick and DeLaune 1977). Previous studies have found that increasing SO_4^{2-} availability in wetland soils can stimulate sulfate-reducing bacteria, and consequently accelerate the loss of CO_2 from the soil (Chambers et al. 2011; Weston et al. 2006b). However, high

SO_4^{2-} availability is also known to repress the activity of methanogens, decreasing the loss of CH_4 (DeLaune et al. 1983; Jackobsen et al 1981). Inundation is known to affect microbially-mediated C loss by creating anaerobic conditions under which microbial activity and efficiency is greatly reduced, and subsequently the rate of CO_2 loss also declines (Wright and Reddy 2001; DeBusk and Reddy 1998). In coastal wetland soils, inundation is inextricably linked to tidal cycle and the rate of CO_2 loss during low tide can be 53 to 310% greater than the rate observed in the same soils during high tide (Chapters 4 and 5). Despite a growing understanding of the effects of salinity (Chambers et al. 2011; Weston et al. 2011; Edmonds et al. 2009; Weston et al. 2006) and tidal cycle (Chapter 4; Neubauer et al. 2000) on coastal wetland C loss, there is still a significant gap in the understanding of the compounding effects of simultaneous increases in both salinity and inundation.

The goals of this study were to: (1) disentangle the effects of increased salinity, increased inundation, and the combination thereof, on soil C loss in an Everglades peat soil, (2) determine the effect of physical environmental factors (temperature, the rising and falling action of tides, and soil macroinvertebrates) on the rate of C loss, and (3) determine the impact of simulated sea level rise on porewater DOC and nutrient availability. Porewater nutrients are strongly coupled with nutrient export in mangroves and can significantly affect C mineralization rates (Bouillon et al. 2007).

I hypothesized that increasing salinity in this system, which is already mesohaline (~10-20 ppt) would not significantly alter the rate of C loss; increasing inundation by ~8 cm would reduce the overall rate of C loss; and the effect of increased salinity and inundation on C loss would be additive. I also expected that temperature and porewater

phosphorus (P) concentration (a limiting nutrient in this system) would be positively correlated with CO_2 flux. I tested these hypotheses by manipulating salinity and inundation for 24 field-replicate peat monoliths collected from Shark River Slough utilizing a tidal mesocosm facility.

Methods

Study Area

Twenty-four peat monoliths were collected in a mature mangrove forest adjacent to lower Shark River Slough (Figure 1; 25°21'52.7"N, 81°4'40.6"W; Florida Coastal Everglades Long-Term Research site SRS 6 (http://fcelter.fiu.edu/research/sites/)) in the SW Everglades (Florida, USA). The collection area is approximately 4 km inland from the Gulf of Mexico and experiences semi-diurnal tides (mean range of 1 m) and seasonally driven (June - Oct.) freshwater inputs (Rivera-Monroy et al. 2007). The forest is comprised of *Rhizophora mangle*, *Laguncularia racemosa,* and *Avicennia germinans* of large stature (10-14 m tall; Chen and Twilley 1999).

The peat monoliths (25-cm deep x 28-cm diameter) were removed from the ground intact, carefully placed in heavily perforated buckets (~16 holes of 3.5-cm diameter; Figure 5-2), and transported to an outdoor tidal mesocosm facility located at the Florida Bay Interagency Science Center (Key Largo, FL, USA). At the time of collection, ambient salinity at Shark River Slough was ~17 ppt.

Experimental Design

The experiment consisted of a randomized split-plot design with repeated observations. The two manipulated factors were salinity (the whole-plot factor with two nested blocks) and inundation (the sub-plot factor). Meanwhile, time (days) and water temperatures (º C) were recorded as potentially important covariant factors. The study

ran for 10 weeks, including a 3-week acclimation period, 1-week salinity ramp, and 6-week experiment.

Once the 24 peat monoliths were brought to the mesocsom facility from the field, standard window screen mesh was affixed to the outside of the buckets to allow for water exchange through the perforations while preventing the loss of soil material (Figure 5-2). Pneumatophores, when present, were clipped to the soil surface and any identifiable litter material was removed. The 24 monoliths were randomly assigned to 1 of 4 “crypts” (cement, water-proof containers, 0.74 m D x 0.80 m W x 2.21 m L) and 1 of 2 water levels. The monoliths assigned to the “control” water level treatment were placed on 7.6 cm tall risers, while those assigned to the “inundated” treatment were placed directly on the crypt floor. A 10-cm diameter PVC collar (10 cm long) was inserted near the center of each peat monolith (Figure 5-2) for placement of a portable 10-cm diameter gas chamber used to collect CO_2 and CH_4 flux measurements. The centralized placement of the collars reduced the likelihood of any soil profile disturbance within the sampling area. A porewater sipper was also inserted (through the side bucket perforations) into the center of each peat monolith at a depth of -10 cm from the soil surface (Figure 5-2). The sipper consisted of a 5 cm long air stone (1-cm diameter) attached to a 1-m long nalgene tube. Oxidation-reduction probes were also installed in a subset of monoliths at a depth of -10 cm. All four crypts were filled with ambient salinity surface water (15-20 ppt) and the monoliths were allowed to acclimate for 3 weeks while exposed to simulated semi-diurnal tides.

The outdoor Key Largo mesocosm facility was constructed in 1995 and consists of 12 large cement water tight crypts, each of which is equipped with a water inflow, a

stand pipe with a ball-value spigot to manipulate high tide (HT) and low tide (LT) water levels, and an outflow drain. Four ~9,500 L head tanks are located on an adjacent earthen mound and deliver water via gravity flow through a system of PVC pipes to a manifold. The manifold allows for the manual mixing of water from multiple head tanks, and the delivery of water to individual crypts. For this experiment, two head tanks were designated at “saltwater,” and were filled with surface water drawn directly from the adjacent Florida Bay (~60 m away) using a hydraulic pump and belowground system of PVC delivery pipes. The other two head tanks were designated as “freshwater,” and were filled with surface water transported via tanker-truck from the C-111 canal (~28 km north). Due to the challenge of maintaining constant head pressure in the tanks during the filling of the crypts, a double hartford loop was constructed using two of the unused crypts, two raised water barrels equipped with stand-pipe drains, and multiple aquarium pumps to circulate the water between the holding reservoirs.

Semi-diurnal tides (every 6 h) were run continuously throughout the entire study using a 20 cm tidal range. The control water level peat monoliths had a LT at -12.7 cm and a HT at +12.7 cm, relative to the soil surface, whereas the inundated treatment had a LT at -5.1 cm and HT at +20.3 cm. Following the 3-week acclimation period, the 2 crypts assigned to the elevated salinity treatment were gradually ramped-up to between 30-35 ppt for the remainder of the study. The remaining 2 crypts continued to receive ambient salinity (15-20 ppt) surface water. All crypts were partially shaded with three layers of mesh window screen to simulate the diffuse sunlight penetration of a natural mangrove canopy.

Soil and Water Properties

Soil properties were determined for 5 initial soil cores (5-cm diameter x 25-cm deep) collected at the same time as the peat monoliths. At the conclusion of the 10-week study, all 24 peat monoliths were destructively sampled for an analysis of soil properties. During destructive sampling, monoliths were cored at the same location the soil collars were previously installed using a 10-cm diameter, 25-cm long PVC tube. The soils were divided into 3 depth segments (0-5, 5-15, and 15-25 cm) and analyzed for % moisture, bulk density, % organic matter, total C, and total N. Moisture content and bulk density were determined after drying a subsample at 70° C to a constant weight. Percent organic matter was estimated by mass loss on ignition (LOI) where dry soils were combusted at 550° C for 5-h and final weight was subtracted from initial weight. Total C and N content were determined using a Carlo Erba elemental analyzer (CE Elantech, Inc., Lakewood, NJ).

Surface water salinity and temperature in the crypts was recorded twice daily at HT using a handheld YSI (YSI Inc., Yellow Springs, OH). General water quality parameters (NO_3^-, NH_4^+, SRP, and DOC) of the source water were gathered from near-by long-term monitoring locations (SFWMD 2012).

CO_2 and CH_4 Flux

Soil respiration (CO_2 flux) was measured ~3 times per week at daytime LT for all 24 soils using a portable infrared gas analyzer (Li-Cor 8100, Lincoln, NB) equipped with a 10-cm diameter chamber. Each flux rate was collected for 75 seconds before manually moving the chamber to another sample collar. Nighttime CO_2 flux was measured once per week on all monoliths at LT using the same procedure as just discribed. Rising and falling tide CO_2 flux measurements were also obtained once per

week on a sub-set of 12 soils for the 3 hours directly proceeding and following the daytime LT. This involved 3-6 consecutive flux readings on each monolith as the tide was rising and falling while concurrently measuring and recording the exact height of soil exposed above the water line at the time of each reading.

Methanogenesis (CH_4 flux) was measured once a week on a sub-set of monoliths using the 10-cm diameter chamber and a trace gas sampling kit (Li-Cor 8100-664, Lincoln, NB) which allowed of in-line gas extraction. For each monolith sampled, the chamber was sealed for 20 min and a 5-mL gas sample was extracted at 5-min intervals and transferred to a 5-mL glass vial (previously capped with a butyl stopper and aluminum crimp-cap and evacuated to -75 kpa). Within 48 h of collection, CH_4 gas samples were run on a gas chromatograph (Shimadzu Scientific Instruments GC 8A, Columbia, MD) fitted with a flame ionization detector (FID). Methanogenesis was calculated as the slope of CH_4-C concentration over time.

DOC and Porewater Nutrients

Soil porewater (60 mL) was extracted from the porewater sippers (10 cm below the soil surface) once per week during HT from each of the monoliths by applying suction with a plastic syringe. Water was field filtered through 0.45 µm filter paper, transferred to a 60-mL nalgene bottle, and stored at -20º C prior to analysis (within 30 d). Porewater was analyzed for NO_3, NO_2, NH_4^+, soluble reactive P (SRP), and DOC at the Southeastern Environmental Research Center Nutrient Analysis Laboratory (Florida International University, Miami, FL). Nitrogen and phosphate were analyzed on a four-channel Alpkem RFA 300 auto-analyzer (OI Analytical, College Station, TX) and DOC was analyzed on a Shimadzu 5000 TOC (Shimadzu Scientific Instruments, Columbia, MD).

Data Analysis

Statistical analysis was performed using SAS 9.1 software (SAS Institute Inc., Cary, NC). A heteroscedastic split-plot repeated measures linear mixed model (Proc GLIMMIX) was developed to test mean differences and interactions between the 4 main factors of interest: salinity, inundation, time, and temperature. The random effects of crypt and replication were also included in the model, along with an auto-regression coefficient that improved model fit. Response variables included: day and night CO_2 flux, DOC, and porewater nutrients. Where time and temperature were not significant factors, such as with methane flux, a two-way ANOVA (Proc GLM) was used. Pearson's Product correlations were calculated to determine correlation coefficients between CO_2 flux, DOC production, porewater nutrients, and environmental variables. All analyses were performed using a significance factor of $\alpha = 0.05$.

Results

Soil and Water Properties

Soil redox potential at -10 cm indicated all soils were under reduced conditions (Figure 5-3). The only treatment that showed a significantly different redox potential between HT and LT was the control water level-elevated salinity treatment (-72 mV at LT and -166 mV at HT). The inundated-ambient salinity treatment had the lowest average redox potential, with an average Eh of -195 mV.

The soil bulk density was 0.24 ± 0.4 g cm^{-3} (mean ± standard deviation) at 0-5 cm, which was significantly higher ($p < 0.001$) than deeper in the soil profile (5-25 cm, 0.17 ± 0.2 g cm^{-3}). After the 10-week study, soils subjected to the increased inundation treatments had significantly lower surface soil (0-5 cm) bulk density (0.20 ± 0.3 g cm^{-3}) than soils maintained at the control water level-ambient salinity treatment ($p = 0.009$;

Figure 5-4). Fiddler crabs (*Uca pugnax*) were inadvertently brought to the mesocosm facility in the peat monoliths. Crab colonization (as indicated by the number of visible burrow holes in the soil surface) was significantly greater in the inundated-ambient salinity treatment (10 ± 4) compared to the inundated-elevated salinity treatment ($p = 0.04$; 4 ± 3) and had a weak negative correlation ($p = 0.08$) with surface soil bulk density.

Average organic matter content in the peat soils was 53 ± 7%, total N averaged 1.3 ± 3%, and total C averaged 22 ± 4%. All three properties were significantly lower ($p < 0.05$) is the surface soil (0-5 cm) compared to deeper in the soil profile (5-25 cm) and were not affected by the inundation or salinity treatment (Table 5-1). Soil pH was between 7.8 and 8.0.

All 4 crypts maintained salinities between 15 and 20 ppt for the first 3 weeks of the study (the acclimation period). During the 4th week, the crypts assigned to the elevated salinity treatment were slowly ramped-up (~2 ppt d^{-1}) to 30-35 ppt, and remained within that salinity range for the remaining 6 week study period. The freshwater (trucked-in from the C-111 canal) had a salinity of <0.5 ppt throughout the study period, while the saltwater (collected directly from Florida Bay) began at ~42 ppt and decreased to ~34 ppt by the conclusion of the study. This decrease was due to the onset of the wet season causing lower salinities in all of Florida Bay. Nutrient concentrations were significantly higher in the fresh source water (Table 5-2), but were always diluted by mixing with saltwater to achieve the ambient (15-20 ppt) and elevated (30-35 ppt) salinities used in the experiment.

CO_2 and CH_4 Flux

Daytime LT CO_2 flux rate was significantly lower in the inundated treatments (644 ± 442 mg CO_2-C m^{-2} d^{-1}) compared to the control water level treatments (987 ± 618 mg CO_2-C m^{-2} d^{-1}; $p < 0.0001$), but the main effect of salinity was not significant during the day ($p = 0.4$; Figure 5-5). The response of CO_2 flux rate to inundation differed according to the salinity treatment (inundation*salinity effect; $p < 0.0001$), with the highest average daytime CO_2 flux observed in the control water level-elevated salinity treatment (1189 ± 699 mg CO_2-C m^{-2} d^{-1}), followed by control water level-ambient salinity (770 ± 426 mg CO_2-C m^{-2} d^{-1}), inundated-ambient salinity (663 ± 419 mg CO_2-C m^{-2} d^{-1}), and inundated-elevated salinity (624 ± 484 mg CO_2-C m^{-2} d^{-1}) treatments. Nearly all of the variability in CO_2 flux rate not explained by the main effects of salinity and inundation were explained by time ($p < 0.0001$; Figure 5-6) and water temperature ($p < 0.0001$; Figure 5-7). Time produced a significant non-linear effect on CO_2 flux and within-treatment variance in CO_2 flux decreased with time (Figure 5-6). The effect of water temperature on CO_2 flux was dependent upon inundation level (temperature*inundation effect, $p = 0.009$), and revealed a polynomial relationship with a steeper slope in the control water level treatment, compared to the inundated treatment (Figure 5-7).

Nighttime CO_2 flux showed a similar pattern to daytime flux with significantly lower flux rates in the inundated treatments ($p < 0.0001$), an overall decrease in CO_2 flux over time ($p < 0.0001$), and a significant interaction between inundation and salinity ($p = 0.02$). However, salinity was a significant main effect for CO_2 flux at night ($p = 0.02$), with the elevated salinity treatment (1134 ± 731 mg CO_2-C m^{-2} d^{-1}) being higher than the ambient salinity treatment (940 ± 610 mg CO_2-C m^{-2} d^{-1}). On average,

nighttime CO_2 flux rate was ~20% higher than daytime flux rate, indicating the presence of photosynthetic activity within the soils during the experiment.

Rising and falling tides did not result in significant differences in the response of CO_2 flux rate. The slope (change in CO_2 flux rate/ change in cm of soil exposed above the waterline) was highest in the control water level treatment (93 to 121 mg CO_2-C m^{-2} d^{-1}) and lowest in the inundated-elevated salinity treatment (42 to 51 mg CO_2-C m^{-2} d^{-1}), but was not significantly different when the tide was rising versus falling (Table 5-3).

Methane flux was significantly lower in the control water level-ambient salinity treatment than all other treatments ($p = 0.001$; Figure 5-8). On average, the inundated-ambient salinity treatment had the highest flux rate (27 mg CH_4-C m^{-2} d^{-1}) and all treatments had high within treatment variance.

DOC and Porewater Nutrients

Porewater DOC was significantly greater (linear mixed model; $p = 0.04$) in the inundated treatments (17.4 ± 7.2 mg L^{-1}) compared to the control water level treatments (13.3 ± 4.7 mg L^{-1};Table 5-4). The response of DOC not explained by the main factors of salinity and inundation, were explained by a positive relationship with porewater salinity (continuous variable; $p = 0.008$) and water temperature ($p < 0.0001$). Porewater nitrite, ammonium, and SRP were all positively correlated with DOC, while CO_2 flux rate was inversely correlated with DOC (Table 5-5).

Porewater nitrate concentration showed a significant non-linear relationship with time and water temperature (both $p < 0.0001$). Neither inundation nor salinity caused a significant response in NO_3^- concentration, but the control water level-ambient salinity treatment had, on average, the highest porewater NO_3^- (1.65 ± 0.29 mg L^{-1}; Table 5-4). There was no difference between treatments in terms of NO_2 concentration (averaging

0.25 ± 0.25 mg NO_2 L^{-1}), but nitrite was affected by time and water temperature (both $p < 0.0001$). Nitrite concentration was positively correlated with the other N-species (NO_3^- and NH_4^+), DOC, salinity, and SRP, but inversely related to CO_2 flux (Table 5-5).

Ammonia concentration was moderately affected ($p = 0.08$) by inundation and significantly affected by the interaction between salinity and inundation ($p = 0.003$), with the inundated-elevated salinity treatment having the highest average NH_4^+ porewater concentration (287.7 ± 78.5 mg L^{-1}; Table 5-4). Ammonium concentration was positively correlated with DOC, salinity, NO_2, and SRP, and inversely related to CO_2 flux (Table 5-5).

Soluble reactive phosphorus concentrations in the porewater were significantly affected by inundation ($p = 0.0002$), with the inundated treatment averaging 9.8 ± 5.2 mg SRP L^{-1} and the control water level treatment averaging 7.0 ± 5.5 mg SRP L^{-1}. A significant interaction between salinity and inundation was also found ($p = 0.04$) with the inundated-elevated salinity treatment having the highest SRP concentration 12.0 ± 3.0 mg L^{-1}. SRP concentrations increased over time and were positively correlated with DOC, salinity, NH_4^+ and NO_2 (Table 5-5).

Discussion

Soil and Water Properties

Sulfate reduction is the dominate pathway for soil respiration in saline wetlands, accounting for 70 to 99% of C mineralization and typically occurring at redox potentials between -100 and -150 mV (Kostka et al. 2002; Howarth 1984; Patrick and DeLaune, 1977). The peat soils of this study were poised for sulfate reduction (Figure 5-3), with the inundated-ambient salinity treatment (and the control water level-elevated salinity

treatment during HT) being reduced enough to support methanogenesis (<-150 mV; Patrick and DeLaune 1977).

Placed at a depth of -10 cm, the redox probes were above the elevation of the waterline in the control water level treatments during LT, but below the waterline in the inundated treatments during LT. Only the control water level-elevated salinity treatments demonstrated significantly different redox potentials between high and low tides (Figure 5-3), suggesting a relatively low hydraulic conductivity in these soils. Peat soils consisting of highly decomposed organic matter, such as those used in this study, have the ability to retain water against the pull of gravity due to great capillary tension in the micropore spaces (Boelter 1965) and can decrease the importance of tidal fluctuations in coastal wetlands by continuing to promote anaerobic conditions even during LT conditions (Chapter 4). In this study, the average increase in CO_2-C flux rate between HT and LT was 83 ± 10% in the control water level treatments and 57 ± 19% in the inundated treatment. The magnitude of this tidal effect on soil respiration rate is comparable to that observed in a freshwater tidal marsh soil with a similar tidal range, but significantly lower than that of a brackish and salt marsh soil, also of a similar tidal range, which demonstrated a 230-310% increase in CO_2 flux from HT to LT (Chapter 4).

Soil bulk density is an indicator of a soils' physical structure (% pore space/ % soil material). In coastal wetlands, significant *increases* in surface soil bulk density are associated with subsidence and peat collapse, whereby pore space is lost when root death reduces the strength of the soil's structural elements, causing compaction (Franzen 2006; Kool et al. 2006; Portnoy and Giblin 1997). This study found a significant *decrease* in surface soil bulk density (0-5 cm) over just a 10 week period in

the inundated treatment, compared to the control water level-ambient salinity treatment (Figure 5-3). Intuitively, it is possible a decrease in soil bulk density might immediately precede peat collapse and compaction. Correlations between decreased soil bulk density, sudden die-back of *Spartina alterniflora*, and longer inundation periods have been noted in the submerging salt marshes of coastal Louisiana (Stagg and Mendelssohn 2010). Vegetation was removed in the present study, and although the severing and death of root structures during the collection of the peat monoliths may have impacted the soil's structural integrity, this does not explain why the inundated treatment soils, in particular, experienced a significant decline in bulk density. One explanation may be abiotic processes, such as increased shear stress or water turbulence when the depth of the water column increased, which has been observed along tidal creeks as water level rises (Fagherazzi et al. 2012). Excessive water-logging has also been shown to reduce soil redox potential and accelerate leaching of certain soil elements, such as iron (Stagg and Mendelssohn 2010; Craft et al. 2002), and may have contributed to a decline in soil material.

The activity of fiddler crabs inadvertently brought from the field to the experimental mesocosms within the peat monoliths are suspected to have played a role in the reduction of the soil bulk density in the inundated treatment. Fiddler crabs can directly reduce the soil bulk density through the construction of burrows within the soil profile, but also ingest and excrete sediments when scavenging for microalgae and other food sources. Over time, the 'processing' of the soil by fiddler crabs likely reduced the structural integrity in the surface soil, creating a 'mushy' film of unconsolidated soil material on the surface of the monolith that was easily sloughed-off with the rising and

falling of the tides. Observation indicated the development of an unconsolidated soil layer that was more prevalent on the inundated monoliths; the sloughing of soil material was also observed to be extensive. The split-plot experimental design prevented the quantification of DOC *export* according to water level treatment, but a weak (p = -0.08) correlation between surface soil bulk density and the number of fiddler crab burrows supports the hypothesis that this macroinvertebrate played a role in reducing soil bulk density. A study conducted in a South Carolina salt marsh found an inverse relationship between the number of fiddler crab burrows, vegetation health, and soil stability (Hughes et al. 2009).

CO_2 and CH_4 Flux

Daytime CO_2 flux was, on average, 34% greater in the control water level treatment, compared to the inundated treatments (Figure 5-5). At LT, 13 cm of soil was exposed above the waterline in control water level treatments, compared to 5 cm exposed in the inundated treatments. The alleviation of electron pressure (i.e., increased O_2 diffusion) during LT is likely the main factor contributing to the difference in CO_2 flux in the two water level treatments (Wright and Reddy 2001; DeBusk and Reddy 1998).

The increase in salinity from 15-20 ppt (ambient) to 30-35 ppt (elevated) alone did not cause a significant change in CO_2 flux during the daytime measurements (p = 0.4), but did significantly affect CO_2 flux at night (p = 0.004). Among all the treatments, average nighttime CO_2 flux was ~20% greater than daytime rates, but the control water level-ambient salinity treatment, in particular, had the greatest difference between day and night flux rates (28%). This suggests photosynthetic activity in the control water level-ambient salinity treatment was greater than the others, possibly due to the

combination of lower ionic stress (lower salinity), greater flushing (larger tidal range), and higher nutrient availability. Nutrient availability was slightly higher in the ambient salinity treatment because it received a larger proportion of water from the freshwater source (during the on-site water mixing), and the freshwater source contained higher N and P concentrations than the saltwater source (Table 5-2). Ammonium and P, in particular, are limiting nutrients for algal production in coastal waters; concentrations of these nutrients were 22 times higher in the fresh source water than the salt source water, possibly promoting higher rates of photosynthesis in the ambient salinity treatment (Boyer 2006; Howarth 1988). Therefore, removing the effects CO_2 fixation by measuring flux rates after dark revealed salinity does exert a significant main effect on soil respiration, but was likely confounded by higher photosynthetic activity during the day.

Increasing both salinity and inundation simultaneously caused the greatest decline in average CO_2 flux rate (Figure 5-5). When considered individually, elevated salinity stimulated CO_2 flux relative to the control, and inundation only slightly suppressed it, so the fact that the inundated-elevated salinity treatment had the lowest average CO_2 flux rate was surprising. Higher salinities have been shown to increase the rate of sulfate reduction and enhance soil respiration (Chambers et al. 2011), but the byproducts of sulfate reduction (HS^- and S^{2-}) can be toxic to plants and microorganisms (Joye and Hollibaugh 1995; Koch et al. 1990). Tidal flushing is critical to the removal of deleterious sulfide compounds (King et al. 1982) and wetland soils with low flushing often develop microzones where SO_4^{2-} becomes depleted and methanogenesis becomes the dominate pathway for C mineralization (King and Wiebe,

1980). In the present study, CH_4 flux was greater in the inundated treatment, compared to the control water level-ambient salinity treatment (Figure 5-8), indicating that the inundated treatment contained more microzones of SO_4^{2-} depletion, lower redox potential (Figure 5-3), and presumably greater sulfide accumulation due to the smaller tidal range and reduced flushing. The synergistic decline in CO_2 flux when salinity and inundation increase simultaneously is an important consideration when predicting the fate of coastal wetland C storage as sea level rises. For example, SLR responses in some coastal wetland areas, such as Taylor Slough, appear to be driven more-so by changes in salinity (Ross et al. 2000), whereas saline marshes already receiving full-strength seawater are more likely to experience changes driven by inundation (Kirwan and Temmerman 2009). Coastal wetlands experiencing both salinity and inundations drivers will be subject to a synergistic decline in the rate of soil C cycling.

Another question this study sought to answer was whether the physical process of a tide rising, versus falling, has an impact on CO_2 flux rate. For example, does the upward momentum of a rising tide push additional CO_2 out of the pore space and therefore accelerate the rate of CO_2 flux? Quantifying the relationship between the instantaneous CO_2 flux rate and the exact height of soil above the waterline during rising and falling tides revealed no significant effect of rising and falling tides on CO_2 flux rate (Table 5-3). However, the lack of difference may have been a consequence of the exclusion of vegetation from the study. Wetland plants are known to translocate and release O_2 and CO_2 from their roots, causing a build-up of gases in the soil that may be physically expelled from the soil during a rising tide. Therefore, this question of rising vs. falling tidal impacts on CO_2 flux should be revisited in a coupled soil-plant system.

Methane flux rates were measured during LT and had a strong correlation with LT redox measurements (r = -0.94; Figs. 5-3 and 5-8). As expected, all CH_4 flux rates were low (between 0.2 and 27 mg CH_4-C m^{-2} d^{-1}) because the abundant SO_4^{2-} in seawater favors the more energy efficient process of sulfate reduction over methanogenesis (Jackobsen et al. 1981). The average methane flux rate in a coastal Louisiana salt marsh was 11.8 mg CH_4-C m^{-2} d^{-1} (DeLaune et al. 1983), which is comparable to the present study. However, in mangroves the pneumatophores are thought to contribute significantly to CH_4 flux by providing labile C substrates; the removal of pneumatophores from this study may have caused a 12-50% underestimation of CH_4 flux rates (Laanbroek 2010).

DOC and Porewater Nutrients

Porewater DOC ranged from 12 to 18 mg DOC L^{-1}, which is slightly higher than reported for other mangroves (e.g., 5 to 10 mg DOC L^{-1} for a mangrove forest in Tanzania; Bouillon et al. 2007). Dissolved OC was significantly greater in the inundated treatment, compared to the control water level treatment ($p = 0.04$). Past studies have found higher DOC concentrations in high marsh (less inundated) areas, than in low marsh areas (Cao et al. 2008) and higher porewater DOC during LT than HT (Bouillon et al. 2007). However, no studies have looked at differences in porewater DOC (or DOC export) as a function of SLR (Henman and Poulter 2008).

It is estimated that wetlands account for ~20% of all DOC export to the ocean (Lugo et al. 1989) and the greater the tidal range, the greater the proportion of C lost to the ocean (Twilley et al. 1992). Previous research has estimated that ~30% of porewater DOC is advected and exported during the ebb tide (Bouillon et al. 2007). If this figure is applied to the current data, an increase in relative water level of 8 cm will

cause the export of *porewater* DOC in Shark River Slough to increase from an average of 4 mg L^{-1} to 5.2 mg L^{-1}. Past estimates of *total* DOC export from Shark River Slough during the summer months range from 8 to 11 mg L^{-1} (Romigh et al. 2006).

The impact of salinity and inundation on N cycling in coastal wetland soils is of interest due to the importance of N in coastal eutrophication and the role of nitrate as an alternative electron acceptor during C cycling. Salinity increases between 0 and ~10 ppt are known to cause the release of significant amounts of NH_4^+ from the soil cation exchange complex into the porewater, but once the salinity has passed a threshold of ~10 ppt, the influence of this abiotic process is believed to be greatly diminished (Baldwin et al. 2006; Weston et al. 2006b; Rysgaard et al. 1999). This is corroborated by the present study, which showed no significant increase in porewater NH_4^+ with elevated salinity (Table 5-4). However, this study did find evidence of increased NH_4^+ concentrations when the affects of inundation and elevated salinity were combined. Under long periods of inundation, NH_4^+ accumulates in the porewater because the anaerobic conditions prevent nitrification (the oxidation of NH_4^+ to NO_3; Reddy and DeLaune 2008). The role of salinity in the accumulation of porewater NH_4^+ at high concentrations of seawater was probably not due to the abiotic release mechanisms mentioned above, but the inhibition of nitrifying and denitrifying bacteria by high concentrations of chloride and sulfide in seawater (Seo et al. 2008; Hale and Groffman 2006; Joye and Hollibaugh 1995). The interaction of both greater anaerobosis and higher concentrations of Cl^- and S^{2-} could account for the highest porewater NH_4^+ in the inundated-elevated salinity treatment (Table 5-4). Similarly, the treatment with the

larger tidal range and lower salinity (the control water level-ambient salinity treatment) had the highest observed NO_3 concentration (Table 5-4).

Soluble reactive P in the porewater was significantly higher in the inundated-elevated salinity treatment compared to the control water level-ambient salinity treatment (Table 5-4). Previous studies have not found a significant relationship between salinity increases and phosphorus availability (Weston et al. 2011) but this effect may be explained by reduced microbial activity in the inundated-elevated treatment, as evidence by the lower rate of CO_2 production in that treatment.

Carbon Budget

Soil C content in this peat soil averaged 2,094 ± 307 g C m^{-2} in the top 0-5 cm, and 6,332 ± 1,198 g C m^{-2} from 5-25 cm. Assuming the majority of C cycling is occurring in the upper 5 cm of soil, the 3 pathways measured in this study (CO_2 flux, CH_4 flux, and DOC export (calculated as 30% of porewater DOC)) represent a mean mass loss of 3.1 ± 1.4% of the total soil C between 0-5 cm. On average, 95% of the total C lost in this study was lost via CO_2 flux, 1% to CH_4 flux, and 4% to DOC export. The control water level-elevated salinity treatment had a significantly higher ($p = 0.02$) % C mineralization over the 10-week study (4.5%), compared to the other 3 treatments (2.6%). However, these predictions of C mineralization may be significantly underestimated because atmospheric CO_2 flux does not include the lateral transport of dissolved inorganic C, which often exceeds DOC export by a factor of 3 to 10 (Bouillon et al. 2008b).

Implications for Everglades Peat Soils

A final goal of this study was to enhance the mechanistic understanding of how SLR may impact biogeochemical processes in the peat soils of Shark River Slough.

The currently mesohaline salinity and low topography in this region of the Everglades suggests Shark River Slough will probably be subjected to simultaneous increases in both salinity and inundation as sea level rises. The findings of this mesocosm simulation indicate the rate of atmospheric CO_2 flux from the soil will decline with SLR. Methanogenesis and DOC production is expected to increase slightly, but represents such a small portion of the C budget (~4%) that the effect on the ecosystem will be negligible. The availability of NH_4^+ and SRP in the porewater will increase significantly. This increase in nutrients, in combination with a decrease in anaerobic soil respiration, may cause an increase in nutrient export to Florida Bay. The increase in inundation could reduce the surface soil bulk density through increased leaching and bioturbation, but under natural conditions, an increase in tidally-deposited sediments could compensate for this decrease.

Summary

The high rate of primary productivity, high density of soil C, and low release of greenhouse gases make mangroves an ideal ecosystem for global C sequestration and storage (Chmura et al. 2003). Unfortunately, mangroves are also highly susceptible to human disturbance and environmental stressors, which have caused a 35% decline in global area since 1980 (Valiela et al. 2001).

Results indicate that among the 3 pathways measured (CO_2 flux, CH_4 flux and porewater DOC) 95% of all soil C lost from this mangrove peat soil was lost through CO_2 flux. Increasing tidal inundation from a LT water depth of -13 cm to a depth of -5 cm significantly *decreased* the rate of CO_2 flux by 14%. Increasing salinity from ambient (15-20 ppt) to 30-35 ppt *increased* the rate of CO_2 flux by an average of 54%. The combination of these two variables (increased inundation and elevated salinity) resulted

in a synergistic decline in the rate of CO_2 flux, 19% less than in the control treatment. The rate of CO_2 flux was positively correlated with water temperature and did not differ significantly whether the tide was rising or falling. Methane flux was low in all treatments (0.2 to 27 mg CH_4-C m^{-2} d^{-1}), but significantly greater in the increased inundation treatment. Porewater DOC was generally higher in the inundated treatment and calculated DOC export represented ~4% of all C lost.

Sulfate reduction was presumed the major pathway of C loss under all conditions. Increasing inundation and salinity resulted in significantly higher porewater NH_4^+ and SRP concentrations, probably due to a combination of decreased soil redox potential, a decline in microbial respiration, and the inhibition of N-cycling by high concentration of chloride and sulfide. Significant physical changes in soil structure as a result of increased inundation were also noted. Specifically, there was a 19% decrease in surface soil bulk density after just 10 weeks of exposure to increased inundation. Past studies have suggested the role of increasing salinity (saltwater intrusion) in prompting peat collapse (Davis et al. 2005), but this study indicates increased inundation may actually contribute more to changes in soil bulk density than salinity in mesohaline mangroves.

Table 5-1. Soil properties. Percent organic matter (loss-on-ignition) total C, and total N according to soil depth. Values represent mean ± standard deviation. Different letters represent significantly different means based on a one-way ANOVA ($p < 0.05$).

Soil Depth	Organic Matter *(%)*	Total N *(%)*	Total C *(%)*
0-5	45.4 ± 5.7 [a]	1.0 ± 0.2 [a]	19.9 ± 3.3 [a]
5-25	56.1± 5.3 [b]	1.5 ± 0.2 [b]	23.5 ± 2.9 [b]

Table 5-2. Surface water properties. Properties of the fresh source water and salt source water mixed to achieve the desired salinities in the mesocosms during the 10-week study. Values represent mean ± standard deviation. Different letters represent significantly different means based on a one-way ANOVA ($p < 0.05$). Saltwater data from DB Hydro site FLAB24 (SFWMD, 2012); freshwater data courtesy of T. Troxler (Florida International University) site JB (25°13'57.7"N, 80°31'28.4"W).

Parameter	Freshwater	Saltwater
Salinity *(ppt)*	<0.5 [a]	38 ± 4 [b]
NO_3^- *(mg L^{-1})*	5.8 ± 3.5 [a]	0.02 ± 0.01 [b]
NH_4^+*(mg L^{-1})*	2.4 ± 0.7 [a]	0.11 ± 0.08 [b]
SRP *(mg L^{-1})*	0.02 ± 0.001 [a]	0.001 ± .001 [b]
DOC *(mg L^{-1})*	7.1 ± 0.4 [a]	6.7 ± 0.3 [a]

SRP = soluble reactive phosphorus; DOC = dissolved organic carbon

Table 5-3. Rising vs. falling tidal affects on CO_2-C flux rate. Relationship between CO_2-C flux rate (mg m^{-2} d^{-1}) and cm of soil exposed above the water line during rising and falling tides; data presented according to treatment and tidal condition.

Water Level	Salinity	Tide	Slope (Δ mg CO_2-C m^{-2} d^{-1} / Δ cm soil exposed)	Difference (Rising-Falling)
Control	Ambient	Rising	121.1	26.3
		Falling	94.8	
Control	Elevated	Rising	93.0	-23.4
		Falling	116.4	
Inundated	Ambient	Rising	74.4	-42.6
		Falling	117.0	
Inundated	Elevated	Rising	41.8	-8.9
		Falling	50.7	

Table 5-4. Soil porewater nutrients. Mean (± standard deviation) porewater concentration of DOC and nutrients presented according to treatment condition. Different letters represent significantly different means based on a one-way ANOVA ($p < 0.05$).

Water Level	Salinity	DOC (*mg L^{-1}*)	NO_3^- (*mg L^{-1}*)	NO_2 (*mg L^{-1}*)	NH_4^+ (*mg L^{-1}*)	SRP (*mg L^{-1}*)
Control	Ambient	14.8 ± 1.6^{ab}	1.65 ± 0.29	0.26 ± 0.05	141.6 ± 57.0^{a}	7.2 ± 2.3^{a}
Control	Elevated	12.0 ± 2.9^{a}	1.28 ± 0.13^{b}	0.27± 0.06	140.9 ± 67.1^{a}	8.6 ± 3.7^{ab}
Inundated	Ambient	18.4 ± 4.2^{b}	1.49 ± 0.20^{ab}	0.27 ± 0.08	211.7 ± 89.9^{ab}	8.5 ± 3.0^{ab}
Inundated	Elevated	17.5 ± 5.0^{b}	1.16 ± 0.22^{b}	0.32 ± 0.13	287.7 ± 78.5^{b}	12.0 ± 3.0^{b}

Table 5-5. Correlations between measured properties. Pearson's product correlation coefficients (r-values with p-values in parentheses) for porewater parameters (n = 206), nighttime CO_2 flux (n = 163), and water temperature (n = 150).

	Time	Temp	DOC	Salinity	NO_2	NO_3^-	NH_4^+	SRP
Temp	-0.873 *(<.0001)*	-						
DOC	NS	NS	-					
Salinity	0.378 *(<.0001)*	-0.271 *(<.0001)*	NS	-				
NO_2	0.503 *(<.0001)*	-0.340 *(<.0001)*	0.223 *(.010)*	0.180 *(.010)*	-			
NO_3^-	0.248 (.0004)	NS	NS	NS	0.341 *(<.0001)*	-		
NH_4^+	0.377 *(<.0001)*	-0.287 *(<.0001)*	0.545 *(<.0001)*	0.323 *(<.0001)*	0.398 *(<.0001)*	NS	-	
SRP	0.332 *(<.0001)*	-0.312 *(<.0001)*	0.413 *(<.0001)*	0.251 *(.0003)*	0.305 *(<.0001)*	NS	0.552 *(<.0001)*	-
CO_2	-0.382 *(<.0001)*	0.394 *(<.0001)*	-0.198 *(.005)*	NS	-0.189 *(.007)*	NS	-0.431 *(<.0001)*	NS

NS = not significant

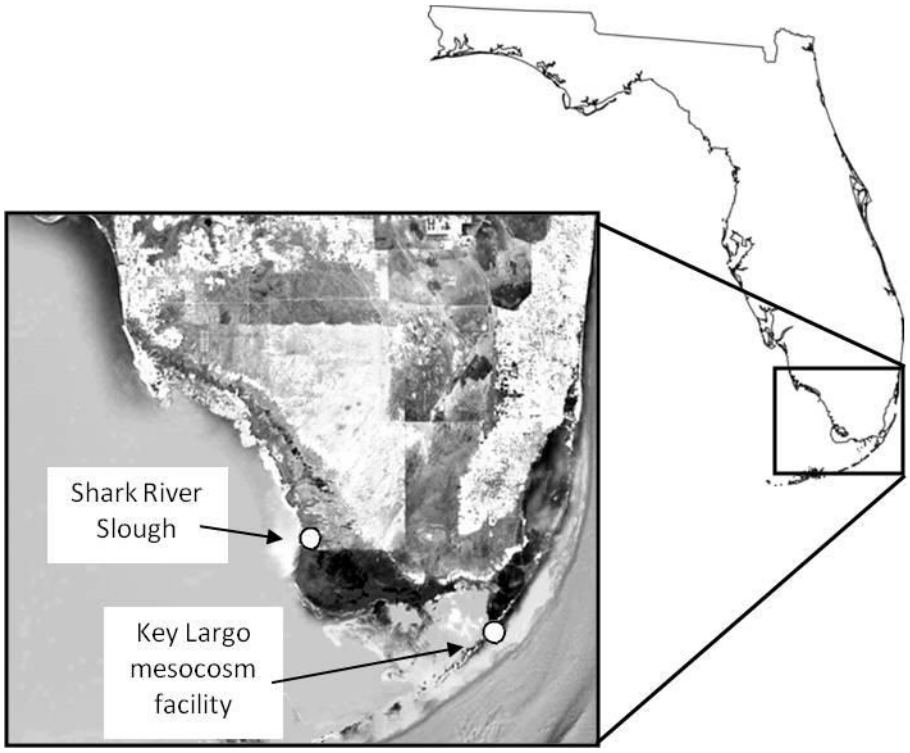

Figure 5-1. Site location map. This study was conducted in south Florida, USA. The aerial photograph indicates where the peat monoliths were collected (Shark River Slough (25°21'52.7”N, 81°4'40.6 W)) and where the experiment took place (Florida Bay Interagency Science Center (25°5'9.21”N, 80°27'6.9"W)).

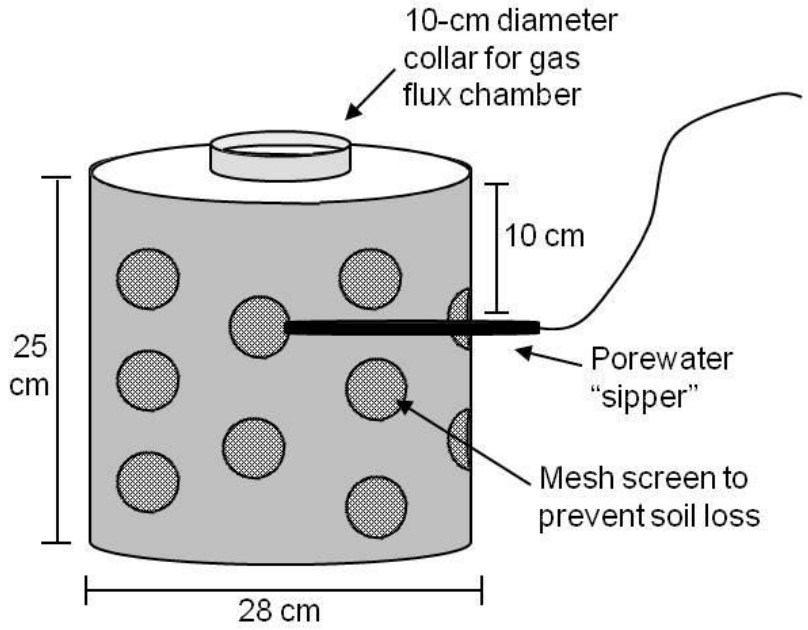

Figure 5-2. Schematic of the peat monolith design. Standard window screen mesh was wrapped around the sides of the monolith to prevent soil loss through the bucket perforation, but the soil surface was not covered. A porewater “sipper” was inserted into the center of the peat monolith (-10 cm depth) from the side of the bucket and a 10 cm diameter collar was centrally located.

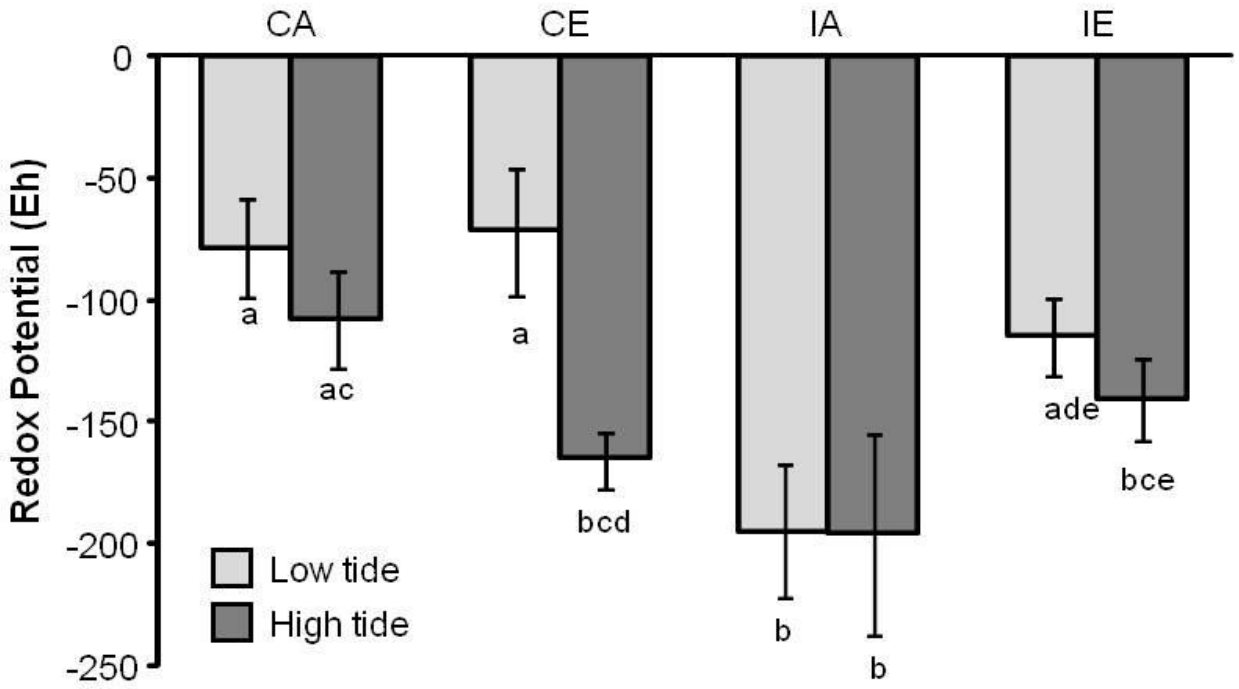

Figure 5-3. Soil oxidation reduction (redox) potential. Readings taken at a depth of -10 cm are presented according to treatment condition (C= control water level; I = inundated water level; A = ambient salinity (15-20 ppt); E = elevated salinity (30-35 ppt)) and tidal condition. Bars represent mean (n = 11); error bars represent standard error. Different letters represent significantly different means based on a two-way ANOVA ($p < 0.05$).

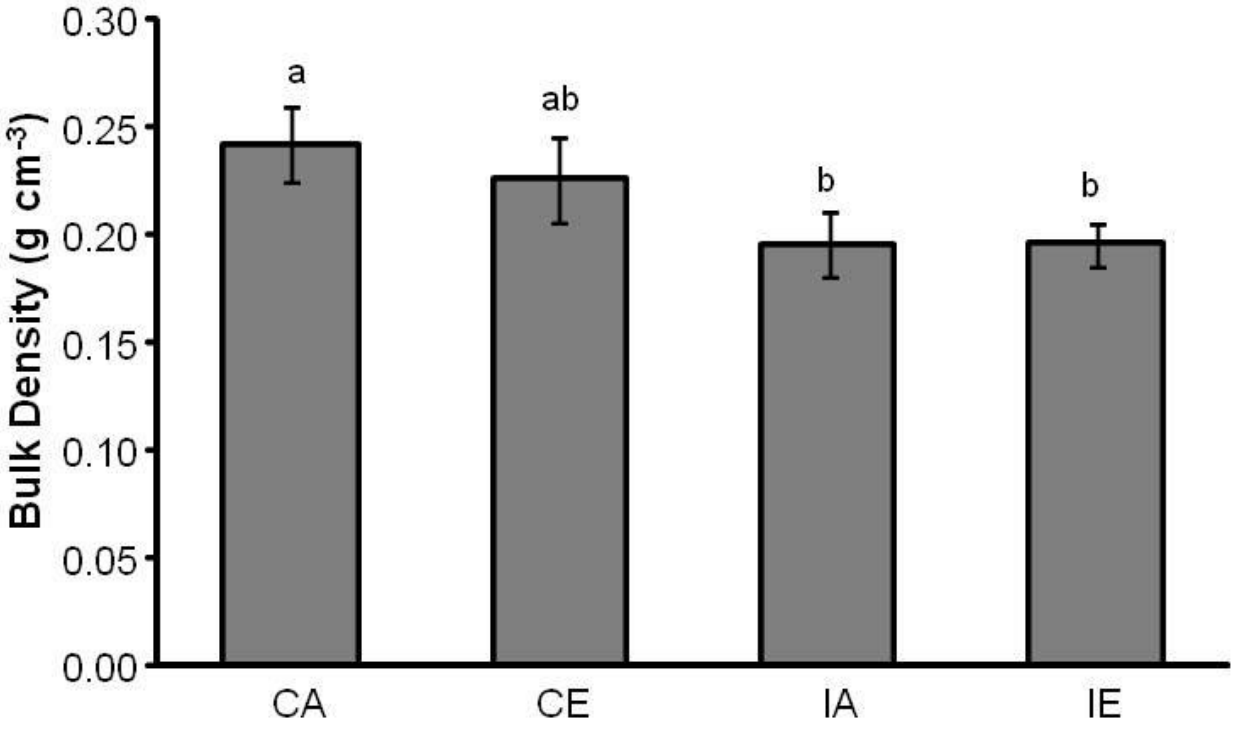

Figure 5-4. Surface soil (0-5 cm) bulk density. Data collected at the conclusion of the 10 week study according to treatment condition (C= control water level; I = inundated water level; A = ambient salinity (15-20 ppt); E = elevated salinity (30-35 ppt)). Bars represent mean (n = 6); error bars represent standard error. Different letters represent significantly different means based on a two-way ANOVA ($p < 0.05$).

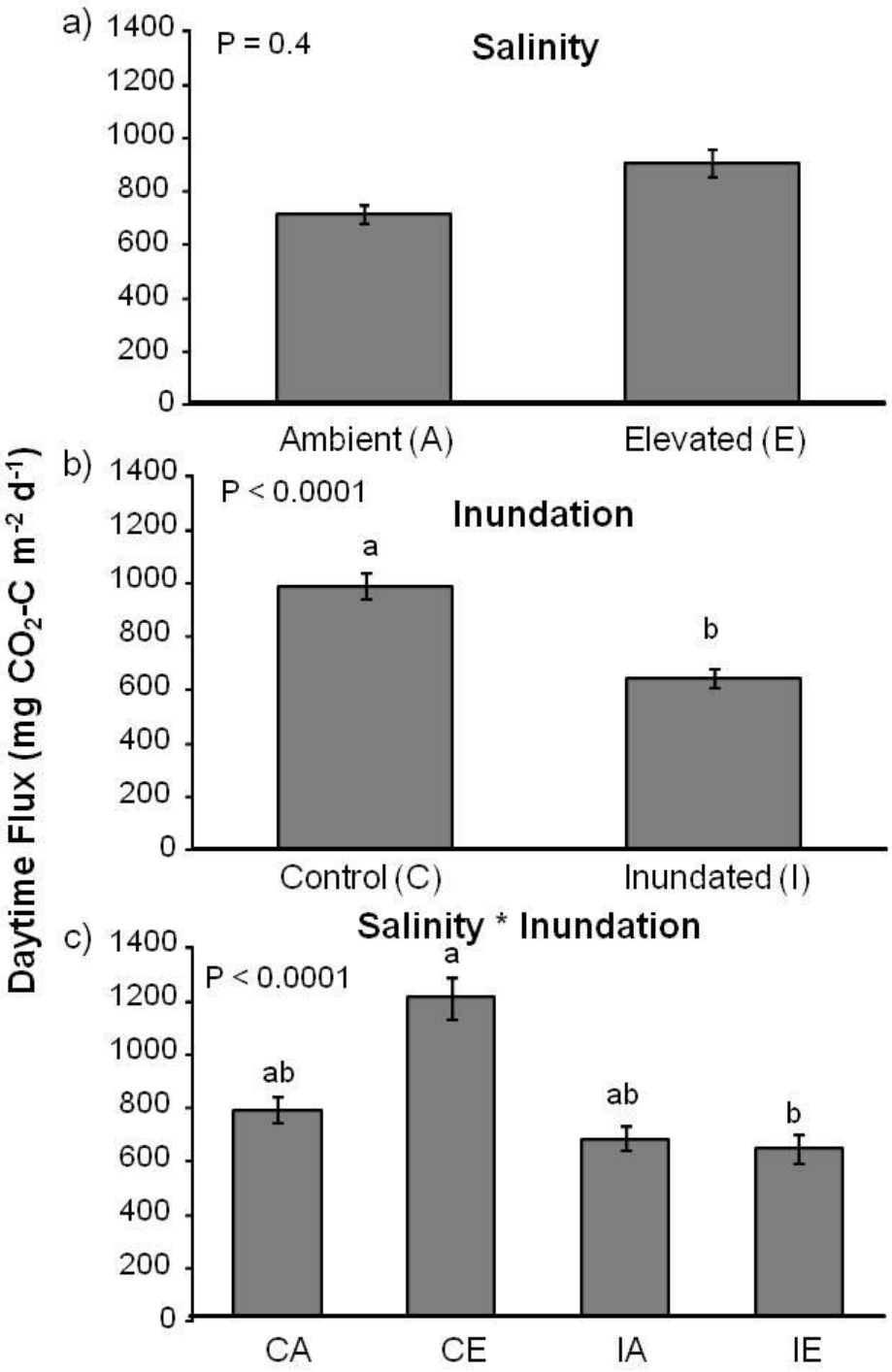

Figure 5-5. Daytime CO_2-C flux by inundation and salinity. Data presented according to a) salinity treatment (n = 155), b) inundation (n = 155), and c) the combination of salinity and inundation (n = 78). Bars represent means; error bars represent standard error. Different letters represent significantly different means based on a heteroscedastic split-plot linear mixed model.

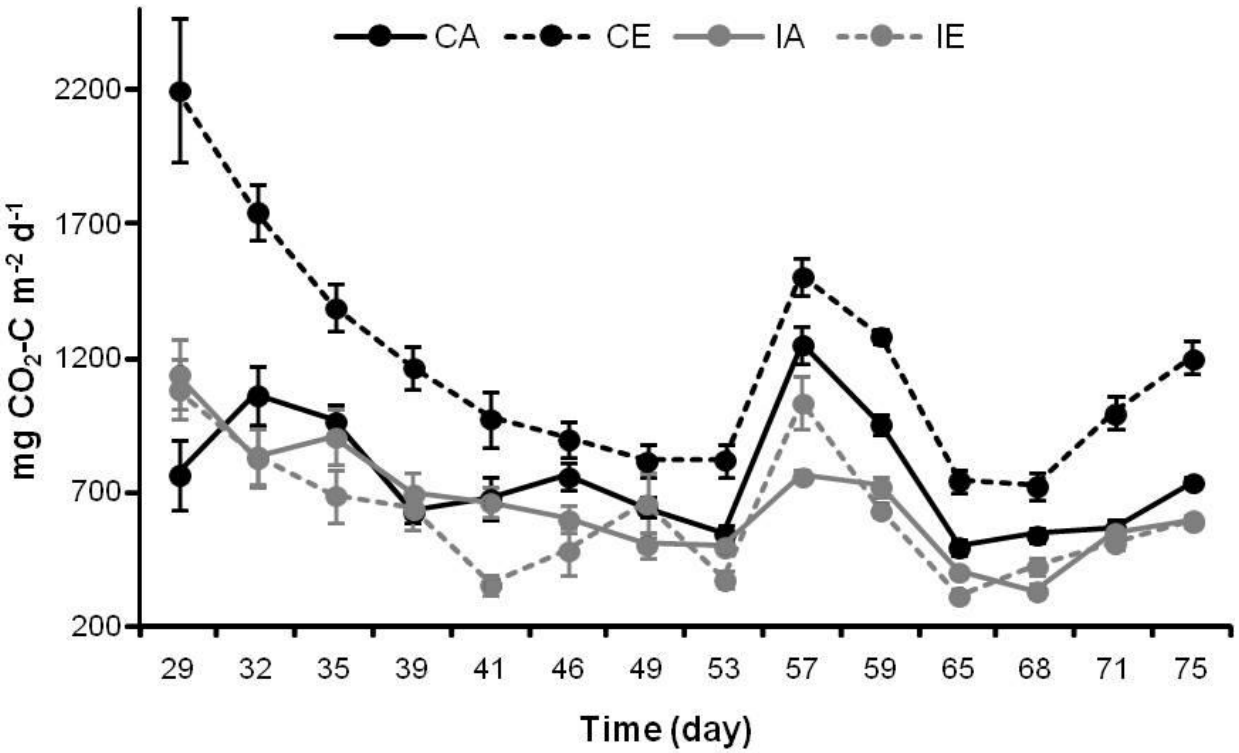

Figure 5-6. Daytime CO_2-C flux over time. The experimental phase began 29 days after soil collection and ended 75 days after collection. Carbon dioxide flux presented according to treatment condition (C= control water level; I = inundated water level; A = ambient salinity (15-20 ppt); E = elevated salinity (30-35 ppt)). Points represent means and error bars represent standard error.

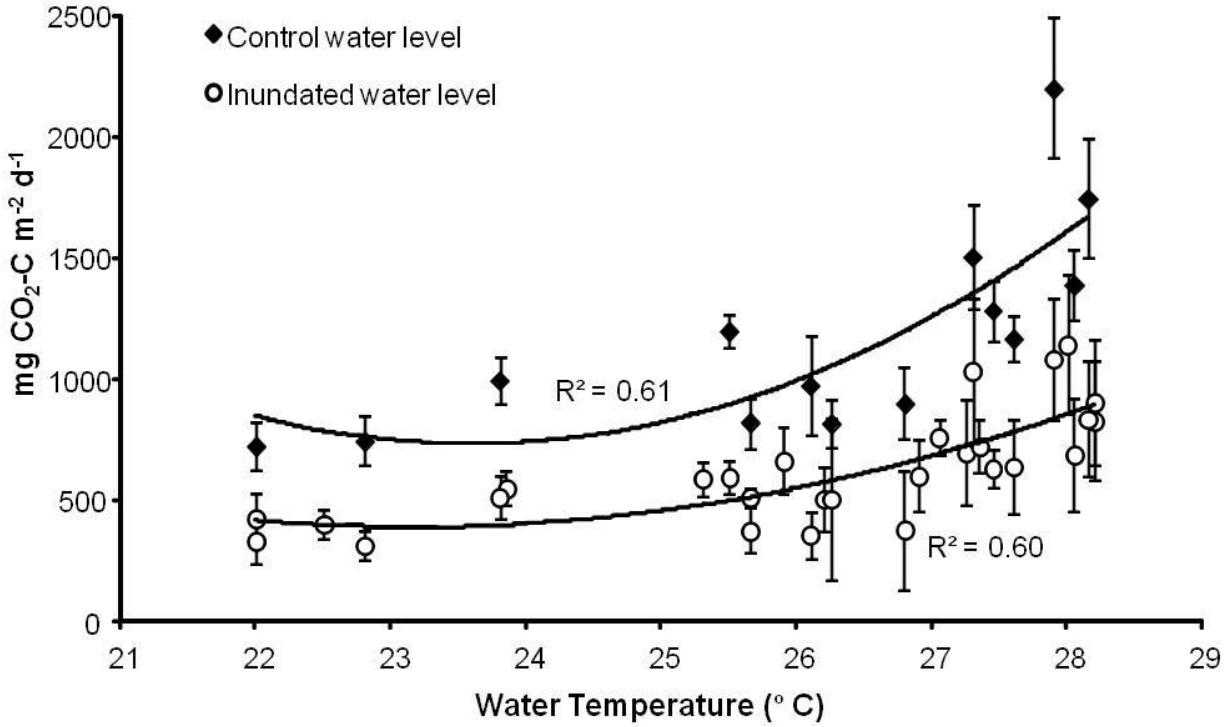

Figure 5-7. Daytime CO_2-C flux over temperature. Relationship between daytime CO_2-C flux and water temperature (ºC) according to water level treatment (control water level or inundated water level). Points represent means; error bars represent standard error. Trend lines are 2nd degree polynomial fits with regression coefficients (r values) indicated.

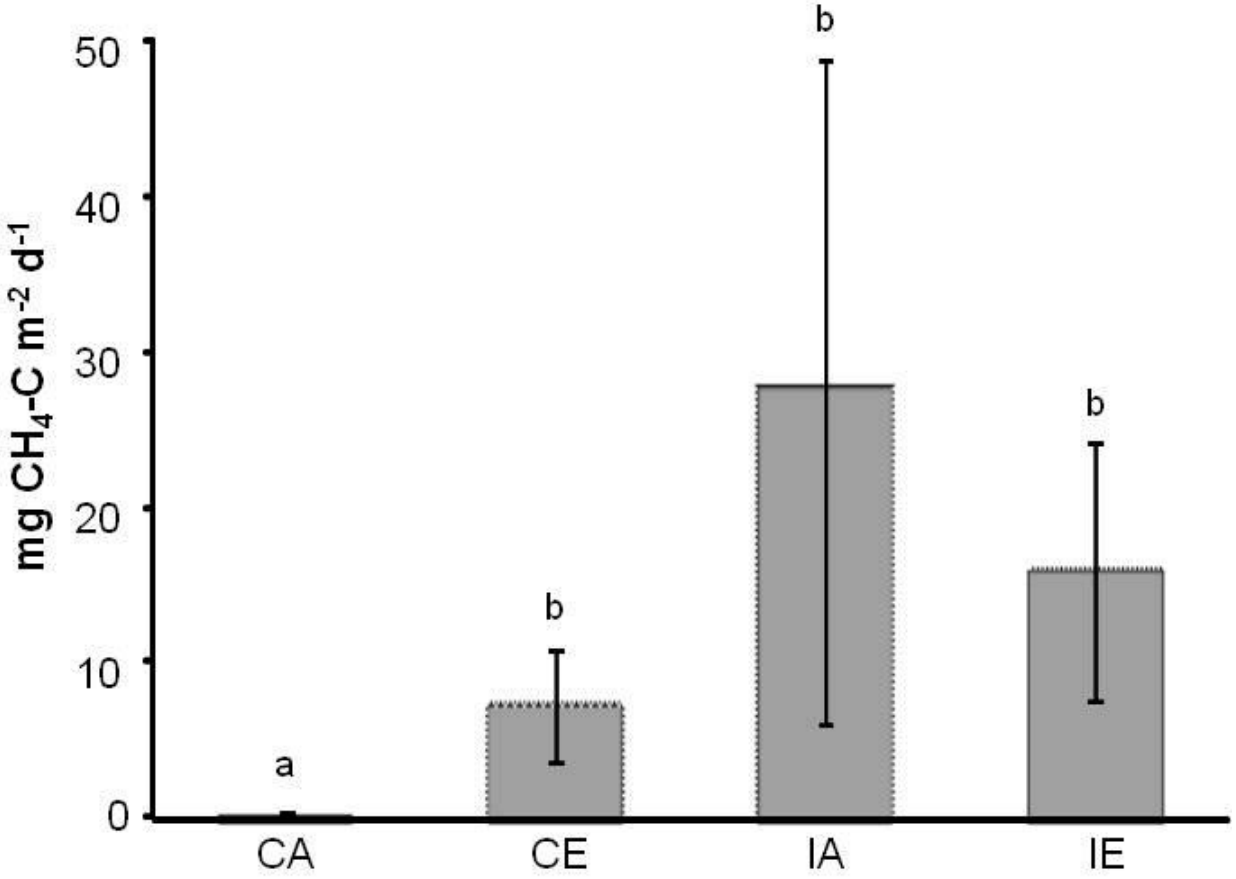

Figure 5-8. Methanogenesis by treatment condition. Methane (CH_4-C) flux at low tide according to treatment condition (C= control water level; I = inundated water level; A = ambient salinity (15-20 ppt); E = elevated salinity (30-35 ppt)) and tidal conditions. Bars represent mean (n = 12); error bars represent standard error. Different letters represent significantly different means based on a two-way ANOVA ($p < 0.05$).

CHAPTER 6
CONCLUSIONS

Background

Coastal wetlands sequester and store an inordinate amount of global carbon (C) relative to their small areal coverage. Over the past century, human development and natural resource harvesting along the world's coastlines have resulted in the degradation and loss of thousands of hectares of coastal wetlands. Today, sea level rise (SLR) is introducing an additional threat to the health and persistence of coastal wetlands. This dissertation evaluates the ability of coastal wetland soils to store C under conditions of increasing sea level. Specifically, this research attempts to answer the question: how do increasing salinity and inundation affect carbon biogeochemistry in coastal wetland soils?

The first goal of this dissertation was to improve the mechanistic understanding of how salinity and inundation affect biogeochemical carbon cycling. This was accomplished by disentangling the components of salinity that affect soil microbial processes (Chapter 3), quantifying the end-products of microbial processes (CO_2, CH_4, and DOC; Chapters 3-5), and measuring changes in the availability of nutrients, electron acceptors, and labile C as potential co-variants impacting wetland biogeochemistry (Chapters 3-5). The second goal was to vary scale (i.e., degree of experimental control) to translate biogeochemical processes into real-world observations. In each successive study (Chapters 3, 4, and 5, respectively), the experimental approach progressed from: (1) a highly-controlled microcosm slurry study (no diffusion barriers, DI water, constant temperature), to (2) an intact soil core study (intact soil profiles, *in-situ* water, constant temperature), to (3) a peat monolith

mesocosm study (large soil area, *in-situ* water, temperature and tidal fluctuations, and macroinvertebrate inclusion). Using this deliberate progression of increasing environmental complexity, specific biogeochemical mechanisms identified in the earlier studies were observed in the context of additional confounding and co-varying factors that are important in natural systems. Finally, the third goal was to provide insight into the broader question of how coastal wetland C storage might be affected by SLR. A review of literature revealed three landscape-scale responses of coastal wetlands to SLR (Chapter 2). Quantifying the release and export of C by the three major microbial pathways (soil respiration, methanogenesis, and DOC production; Chapters 3-5) suggested there are physical, chemical, and biological characterisitcs that help to predict the response trajectory of a specific coastal wetland to SLR. In the subsequent section, each research objective presented in the introduction (Chapter 1) is re-evaluated in the context of the new knowledge gained from this research and the three over-arching goals are further discussed and dissected.

Objective 1: Review of Literature

Coastal wetland C cycling is controlled by three main regulators, (1) the quantity and quality of C, (2) the availability of electron acceptors, and (3) the size, structure, and activity of the soil microbial community (Chapter 2). The quantity and quality of C in a wetland is a function of C inputs (primary production and inflows/deposition), the legacy of organic matter accumulation, and soil development. According to the literature, the rate of primary productivity is mainly driven by system-specific characteristics (e.g., temperature and nutrient availability), rather than salinity and inundation. However, a few general trends do orient along salinity gradients: plant diversity, litter quality, and organic soil C are inversely correlated with salinity, while bulk density and inorganic soil

C are directly correlated with salinity. In terms of electron acceptor availability, SO_4^{2-} and NO_3^- are most affected by changes in salinity. Sulfate is the third most abundant ion in seawater and is responsible for nearly all anaerobic soil respiration at seawater salinities >10 ppt. The N-cycle (and NO_3^- available for denitrification) experiences multi-faceted consequences from salinity increases. At low salinities, an aboitic release of NH_4^+ from the soil commonly occurs. At higher salinities, the accumulation of sulfide (a by-product of sulfate reduction) and chloride can reduce the activity of nitrifiers and denitrifiers. In coastal wetlands with significant iron content, salinity can also affect Fe dynamics by promoting a shift from Fe-P complexes to Fe-S complexes, resulting in increased P-availability. Current knowledge regarding the soil microbial community response to SLR is incomplete and includes numerous contradictions. In general, it is believed that microbial communities adapt quickly to changes in salinity and inundation, and that more saline wetlands tend to have lower rates of soil respiration and enzyme synthesis. Saline coastal wetlands (>18 ppt) also have significantly lower global warming potential than tidal freshwater wetlands due to low rates of CH_4 production and generally high rates of accretion from greater tidal deposition. Some of the most important knowledge gaps in the current literature include: (1) how does time-scale (short-term vs. long-term) influence the observed changes in C biogeochemistry resulting from SLR, (2) what is the mechanism for N-cycling suppression, (3) how do microbial and fungal biomass vary along salinity gradients, and (4) how do microbial-scale biogeochemical processes relate to landscape-scale responses of coastal wetland C storage.

Objective 2: Salinity and Carbon Cycling

Most of the research investigating biogeochemical responses to salinity to date has been performed in agricultural and uplands soils (e.g., Gennari et al. 2007; Muhammad et al. 2006; Pattnaik et al. 2000). Previous studies indicated significant decreases in the rate of C cycling with increasing salinity, but may have limited applicability to coastal wetlands exposed to SLR because of the central importance of anaerobic conditions and sulfate availability in wetland C cycling. Therefore, the goal of the microcosm study presented in CHAPTER 3 was to determine the mechanism by which salinity alters C mineralization rates in wetland soils. This was done by quantifying the relative importance of ionic stress, compared to the addition of sulfate, on the production of CO_2 and CH_4. A batch incubation study measured potential anaerobic respiration and methanogenesis over time in a freshwater wetland soil exposed to varying concentrations (3.5, 14, and 35 ppt) of seawater or salt (NaCl) solutions. Seawater (sulfate) addition induced a short-term (2 week) stimulation of CO_2 production (20-32% greater than the freshwater control) and a continuous suppression of CH_4 production (up to 94% less than freshwater). Ionic stress (NaCl) did not reduce CO_2 production, but did decrease CH_4 production for 2 weeks in both the 14 and 35 ppt NaCl treatments. Results indicate microbial populations rebound quickly from ionic stress. The intrusion of dilute seawater (3.5 ppt) to freshwater wetlands can accelerate organic C mineralization through the short-term increase in sulfate-induced respiration without inhibiting methanogenesis. Overall, organic C mineralization rate was 17% higher under 3.5 ppt seawater than the freshwater control.

Objective 3: The Importance of Time-Scale

The temporary nature of the microbial response in Chapter 3 suggested "pulses" of seawater may have a greater influence on the rate of C cycling in freshwater wetlands than gradual SLR. Therefore, Chapter 4 focused on simulating pulses of higher (or lower) salinity water in coastal wetlands, such as would typically occur during storm surges, extreme tides, heavy rains, or urban run-off. This study quantified the impact of salinity pulsing events on soil organic C (SOC) loss (CO_2 flux at high and low tide, CH_4 flux, and DOC release) in three intertidal wetlands in Jacksonville, FL (USA). Twelve intact soil cores from a freshwater tidal, brackish, and salt marsh were exposed to simulated tides and 3 salinity pulsing events during a 53-day laboratory experiment. Results indicated the freshwater marsh was highly sensitive to brackish (13 ppt) pulses, causing a 112% increase in LT respiration from accelerated sulfate reduction and N-cycling, a decrease in both CH_4 flux and DOC export, and a significant change in the partitioning of SOC loss through the 3 biogeochemical pathways studied. Low tide soil respiration rate and DOC export both increased significantly in the salt marsh pulsed with fresh (0.5 ppt) water, suggesting urban run-off may decrease a salt marsh's ability to keep pace with SLR. Overall, this study indicated pulses of different salinities had the greatest impact in the tidal freshwater marsh (TFM) and salt marsh, and the effects on soil respiration were often evident as 'legacy effects' occurring during the low tide following the recession of the surface water salinity pulse.

At the opposite-end of the time spectrum, a more measured increase in salinity was simulated in Chapter 5. In the tidal mesocosm study, a 10-15 ppt increase in salinity (from 15-20 to 30-35 ppt) was gradually introduced over a 1-week period, and then the SOC cycling response was monitored for an additional 6 weeks. Based on

previous findings that the major shifts in biogeochemical pathways occur between 0 ppt and 14 ppt, and that the microbial population can adapt quickly to changes in salinity (Chapters 2-4), this increase was not hypothesized to cause a significant change in the rate of SOC loss. However, a significant and persistent increase in CO_2 flux was observed in Chapter 5 as a result of elevated salinity, which was particularly evident during nighttime CO_2 flux sampling.

There may be intrinsic characteristics of the mangrove peat soils used in Chapter 5 that caused the soil to be stimulated by the sulfate addition for the long-term. For example, high microbial activity caused by high temperatures, high DOC, and consistent flushing of the soil by tides could have created a circumstance where electron acceptor availability was the limiting factor for microbes. In which case, increasing sulfate availability could persistently raise the baseline CO_2 flux rate. In contrast, the microcosm soil slurries (Chapter 3) experienced a confounding limitation in labile C availability, preventing a long-term increase in the rate of soil respiration.

Objective 4: Tidal Cycle Effects

Despite extensive previous work on the effects of water table on soil respiration in inland wetlands, there had been almost no investigation of how tidal cycles impact CO_2 flux in coastal wetlands. In inland wetlands, a fairly straightforward relationship exists between increasing inundation, a decrease in soil respiration rate, and an increase in methanogenesis (Wright and Reddy 2001; DeBusk and Reddy 1998; Clymo 1983). In coastal wetlands, tidal inundation also involves an influx of sulfate, which has been shown to poise the redox potential of wetland soils at an Eh that promotes high rates of sulfate reduction (Mendelssohn et al. 1999). Additionally, significant variations in inorganic sediment deposition along coastal wetland gradients can result in large

differences in soil properties, which also influence SOC loss (Craft 2007; Nyman et al. 1990). The effect of tidal cycle was investigated in both Chapters 4 and 5. On average, low tide (LT) CO_2 flux was higher than high tide (HT) CO_2 flux, but the magnitude of the difference between LT and HT varied significantly depending on the coastal wetland type (Figure 6-1). For the TFM, brackish marsh, salt marsh, and mangrove, the difference in CO_2 flux between HT to LT was 53, 230, 310, and 83%, respectively. Soil properties (organic matter content, total C, bulk density) did not explain these variations in tidal effect, but significant differences in soil drainage rates were observed between wetland types. This suggests soil hydraulic conductivity (based on the size and distribution of pore spaces) may drive the relationship between CO_2 flux and tidal cycle as much as biogeochemical processes.

Objective 5: Inundation and Carbon Cycling

While objective 3 addressed differences in C loss between HT and LT, objective 4 asked how reduced soil exposure during LT (an overall increase in inundation) affected SOC loss rate. Results of the numeric model developed in Chapter 4, more saline wetlands will store more SOC as inundation increases, while TFMs looses more SOC. TFMs have high rates of SOC loss via HT-CO_2 flux, CH_4 flux, and DOC export; under longer durations of HT, this can lead to an overall increase in the rate of SOC loss. In comparison, brackish and salt marshes demonstrated low rates of HT-CO_2 flux, translating into a decrease in the rate of SOC loss as inundation increases.

Chapter 5 directly addressed this objective with a water level manipulation that decreased the elevation of the soil surface by -8 cm relative to the water table. This increase in inundation caused a 35-37% decrease in the average CO_2 flux rate, compared to the control water level. Methane flux also increased significantly

compared to the control, but remained low, while DOC concentration increased by approximately 31%.

Objective 6: Interaction of Salinity and Inundation

Based on the geomorphological characteristics of a coastal wetland, either salinity or inundation may exert a stronger influence on the biogeochemical response to SLR. However, other wetlands will be influenced by simultaneous increases in salinity and inundation. Chapters 3 and 5 clearly demonstrated an increase in the rate of SOC loss with increasing salinity over both short and long time scales. In Chapter 5, an increase in salinity from 15-20 ppt to 30-35 ppt caused a 54% increase in the rate of CO_2 flux. In the same system, increased inundation caused a 14% decrease in the rate of CO_2 flux. Interestingly, when these two drivers were combined, rather than the increase and decrease in rates canceling each other out, there was a synergistic decline of 19%. This data and pervious research suggests the synergistic decline may be caused by the deleterious by-products of increased sulfate reduction (sulfide) accumulating in the soil as salinity increases. This, in combination with the low redox potential and limited water exchange caused by the increase in inundation, prevented these compounds from being flushed from the soil, leading to the overall lowest rate of soil respiration in the inundated-elevated salinity treatment.

Objective 7: Importance of Environmental Variables

Coastal wetlands exist in a complex environment with each individual ecosystem having unique biological, chemical, and geological characteristics that play a role in determining its response to SLR. Most of this dissertation has investigated SLR in a 'simplified' version of reality- one in which climate drivers, megafauna, and especially C inputs (vegetation and sediment deposition) have been excluded. Providing these

artificial boundaries to the soil system allowed for the isolation of individual processes, but also reduced the applicability of the results to natural systems. Still, the inclusion of natural variables increased with each successive research study and did allow for some general conclusions regarding important co-variants in coastal wetlands.

- The brackish marsh soil had a higher bulk density and greater inorganic material >0.025 mm, as well as lower % organic matter, total C, and total N than the TFM, salt marsh, and mangrove soils (Chapters 4 and 5).
- Surface water DOC was inversely correlated with salinity (Chapters 4 and 5) and was positively correlated with HT soil respiration (Chapter 4).
- The salt marsh soil had higher labile C availability and MBC than the TFM and brackish marsh soils (Chapter 4).
- Surface water soluble reactive P was inversely correlated with salinity and positively correlated with HT soil respiration and DOC release (Chapter 4).
- Water temperature caused a positive non-linear response in CO_2 flux rate (Chapter 5).
- Bioturbation by fiddler crabs appeared to be driven partly by soil inundation level and may increase soil porewater DOC concentration (Chapter 5).

Synthesis and Future Research

This body of research answers the questions and objectives presented in the introduction, as outlined above. Carbon dioxide flux was identified as the major pathway of SOC loss in all the studies, representing over 90% of total SOC lost through the measured pathways in each coastal wetland type. Using the conceptual diagram presented in Chapter 1, the response of CO_2 flux to each of the factors and processes of interest in this dissertation is presented in Figure 6-2.

This research also fills many of the research gaps identified in the literature review (Chapter 2). For example, this work found the impacts of salinity can be observed over both short *and* long time scales. Short-term impacts are abiotic, such as ion exchange

on the soil surface (Chapter 4), and biotic, such as quick spikes in sulfate reduction or reduced microbial respiration due to osmotic stress (Chapter 3). Whether a short-term response persists over time depends on the availability of other potentially limiting factors. For example, in a system with a limited supply of labile C (a condition artificially created in Chapter 3), excess SO_4^{2-} becomes inconsequential to soil microbes over time. Whereas, systems not limited by substrate availability or microbial population, an increase in SO_4^{2-} availability can create a long-term increase in the rate of CO_2 flux (Chapter 5). Therefore, the most appropriate question is not what effect salinity exerts on the system, but rather: (1) is the system currently limited by electron acceptor availability and (2) how much of an increase in biogeochemical cycling can result from the alleviation of electron pressure before another factor (electron donor availability, enzyme synthesis, nutrient availability, etc.) becomes limiting? It is the availability of *other* critical components of the biogeochemical C cycle that ultimately dictates the duration of the salinity effect.

The *mechanism* for the suppression of N cycling is still unknown, but the results presented herein provide ample new evidence for a significant interaction between N and C cycling as salinity and inundation increase in coastal wetland soils. An accumulation of NH_4^+ in the soil porewater can be initiated by cation exchange, organic matter mineralization, and increased inundation. Such an increase in NH_4^+ was observed following pulses of higher salinity water in TFM soil (Chapter 4) and with increased inundation in mangrove soil (Chapter 5). This increase in NH_4^+ availability is an indicator of a bottleneck in the process of nitrification which was also shown to be alleviated by increasing the soil redox potential with a LT event (Chapter 4). Any

disruption of nitrification can have important ecological consequences for coastal system because NH_4^+ availability is positively correlated with coastal eutrophication and algal blooms (Howarth 1988). Whether the ultimate cause of the NH_4^+ accumulation was related to physical conditions (redox potential) or biological toxicity (high sulfide and/or chloride concentrations inhibiting nitrifiers) remains an unanswered question that deserves additional attention.

The scaling-up process initiated with this dissertation needs to continue so that some of the important processes identified herein can be used to assist in predicting landscape-scale changes in coastal wetland C storage as sea level rises. Some important inroads to understanding the fate of coastal wetlands were made in Chapter 4. Coastal wetlands adjacent to urban development are already prohibited from migrating landward in response to SLR and must rely exclusively on vertical accretion to combat submergence. Pulses of fresh surface water (such as urban stormwater discharge) can significantly accelerate SOC loss from salt marsh soils, further increasing the need for C inputs to compensate for both SLR and increased soil mineralization in coastal wetlands adjacent to human development. Additionally, Chapter 5 demonstrated how increased inundation can impact soil structure through a significant decline in soil bulk density after only 10-weeks of water level manipulation. Although the mechanism for the loss of soil structure needs to be confirmed, it is plausible the decrease in bulk density is a precursor to peat collapse, which often leads to wetland submergence.

I believe the logical next steps for biogeochemical research in coastal wetlands exposed to SLR is a focus on three main research avenues: (1) coupled

biogeochemical cycles affected by sulfate and inundation (especially N and Fe dynamics), and (2) plant-soil interactions influencing biogeochemical cycling (such as substrate availability, rhizosphere microzone dynamics, and nutrient and gas translocation in and out of the soil), and (3) disentangling abiotic soil responses to salinity and inundation (leaching, solubilization, dispersion) from biotic responses (mineralization). Ecological systems are both complex and individually unique. Understanding micro-scale processes, mechanisms, and drivers is critical to being able to make accurate predictions about how other systems that have not been directly studied may respond to SLR. Continuing to research the fundamental processes underlying the response of coastal wetland C to SLR in a deliberate, sequential manner of increasing complexity is the most effective way to accrue knowledge that will lead to robust landscape-scale predictions regarding the fate of coastal wetlands as a C sink/source during SLR.

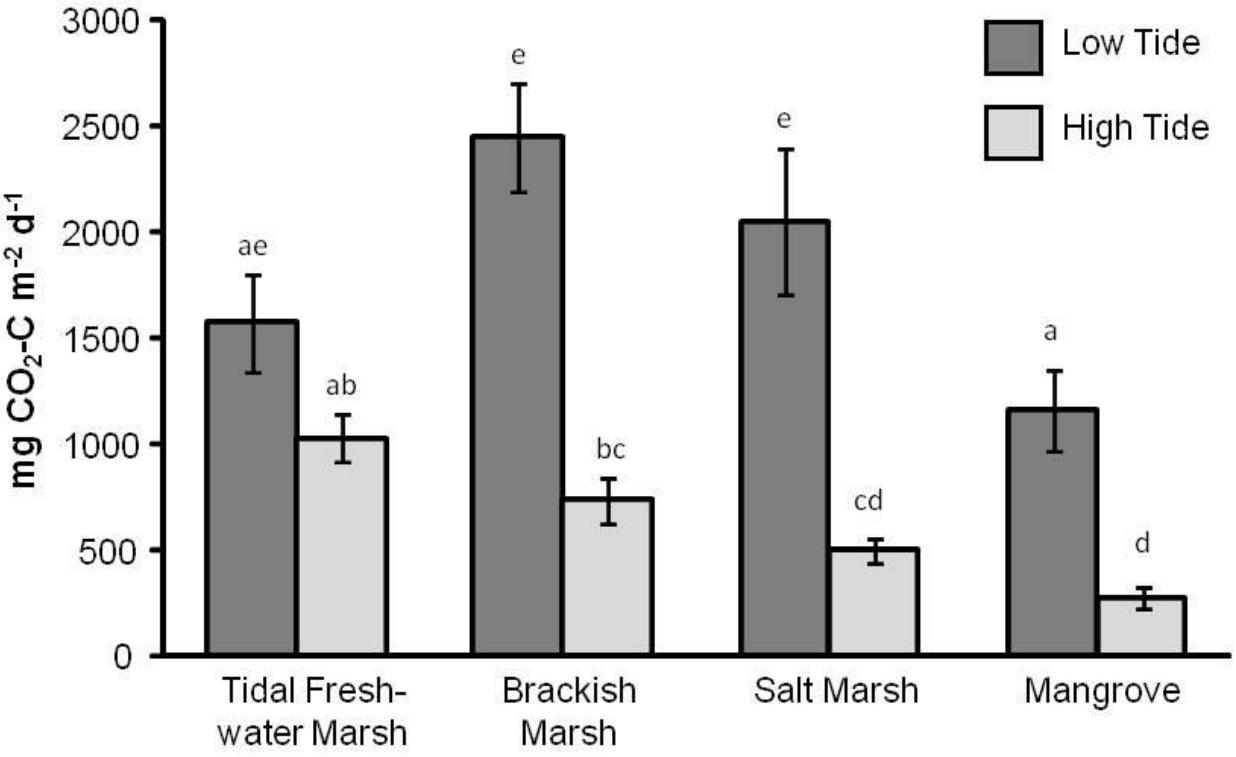

Figure 6-1. Tidal effects by wetland type. Rate of CO_2 flux during high and low tide (all 20 cm tidal range) for each of the 4 wetland types studied.

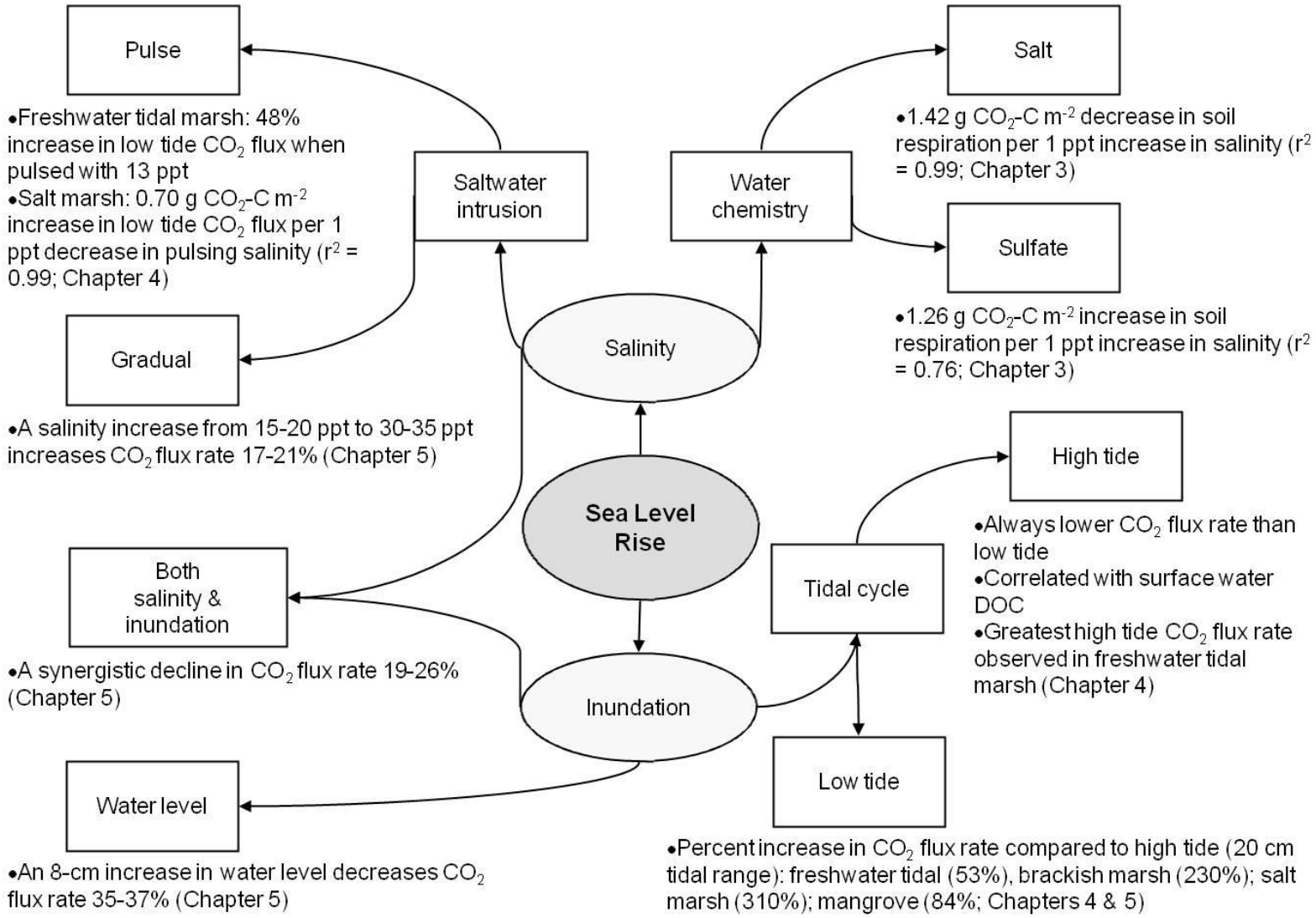

Figure 6-2. Conceptual diagram with comprehensive soil respiration results.

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BIOGRAPHICAL SKETCH

Lisa Gardner Chambers grew up in North Canton, Ohio with her parents, Bruce and Marcia Gardner, and older brother, Chris Gardner. Her family instilled in her a great appreciation for nature through weekend trips to the lake and family vacations at America's National Parks. Attending Ohio State University (Columbus, Ohio), Lisa graduated magna cum laude with a Bachelor of Science in natural resources in 2003. At Ohio State, her desire to study wildlife veterinary medicine propelled her to enroll in an environmental science course, which permanently changed her academic focus toward a career in ecology and conservation. Her undergraduate mentor, Dr. Virginie Bouchard, was instrumental in honing this interest to a concentration in wetlands.

Following her undergraduate degree, Lisa worked for two year as a Wetland Consultant and one year as a Watershed Director for a an environmental non-profit near Dayton, Ohio. However, her passion for academia and interest in large-scale wetland restoration projects led her to accept a fellowship at Louisiana State University in Baton Rouge, Louisiana, under Dr. John White. Her master's research focused on the biogeochemical impacts of a Mississippi River Freshwater Diversion on coastal wetlands in southern Louisiana. She graduated from the Department of Oceanography and Coastal Sciences with the Outstanding Thesis award in 2008.

In the summer of 2008, Lisa received both a National Science Foundation Integrative Graduate Traineeship (IGERT) fellowship and an Alumni Fellowship from the Soil and Water Science Department to begin her Ph.D. at the University of Florida in Gainesville, Florida, under Dr. K. Ramesh Reddy. Her Ph.D. program focused on interdisciplinary science and included a life-changing summer studying in southern Africa. Lisa followed her enthusiasm for coastal wetlands in her Ph.D. program,

developing an externally-funded research initiative focused on the biogeochemical effects of sea level rise on coastal wetland carbon cycling. During this time, Lisa also met and married her husband, Dr. John Chambers. Lisa has dedicated her career to studying the fundamental science behind globally important ecosystems and being a mentor and leader in the field of wetland science.