SEDIMENT ORGANIC CARBON POOLS AND SOURCES IN A RECENTLY CONSTRUCTED MANGROVE AND SEAGRASS ECOSYSTEM

By

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To my parents, Michelle and Richard Hicks, for their wonderful support of all my academic endeavors from preschool onwards

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Coastal ecosystems are significant natural carbon sinks. If constructed coastal ecosystems can obtain the same carbon sink capacity as their natural counterparts, then construction and restoration of these systems has the potential to become a tool for reducing atmospheric CO2. In this study, sediment organic carbon (OC) of a recently constructed mangrove and seagrass system in the Indian River Lagoon, Florida was compared with sediment OC of nearby mature, reference systems. Total OC, extractable OC, and microbial biomass C pools were measured to compare C storage. Organic C lability in the constructed and reference sites was also measured. The main sediment OC sources were determined using 13C isotopes and C:N ratios and were compared among systems. Organic C pools were generally larger in sediments of reference systems than in sediments of the constructed systems, but differences in pool sizes were much greater between the constructed and reference mangrove systems. Organic C lability was greater in the constructed systems indicating their sediments could not store OC for as long as the references. Seston was a major source of sediment OC in all systems. Other main sources of OC were higher plant-derived in constructed and reference mangrove and reference seagrass sediments, but were algal-derived in constructed seagrass sediments. After one year, the C sink capacity of the constructed systems is less than the capacity of the reference systems, but the

constructed seagrass system is functioning more like its reference than the constructed mangrove system. In the long term, however, the potential C sink capacity of the constructed mangrove system is greater.

CHAPTER 1
INTRODUCTION

Restoration and construction of coastal ecosystems may help mitigate the effects of climate change by reducing atmospheric carbon dioxide (CO2). Global climate change has become a major environmental concern over the past 50 years. The anthropogenic release of greenhouse gases is the major cause of global climate change (IPCC 2001). Atmospheric concentrations of CO2 and methane (CH4), the biggest contributors to climate change, are increased by fossil fuel burning and deforestation, and livestock production, respectively. Highly productive coastal ecosystems including salt marshes, seagrass beds, and mangrove forests are carbon (C) sinks. Salt marshes and mangroves store at least 44.6 Pg C in their sediments (Chmura et al. 2003). Seagrass beds, which make up only 0.15% of global marine area, account for 15% of global marine organic C (OC) storage (Hemminga and Duarte 2000). Sediment C storage values are even larger when stores of inorganic C like carbonates are taken into account (Zhu et al. 2002).

The C cycle in coastal ecosystems is an open cycle because OC is imported into and exported out of systems by water currents and tides. In a seagrass bed, seagrasses and macroalgae (drift and epiphytic) take up CO_2 and HCO_3^- from the water column to produce OC through photosynthesis (Fig. 1-1). When seagrass fronds senesce or break, they (and their associated macroalgae) become litterfall on top of sediments or are exported out of the system. Litterfall OC is either decomposed by microbes or incorporated into the sediment OC (SOC) pool by leaching, bioturbation, or burial. Imported OC, which may include terrestrial and mangrove detritus, is trapped by seagrass fronds and settles on the sediment. Seston, comprised of plankton, bacteria, and dissolved and particulate OC from in and outside the system, is also trapped by seagrass fronds. The fate of trapped OC is the same as litterfall. Seagrass root OC from exudates or dead tissue is immediately part of the SOC pool and can be used by microbes.

SOC can be part of three pools—microbial biomass C, labile OC, or recalcitrant OC. Generally, microbes consume mainly labile OC, which they respire as CO_2 or incorporate into their biomass. When microbes die, their OC becomes part of labile and recalcitrant pools. The more OC is reworked by microbes, the more recalcitrant it becomes. The recalcitrant pool is where OC is sequestered long-term and where OC undergoes abiotic condensation into complex humic materials. In mangrove forests, the C cycle is basically the same except for the C sources (Fig. 1-2). The inorganic C source used by mangroves is atmospheric CO_2, the litter is mangrove leaves, and imported OC trapped in litter by mangrove roots is seston and seagrass detritus.

The capacity of coastal ecosystems to sequester OC is greater than the capacity of terrestrial ecosystems. Coastal ecosystems are natural C sinks, while terrestrial systems reach an equilibrium where the net C fixed annually is about zero (Rabenhorst 1995). Constant accumulation of C in coastal ecosystems is due to their anoxic sediments. In these sediments, oxygen is depleted so electron acceptors that are not as efficient must be utilized by microbes to decompose OC. Coastal ecosystems also have a greater OC sequestration capacity than freshwater wetlands because they, unlike freshwater wetlands, do not use CO_2 as a terminal electron acceptor and therefore emit less CH_4 (Bridgham et al. 2006). In coastal ecosystems, sulfate is the terminal electron acceptor, and high sulfate levels inhibit methanogenesis (Capone and Kiene 1988). A study of mangrove forests did not detect CH_4 either dissolved in sediment porewaters or fluxing out of sediments and 51 to 75% of OM oxidation was occurring through sulfate reduction (Alongi et al. 2004). Coastal ecosystems, like salt marshes, mangrove forests, and seagrass beds, may therefore be highly significant C sinks because they accumulate C in sediments without emitting CH_4.

Many salt marsh, mangrove, and seagrass ecosystems have been degraded or lost through disturbances such as dredging channels and developing coastlines for human habitation (Valiela et al. 2001; Kennish 2002; Zedler 2004). This degradation and loss affects the biogeochemical functioning of coastal systems including C sequestration. Loss and degradation of coastal systems therefore affects the global C cycle and may increase the affects of climate change (Duarte et al. 2005; Bridgham et al. 2006). Globally, 50% of wetlands (freshwater and coastal) have been lost (Moser 1996). The continuous United States has lost 53% of its wetlands since the 1780's (Dahl 1990). Since 1989, the United States has had a policy of no net wetland loss that includes coastal wetlands (Zedler 2004). In Florida, state policy applies this principle to seagrass systems as well. Therefore when mangrove and seagrass ecosystems are destroyed, their loss must be mitigated by restoring or creating these systems elsewhere. It is important to know whether mitigation of coastal ecosystems restores the accumulation and storage capacity of these important C sinks. Such research can indicate whether mitigation is truly effective and whether coastal ecosystem restoration can become a policy tool for reducing CO_2 emissions, as was suggested by Connor et al. (2001). Functional trajectory studies of constructed systems and studies comparing constructed systems with natural systems are used to determine the effectiveness of mitigation in restoring ecosystem functions, like C storage.

Functional trajectories are used to monitor the development of ecological functions in constructed ecosystems over time. When constructed systems' functions equal those of reference systems, the constructed systems are said to be functionally equivalent. Studies that documented functional trajectories of OC in restored and constructed salt marshes concluded that it takes a long time for the restored/constructed marshes to develop SOC pools equal to their natural counterparts (Simenstad and Thom 1996; Craft 2001; Havens et al. 2002; Morgan and

Short 2002; Craft et al. 2003). Functional trajectory studies, with one exception (Evans and Short 2005), have been limited to temperate brackish and salt water marshes. There is a need to study functional trajectories in constructed mangrove forests and seagrass beds. Functional trajectory studies generally measure a suite of ecological functions, so SOC is usually the only variable measured that pertains to ecosystem C storage. Studies that examine multiple OC pools, OC lability, and OC sources are needed to more fully understand the recovery of C storage functioning in constructed systems. Studies that examine short term changes immediately following construction are also lacking. Short term trajectory studies are important because certain aspects of OC storage may recover quickly.

Whether constructed mangrove and seagrass ecosystems provide the same ecological services as their natural counterparts with respect to C storage, and whether restoration of these services follow a functional trajectory is currently unknown. In this thesis, the trajectories of SOC pools in constructed seagrass and mangrove systems were monitored during the first year after construction completion. SOC pools in the constructed systems were also compared with SOC pools in adjacent natural systems. Sediments were the focus of this research because they are the sites of long term C storage. Variables measured include the amount of OC in three pools (total OC, extractable OC, and microbial biomass C), the lability of SOC, and the C to nitrogen ratios and $\delta^{13}C$ of sediments and potential SOC sources. The constructed site was a former spoil island called SL 15 in the Indian River Lagoon, FL that was converted to a mangrove and seagrass ecosystem in November 2005. The reference sites were the natural seagrass beds that surround SL 15 and the nearby mangrove forests that occupy the edges of adjacent spoil islands.

The main research objectives were: 1) to determine short term trajectories of SOC pools in a constructed mangrove forest and seagrass bed; 2) to compare SOC pools in the constructed

system with those in more natural, reference systems; 3) to compare the lability of SOC in the constructed and reference systems; 4) to determine and compare significant sources to the total SOC pool in the constructed and reference systems.

The hypotheses were: 1) in the short term, storage in the three OC pools studied would increase in the constructed systems, but would not reach the level of storage in the references' OC pools; 2) OC lability would be greater in sediments of constructed systems than in reference sediments; 3) SOC sources in constructed systems would be macroalgae or plankton, while SOC sources in reference systems would be vascular plants, like mangroves and seagrass.

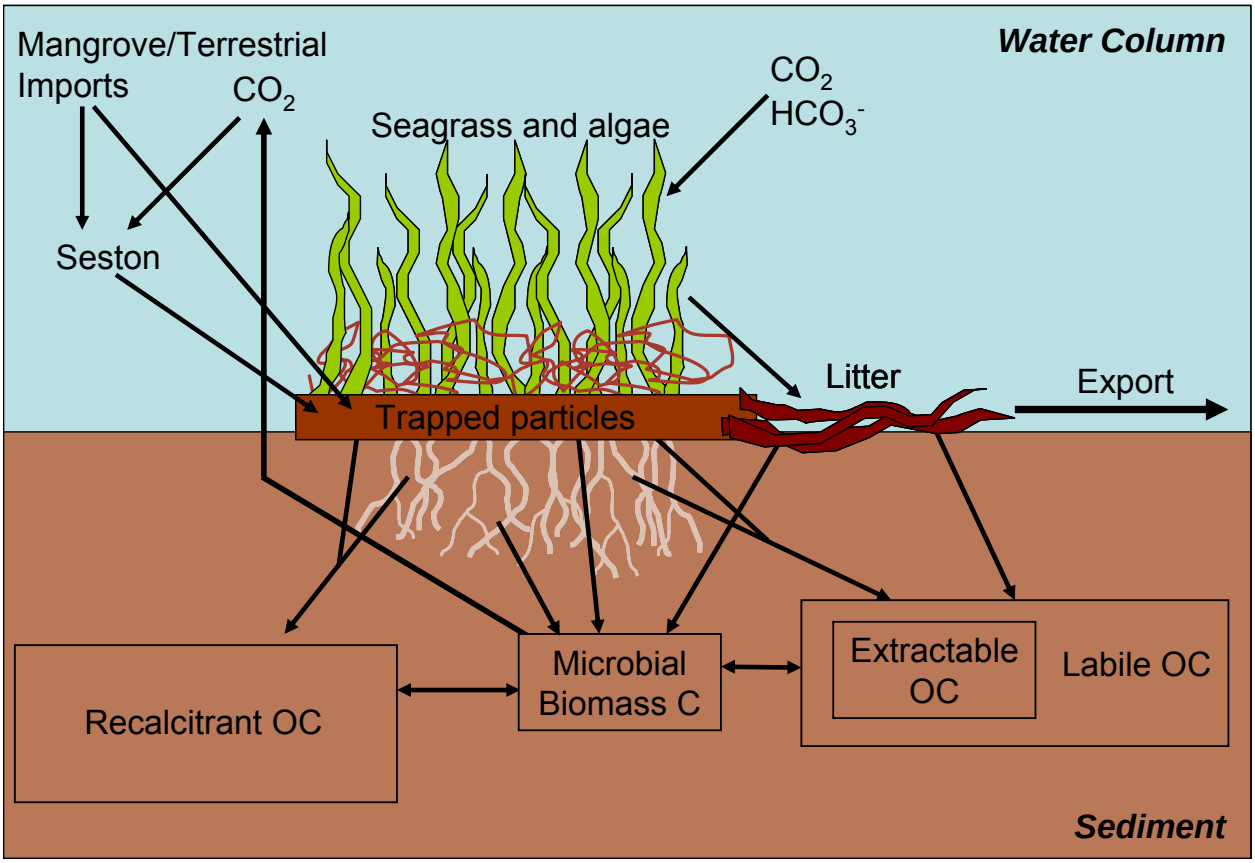


Figure 1-1. The carbon cycle in seagrass beds.

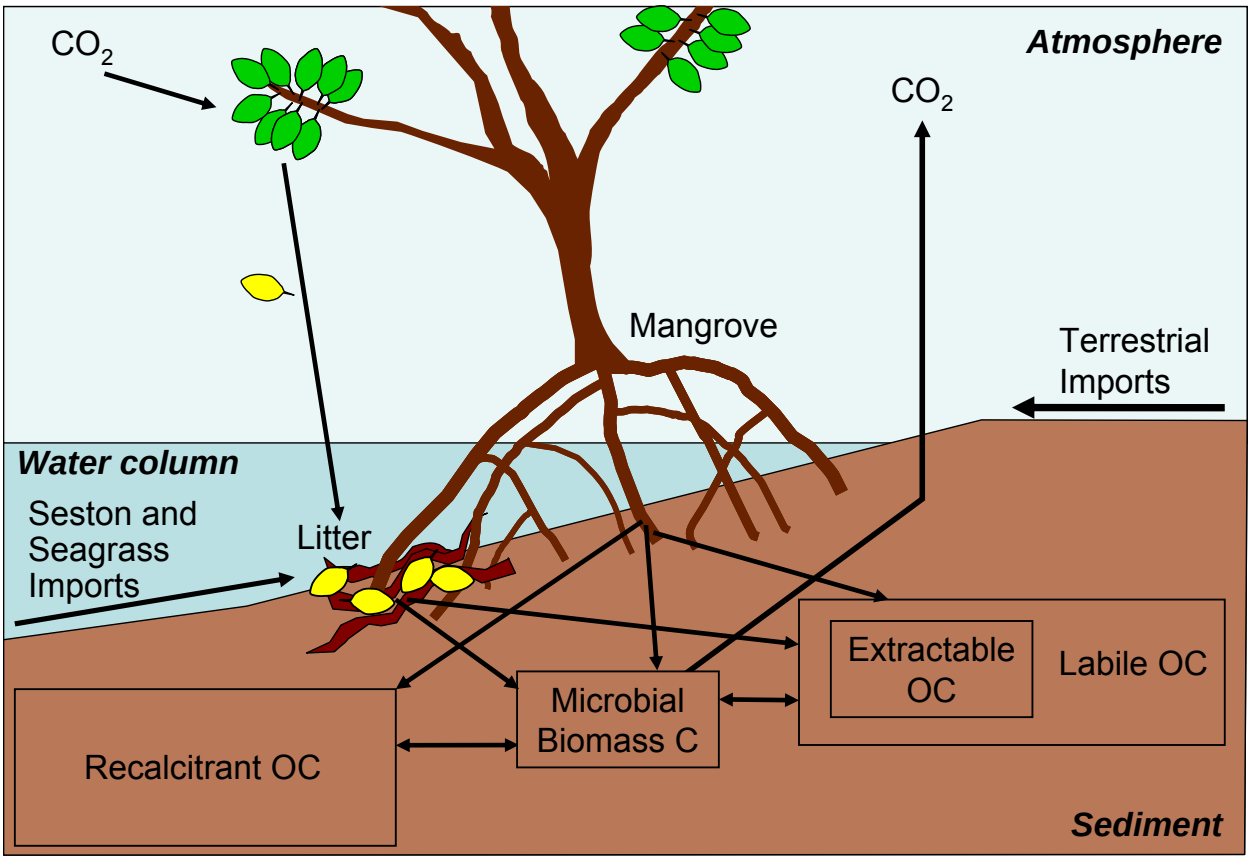


Figure 1-2. The carbon cycle in mangrove forests.

CHAPTER 2
LITERATURE REVIEW

Introduction

In this literature review, rates of organic carbon (OC) accumulation are compiled and compared for three coastal ecosystems—salt marshes, mangrove forests, and seagrass beds. Studies comparing sediment organic carbon (SOC) pools in restored or constructed salt marshes to SOC pools in natural salt marshes are then examined. This section does not discuss mangrove forests or seagrass beds because the literature on the functioning of restored or constructed coastal ecosystems is currently limited to salt marshes. Third, methods for determination of SOC sources are discussed for the three coastal ecosystems. These coastal ecosystems are dominated by vascular, halophytic macrophytes, with mangroves dominated by trees and salt marshes and seagrass beds dominated by grasses and other herbaceous species. Sediments in these systems are C sinks due to their high net primary production, trapping of material from the water column, and O_2 limited conditions.

These systems are globally distributed. Salt marshes and mangroves occupy non-rocky, sedimentary-driven intertidal zones of the world. Salt marshes predominate in temperate climates, while mangroves predominate in subtropical and tropical climates. Salt marshes are generally replaced by mangroves at a latitude of 25° N or S (Mitsch and Gosselink 2000). Seagrass systems are subtidal and are found from tropical through temperate climates where needs such as low light attenuation in the water column are met (Hemminga and Duarte 2000). Seagrasses are often found adjacent to their intertidal counterparts—salt marshes or mangroves. Multiple estimates of global area covered by each system differ, but in each system the estimates are within the same order of magnitude. According to the average of the estimates, mangrove forests cover 220,000 km^2, salt marshes cover 350,000 km^2, and seagrass beds cover 450,000

km^2 (Table 2-1). Together these systems occupy only 0.8% of the global ocean area, but they contribute 30% of the total ocean C storage (Duarte and Cebrian 1996). This observation indicates that these systems play a significant role in global sequestration of C.

Coastal ecosystems are better C sinks than terrestrial systems and freshwater wetlands. Coastal ecosystems and freshwater wetlands can accumulate C indefinitely while terrestrial systems reach an equilibrium where C fixed equals the amount respired annually (Rabenhorst 2005). Coastal ecosystems and freshwater wetlands' abilities to continually accumulate C are due to their anoxic sediments where electron acceptors other than O_2 must be utilized to decompose OC. These electron acceptors yield less energy to microbes than O_2, slowing decomposition rates (Schlesinger 1997).

Coastal ecosystems are better C sinks than freshwater wetlands, because they release orders of magnitude less CH_4, a potent greenhouse gas (Bridgham et al. 1996). CH_4 has a higher radiative forcing capacity than CO_2, so its global warming potential (GWP), a measure of its radiative forcing capacity per one unit mass relative to the radiative forcing capacity of one unit mass of CO_2, is by definition greater than the GWP of CO_2 (IPCC 2001). CH_4 release occurs because methanogenesis, the process where CO_2 is reduced to CH_4 in order to breakdown organic matter (OM), is the dominant decomposition pathway in most freshwater systems. In coastal ecosystems high sulfate levels inhibit methanogenesis as sulfate is a more energetically efficient electron acceptor than CO_2 (Capone and Kiene 1988).

Rates of Organic Carbon Sequestration

Before any discussion on rates of C accumulation, terminology and resulting caveats must be addressed. Not all studies use the same terminology when reporting rates of C accumulation and often studies do not specifically define their rate terminology. Terms used in the literature that all essentially meant "rate at which OC builds up in soil" were "rate of OC accumulation,"

"rate of OC sequestration," "rate of POC burial," "rate of refractory accumulation," and "organic accumulation rate." Nuances of these terms could be gleaned from methodology. Some like "rate of C accumulation" referred to additions of both labile and refractory OC to the SOC pool (Craft et al. 2003). Others like "rate of refractory accumulation" referred to long-term burial of OC that is unlikely to decompose on a human time scale (Cebrian 2002), and others like "POC burial" were vague (Alongi et al. 2005). Some studies reported OM accumulation, not OC accumulation. Those rates were divided by two to obtain OC accumulation rates. Also it was assumed that "C accumulation rates" referred to accumulation rates of OC, not total C, because studies that used the term reported measuring OC. Lastly, for indirectly measured rates (modeled or based on mass balance equations) it was not always clear whether rates included amounts of OC from both autochthonous and allocthonous sources. This review reports all values as "C accumulation rates," which refers to the build up of OC in sediments though there may be discrepancies in the lability of accumulating OC. Generally, the longer the timescale of a study, the more likely rates represent long-term burial. Only the term "C burial rates" definitively refers to long-term storage of refractory OC. There is a need for future studies to clearly define rate terminology and to be consistent in its use.

Global Rates

Many scientists have estimated global rates of C accumulation for coastal ecosystems due to their important role in the global C cycle (Table 2-2). Global rates of C accumulation for these systems are calculated in several ways. The most common way was averaging published accumulation rates for many sites (Duarte and Cebrian 1996; Chmura et al. 2003). Other methods included graphing frequency distributions of published accumulation rates (Cebrian 2002), scaling up from model-derived rates (Suzuki et al. 2003), or using mass balance equations derived from production and burial estimates (Jennerjahn and Ittekkot 2002). Despite the

different ways of calculating global rates, accumulation rates for intertidal systems are basically in agreement (Table 2-2). Estimated global accumulation rates for mangrove forests range from 92 to 200 g C m^{-2} yr^{-1} and rates for salt marshes range from 50 to 175 g C m^{-2} yr^{-1} (ignoring the high estimate of Rabenhorst (1995). Rates for seagrass beds are more variable and range from 16.5 to 270 g C m^{-2} yr^{-1}. Higher variability for seagrass ecosystems is likely because C accumulation rates in seagrass sediments have been studied less than in mangroves and salt marshes. Suzuki et al. (2003) estimated that seagrasses caused an accumulation of 1.2 g C m^{-2} yr^{-1} in deep ocean sediments due to export of their primary production to the open ocean and its subsequent burial. While this review concentrates on *in situ* accumulation, it is important to recognize that there are other ways these systems contribute to the global C sink.

Coastal ecosystems accumulate C at a rates several orders of magnitude greater than rates in terrestrial systems and the open ocean (Table 2-2). C cycling in terrestrial systems should reach a steady-state condition, making them neither a C source nor C sink (Hussein et al. 2004). Disturbances such as fire, however, occur before climax stages causing terrestrial systems to become C sources to the atmosphere. Coastal ecosystem C accumulation rates are greater than open ocean rates because their primary producers differ. Open ocean phytoplankton have a much lower net primary production (NPP) per unit area, have a greater percentage of their NPP consumed by herbivores, and contain more easily decomposed OM than coastal macrophytes (Duarte and Cebrian 1996; Cebrian 2002).

Local Rates

Mean global rates of C accumulation (2-2) were calculated using rates of C accumulation from numerous local studies (Table 2-3). The majority of C accumulation rates were measured in salt marshes while accumulation rates in seagrass beds were the least measured. Accumulation rates in mangrove forests ranged from 33 to 841 g C m^{-2} yr^{-1} with the lowest rate

measured in Terminos Lagoon, Mexico (Gonneea et al. 2004) and the highest rate measured at the low marsh in Jiulonglijang Estuary in China (Alongi et al. 2005). Rates in salt marshes ranged from 2 to 300 g C m^{-2} yr^{-1} with the lowest rate measured at a natural site in Dell's Creek, North Carolina (Craft et al. 2003) and the highest rate measured behind a continuous canal in Lafourche Parish, Louisiana (Cahoon and Turner 1989). Rates in seagrass beds ranged from 19 to 191 g C m^{-2} yr^{-1}, a range measured offshore of Cala Culip, Spain (Romero et al. 1994).

Comparing the compiled rates for these systems, there were no trends of one system having consistently higher C accumulation rates than the other systems (Table 2-3). The system accumulating C at the highest rates even varied within the same region. For example, in Celestun Lagoon, Mexico, mangroves accumulated more carbon in their sediments than seagrasses, but in Terminos Lagoon, Mexico, the reverse was true (Gonneea et al. 2004). This lack of a trend is supported by Chmura's (2003) review that found no significant differences between C accumulation rates in salt marshes and mangroves. It should be noted, however, that contributions of mangrove forests to C storage on an ecosystem scale may be greater than salt marshes and seagrass beds because large amounts of C are stored for decades in woody biomass of mangrove trees (Twilley et al. 1992).

Measuring Rates of Carbon Accumulation

Calculating rates of C accumulation typically involves three steps. The first step is to measure SOC pools. SOC pools for local rate studies were directly measured using either an elemental analyzer after acidification of the sample to get rid of carbonates (Gacia et al. 2002), a TOC analyzer (Brunskill et al. 2002; Alongi et al. 2004), or a mass spectrometer (Choi and Wang 2004). SOC pools were indirectly measured by using loss-on-ignition (LOI) values in regression equations describing the relationship between SOM and SOC (Connor et al. 2001). The second step is to age the sediment or measure rates of sediment accretion. Sediment age and

accretion rates are less straightforward measurements than SOC pool measurements. Radioisotope dating of cores using either ^{210}Pb and ^{14}C activity or δ^{137}Cs and ^{14}C peaks from nuclear bomb fallout were the most commonly used methods to date sediments (e.g. Callaway et al. 1997; Connor et al. 2001; Choi and Wang 2004; Hussein et al. 2004; Alongi et al. 2005). Other methods of dating sediments were Romero's (1994) use of a shipwreck whose date was known and that had been buried by seagrasses over hundreds of years and Chmura et al.'s (2001) use of pollen stratigraphy. Short term (1-3 years) accretion rates were measured with feldspar markers (Cahoon and Turner 1989; Cahoon 1994; Cahoon and Lynch 1997) or sediment traps (Gacia et al. 2002). The third step is to calculate C accumulation rates. The amount of OC in a unit of sediment is divided by the age of that sediment unit, or OC in a unit of sediment is multiplied by the rate at which that sediment unit accreted. Sediment ages in restored or constructed systems do not have to be determined because the site ages are known. C accumulation rates can be calculated by the difference between SOC content at the beginning of the restoration process and SOC content at subsequent points after the initial restoration, divided by site's age (Cammen 1975; Craft et al. 2003).

Calculated rates of C accumulation may be dependent on time scale, which is dependent on the method used. With a half-life of 5730 years, ^{14}C methods are suitable for measuring rates over many millennia, while with a half-life of 22.3 years, ^{210}Pb methods are suitable for measuring rates over a century (Bierman et al. 1998). Bomb fallout methods using δ^{137}Cs and ^{14}C peaks can only measure rates over the last 40 years as the peaks generally occur in 1963. Many of the highest rates of C accumulation were measured using the feldspar marker technique, which measures C accumulation rates over a year or two. These rates may be high because surface pools of SOC are relatively labile compared to deeper pools of SOC. Much of the

surface SOC may be mineralized by the time it is buried deeper in the soil profile, where it would be measured if longer term methods were used. Long term rates calculated by ^{14}C dating were slower than rates measured over a decadal (Choi and Wang 2004) or an 100 year time scale (Hussein et al. 2004). Choi and Wang (2004) did not attribute this difference to methodology and speculated that greater C accumulation rates are due to increases in primary production over the last 100 years caused by increased CO_2 and nutrients.

Comparing Organic Carbon in Restored and Reference Coastal Marshes

Highly productive habitats like coastal ecosystems are C sinks as their high C accumulation rates demonstrate. In these coastal ecosystems atmospheric CO_2 becomes stored as OC for long periods of time. Restoration and construction of coastal ecosystems may therefore help mitigate the effects of climate change by reducing atmospheric CO_2 (Connor et al. 2001). If limits are placed on CO_2 emissions in the United States, coastal ecosystem restoration and construction may then become a viable option for C offsetting. C offsetting occurs when an industry needs to reduce its net CO_2 emissions but can or will not reduce their own emissions, so they invest in projects that reduce emissions elsewhere, such as tree planting. Anthropogenic release of greenhouse gases is the major cause of global climate change (IPCC 2001). CO_2 and CH_4 are greenhouse gases with the biggest effect on climate change due to their concentrations in the atmosphere and radiative forcing capacity (IPCC 2001). Humans increase atmospheric concentrations of CO_2 through fossil fuel burning and land use change and concentrations of CH_4 through livestock production. This section of the review focuses on salt marshes due to the dearth of literature on functional trajectories in restored or constructed mangrove and seagrass systems.

Despite the numerous important ecological functions coastal ecosystems and wetlands provide, which extend well beyond their function as C sinks, many were viewed as wastelands

until recently (Broome et al. 1988). These systems were seen as wasted space that could be utilized for agriculture or valuable development. Wetlands, including salt marshes, were summarily destroyed without much thought to the consequences of their destruction through the 1980's. The lower 48 U.S. states lost 53% of its wetlands from the 1870's to the 1980's (Dahl 1990). Globally, it is estimated that 50% of the wetlands have been lost (Moser 1996). When these systems are lost, we lose a sink for anthropogenically-derived CO_2. For example, Connor et al. (2001) estimated that if 85% of the coastal marshes in the Bay of Fundy had not been altered for agricultural uses, 3.8 x $10\delta^{13}$ g C could have been stored over the past 160 years. The loss of coastal ecosystems and wetlands therefore disrupts the global C cycle and may increase the affects of climate change.

Since 1989, the U.S. has had a policy of no net wetland loss that includes coastal marshes (Zedler 2004). The policy calls for mitigation if alternatives to destroying wetlands in the course of development projects are unavailable. This mitigation comes in the form of creating new wetlands onsite or nearby to the lost wetland, restoring an existing, degraded wetland, or buying into wetland mitigation banks (Zedler 2004). Because of coastal marshes' importance as C sinks and the widespread replacement of natural marshes with created marshes, it is important to know whether restored and constructed marshes have OC accumulation rates and storage capacities equivalent to those of natural marshes. Such research can indicate whether marsh creation can become a policy tool for reducing CO_2 emissions. Connor et al. (2001) suggested that restoring coastal marshes may help countries reduce their CO_2 emissions to the standards set by the Kyoto protocol. Monitoring functional trajectories of constructed marshes helps researchers understand if constructed marshes' OC storage can equal the storage of natural marshes.

Monitoring Constructed Coastal Marshes Using Functional Trajectories

Functional trajectories are used to track the progress of constructed ecosystems and to compare constructed and natural ecosystems (Simenstad and Thom 1996; Zedler and Callaway 1999; Morgan and Short 2002). Functional trajectory studies often examine a whole suite of "ecological attributes" (Craft et al. 2003) that act as indicators for more complex ecological functions (Simenstad and Thom 1996). Attributes are measured in the same constructed system over time, or in several different-aged constructed systems in the same region using a space-for-time substitution, to obtain a range of attribute values that can be plotted against time (Kentula 1992). In coastal marshes, OC parameters are often just several of many attributes measured. Data are then fitted to a curve and compared with values from natural marshes. The resulting trajectory represents how the attribute develops in a restored or constructed marsh over time (Morgan and Short 2002). There are two main questions that functional trajectories studies seek to answer: 1) how long does it take for the attribute in the restored or constructed marsh to reach functional equivalence (i.e. the mean value of that attribute in a natural marsh); 2) is the mean value of an attribute in a natural marsh the correct endpoint for the development of that attribute in the restored or constructed marsh?

Not all attributes have the same trajectory, and trajectories of the same attribute may differ across different marshes and depending on the natural reference marsh used. There are many different trajectories that attributes like SOC pools can follow (Kentula et al. 1993; Fig. 3). Some attributes may not even follow a trajectory and instead stay relatively constant through time (Zedler and Calloway 1999). Craft et al. (2003) proposed that different attributes follow one of three trajectories depending on whether they are part of hydrologic, biological, or soil development processes. OC pool formation is part of soil development, which in most cases is the slowest trajectory to reach functional equivalence (Craft et al. 2003). If a trajectory fits OC

data well, it can be used to predict future levels of OC thereby helping agencies set standards for mitigation project monitoring or determine the amount of C emission credits a created marsh is worth. In theory, functional trajectories are a simple way to evaluate the current success and predict the future success of constructed marshes; data, however, do not always fit a smooth line. Often, there is high variability between constructed marshes (Craft et al. 2003) and between years in the same study (Zedler and Calloway 1999). The reference marshes used can also influence the predicted success or failure of a constructed marsh as a result of their age, variability (Simenstad and Thom 1996), or stress level. Furthermore, predictions from functional trajectories should be considered with caution because they do not take into account disturbances that may alter the trajectory.

Functional Trajectory Case Studies

The studies reviewed here examine the equivalence in constructed and restored marshes that are one (Morgan and Short 2002) to 42 years old (Craft 2001). The first prediction of functional equivalence for SOC in a salt marsh was made by Seneca et al. (1976) for one of the first salt marsh creation projects using dredge spoil, which is essentially devoid of OC. They predicted it would take 4 to 25 years for the constructed marsh to store as much C as the natural marsh. More recent studies show that it probably takes *at least* 25 years for OC to reach functional equivalence (Table 2-4). SOC and the related attribute, sediment organic matter (SOM), seem to be one of the last attributes to reach functional equivalence in marshes after aboveground biomass, sedimentation rates, and diversity of flora and fauna. There is also the possibility that OC will never reach functional equivalence as most studies did not follow marshes for a sufficient duration of time to show equivalence.

Most studies on the eastern coast of the United States found a trend of increasing SOC/SOM over time (Craft 2001; Havens et al. 2002; Morgan and Short 2002; Craft et al. 2003).

A study of different-aged New England salt marshes found that SOM increased steadily from 2% at a 1-year-old site to 15% at a 15-year-old site (Morgan and Short 2002). Studies from the western coast did not find strong directional trends of SOM over time. In Tacoma, Washington SOM stayed between 2-4% over 5 years (Simenstad and Thom 1996) and in San Diego, California only a slight increase of 3% was found over 11 years (Zedler and Calloway 1999). These differences in trajectories may be more a case of land use than geography. Both of the west coast studies took place in large urban areas, whereas the east coast studies took place in a variety of locales, none as developed as Tacoma and San Diego.

Only two studies documented tidal marshes that reached functional equivalence with their natural references in terms of SOC. The tidal marshes were 25 (Craft et al. 1999; Craft et al. 2003) and 42 (Craft 2001) years old. Both these marshes are located in the southeastern U. S. These marshes achieved functional equivalence possibly because they, or their references, differed from most of the marshes studied. The 42-year-old marsh differed because it was a restored marsh and not a marsh constructed from dredge spoil. Instead, it had been disturbed by a dike that prevented tidal inundation but was removed after only 8 years (Craft 2001). The 25-year-old marsh differed because its reference marsh was a relatively new natural salt marsh, which contrasted to other reference marshes that are greater than 2,500 years old (Craft et al. 1999). Because the reference was relatively young, its soils resembled spoil (90% sand) more than a histosol (>10% OM). They were mineral entisols with a high bulk density and low OC content (<1.4%). Reference marshes can determine whether or not a constructed marsh reaches functional equivalence because their mean attribute values represent functional equivalence "finish lines."

Factors Affecting Functional Equivalence

The reference marsh used affects the functional equivalence of the constructed marsh. In the last example (Craft et al. 1999), if the SOC pool of the 25-year-old constructed marsh had been compared to the SOC pool of the 2,500-year-old natural marsh with a high OM content, the authors would have concluded that the constructed marsh had not yet reached functional equivalence. Many studies choose nearby natural marshes as references without regard to their similarities to constructed marshes. Studies in urban areas are particularly limited by reference sites as the restored site is often the only large area of marsh remaining (Simenstad and Thom 1996). Morgan and Short (2002) solved some of the problems associated with reference site choice when they chose reference sites after comparing constructed sites to potential reference sites using a principle components analysis (PCA) based on physical attributes like aspect, slope, and size. They used the PCA to choose two well-matched reference sites for each constructed site. Because reference marsh is a major factor in whether a constructed marsh reaches functional equivalence, it should not be chosen arbitrarily.

While between-system factors affect whether a constructed wetland reaches functional equivalence, so do within-system factors like elevation, depth in the soil profile, and variation in sedimentation rates. Even when a constructed marsh as a whole is far from reaching functional equivalence in terms of SOC, some parts of it may be closer than others. Several studies found higher SOC at low elevations in constructed marshes (Lindau and Hossner 1981; Craft et al. 2002). Lower elevations are inundated by tides for longer periods of time, which leads to more highly reducing conditions that can encourage OC storage. In most soils or sediments, OC naturally decreases with depth, which may hinder the ability of lower depths to reach functional equivalence. In one of the only studies to examine OC at different depths in the soil profile, upper depths reached functional equivalence quickly while OC values at lower depths did not

increase over 7 years (Havens et al. 2002). Sedimentation of mineral particles dilutes SOC concentrations. Creek banks often have lower OC concentrations than the interior of marshes (Craft et al. 2002) because they experience greater sedimentation of mineral particles (e.g. Temmerman et al. 2003). Simenstad and Thom (1996) cited sedimentation as a reason why SOM in a restored marsh did not increase with time.

Storing Carbon Versus Sinking Carbon

Even though most constructed marshes do not yet store the same amount of C as their natural counterparts, they may still be acting as C sinks. A few studies examined OC accumulation rates as well as SOC pools and found that OC accumulation rates in constructed marshes are as high as or higher than rates in constructed marshes (Cammen 1975; Craft et al. 2002; Craft 2001). The mean OC accumulation rate of 8 different-aged constructed wetlands in North Carolina was 42 g C m^{-2} yr^{-1} compared to 43 g C m^{-2} yr^{-1} in the reference wetlands, even though the OC pools (g C m^{-2}) in the constructed wetlands were significantly lower (Craft et al. 2003). Additionally, some young marshes have high sedimentation rates (Morgan and Short 2002). Sedimentation may encourage OC accumulation while reducing SOC concentrations resulting in a reciprocal relationship as was demonstrated in Bay of Fundy marshes (Connor et al. 2001). High sedimentation rates may have prevented SOC pools from increasing in the Tacoma and San Diego constructed marshes while encouraging OC accumulation, which unfortunately was not measured in those studies.

New Directions

The extensive studies on coastal marsh functional trajectories have been broad in scope and therefore unable to examine OC dynamics in constructed marshes with sufficient detail. SOC is a conglomeration of pools that include a labile pool, a slowly oxidized pool, a very slowly oxidized pool, and a recalcitrant pool (Eswaran et al. 1995). The pool matters, as the one

containing the most OC affects the overall sequestration abilities of a wetland. A wetland with most of its OC in the recalcitrant pool is going to sequester C longer than a wetland with most of its OC in a labile pool like microbial biomass, which has frequent turnover. A study of macro organic matter (MOM), precursor of SOM, in constructed marshes showed that younger marshes had more labile MOM than older marshes indicating they were less likely to sequester OC in the long term (Craft et al. 2003).

Sources of SOC may also be important as they influence OC lability, carbon to nitrogen ratios (C:N), and the rate at which OC accumulates. Morgan and Short (2002) hypothesized that the lag time in OC accumulation is because macrophytes must first become established before they contribute to the SOM pool. Others claim that seston, a mixture of plankton and detritus, is the main source of SOM so accumulation should occur whether a site has macrophytes or not (Cammen 1975). Organic matter C:N ratios may also be a significant parameter because the ratios indicate whether accumulation of C is likely. If the C:N ratio is low, the microbes may be starved for C, and therefore more likely to decompose OC and respire CO_2.

Because these studies have been so broad in scope, they also do not take the time to use the best methodology for measuring OC. While loss on ignition (LOI) is the easiest way, the high carbonate content of coastal sediments/soils may interfere with the results (Nieuwenhuize et al. 1994). Furthermore, LOI is a measure of OM so conversion factors, with their associated errors, need to be used to convert an OM value to an OC value. Older studies (e.g. Cammen 1975) used the Walkley-Black chromic acid oxidation method to determine OC, which is only 75-90% efficient at obtaining a true OC value (Nieuwenhuize et al. 1994). While errors in the method are not a significant problem for comparison studies reviewed here, they are a concern if constructed wetlands are to be used for C emission offsetting. Future work should consider *in*

situ acidification techniques and subsequent analysis with an elemental analyzer as the standard method for OC measurements (Nieuwenhuize et al. 1994).

Lastly, research is needed that addresses the permanency of C storage in constructed and restored coastal systems. Disturbances like changes in nutrient loading, invasive species, and hurricanes can affect C storage. A nutrient loading experiment in a North Carolina salt marsh increased microbial respiration and caused a subsequent net loss of SOC over 12 years (Morris and Bradley 1999). Alternatively, the spread of a native, yet invasive, grass species in a natural coastal marsh in France was found to increase SOC storage (Valery et al. 2004). These studies occurred in natural marshes, and studies that examine disturbance effect on SOC in constructed coastal systems are needed because constructed systems may be less resilient than natural systems. In order for constructed coastal systems to become a viable option for C offsets, these effects need to be understood and quantified.

More thorough studies are needed on the C sink capabilities of restored and constructed coastal ecosystems. Thus far, the vast majority of studies have been carried out in salt marshes. Studies are needed in coastal ecosystems like mangrove forests and seagrass beds whose destruction is also routinely mitigated with restoration and construction. If researchers can prove that constructed systems are effective C sinks by demonstrating that they not only follow trajectories of increasing SOC, but also have OC accumulation rates similar to natural ecosystems, then constructing coastal ecosystems may become an accepted way to offset CO_2 emissions. Institutions such as Climate Neutral (www.climateneutral.org) and the Chicago Climate Exchange (www.chicagoclimatex.com) could use coastal ecosystem construction to offset emissions like they now do with certain forestry and agricultural practices.

Sediment Organic Carbon Source Determination

One of the new directions functional trajectory studies could take is examining sources of SOC in constructed coastal systems. Determining SOC sources is important to the study of OC storage in coastal ecosystems as the identity of sources is one of the factors that determine OC lability and accumulation rates. Hedges (1992) stated that understanding the types of OM that accumulate in marine sediments was one of the key questions that needs to be answered in order to better understand global biogeochemical cycles. The source determination question most often studied is whether the SOC is of allochthonous (via sedimentation) or autochthonous origin (Middelburg et al. 1997; Bouillon et al. 2003; Golding et al. 2004). If most SOC is of autochthonous origin, then contributions to SOC from the primary producers needs to be teased apart, but this detailed question is harder to answer and rarely studied (Bouillon et al. 2003). There are many possible SOC sources in seagrass beds, mangroves, and salt marshes. Coastal ecosystems can have allochthonous OC inputs of planktonic origin from the open sea or of terrestrial plant and anthropogenic origin. These systems also have numerous potential autochthonous OC inputs. Within a seagrass bed OC can come from different species of seagrasses, epiphytes, macroalgae, or micro-benthic algae. Seagrass beds can also receive OC inputs from adjacent mangroves (Kennedy et al. 2004; Lin et al. 1991). The complexities of seagrass beds, mangroves, and salt marshes make OC source determination difficult. However, making sense of complex OC sources and their role in C accumulation and storage is important for the conservation of coastal ecosystems in the face of increased nutrient loading and sea level rise and the maintenance of their C sink capabilities.

Many methods have been used to determine SOC sources; however, no single method has offered a definitive answer among and within system types. Some methods were developed for two end-member systems—systems in which there are only two distinct sources of OC such as

allochthonous terrestrial plant matter and autochthonous marine plankton. Such simple systems may be encountered in estuaries that lack submerged aquatic vegetation (Golding et al. 2004). Sometimes researchers simply group the sources of OC into two end-member groups. For example, in salt marshes the SOC inputs from *Spartina* can be distinguished from the inputs from all other sources because they differ in their $\delta^{13}C$ values (Middelburg et al. 1997). These two end-member models are often useful in estimating the major categories of OC sources (i.e. whether allochthonous or autochthonous), but they cannot fully partition the individual SOC sources.

The variety of methods used to determine OC inputs range widely in terms of time and equipment involved. Methods can be as simple as comparing C:N ratios of possible sources with sediment C:N ratios or as complicated as searching for a biomarker and then isolating and concentrating that specific compound for isotopic analysis. The most widely used method involves stable isotopes—either comparing bulk composition of $\delta^{13}C$ in possible sources and sediments or comparing composition of $\delta^{13}C$ in lipids found in possible sources and sediments. Lipids and other biomarkers can also be used singly to determine sources. Other methods, which include petrographic analysis and nuclear magnetic resonance spectroscopy (NMR), involve comparing relative amounts of different OC structures in the soil.

Stable Isotopes

In salt marshes, mangrove forests, and seagrass beds many researchers have tried to determine SOC sources by matching the $\delta^{13}C$ isotopic signatures of the bulk sediment to the $\delta^{13}C$ isotopic signatures of the sources via strait comparison of the numbers, mixing models, or diagrams (Table 2-5). In order for stable isotopes to elucidate OC sources, the sources need to have consistently distinct isotopic signatures (Papadimitriou et al. 2005). The various primary producers in coastal systems develop distinct isotopic signatures through their discrimination

against heavy isotopes during carbon uptake and fixation. Discrimination against the heavy isotope is highest when the inorganic C exceeds supply. Generally, C_3 plants are lighter ($\delta^{13}C$ = -35 to -20 ‰) than C_4 plants ($\delta^{13}C$ = -15 to -9 ‰) in their $\delta^{13}C$ signatures due to the strong isotopic discrimination of the carboxylase Rubisco, an enzyme that is not found in the C fixation pathway of C_4 plants (Hemminga and Mateo 1996; Hemminga and Duarte 2000). Luckily for C source determination in coastal systems, the principal primary producers of seagrass beds, mangrove forests, and salt marshes all have isotopic signatures distinct from the signatures of the less abundant primary producers within these systems. Seagrasses are relatively heavy isotopically with average $\delta^{13}C$ values of -10 to -11 ‰ (Hemminga and Mateo 1996). Mangroves, a C_3 plant, have isotopic signatures close to that of many terrestrial primary producers with $\delta^{13}C$ values around -28 ‰ (Jennerjahn and Ittekkot 2002; Kennedy et al. 2004). *Spartina* species that dominate salt marshes are C_4 plants with $\delta^{13}C$ values around -12 to -13 ‰ (Haines 1976; Middelburg et al. 1997). The isotopic signatures of other primary producers such as plankton and epiphytes generally fall below that of seagrasses and *Spartina* and above that of mangroves (Kennedy et al. 2004; Papadimitriou et al. 2005), but this is not always the case.

In order for the bulk stable isotope method to be accurate, the $\delta\,\delta^{13}C$ signature of the sources must not change during decomposition, or if they do change, the magnitude of the change needs to be small when compared to inter-source differences (Papadimitriou et al. 2005). Changes during decomposition are often small, like the 0.7 ‰ difference found between fresh and senescent mangrove leaves in Brazil (Jennerjahn and Ittekot 2002), but are variable in direction and magnitude depending on the plant (Dai et al. 2005).

A study of OC inputs into seagrass (*Posidonia oceanica*) sediments of 22 sites in the northwestern Mediterranean by Papadimitriou et al. (2005) is a good example of the potential of

bulk isotopic studies and their inherent weaknesses. They measured $\delta^{13}C$ and ^{15}N isotopic signatures of the top 2cm of fine fraction (>63um) sediments and of potential sources—seston (assumed to represent phytoplankton), above- and below-ground seagrass tissues, and epiphytes. $\delta^{13}C$ values of the sediments ranged from -15.8 ‰ to -21.5 ‰ and average $\delta^{13}C$ values of seston, epiphytes, below-ground seagrass tissues, and above-ground tissues were -22.1 ‰, -17.8 ‰, -12.1 ‰, and -12.6 ‰, respectively. No systematic differences in the ^{15}N values of the potential sources were found; most likely because discrimination against different N isotopes is not due to physiology of primary producers and because N is often a limiting nutrient. At all sites, SOC was more depleted isotopically than seagrass tissues but less depleted than seston. Using a mixing equation based on one developed by Dauby (1989), they were able to find a range of fractional contribution values of each source.

$$^{13}C_{sediment} = f_{seston}\delta^{13}C_{seston} + f_{epeiphytes}\delta^{13}C_{epiphytes} + f_{seagrass}\delta^{13}C_{seagrass} \qquad (2\text{-}1)$$

In equation 2-1, f_i is the unknown proportion of the OC from source *i* in the SOC pool and $\delta^{13}C$ is the isotopic signature of source *i*. This equation is used to find the range of *f* values for each source needed to satisfy the equation and equal the sediment $\delta^{13}C$ value. With this model, they were able to determine which sites had seston as the major contributor to SOC and which sites had seagrass as the major contributor to SOC. If this were simply a two end member system involving seagrasses and seston, the elucidation of sources to the sediments using this model would have been straightforward. But these sites also included epiphytes, and their intermediate $\delta^{13}C$ signature made it impossible for the model to assign them reasonable contribution ranges (often the ranges included a 0% contribution). Thus the relative contribution of epiphytes to SOC could not be determined by bulk isotopic methods alone.

A similar method was employed by Kennedy et al. (2004) when they examined SOC sources in seagrass beds, mangroves, and mixed seagrass/mangrove systems in the South China Sea. They measured $\delta^{13}C$ values of sediments, particles in sediment traps, and potential sources (seagrass leaves, mangrove leaves, epiphytes, and seston). They found consistent and distinct differences in the $\delta^{13}C$ values of potential sources. The use of the mixing equation gave broad estimates of source contribution, which suggested that seagrasses and mangroves contributed to the SOC in their respective systems, but that seston and epiphytes were probably the dominant sources. As with the study by Papadimitriou et al. (2005), the presence of intermediate signatures (epiphytes and seston) between the two end members (seagrass and mangroves) made determination of contributions from sources with intermediate $\delta^{13}C$ values difficult.

In salt marshes, similar problems are encountered. While the importance of the main primary producer's contribution can be easily elucidated, the contributions of other sources with less distinct $\delta^{13}C$ signatures cannot be. In one of the first studies that used C isotopes to examine SOC sources, *Spartina* had the distinctive enriched $\delta^{13}C$ values (-12.3 to -13.6 ‰) of C_4 plants, but all other vascular plants including species as disparate as *Juncus roemerianus* and *Salicornia virginica* had signatures between -22.8 and -26 ‰ because they were C_3 plants (Haines, 1976). Benthic diatoms in this study were plagued with the same intermediately-valued problem as the previously-discussed epiphytes with $\delta^{13}C$ values between -16.2 and -17.9 $^{0}/_{00}$. Through comparing the primary producer and sediment values, Haines concluded sediment $\delta^{13}C$ values generally reflected values of plants growing in the sediments. Sediments beneath C_4 plants were slightly more depleted in $\delta^{13}C$ than the C_4 plants, and sediments beneath the C_3 plants were slightly more enriched in $\delta^{13}C$ than the C_3 plants. The sediments' differences from *in situ* vegetation may have been due to C_3 and C_4 plant detritus mixing or input from benthic diatoms.

Inputs to SOC from individual species of C_3 plant were unknown because their signatures were not distinct.

Middelburg et al. (1997) avoided problems associated with intermediate and indistinct values by using $\delta^{13}C$ isotopes for the sole purpose of determining the amount of *Spartina*-derived SOC in salt marshes in Massachusetts (Great Marsh) and the Netherlands (Waarde Marsh). In Great Marsh, high marsh SOC $\delta^{13}C$ value (-13.4 to -14.5 ‰) was similar to the *Spartina* value (-12.5 ‰), but low marsh SOC $\delta^{13}C$ value (-21 to -19.5 ‰) was not. In Waarde Marsh SOC was 9-12 ‰ less than the *Spartina* value (-12.7 ‰). They hypothesized that depletions of SOC values in Waarde marsh and the low marsh of Great Marsh were due to the input of allocthonous OM such as marine plankton and non-local macrophytes, but since they did not measure these sources they could not definitively identify which contributed to the depletion. They concluded Great Marsh was a peaty marsh where C accumulation was due to *Spartina* inputs and Waarde marsh was a mineral marsh where accumulation was due to sedimentation.

Problems with intermediate values were encountered by all previously discussed studies that tried to comprehensively measure $\delta^{13}C$ values of all major sources. These studies often used either a variation of the mixing equation developed by Dauby (1989) or a simple comparison of sources and sediment isotope values. However, other ways to calculate source contributions may partially eliminate problems with intermediate values. Gonneea et al. (2004) used a ternary mixing diagram to elucidate relative source contributions of seagrass, mangroves, and seston to SOC. With a ternary mixing diagram, all sources were end members as they formed a triangle on a graph of C:N ratios plotted against $\delta^{13}C$ values. Sediment C:N and $\delta^{13}C$ values were also plotted on this diagram, which had a 10% tolerance interval to account for natural variability in source values. Sediment samples that fell in the middle of the triangle were

assumed to be a mixture of all three sources, samples that fell along a line connecting two end-members were considered a mixture of those two sources, samples that fell near one end member were assumed to have OC predominantly from that source, and samples that fell outside the triangle were assumed to have OC contributions from additional sources. This method is limited to systems with three main sources. Conclusions of research, like Papadimitriou et al.'s (2005) study of seagrass, seston, and epiphytes, could have benefited from this method if had they measured C:N ratios.

Comparisons of actual values to values from a predicted model can sometimes help elucidate sources better than a mixing equation based on the actual data. These models are based on biomass of potential sources (Chmura et al. 1987), primary productivity (Bull et al. 1999), or %SOC (Middelburg et al. 1997). The problem with these models is that they assume sources contribute to SOM in the same relative proportions as their biomass/productivity. This assumption may not be correct because sources differ in their degrees of lability, in their litterfall, and in the amount of their biomass that is exported out of the system. However, models are good approximations, especially in more peaty coastal wetlands where sediments have high OC and sedimentation of allocthonous OC inputs is minimal.

For the above methods of calculating SOM sources from isotope values, parameters other than the $\delta^{13}C$ values, such as biomass or C:N ratios, are needed. These other parameters also support conclusions based on isotopic values alone. Many studies combine C:N ratios with isotopic measurements (Middelburg et al. 1997; Bouillon et al. 2003; Soto-Jimenez et al. 2003; Thimdee et al. 2003; Gonneea et al. 2004). Correlations between C:N ratios or %SOC and $\delta^{13}C$ values are used to assist in determining SOC sources. A mild relationship ($R^2 = 0.26$) was found to exist between $\delta^{13}C$ values and C:N ratios in a Mexican salt marsh where less negative $\delta^{13}C$

values corresponded to lower C:N ratios (Soto-Jimenez et al. 2003). In the Mexican marsh lower C:N ratios were thought to be indicative of marine producers, specifically plankton. A brief review of sediment $\delta^{13}C$ and C:N values from mangrove literature also showed an inverse relationship between the two variables (Bouillon et al. 2003). Similar trends were found when comparing sediment $\delta^{13}C$ and %SOC values in mangroves (Bouillon et al. 2003) and salt marshes (Middelburg et al. 1997). More depleted $\delta^{13}C$ values corresponded with higher %SOC in mangroves and more enriched $\delta^{13}C$ values corresponded with higher %SOC in salt marshes. Generally, the higher the sediment %OC values, the closer the sediment $\delta^{13}C$ values are to the $\delta^{13}C$ values of the dominant vegetation (Bouillon et al. 2003).

There are other complications with the use of stable isotopes for OC source determination. Problems not already discussed include inherent variation of isotopic signatures within different tissues of a single individual (Papadimitriou et al. 2005) and within a single species (Hemminga and Mateo 1996) across sites (Kennedy et al. 2004), seasons, and years (Anderson and Fourqurean, 2003; Fourqurean et al. 2005). These variations are most pronounced in seagrasses (Thimdee et al. 2003). Such variation may be due to changes in relative uses of dissolved CO_2 and HCO_3^- (sources of inorganic C in water) (Lin et al. 1991), and changes in irradiance, photosynthesis rates, and temperature (Hemminga and Mateo 1996). Kennedy et al. (2004) found that isotopic signatures of sources such as seagrasses ($\delta^{13}C$ = -5.8 to -13.3 ‰) and seston ($\delta^{13}C$ = -9.6 to -22.9 ‰) varied greatly among 15 different sites in the South China Sea. The order trend of potential sources' $\delta^{13}C$ signatures (seagrass > epiphyte > seston > mangrove) remained constant, however. Variation by location means that conclusions based on measurement of SOC $\delta^{13}C$ values without measuring potential sources may not be valid. Soto-Jimenez et al. (2003) inappropriately used isotopes when they only measured sediments

signatures in a Mexican marsh. Average $\delta^{13}C$ value of sediment was -20.4 ‰ and they assumed, based on previously published $\delta^{13}C$ signatures of sources in *temperate* estuaries, that dominant SOC sources were plankton and macrophytes. While $\delta^{13}C$ values of putative sources at each site need to be measured at least once per site, Fourqurean et al. (2005) proposed further determination of source $\delta^{13}C$ values seasonally and annually.

Lipid Biomarker Compounds

The use of specific organic compounds, called biomarkers, to identify SOC sources in coastal ecosystems is becoming more common. These compounds are generally lipids including sterols, fatty acids, and hydrocarbons. The ways these organic compounds are used vary because the compounds vary in their specificity—some can identify groups of organisms such as vascular plants or algae while others may be specific to one genera or species (Canuel et al. 1997). Less specific biomarkers can be used in conjunction with stable isotopes to further differentiate sources from general groups (i.e. vascular plants into C_3 and C_4 groups). Many studies used biomarkers in concert with bulk stable isotopes (Hernandez et al. 2001; Wang et al. 2003) or measured the stable isotopic composition of biomarker compounds in sources and sediment (Canuel et al. 1997; Bull et al. 1999; Hernandez et al. 2001; Mead et al. 2005).

This method uses a gas chromatography (GC) to determine lipids after a complex and lipid-type specific extraction process. The different lipids are separated by the GC column due to their different retention time within the column. Different lipids can be identified by comparing their relative retention times on the resulting gas chromatogram with relative retention times on a gas chromatogram of a known standard. Relative amounts of each lipid can also be determined by calculating areas underneath each peak on the chromatogram—larger areas correspond to a larger amount of that lipid in the sample. Isotopic signatures of these lipids can be determined when the GC is connected to a mass spectrometer in a method known as

isotope ratio-monitoring gas chromatography-mass spectroscopy (irm-GCMS) (Canuel et al. 1997).

Canuel et al. (1997) examined the usefulness of isotopic signatures of specific lipid compounds to identify SOC sources in coastal ecosystems. The study examined isotopic signatures of bulk organic matter, total lipid extracts, and a whole suite of lipid compounds in three vascular plants, *S. alterniflora, J. roemerianus*, and *Zostera marina*, suspended particulate matter (SPM), and sediment in North Carolina. Vascular plants had similar molecular compositions of sterols and fatty acids but differed in hydrocarbon compositions, specifically in ranges and maxima of *n*-alkanes and the presence of monosaturated alkenes. SPM had a different lipid composition than vascular plants; the majority (>50%) of SPM's hydrocarbons were C_{25} highly branched isoprenoids (HBI) alkenes. Among different vascular plant lipids there was a variety of isotopic signatures with an average depletion of 3-5 ‰ in lipid $\delta^{13}C$ values relative to bulk values. Lipids in *Z. mostera*, *S. alterniflora*, and *J. roemerianus* followed the same trend in $\delta^{13}C$ values as bulk tissues with mean $\delta^{13}C$ values (in ‰) of -14.8 to -18.9, -18.4 to -22.6, and -29.0 to -33.8 for lipids and of -10.0, -12.6, and -26.0 for bulk tissues, respectively. Differences between bulk and lipid signatures demonstrated another reason caution should be used in analyzing bulk isotopic studies because compounds preserved in SOC may not have the same signature as bulk plant matter (Canuel et al. 1997). $\delta^{13}C$ values of lipids in sediments were different than those for the same lipids in vascular plants, but similar to SPM lipids. Sediments had a higher diversity of lipids than vascular plants, small amounts of major vascular plant biomarkers like C_{21} and C_{29} (maxima observed in the *Z. mostera* and *S. alterniflora* tissues), and a lot of the major SPM biomarker, C_{25} HBI. The study concluded vascular plants were only minor contributors to SOC.

The North Carolina study shows how the molecular distribution (diversity of types and dominant types) of lipids and isotopic signatures of lipids can be used to determine SOC sources. The method was not without problems, however. Use of compound classes that may not be the "most" diagnostic for vascular plants may have skewed results. Furthermore, this technique is biased toward extractable, not bound, lipids in sediments (Canuel et al. 1997). It is important to note that only the top 0.5 cm of sediment was analyzed in this study. Thus, depths where macrophyte roots may contribute to SOC through exudates or senescent tissue were ignored.

Not all studies examine a wide range of lipids. It is common to examine only one lipid class such as *n*-alkanols (Bull et al. 1999) or n-alkanes (Wang et al. 2003). Studying the $\delta^{13}C$ values of one type of lipid biomarker can help solve the intermediate-value problem that muddles analysis of SOC sources in bulk isotope studies. The use of compounds that are specific to vascular plants (n-alkanes) or to plankton and algae (HBI alkenes; Canuel et al. 1997) for isotope studies can help clarify their contributions to SOC (i.e.: whether a sediment bulk $\delta^{13}C$ value of -18 ‰ is due to an even mix of C_4 and C_3 plants, only plankton, or a mixture of all three). The n-alkanol homologue, C_{32}, was chosen for a study addressing contributions of *S. alterniflora* and *Puccinellia maritima* to salt marsh SOC in the United Kingdom (Bull et al. 1999). By only examining $\delta^{13}C$ values of an n-alkanol, which plankton cannot produce, plankton's confounding intermediate $\delta^{13}C$ value was removed as a factor from the isotopic mixing equation. Using a two-member mixing model based on $\delta^{13}C$ values of the C_{32} n-homologue, contributions of *S. alterniflora* to SOC were calculated. *S. alterniflora* contributed about 100% of primary biomass to sediments directly beneath *S. alterniflora* stands and about 50% to sediments beneath *P. maritima* stands. To fully understand all sources to SOC, this method should be expanded to include group-specific biomarkers for both vascular plants and plankton. Otherwise when

analyzing only $\delta^{13}C$ values of a biomarker for one plant group, contributions of plants outside that group remain unknown.

Mead et al. (2005) took the examination of group-specific series of homologues a step farther when they used an n-alkane-based proxy, P*aq*, along with compound-specific stable isotopes to elucidate sources along a gradient of freshwater marsh to estuarine mangrove forests to marine seagrass beds in the Florida Everglades. P*aq* is calculated from abundances of different *n*-alkane homologues.

$$Paq = (C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31}) \quad (2\text{-}2)$$

In equation 2-2, C_x is the amount of the C_x *n*-alkane. Submerged and floating macrophytes like seagrasses contained more abundant mid chain *n*-alkanes and therefore had a higher P*aq* than emergent macrophytes and terrestrial plants like mangroves. This method was able to resolve sources to a greater extent than studies using only isotopes or only biomarkers in estuaries because sources with similar P*aq* values were differentiated using n-alkane $\delta^{13}C$ values and vice versa. Generally, as the gradient went from freshwater marsh to seagrass beds there was a trend of increasing sediment $\delta^{13}C$ values and increasing P*aq* values. These trends were further connected to contributions of individual sources through a PCA based on compound specific $\delta^{13}C$ and P*aq*.

An example using a species-specific biomarker is the study of different homologues of the *n*-alkane-2-ones lipid series to elucidate SOC sources in the Harney River estuary and the adjacent Florida shelf (Hernandez et al. 2001; Mead et al. 2005). Lipids in this series generally have odd-numbered C chains ranging from 19 to 33 C's in length. There has been some debate about whether n-alkane-2-ones arise is sediments directly from plant detritus or whether they arise from microbial oxidation of alkanes. However, Hernandez et al. (2001) were able to find

significant amounts of n-alkane-2-ones in tissues of seagrasses and mangroves. In seagrasses, the most common (82% to 88% of the ketone fraction) n-alkane-2-one was the C_{25} homologue, and in mangroves the most common n-alkane-2-ones were the C_{27}-C_{31} homologues. Gas chromatograms of sediments in the lower estuary and the shoreward section of the Florida shelf showed a predominance of seagrass-derived C_{25} homologues, implying that seagrass was a major SOC source there. In upper estuarine sediments, there was a predominance of higher molecular weight homologues implying mangroves were the major SOC source. Isotopic measurements of bulk SOC and n-alkane-2-ones confirmed these conclusions about primary SOC sources because sediment $\delta^{13}C$ values became more enriched (i.e. more like seagrass-derived SOC) as the samples went from the upper estuary to the Florida shelf. By using biomarkers specific to vascular plants, however, contributions to SOC from algae and plankton were unknown.

As with the use of bulk stable isotope measurements, there are caveats with the use of lipid biomarkers. First, this method has not been as extensively studied as the use of bulk isotopes. Inherent variation of molecular distributions and compound specific isotope signatures within different tissues of an individual plant, within plants of the same species, across geographical areas, and across seasons has yet to be documented (Canuel et al. 1997). Also, the more specific biomarkers may not be applicable to all species of the same plant type. The temperate seagrass, *Z. marina*, did not have the predominant C_{25} n-alkane-2-one homologue that sub-tropical seagrass species had (Hernandez et al. 2001). Not all major ecosystem components will have appropriate species-specific biomarkers, so a combination of species-specific and group-specific biomarkers may have to employed (Mead et al. 2005). Biomarkers confirm the presence of a certain source in SOC, but they do not necessarily yield relative contributions of sources because not all sources are represented in each lipid type. Just because the isotopic mixing equation

indicates that 50% of a biomarker is from *S. alterniflora* and the other 50% is from *P. maritima* does not mean each species contributes to 50% of the bulk SOC. Furthermore, when examining isotopes of group-specific lipids, one must make sure that the lipids being examined have similar abundances in each species. Otherwise, what seems like a greater abundance of one species in SOC might actually be due to a greater abundance of that biomarker in tissues of that species relative to other species. In cases where biomarkers are not likely to be at the same concentration among species, relative abundances of biomarkers within each plant should be included in isotopic mixing equations (Bull et al. 1999).

Petrographic Analysis

Petrographic analysis of sediments is a lesser-used method to determine SOC sources. Petrographic analysis microscopically examines organic matter for recognizable organic components such as macrophytic tissues, differentiated based on their level of decomposition, and algae. Marchland et al. (2003) examined SOC sources in mangrove forests of various ages using six different categories of plant tissues: Translucent ligno-cellulosic debris (TLC), which exhibited preserved cell wall structures, degraded ligno-cellulosic debris (DLC), which exhibited decaying cell walls, gelified particles (GP), which were orange brown gel-like particles produced by cellulose degradation, reddish amorphous organic matter (RAOM), in which the cellulose is completely degraded, oxidized opaceous ligno-cellulosic debris (OLC), which were dark and structureless refractory land-derived OM, and grayish amorphous organic matter (GAOM), which were the remains of algae and phytoplankton. This study looked at relative proportions of these various components to understand whether SOC sources to mangrove forests were autochthonous algae, mangroves, or allocthonous riverine detritus. Combining proportions of these OM components with C:N ratios, they found that sediments of younger mangrove forests, with their low C:N ratios and high proportion of GAOM, were dominated by algal-derived OM

and that more mature forests, with their higher C:N ratios and ligno-cellulosic debris, were dominated by mangrove-derived OM. They also found that the upper sediments of the younger forests and the deeper sediments of the older forests had a lot of OLC, indicating a trapping of allochthonous OM from the river. With this method, known proportions of various OM components can be measured directly, in contrast to isotopic methods. However, OM components such as TLC and GP cannot be directly attributed to any one species of primary producer, but rather to broad classes of producers. This study did not take seagrasses into consideration, which may have similar-looking partially decomposed ligno-cellulosic tissues as mangroves, making it hard to differentiate between those two sources using this method.

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR), specifically ^{13}C-NMR, is another method that can be used to identify SOC sources. However, no known studies document this method in seagrass, mangrove, or salt marsh sediments, and therefore an estuarine study is used to illustrate this method. In NMR spectroscopy, a sediment sample is subjected to a magnetic field which causes the nuclei in the ^{13}C atoms to precess as a gyroscope does (Stevenson 1994). A second alternating magnetic field is then added, and when the frequency of that second magnetic field matches the frequency of the nuclei's precession, the nuclei of the atom then resonate causing a voltage change that is amplified and recorded. A spectrum is produced from this resonance signal. The nuclei resonate at different frequencies depending on their chemical environment. Each sample resonates at several frequencies, and from the different resonance signals, spectra with several distinct peaks are produced. Spectra are plotted using the chemical shift—the difference between resonance frequencies of samples and the resonance frequency of a standard, tetramethylsilane (TMS) solution. This chemical shift calculation is analogous to the calculation of δ^{13}C values based on how much the samples' values differ from the PDB standard.

Each organic structure, such as an aromatic ring or a carboxyl group, has a different resonance subsequent chemical shift; therefore this method allows scientists to assign categories of OM to specific chemical shifts (Golding et al. 2004). Using this method, types and relative amounts of OM structures in sediments can be elucidated.

Golding et al. (2004) used ^{13}C-NMR to study whether SOM was terrestrial- or marine-derived in upper (fluvial) and lower (marine) sections of Australian estuaries. They studied four groups of organic carbon structures—carbonyls, aromatics, *O*-alkyls, and alkyls. They associated both *O*-alkyl C and aromatic C with terrestrial plant sources because they assumed *O*-alkyl C was from cellulosic carbohydrates and aromatic C was from lignin and tannins of vascular plants. The presence of alkyl C indicated marine origins because they associated it with planktonic material. They cautioned, however, that alkyl C may also be present due to microbial decomposition of terrestrial OM. The authors concluded that upper portions of estuaries had higher proportions of *O*-alkyl C and aromatic C, and therefore higher amounts of terrestrially-derived SOC, than lower portions of estuaries.

NMR has similar problems as petrographic analysis because structures being studied cannot be directly assigned to specific primary producers; the relationship between the producer and the structure must be inferred, and one structure type can come from several producers. This technique may be best suited to situations where sources are grouped into a couple of components such as a study of seagrass/mangrove-derived SOC and planktonic SOC. Despite problems associated with SOC source determination using ^{13}C-NMR, this tool may help scientists better elucidate roles of plankton and algae, whose proportions in SOC are difficult to determine via stable isotopes because of their variable and intermediate δ^{13}C values. This method also helps scientists understand the OC structures, not just the OC sources in coastal sediments.

Conclusion

This review sought to cover SOC topics relevant to this thesis research in three types of coastal ecosystems—salt marshes, mangrove forests, and seagrass beds. The original research in this thesis covers OC pools and sources in a constructed mangrove and seagrass system. This review covered salt marshes in order to add both depth and breadth because C accumulation and constructed ecosystem development are currently better understood in salt marshes than in mangrove forests and seagrass beds. This review discussed C accumulation rates of salt marshes, mangrove forests, and seagrass beds, functional trajectories of OC attributes in restored and constructed salt marshes, and SOC source determination methods in salt marshes, mangrove forests, and seagrass beds. The C accumulation section showed that these coastal ecosystems are globally significant C sinks. The functional trajectory section showed how OC functions in constructed salt marshes and emphasized the need for further and more in-depth studies of OC in constructed coastal ecosystems. The SOC source determination section showed pros and cons of different SOC determination methods, including bulk stable isotopes, which are utilized in the original thesis research.

Table 2-1. Global area of mangrove forests, salt marshes, and seagrass beds.

System	Global area (km^2)	Data source[a]
Mangrove forests	200000	1
	218000	2
	240000	3
Salt marshes	300000	2
	400000	4
Seagrass beds	300000	5
	600000	6

[a]1, Jennerjahn and Ittekkot 2002; 2, Twilley et al. 1992; 3, Mitsch and Gosselink 2000; 4, Duarte and Cebrian 1996; 5, Suzuki et al. 2003; 6, Hemminga and Duarte 2000.

Table 2-2. Global rates of carbon accumulation in coastal ecosystem sediments.

System	Average type	Global areal rate ($g\ C\ m^{-2}\ yr^{-1}$)	Global rate ($Tg\ C\ yr^{-1}$)	Data source[a]
Mangrove forests	Mean[1]	92	20	1
	Mean	100	22	2
	Estimate[2]	200	44	3
	Mode[1]	115	25	4
Salt marshes	Mean	50-5000	17.5-1750	5
	Mean	100	35	1
	Mean	175	61	2
	Mode	115	25	4
Intertidal[3]	Mean	210	120	6
Seagrass beds	Estimate[4]	1.2	0.54	7
	Mean	133	60	2
	Estimate	270	122	8, 9
	Mode	36.5	16.5	4
Open ocean	Mean	0.22	170	2
Terrestrial systems[5]				
Tundra		0.2-2.4		10
Temperate forest		0.7-10		10
Tropical rainforest		2.3		10
Temperate grassland		2.2		10
Temperate desert		0.8		10

[a]1, Twilley et al. 1992; 2, Duarte and Cebrian 1996; 3, Jennerjahn and Ittekkot 2002; 4, Cebrian 2002; 5, Rabenhorst 1995; 6, Chmura et al. 2003; 7, Suzuki et al. 2003; 8, Duarte and Chiscano 1999; 9, Hemminga and Duarte 2000; 10, Schlesinger 1990.

[1]Both the mean and mode numbers were derived from compiling numbers from published studies. [2]The estimates were either scaled up from a single study or derived from a rough "back-of-the-envelope" calculation. [3]Number includes contribution of both mangrove forests and salt marshes. [4]Estimate is of amount being exported and subsequently buried in the open ocean sediments, not *in situ* accumulation. [5]These numbers represent long term accumulation rates measured since the end of the last ice age.

Table 2-3. Rates of carbon accumulation in coastal ecosystem sediments and the methods used to calculate the time component of the rates.

Location	Site	C accumulation (g C m^{-2} yr^{-1})	Time scale	Method	Data source[a]
Mangrove forests					
Herbert River Estuary, Australia		180	Century	^{210}Pb profiles	1
Jiulonglijang Estuary, China	High intertidal	168	Century	^{210}Pb profiles	2
	Mid intertidal	204	Century	^{210}Pb profiles	2
	Low intertidal	841	Century	^{210}Pb profiles	2
Florida Keys, Florida	*Rhizophora mangle*	159[1]	30 Year	^{137}Cs profiles	3
	Avicennia germinans	105[1]	30 Year	^{137}Cs profiles	3
Rookery Bay, Florida	Fringe	228[1]	Annual	Feldspar marker	4
	Basin	328[1]	Annual	Feldspar marker	4
	Exposed island	291[1]	Annual	Feldspar marker	4
	Sheltered island	191[1]	Annual	Feldspar marker	4
Matang Forest Preserve, Malaysia		150	8,000 Year	Estimate	5
	5-yr-old stand	101	Century	^{210}Pb profiles	6
	18-yr-old stand	110	Century	^{210}Pb profiles	6
	85-yr-old stand	127	Century	^{210}Pb profiles	6
Celestun Lagoon, Mexico		55-70	Century	^{210}Pb profiles	7
Chelem Lagoon, Mexico		67-104	Century	^{210}Pb profiles	7
Terminos Lagoon, Mexico		33	Century	^{210}Pb profiles	7
Sawi Bay, Thailand		184-281	Decadal	^{137}Cs and ^{210}Pb profiles	8
Brackish Marshes					
Cameron Parish, Louisiana	Natural waterway	700[1]	Annual	Feldspar marker	9
	Restricted canal	35[1]	Annual	Feldspar marker	9
	Restricted natural waterway	30[1]	Annual	Feldspar marker	9
Fina La Terre, Louisiana	Unmanaged	75[1]	Annual	Feldspar marker	10
	Managed	10[1]	Annual	Feldspar marker	10
Rockefeller Refuge, Louisiana	Unmanaged	335[1]	Annual	Feldspar marker	10

Table 2-3. Continued

Location	Site	C accumulation (g C m^{-2} yr^{-1})	Time scale	Method	Data source[a]
Salt marshes					
Upper Bay of Fundy, Canada	Low marsh	39	30 Year	^{137}Cs profiles	11
	High marsh	194	30 Year	^{137}Cs profiles	11
Outer Bay of Fundy, Canada	Low marsh	76	30 Year	^{137}Cs profiles	11
	High marsh	188	30 Year	^{137}Cs profiles	11
St Marks NWR, Florida	Low marsh	117	12 Year	^{14}C bomb uptake[2]	12
	Mid marsh	101	12 Year	^{14}C bomb uptake[2]	12
	High marsh	65	12 Year	^{14}C bomb uptake[2]	12
	Low marsh	25	400-600 Year	^{14}C profiles[2]	12
	Mid marsh	22	400-600 Year	^{14}C profiles[2]	12
	High marsh	20	400-600 Year	^{14}C profiles[2]	12
Lafourche Parish, Louisiana	Continuous canal	300[1]	Annual	Feldspar marker	10
	Discontinuous canal	200[1]	Annual	Feldspar marker	10
	Natural waterway	650[1]	Annual	Feldspar marker	10
Cedar Creek, Maryland		89	150 Year	^{210}Pb profiles[2]	13
		18.5	Millennia	^{14}C profiles[2]	13
Hell Hook, Maryland		78	150 Year	^{210}Pb profiles[2]	13
		39.8	Millennia	^{14}C profiles[2]	13
Barnstable, Massachusetts		96	NA	Modeled	14
Biloxi Bay, Mississippi		180	Decadal	^{137}Cs profiles	3
Waarde Marsh, Netherlands		105	NA	Modeled	14
Consultant, North Carolina	3-yr-old constructed	39	3 Year	ΔOC / Time[2]	15
	Natural reference	35-51	Decadal	^{137}Cs and ^{210}Pb profiles	15
Drum Inlet, North Carolina	Bare spoil	80	16 Month	ΔOC / Time[3]	16
	Spoil planted with *Spartina*	87	16 Month	ΔOC / Time[3]	16
	Fertilized spoil with *Spartina*	96.8	16 Month	ΔOC / Time[3]	16
Dill's Creek, North Carolina	13-yr-old constructed	62	13 Year	ΔOC / Time[3]	15

Table 2-3. Continued.

Location	Site	C accumulation (g C m^{-2} yr^{-1})	Time Scale	Method	Data Source[a]
"DOT," North Carolina	1 yr-old constructed	99	1 Year	ΔOC / Time[3]	15
	Natural reference	30-36	Decadal	^{137}Cs and ^{210}Pb profiles	15
Jacob's Creek, North Carolina	Irregularly-flooded streamside	146	Decadal	^{137}Cs profiles	17
	Irregularly-flooded backmarsh	107	Decadal	^{137}Cs profiles	17
"Marine Lab," North Carolina	26-yr-old constructed	34	26 Year	ΔOC / Time[3]	15
	Natural reference	15	Decadal	^{210}Pb profiles	15
Oregon Inlet, North Carolina	Regularly-flooded streamside	58.9	Decadal	^{137}Cs profiles	17
	Regularly-flooded backmarsh	21.3	Decadal	^{137}Cs profiles	17
Pine Knoll Shores, North Carolina	21-yr-old constructed	125	11 Year	ΔOC / Time[4]	18
	Natural reference	115	11 Year	ΔOC / Time[4]	18
"Port," North Carolina	8-yr-old constructed	27	8 Year	ΔOC / Time[3]	15
	Natural reference	28-32	Decadal	^{137}Cs and ^{210}Pb profiles	15
Snow's cut, North Carolina	25-yr-old constructed	99	11 Year	ΔOC / Time[4]	18
	Natural reference	159	11 Year	ΔOC / Time[4]	18
Swansboro, North Carolina	11-yr-old constructed	18	11 Year	ΔOC / Time[3]	15
	Natural reference	105-115	Decadal	^{137}Cs and ^{210}Pb profiles	15
Aransas NWR, Texas		167[1]	Decadal	^{137}Cs profiles	3
San Bernard NWR, Texas		207[1]	Decadal	^{137}Cs profiles	3
United States Average		83	NA	Compiled	19
Seagrass Beds					
Aburatsubo Bay, Japan		1.2-1.5[5]	NA	Modeled	20
Celestun Lagoon, Mexico		40	Century	^{210}Pb profiles	7
Terminos Lagoon, Mexico		53-65	Century	^{210}Pb profiles	7
Cala Culip, Spain		19-191	600 Year	Shipwreck	21
Fanals Point, Spain		182	Annual	Sediment trap	22

[a]1, Brunskill et al. 2002; 2, Alongi et al. 2005; 3, Callaway et al. 1997; 4, Cahoon and Lynch 1997; 5, Ong 1993; 6, Alongi et al. 2004; 7, Gonneea et al. 2004; 8, Alongi et al. 2001; 9, Cahoon and Turner 1989; 10, Cahoon 1994; 11, Connor et al. 2001; 12, Choi and Wang 2004; 13, Hussein et al. 2004; 14, Middelburg et al. 1997; 15, Craft et al.

2003; 16, Cammen 1975; 17, Craft et al. 1993; 18, Craft et al. 1999; 19, Hopkinson 1988; 20, Suzuki et al. 2003; 21, Romero et al. 1994; 22, Gacia et al. 2002.

[1]This author reported organic matter accumulation rates, so rates were divided by 2 in order to obtain these numbers. [2]Modeled sediment profiles instead of measuring them directly. [3]Calculated by subtracting the OC in 0-30 cm from the OC in top 10 cm, divided by the age of the site [4]Calculated by subtracting the OC at time 0 from the OC at time 1, divided by time 1-time 0 [5]Denotes carbon buried after exportation to the open ocean not in situ.

Table 2-4. Studies comparing organic carbon in restored and constructed coastal marshes to OC in natural reference marshes.

Location	Site	Age (years)	Constructed OC (units)	Reference OC (units)	Depth sampled (cm)	Method[a]	Source[b]
Tacoma, Washington[1]	Gog-Le-Hi-Te, Site 1	1	3.5 %	3.3 – 8.7 %	0-2	1	1
		2	3.0				
		3	4.0				
		6	3.5				
	Gog-Le-Hi-Te, Site 2	1	4.0				
		2	4.5				
		3	5.5				
		6	9.0				
	Gog-Le-Hi-Te, Site 3	1	2.5				
		2	2.0				
		3	2.2				
		6	1.2				
	Gog-Le-Hi-Te, Site 4	1	2.0				
		2	2.0				
		3	3.0				
Maine, New Hampshire[1,2]	Great Bay Estuary	1	2.0 %	mean = 23 %	0-5	1	2
		2	1.5				
		3	3.0				
		6	2.5				
		14	16				
Core Banks, North Carolina	Sound-side marsh, site 1	0	77.3 g OC m^{-2}	362.7 g OC m^{-2}	0-13	2	3
		1.3	184.3				
	Sound-side marsh, site 2	0	77.3				
		1.3	193.3				
	Sound-side marsh, site 3	0	77.3				
		1.3	206.4				
San Diego, California[1]	San Diego Bay	2	3.5 %	7.5 – 11 %	Not reported	1	4
		4	5.5				
		8	7.5				
		11	7/0				

Table 2-4. Continued

Location	Site	Age (years)	Constructed OC (units)	Reference OC (units)	Depth sampled (cm)	Method[a]	Source[b]
Georgia	Sappelo Island	42	1264 g C m^{-2}	1372 g C m^{-2}	0-10	1	5
North Carolina	Pamlico River Estuary	5	886 kmol C ha^{-1}	10270 kmol C ha^{-1}	0-30	3	6
		15	1866				
Virginia	Gloucester Point	5	95 g C m^{-2}	129 – 163 g C m^{-2}	0-2	1	7
		12	120				
		5	50	146 – 174	14-16		
		12	53				
North Carolina[2]	"DOT"	1	400 g C m^{-2}	3800 g C m^{-2}	0-30	1	8
	Consultant	3	600	4600			
	Port	8	900	2000			
	Swansboro	11	1000	4600			
	Dill's Creek	13	1800	4900			
	Pine Knoll	24	1200	1000			
	Marine Lab	26	2900	5100			
	Snow's Cut	28	2900	10000			

[a]1, loss-on-ignition; 2, Walkley-Black oxidation; 3, CHN analyzer. [b]1, Simenstad and Thom 1996; 2, Morgan and Short 2002; 3, Cammen 1975; 4, Zedler and Calloway 1999; 5, Craft 2001; 6, Craft et al. 2002; 7, Havens et al. 2002; 8, Craft et al. 2003

[1]Signifies study measured organic matter (OM) only, not organic carbon (OC). [2]Signifies study did not measure the same wetland overtime but instead used a space-for-time substitution.

Table 2-5. Stable Isotope values and dominant source conclusions from carbon source determination studies in coastal ecosystems.

Location	Potential sources	Source $\delta^{13}C$	Site description	Sediment $\delta^{13}C$	Main sources[a]	How main sources determined	Data source[b]
Mangrove forest							
Eastern Brazil	Seston	-21 to -22[1]	Mangroves	-26.9	4	Comparison	1
	Spartina	-26.8[2]	Riverine	-23.8	4		
	Mangroves	-27	Shelf	-21.3	2		
			Slope	-20.5	2		
Gazi Bay, Kenya	Mangroves	-28.25	*Rhizophora mucronata*	-25.3	4	Comparison	2
Gazi Bay, Kenya	Mangroves	-24.12	*Ceriops tagal*	-22.7	4	Comparison	2
Southeast Asia	Seston	-20.5 to -23[3]	Coringa Wildlife	-29.4 to	2	Compared to curve of	3
	Mangroves	-27 to -29[3]	Sanctuary, India	-20.6[3]		2 source mixing model	
			Galle, Sri Lanka		4		
			Pampala, Sri Lanka		4		
Mangroves and salt marsh							
Chiricahueto, Mexico	NR		Marsh	-20.4	2	Compared to literature values	4
Salt Marsh							
Florida	NR		*Spartina alterniflora*	-16.9		Comparison	5
			Juncus roemerianus	-23.9			
Sapelo Island, Georgia	Diatoms	-17.0	Bare creekbank	-18.9	NR	Comparison	6
	S. alterniflora	-12.9	Tall *Spartina*	-16.0	NR		
	S. virginica	-26.0	Short *Spartina*	-17.9	5		
	D. spicata	-13.1	*S. virginica* high marsh	-21.6	NR		
	S. virginicus	-13.3	Sand flat	-22.6	NR		
	J. roemerianus	-22.8	Mixed vegetation	-19.3	NR		
	B. frutescens	-26.0					
Barataria Bay, Louisiana	*S. Alterniflora*	-12.1 to -13.6	Marsh	-16.2	5	Compared to predicted values based on producer biomass	7

Table 2-5. Continued

Location	Potential sources	Source $\delta^{13}C$	Site description	Sediment $\delta^{13}C$	Main sources[a]	How main sources determined	Data source[b]
Plum Island, Massachusetts	*S. Alterniflora*	-13.3	Mid marsh	-18.9[4]	both	Comparison and distributions of long chain n-Alkanes	8
	T. latifolia	-25.3	Upper marsh	-22.81[4]	both		
			Mudflat	-19.39[4]	Both		
Waarde Marsh, Netherlands	*Spartina*	-12.7[2]	Marsh	-22 to -24.6	6	Compared to curve of 2 source mixing model	9
	Allochthonous OM	-25.5					
Cape Lookout Bight, North Carolina	Seston	-18.4	Fall	-17.8	2	Comparison with lipid distributions and lipid $\delta^{13}C$	10
	Seagrass	-10.0	Spring	-20.3	2		
	Spartina	-12.6					
	J. roemerianus	-26.0					
Dorset, United Kingdom	*Spartina anglica*	-12.1	*S. anglica*	-17.6	5	Mixing model using compound specific $\delta^{13}C$	11
	Pucinella maritima	-26.9	*P. maritima*	-21.4	5 (50%)		
			Mudflat	-20.4	5 (40%)		
Barnstable, Massachusetts	*Spartina*	-12.5[1]	High marsh	-13.4 to -14.5	5	Compared to curve of 2 source mixing model	9
	Allochthonous OM	-25.5[1]			6		
			Low marsh	-21 to -19.5			
Seagrass beds							
Gazi Bay, Kenya	Seagrass	-19.7	Closest to mangroves	-22.9	4,1	Comparison	12
	Mangroves	-26.7[5]					
	Sediment Traps	-23.3					
Gazi Bay, Kenya	Seagrass	-18.3	Closer to mangroves	-20.6	4,1	Comparison	2
	Mangroves	-26.7[5]					
	POM	-22.5					
Gazi Bay, Kenya	Seagrass	-15.8	Farther from mangroves	-18.5	1	Comparison	2
	Mangroves	-26.7[5]					
	POM	-19.2					
Gazi Bay, Kenya	Seagrass	-10.70	Farthest from mangroves	-15.14	1	Comparison	2
	Mangroves	-26.7[5]					
	POM	-13.7					

Table 2-5. Continued

Location	Potential sources	Source $\delta^{13}C$	Site description	Sediment $\delta^{13}C$	Main sources[a]	How main sources determined	Data source[b]
Chale Lagoon, Kenya	Seagrass Mangroves	-10.72 -26.7[5]		-14.8	1	Comparison	12
Silaqui, Philipines	Seston Seagrass Epiphytes	-16.4 -5.8 -9.6		-10.3	3	Percent contribution ranges from mixing equation	12
Pislatan, Philipines	Seston Seagrass Epiphytes	-16.5 -7.5 -10.5		-14.9	2	Percent contribution ranges from mixing equation	12
Spain	Seston Seagrass Epiphyte	-22.1[3] -12.4[2,3] -17.8[3]	Iberian Coast Balearic Islands	-15.8 to -21.6[3] -15.8 to -21.6[3]	2,1 (3?) 1,2 (3?)	Percent contribution ranges from mixing equation	13
Fanals Point, Spain	Seston Seagrass Epiphyte POM	-24.7 -12.2 -17 -21.5		-20.07	2	Percent contribution ranges from mixing equation and microscopic examinations	14
Can Rhan Lagoon, Vietnam	Seston Seagrass	-19.6 -8.6		-18.6	NR	Percent contribution ranges from mixing equation	12
Dam Ghia Bay, Vietnam	Seston Seagrass Epiphyte	-17.7 -6.0 -8.6		-15.8	2	Percent contribution ranges from mixing equation	12
Mi Giang II, Vietnam	Seston Seagrass	-12.1 -7.6		-13.2	NR	Percent contribution ranges from mixing equation	12
Seagrasses and mangroves							
Celestun, Mexico	Seston Seagrass Mangrove	-22.1 -16.1[2] -28.6[2]	Fringing mangrove Lagoon center	-24 -20	4,2 1,2	Ternary mixing diagram of $\delta^{13}C$ and N:C	15

Table 2-5. Continued

Location	Potential sources	Source $\delta^{13}C$	Site description	Sediment $\delta^{13}C$	Main sources[a]	How main sources determined	Data source[b]
Chelem, Mexico	Seston	-22.1	Fringe mangrove	-23.1 to -26.1[6]	1,2	Ternary mixing diagram of $\delta^{13}C$ and N:C	15
	Seagrass	-15.4[2]			4,2		
	Mangrove	-27.1[2]	Seagrass bed	-17.2 to -22.4[6]			
Terminos, Mexico	Seston	-25.3	Fringe mangrove	-26	4,2	Ternary mixing diagram of $\delta^{13}C$ and N:C	15
	Seagrass	-11.9	Seagrass bed	-16	1,2		
	Mangrove	-28.6[2]					
Santa Barbara, Philipines	Seston	-19.0	Seagrass bed	-22.7	4	Percent contribution ranges from mixing equation	12
	Seagrass	-10.9					
	Epiphyte	-12.9					
	Mangrove	-28.6					
Buenavista, Philipines	Seston	-17.7	Seagrass bed	-15.7	1	Percent contribution ranges from mixing equation	12
	Seagrass	-11.7					
	Epiphyte	-13.1					
	Mangrove	-28.1					
Umalagan, Philipines	Seston	-27.6	Seagrass bed	-26.6	2 or 4	Percent contribution ranges from mixing equation	12
	Seagrass	-12.3					
	Epiphyte	-22.9					
	Mangrove	-28.4					
Khung Krabaen Bay, Thailand	Seston	-20.6[2]	Canals	-26.5	4	Comparison	16
	Seagrass	-10.5	Mangroves	-26.3	4		
	Macroalgae	-15.6[5]	Inner bay	-15.1	1,7		
	Mangrove	-28.8[2,5]	Mouth of bay	-19.2	2		
	Shrimp feed	-22.5	Offshore	-17.5	2		
Ghia Luan, Vietnam	Seston	-21.6	Seagrass	-24.6	4	Percent contribution ranges from mixing equation	12
	Seagrass	-13.3					
	Mangrove	-27.9					

[a]The numbers in the main sources column signify the following: 1, seagrass; 2, seston; 3, epiphytes; 4, mangroves; 5, *Spartina*; 6, other; 7, macroalgae.
[b]1, Jennerjahn and Ittekkot 2002; 2, Hemminga et al. 1994; 3, Bouillon et al. 2003; 4, Soto-Jimenez et al. 2003; 5, Johnson and Calder 1973; 6, Haines 1976; 7, Chmura et al. 1987 ; 8, Wang et al. 2003; 9, Middelburg et al. 1997; 10, Canuel et al. 1997; 11, Bull et al. 1999; 12, Kennedy et al. 2004; 13, Papadimitriou et al. 2005; 14, Gacia et al. 2002; 15, Gonneea et al. 2004; 16, Thimdee et al. 2003.

[1]The values were not measured in the study and were taken from published values in the literature. [2]Averaged values of leaf, root, rhizome and litter tissue or across sites to obtain one stable isotope value. [3]Average or range of entire study because the authors did not provide the specific values for each site. [4]Averaged values of e ach 2 cm section in the top 10 cm of sediment. [5]Average of several species. [6]Range taken from a graph. NR = not reported

CHAPTER 3
SEDIMENT ORGANIC CARBON STORAGE IN A CONSTRUCTED MANGROVE AND SEAGRASS SYSTEM

Introduction

Coastal ecosystems such as salt marshes, mangrove forests, and seagrass beds are being degraded and lost worldwide as a result of the eutrophication, sedimentation, and destruction that accompany coastal development for human habitation, agriculture, and aquaculture (Valiela et al. 2001; Kennish 2002; Zedler 2004). In the United States development and infilling are the main causes of coastal ecosystem loss (Dahl 2000). In the last two decades, humans have caused the loss of 18% of the known worldwide area of seagrass beds (Green and Short 2003), and in the last five decades, have caused the loss of about 35% of the world's mangrove forests (Valiela et al. 2001; Alongi 2002). In the United States, about 50% of salt marshes have been lost historically (Kennish 2001) and 25% of mangrove forests have been lost since the 1950's (Bridgham et al. 2006). United States seagrass beds had a relatively constant area between 1986 and 1997 in, what is to our knowledge, the only nationwide seagrass inventory (Dahl 2000). Smaller scale studies, however, have demonstrated local declines in the extent of seagrasses (Zieman et al. 1999; Short et al. 2006). When coastal systems are lost, we lose not only wildlife habitat, storm surge protection, and economically-important fish and shellfish nurseries, but also biogeochemical functions like phosphorus retention, denitrification, and carbon (C) sequestration (Alongi 2002; Duarte 2002; Zedler and Kercher 2005).

The United States has a policy of no net wetland loss that includes coastal wetlands as part of the Clean Water Act (Zedler 2004; Zedler and Kercher 2005). Florida policy applies this no-net-loss principle to seagrass beds as well (Florida Administrative Code, Chapter 18-21). Destruction of mangrove and seagrass ecosystems in Florida requires compensatory mitigation via restoration of an existing ecosystem or construction of a new ecosystem. Mitigation can

result in the replacement of fully functioning ecosystems with ineffective surrogates that do not provide the same functional value (Zedler 2004). Success of most mitigation projects is judged on the survival of macrophytes, not on proper functioning of the ecosystem. With the majority of ecosystem functions are not assessed, the true success of mitigation projects is usually unknown.

One major function of coastal ecosystems is C sequestration. The value of this ecosystem function is increasing with mounting concern about climate change. Anthropogenic release of greenhouse gases like carbon dioxide (CO_2) and methane (CH_4) through fossil fuel burning and deforestation, and livestock production, respectively, is the major cause of global climate change (IPCC 2001). Coastal ecosystems dominated by macrophytes including salt marshes, seagrass beds, and mangrove forests are high productive habitats that act as sinks for CO_2 and therefore mitigate climate change. Worldwide, salt marshes and mangroves store at least 44.6 Pg C in their sediments (Chmura et al. 2003). Seagrass beds, which make up only 0.15% of the global marine area, account for 15% of the global marine organic C (OC) storage (Hemminga and Duarte 2000). Global rates of C sequestration in vegetated marine sediments are estimated between 111 and 216 Tg C y^{-1} (Duarte et al. 2005). Based on the low estimate, globally mangroves bury 23.6 Tg C y^{-1}, salt marshes bury 60.4 Tg C y^{-1}, and seagrass bury 27.4 Tg C y^{-1} (Duarte et al. 2005). In the United States, salt marshes store 400 Tg C and sequester 4.4 Tg C y^{-1}, and mangroves store 61 Tg C and sequester 0.5 Tg C y^{-1} (Bridgham et al. 2006); the C stored and sequestered by seagrass systems is unknown. Coastal ecosystems also export C to the oceans where another portion is buried (Duarte et al. 2005).

The capacity of coastal ecosystems to sequester C, like freshwater wetlands, is greater than the capacity of uplands. These “wetlands” are a natural C sink, while upland systems

eventually reach an equilibrium where amount of C fixed equals the amount respired annually, if disturbances like fire do not cause a loss of C first (Rabenhorst 1995). Constant accumulation of C in wet ecosystems is due to their anaerobic sediments where alternate electron acceptors, which are not as efficient as oxygen, must be utilized to decompose C. The capacity of coastal ecosystems to sequester C is also greater than that of freshwater wetlands (Bridgham et al. 2006). Bridgham et al. (2006) found that estuarine wetlands sequestered C 10 times faster on an areal basis than other wetlands. These high rates are due to estuarine wetlands' high sedimentation rates, high percent soil C, and burial due to sea level rise (Connor et al. 2001; Bridgham et al. 2006). Coastal ecosystems have another advantage over freshwater wetlands. They have lower rates of methanogenesis, so the C they store is not being converted to CH_4, a more potent greenhouse gas than CO_2. In the United States, freshwater mineral wetlands emit 2.4 Tg CH_4 y^{-1} while salt marshes and mangroves emit only 0.027 and 0.004 Tg CH_4 y^{-1}, respectively (Bridgham et al. 2006).

When these coastal ecosystems are impacted, a portion of the biosphere's C storage and sequestration capacity is lost, which may exacerbate climate change by causing more CO_2 to be in the atmosphere than would be if these systems were intact. Loss of vegetated coastal ecosystems has caused at least a 25% decrease in their global C sequestration capacity (Duarte et al. 2005). Bridgham et al. (2006) estimated that losses of salt marshes and mangroves in the conterminous United States have caused a net flux of 402 Tg C y^{-1} into the atmosphere.

The upside is that restoration and construction of coastal systems may help mitigate the effects of climate change by increasing C sequestration. For example, if all dyked salt marshes in Canada were restored, an additional 2.4 to 3.6 x 10^{11} g C y^{-1} would be sequestered, which would contribute 5% to Canada's CO_2 emissions reduction identified in the Kyoto Protocol

(Connor et al. 2001). It is therefore important to know if restoration and construction of coastal systems returns the C accumulation and storage capacity of these C sinks. Such research can indicate whether mitigation is effective and if coastal wetland restoration can become a policy tool for reducing CO_2 emissions as was suggested by Connor et al. (2001). Studies that focus on functional trajectories of OC in restored/constructed systems and compare OC between restored/constructed and natural systems help answer these questions.

Functional trajectories are used to track the progress of constructed systems over time and to compare constructed and reference systems (Simenstad and Thom 1996; Zedler and Callaway 1999; Morgan and Short 2002). Functional trajectory studies examine many "ecological attributes" that act as indicators of more complex ecosystem functions (Simenstad and Thom 1996; Craft et al. 2003). Attributes reach functional equivalence when they have a value similar to the reference. Functions can follow linear, asymptotic, and sigmoidal trajectories (Kentula et al. 1993) or no trajectory at all (Zedler and Calloway 1999). Craft et al. (2003) proposed that different attributes follow one of three trajectories depending on whether they are part of hydrologic, biological, or "soil" development processes. OC pool formation is a soil development process, and soil development processes generally follow the longest trajectory before reaching functional equivalence (Craft et al. 2003). There have been many studies documenting functional trajectories of sediment OC (SOC) or organic matter (OM) in restored and constructed tidal marshes (Simenstad and Thom 1996; Craft 2001; Havens et al. 2002; Morgan and Short 2002; Craft et al. 2003) but, to our knowledge, only one in seagrass beds (Evans and Short 2005) and only a comparison study in mangrove forests (McKee and Faulkner 2000).

Given the limited scope of these studies, many questions remain unexplored. First, the majority of studies on restored coastal systems have been performed in temperate salt and brackish marshes. Second, these studies only measured SOC or sediment OM as one of a suite of variables and did not deeply examine various SOC pools or characteristics. Third, these studies only examined long term trends and not short term changes that may occur immediately following construction of an ecosystem.

Whether constructed mangrove and seagrass ecosystems provide the same ecological services as their natural counterparts with respect to the C sink, and if the restoration of this service follows a functional trajectory is currently unknown. In this study, OC storage in a constructed seagrass and mangrove system in the Indian River Lagoon, FL was examined and its OC storage functioning was compared with the functioning of adjacent mature systems. Specific objectives were to: 1) determine whether extractable OC, microbial biomass C, total OC pools, and OC lability follow a short term trajectory in sediments of a constructed mangrove forest and seagrass bed and 2) evaluate whether the constructed system has reached functional equivalence by comparing SOC between constructed and natural systems. We hypothesized that, in the short term, SOC storage would increase in the constructed system but would not reach the level of SOC storage in natural systems.

Methods

Study Site

SL 15 (Fig. 3-1) is a mitigation site located in the Indian River Lagoon (IRL) adjacent to Fort Pierce, Florida. It is one of many spoil islands created in the IRL during the construction of the Atlantic Intracoastal Waterway that sit several meters above sea level. These islands are populated by many exotics, such as Australian Pine (*Casuvina casuvina*) and Brazilian Pepper (*Shinus terebinthifolius*), in their interiors and by native red, black, and white mangroves

(*Rhizophora mangle*, *Avicennia germinans*, and *Laguncularia racemosa*) around their margins. To mitigate destruction of a nearby mangrove forest and seagrass bed, seagrass and mangrove systems were created on SL 15. These systems were created by burning and removing interior vegetation and removing dredge spoil to create several different elevations. The seagrass bed, which remains submerged during low tide, is at the lowest elevation, the mangrove forest, which is exposed at low tide, is at the middle elevation, and a maritime forest occurs above sea level at the highest elevation. The mangrove fringe of SL 15 was left intact except for a few flushing channels. Between the constructed seagrass and mangrove systems a thin *Spartina alterniflora* buffer was planted. The mangrove forest was planted with *R. mangle*, and maritime forests were planted with *Coccoloba uvifera*, *Borrichia frutescens*, *Rapanea guinensis*, *Conocarpus erectus*, and *Distichlis spicata*, but seagrasses were left to colonize naturally. Natural systems near SL 15 include its original mangrove forest fringe, surrounding seagrass beds, and mangrove fringes of adjacent spoil islands, which are at least 40 years old.

Sediment Sampling

Four, 2 m x 2 m plots were established in the mangrove forest and in the seagrass bed on SL 15 (Fig. 3-1). Three, 7 cm in diameter sediment cores from each of these plots were retrieved in November 2005, January (mangrove only), February (seagrass only), May, July, and November 2006. Cores were taken from different areas of the plots each time to ensure an area was not re-sampled. For references, three randomly-selected plots were established in natural mangrove forests and seagrass beds within 1 km of SL 15. These plots were sampled in July and November 2006 using the same procedure as for SL 15 plots. Sediment cores were sectioned in the field and stored in plastic bags on ice for transport and then in a 4ºC refrigerator. SL 15 cores were initially divided into 0-5 cm and 5-10 cm sediment depths. In subsequent samplings, material had accumulated on top of the seagrass bed, which was collected and analyzed

separately from the original sediment depths as an accreted layer. Surface layers—floc from seagrass systems, algal mats from the SL 15 mangrove system, and litter layers from the reference mangrove system—were collected from each core and were composited for each plot. Differences in color and texture were used to separate accreted and surface layers from original depths except for floc, which was the fraction of the accreted layer that poured off (Fig. 3-2). Average heights of accreted and surface layers were measured for bulk density calculations. One core per plot was retrieved in September 2006 and brought intact to the laboratory for pH and Eh (redox potential) measurements.

Laboratory Analyses

Sectioned sediments and surface layers were weighed to determine bulk density. Rocks, roots, and detritus were removed from the sample before homogenization, and the volume and weight of large rocks were taken into account when calculating bulk density. After homogenization of each sample, a subsample was weighed to determine moisture content and the remaining sample was split into two parts. One part (wet sample) was stored in airtight containers at 4ºC and the other was freeze-dried for 48 hours. Moisture content was determined after subsamples were dried at 105ºC for 24 hours.

Intact cores from September 2006 were incubated upright in tanks filled with 25 ppt saltwater made with Instant Ocean (Marineland Labs, Moorpark, CA). Platinum electrodes were inserted into each core at 2.5 cm, at 7.5 cm, at 12.5 cm (reference seagrass only), and halfway through the accreted layer (SL 15 seagrass only). Platinum electrodes stabilized for 24 hours, and then Eh was measured using an Accumet AP71 handheld meter and an Accumet calomel reference electrode. Eh values were corrected relative to a standard hydrogen electrode. Cores were then sectioned into 0-5 cm, 5-10 cm, and 10-15 cm or accreted depths as previously described. pH was measured on 5 g of each depth using a Fisher Accumet AR50 pH meter.

Total OC (TOC) and total nitrogen (TN) were measured on freeze-dried sediment and surface layer samples. Freeze-dried samples were composited by plot and sieved through a 1 mm mesh screen to remove large shell pieces and carbonate rock, which were weighed so their mass could be accounted for in calculations. Samples were then ball-milled to a fine powder in stainless steel canisters. Inorganic C (IC) in was removed from samples via vapor acidification (Hedges and Stern 1983; Harris et al. 2001). Samples were weighed out into 9 x 5 mm or 10 x 10 mm silver capsules (Thermo Scientific, Waltham MA and CE Elantech, Lakewood, NJ), moistened with deionized water, and placed in an airtight container with a beaker of concentrated HCl (12 *M*) for 24 hours before being dried at 60ºC for 24 hours. Samples were then rolled and analyzed for OC on an elemental analyzer (ECS 4010, Costech Analytical Technologies, Valencia, CA). Peach leaves (NIST 1547) were used for calibration standards, and sucrose and an internal soil standard were used for quality control. Tests were run on sand samples with various carbonate percentages and total weights to assess the efficacy of vapor acidification and to determine the maximum sample mass that still ensured complete removal of IC. Furthermore, concurrent measures of ^{13}C were used to confirm complete removal of IC, and if incomplete IC removal was suspected, samples were rerun at a lower total mass. Unacidified samples were run separately in tin capsules (Costech) on a Flash EA 1112 series elemental analyzer (Thermo Scientific, Waltham, MA) for TN. Acetinilide was used for calibration standards, and peach leaves (NIST 1547) and an internal soil standard were used for quality control.

Extractable organic C (ExOC) and microbial biomass C (MBC) were measured using a modified fumigation-extraction procedure (Vance et al. 1987; Joergensen and Mueller 1995). Approximately 5 g of moist sample was weighed out in duplicate for sediment, algal mat, and litter samples and 10 g was weighed out for floc samples. One set of samples was immediately

extracted with 25 mL of 0.5 M K_2SO_4 for an hour and then filtered through a Whatman 42 filter. The second set was fumigated in an ethanol free-chloroform atmosphere for 24 hours before being extracted as above. Extracts were diluted, acidified, and run for OC on a Shimadzu TOC-5050A (Shimadzu North America, Columbia, MD). OC in non-fumigated samples was ExOC. The difference between OC in fumigated and non-fumigated samples, multiplied by a correction factor of 2.22 (Wu et al. 1990; Joergensen 1996; Jenkinson et al. 2004), was MBC.

Sediment oxygen demand (SOD; APHA 1992), normalized to TOC, was used as a measure of OC lability. SOD was measured by mixing 10 mg of wet sample with about 300 mL of oxidized, salt water in dark biological oxygen demand (BOD) bottles. The salt water was created by dissolving Instant Ocean Sea Salt (Marineland Labs) into deionized water until the solution reached 25 ppt. Dissolved oxygen (DO) content of the water was measured initially and after 24 hours by a Fisher Accumet AR40 DO meter. Measurements were taken after the water and sample in each BOD bottle were thoroughly mixed on stir plates for 30 minutes. While abiotic and chemotrophic reactions can cause decreases in DO, these reactions most likely did not cause a significant O_2 reduction during this experiment because samples were already exposed to O_2 during processing. Furthermore, NH_4^+ levels in the samples were low (unpublished data) and pH did not change during incubation, which would have indicated oxidation of sulfide in the samples,. The majority of O_2 depletion was therefore assumed to be due to biological, heterotrophic oxidation of OC.

OC accumulation rates (g OC m^{-2} y^{-1}) in SL 15 were calculated using equation 3-1 (Cammen 1975; Craft et al. 1999).

$$OC_{accumulation} = \frac{OC_f - OC_i + OC_a}{A_{system}} \qquad (3\text{-}1)$$

In equation 3-1, OC_f is the final amount of TOC (g OC m^{-2}) in the top 0-10 cm, OC_i is the initial amount of TOC in the top 0-10 cm, OC_a is the amount of TOC in the accreting layer, and A_{system} is the age of the system in years. Without dating sediments using ^{137}Cs, ^{210}Pb, or ^{14}C profiles, OC accumulation rates in reference systems could not be calculated.

Statistical Analyses

Repeated measures analysis of variance (ANOVAs) were run to investigate if parameters in SL 15 sediments and surface layers followed a functional trajectory over time. ANOVAs were run with a spatial power covariance structure to account for the unequal spacing between time points. Subjects were SL 15 plots and the repeated factor was month. The 0-5 and 5-10 cm depths were run together in each system in ANOVAs with depth as a main effect. Floc, algal mat, and accreted layers were run separately in ANOVAs. Replicate cores had to be averaged for each plot and month so the data fit the structure required for repeated measures analysis. A parameter followed a trajectory if its repeated measures ANOVA had a significant time effect and it demonstrated an increasing or decreasing (in the case of bulk density) trend over time. Analyses were run using the mixed procedure in SAS Version 8 (SAS Institute, Cary, NC).

Comparisons between SL 15 and reference sites were analyzed using one factorial ANOVA each for the mangrove and seagrass sediments and one factorial ANOVA each for the mangrove and seagrass surface layers. Sediment ANOVAs consisted of three fixed factors—site, month, and depth. Surface layer ANOVAs consisted of site and month factors. All two way interactions were tested. Plot data were pooled into two site treatments, SL 15 and reference. July and November 2006 were the months. For seagrass sediment analysis, SL 15 and reference depths were assigned to 3 categories in order to make comparisons: SL 15 accreted and reference 0-5 cm were depth 1, SL 15 5-10 cm and reference 0-5 cm were depth 2, and SL 15 5-10 cm and reference 10-15 cm were depth 3. Factorial ANOVAs only compare the same

depths across different sites and not different depths across different sites (*i.e.*: it compares SL 15 mangrove 0-5 cm to reference 0-5 cm but not SL 15 mangrove 0-5 cm to reference 5-10 cm), so one-way ANOVAs were also run when site*depth interactions of the factorial ANOVAs did not reveal all interesting trends. Data were averaged by each site and depth over July and November samplings for these one-way ANOVAs. Factorial and one-way ANOVAs were run on JMP Version 6 (SAS Institute, Cary, NC).

For all analyses most data were transformed to meet the normality requirement (see Appendix A for details). Post hoc multiple comparisons were carried out on significant effects using the Tukey test. Significance was decided using an alpha level of 0.05.

Results

Sediment Characteristics

SL 15 sediments (0-5 cm and 5-10 cm) had higher bulk densities than reference sediments (Table 1; site effect, $p<0.0001$, Table 2) as did the SL 15 mangrove algal mat. The seagrass accreted layer had a bulk density similar to the 0-5 cm depth of the seagrass reference. In seagrass sediments, bulk densities were greatest in the lowest depths, but in mangrove sediments were greater in 0-5 cm depths (Table 1; depth effect, $p<0.026$, Table 2). SL 15 seagrass sediments had orders of magnitude more shell fragments than reference sediments, while SL 15 and reference mangrove sediments had similar amounts of shell fragments (Table 1). pH in SL-15 seagrass and reference sediments and in SL-15 mangrove sediments ranged from 8.0 – 8.3. Reference mangrove sediments had a pH of 7.5 (Table 1). Redox potentials in the upper sediment depths were similar between SL-15 and reference sites, but were more negative in the lower depths of the reference sediments (Table 1).

Trajectory of Constructed System

Parameters measured in SL 15 sediments did not follow a trajectory over time, except for mangrove sediment bulk density, which significantly decreased with time (month effect, $p<0.0001$, Table 3, Fig. 3-3). OC parameter values seemed to shift randomly when there were significant monthly changes as for MBC in all sediments, and ExOC and TOC in seagrass 0-10 cm sediments (month effect, $p<0.021$, Table 3, Fig. 3-4). OC parameters followed a pattern in seagrass sediments in which low values occurred in February and July while high values occurred in May and November (Fig. 3-4). TN and C:N also changed without direction when they did change significantly (month effect, $p<0.041$, Table 3). There were no significant changes in lability for either mangrove or seagrass sediments. Significant differences between depths were few. In mangrove sediments, 0-5 cm depths had greater bulk density and TN, and in all sediments, 0-5 cm depths had greater lability (depth effect, $p<0.031$, Table 3).

SL 15 surface layers (mangrove algal mat and seagrass floc) followed a trajectory of significantly increasing MBC ($p<0.0051$, Table 3, Fig. 3-5). Extractable OC, TOC, and TN significantly changed with time in floc, with TOC and TN generally increasing ($p<0.050$, Table 3, Fig. 3-5). C:N significantly changed without a trend in floc ($p<0.043$, Table 3). Lability of OC in the mangrove algal mat significantly increased with time, while lability in seagrass floc significantly decreased with time ($p<0.052$, Table 2).

Constructed and Reference Comparisons

TOC was significantly higher in reference than in SL 15 mangrove and seagrass systems on both a concentration and storage basis, except in seagrass floc where TOC was similar between sites (site effect, $p<0.0005$, Table 2; Table 4). TOC differences between sites were greatest in mangrove sediments (Fig. 3-6). On a concentration basis in seagrass sediments, sites had similar TOC in depth one, but had different TOC in depths two and three (site x depth

interaction, p=0.018, Table 2; Fig. 3-6b). On a storage basis, all layers had lower TOC in SL 15 so there was not a significant interaction, but a Tukey revealed layers one and three had similar TOC across sites (Fig. 3-6b; one-way ANOVA, df=5, p<0.0001). In seagrass sediments, TOC was greatest in depth one (depth effect, p>0.013, Table 2; Table 4).

TN was significantly higher in reference than in SL 15 mangrove and seagrass systems (site effect, p<0.0001, Table 2; Table 4), except in seagrass floc where month affected which site had higher TN (site x month interaction, p=0.041, Table 2; Table 4). C:N was significantly higher in the sediments and surface layers of mangrove references but was similar in the sediments and surface layers of seagrass sites (site effect, p<0.0097, Table 2; Table 4).

In mangrove sediments, ExOC was significantly higher in references but, in seagrass sediments, was significantly higher in SL 15 (site effect, p>0.0013, Table 2, Table 5). ExOC (storage basis) of the 0-5 depth in SL 15's mangrove system was similar to reference depths while SL 15's 5-10 depth had significantly lower ExOC (site x depth interaction, p=0.058, Table 2; Fig. 3-7a). In the seagrass systems, ExOC (concentration basis) was similar in depths two and three across sites while depth one in SL 15 had greater ExOC than depth one in the reference (site x depth interaction, p<0.0001, Table 2; Fig. 3-7b). On a storage basis, however, ExOC of depths two and three in SL 15 were higher than the references, but depth one had similar ExOC across sites (site x depth interaction, p=0.0017, Table 2; Fig. 3-7b). Upper depths had significantly more ExOC in both mangrove and seagrass sediments (depth effect, p<0.0038, Table 2; Table 5). Surface layer ExOC did not significantly differ except for seagrass floc where ExOC was greater on a concentration basis in SL 15 (site effect, p=0.020, Table 2; Table 5).

MBC was significantly higher in reference sites for mangrove and seagrass sediments on a concentration and storage basis (site effect, p<0.0001, Table 2; Tables 5; Fig. 3-8). In mangrove

sediments, SL 15 0-5 cm depths had similar MBC to reference 5-10 cm depths on a storage basis (Fig. 3-8a; one-way ANOVA, df=3, $p<0.0001$). On a concentration basis, depths two and three of SL 15 seagrass sediments had significantly lower MBC than those depths in reference sediments, while depth one MBC was similar across sites (Fig. 3-8b; one-way ANOVA, df=5, $p<0.0001$). On a storage basis, depths two and three had similar MBC across sites, but depth one had significantly lower MBC in SL 15 (site x depth interaction, $p<0.0001$, Table 2; Fig. 3-8b). MBC was significantly greater in November than in July for both mangrove and seagrass sediments (month effect, $p<0.0009$ Table 2; Table 5). MBC was significantly greater in upper depths of both mangrove and seagrass sediments (depth effect, $p<0.0066$, Table 2; Table 5 and 6). Surface layers had similar MBC to respective references (Table 2; Table 5).

SL 15 systems had significantly greater OC lability than reference systems in all sediments and surface layers except for floc (site effect, $p<0.013$, Table 2; Table 6). Only depth one in seagrass sediments was similar across sites (site x depth interaction, $p<0.0001$, Table 2; Table 6). In mangrove sediments, the 0-5 cm depth had significantly greater lability than the 5-10 cm depth while in seagrass sediments, depth two had the greatest lability (depth effect, $p<0.0027$, Table 2; Table 6). In mangrove surface layers, lability of the SL 15 algal mat increased while lability of reference litter decreased from July to November (site x month interaction, $p<0.0001$, Table 2; Table 6).

Organic Carbon Accumulation Rates

OC accumulation rates in SL 15 sediments were between 168 to 231 g OC m^{-2} y^{-1} in the seagrass sediments, but were between -119 to -148 g OC m^{-2} y^{-1} in the mangrove sediments. When algal mat accumulations were added to mangrove sediments accumulations, rates ranged from 29 to 236 g OC m^{-2} y^{-1}. Floc OC accumulations were not added to seagrass sediments due to the transient nature of floc, which is easily swept away by currents.

Discussion

Sediment Characteristics

SL 15 and reference sediments are physically different from one another because SL 15 sediments' parent material is dredge spoil, as is apparent from their high amount of shell fragments (Table 1). Furthermore SL 15 sediments were compacted during construction. SL 15's accreted layer differs from other SL 15 sediments because it is a layer of post-construction deposition and was not compacted by equipment. In comparisons of constructed and reference salt marshes and mangrove forests, bulk density was almost always greater in constructed sites (Craft et al. 1999; McKee and Faulkner 2000; Craft et al. 2002). Redox potentials of all sites were negative implying anaerobic conditions and a slow rate of decomposition. Redox potentials in this study are generally more negative than those found in other mangrove (McKee 1993, Otero et al. 2006) and seagrass sediments (Terrardos et al. 1999), and sediment pH in this study are generally higher than in other mangrove sediments (McKee and Faulkner 2000; Otero et al. 2006) but similar to other seagrass sediments (Burdige and Zimmerman 2002; Daby 2003).

C:N ratios only differed between mangrove constructed and reference sediments (Table 4). Lower C:N ratios in the mangrove SL 15 sediments are due to their very low TOC. The rest of the C:N ratios are the same between SL 15 and reference sites due to similar proportions of C and N despite SL 15 having lower amounts of C and N overall. In this study, C:N ratios could therefore not be used as the ultimate metric of restoration success as was suggested for salt marshes by Craft (2001).

Trajectory of Constructed Site

In SL 15 sediments, only mangrove bulk density followed a functional trajectory in which it decreased within 2 months of construction completion but remained higher than the reference values (Fig. 3-3). This initial decrease may have occurred as these sediments decompressed,

aided by water movement into interstitial spaces, once compaction-causing construction ceased and tides could access the site. The seagrass section of SL 15 was completed a month before the rest of SL 15. Seagrass sediments therefore decompressed earlier and may have experienced a similar bulk density decrease before sampling began.

OC parameters in SL 15 sediments did not follow a trajectory, although OC pools in SL 15 seagrass sediments seemed to follow a pattern (Fig. 3-4). External, seasonal factors, not ecosystem development, were likely the force driving these patterns. A review of physical and chemical water column data in IRL from November 2005 to November 2006 revealed potential correlations that could explain the pattern (SFWMD 2007; station IRL 36). Lows in OC parameters corresponded with lows in salinity, highs in total Kjeldahl nitrogen, and the lowest (February) and highest (July) water temperatures of the year. Nitrogen probably did not cause these trends because N levels in the IRL are not high enough to be toxic to bacteria, but temperature or salinity may have. If the overlying water affected OC parameters in seagrass sediments, it explains why mangrove sediments, which are only in contact with water at high tide, experienced the pattern to a much lesser extent.

In both SL 15 surface layers, TOC and MBC followed a trajectory where they increased over time (Fig. 3-5). As a surface layer, seagrass floc is more likely to respond to water column changes than sediments. Floc TOC and MBC, however, followed a different pattern than seagrass sediments and IRL salinity and temperature. Floc OC pool increases match increases in IRL total suspended solids from February to November 2006 (SFWMD 2007; station IRL 36). Since the floc is mostly water (95%), it is likely that its solids are correlated to water column solids, which include OC substrate and microbes. Algal mat MBC increases are likely due to the algal mat's maturation as it became larger and denser throughout the year (personal observation).

Overall, during the first year following construction, with the exception of the mangrove algal mat, OC changes in SL 15 are due to seasonality and water quality. These seasonality-caused changes are large and may obscure any changes due to increasing functions. High interannual variability that mask directional changes has been observed in a restored California salt marsh (Zedler and Callaway 1999). SL 15 changes were greatest in ExOC and MBC, pools with fast turnover rates. One year may not be ample time to observe changes in more stable OC pools like TOC.

Constructed and Reference Equivalence

Organic carbon pools

A lack of trajectories does not preclude OC on SL 15 from being functionally equivalent to reference OC. Examining depths separately, 0-5 cm SL 15 mangrove sediments approached functional equivalence on a storage basis for ExOC and MBC (Fig. 3-7 and 3-8). Most depths of SL 15 seagrass sediments were at or exceeded functional equivalence for all OC pools on a storage basis (Fig. 3-7 and 3-8). The reason for this equivalence was bulk density. Because bulk density of SL 15 0-10 cm sediments is greater than reference sediments, when OC concentrations are multiplied by bulk density in order to be reported on a storage basis, the resulting parameters in SL 15 are often greater than or equal to the resulting parameters in reference sediments. Accreted layers were an exception because their bulk densities were the same as the references' and their heights were usually less than the references' 5 cm.

TOC equivalence did not occur on a concentration or a storage basis in the mangrove sediments but occurred for accreted and 0-5 cm depths in seagrass sediments. Accreted layers reached equivalence because the material accumulating from the water column is likely the same material being trapped by seagrasses in reference sediments. It is odd, at first, that 5-10 cm depths reached equivalence before 0-5 cm depths because inputs of OC to SL 15 sediments were

most likely coming the water column and benthic vegetation, which in the first year did not include deeply rooting plants. The 5-10 cm depth, however, was not completely dredge spoil. It contained mangrove clay from pre-construction mangrove areas and a buried "A horizon" from the seagrass bed that occupied the site before spoil island creation (Fischler 2006). These other sediments were exposed and mixed with dredge spoil during construction and had more OC than dredge spoil due to their origins in vegetated systems.

In the surface layers, the seagrass floc reached or exceeded equivalence in terms of all OC pools. SL 15 floc may have exceeded reference values due to its position inside the mangrove fringe of SL 15. In the subtidal portion of SL 15 there were areas of slower tidal flow that caused settling of water column material (Fischler 2006), which would include OC. The algal mat reached equivalence in ExOC and MBC but not TOC. Lower TOC in the algal mat than in the litter layer is because the litter layer consisted of higher plant material like mangrove leaves and seagrass that contain more recalcitrant C than algae (Kristensen 1994). Surface layers are first to receive inputs that contribute directly and indirectly to OC pools, such as of light, water column nutrients, and detritus. Therefore, it is not surprising that most of their OC parameters would reach equivalence within the first year. Upper depths reached OC functional equivalence quickly while lower depths failed to increase over 7 years in a constructed Virginia salt marsh (Havens et al. 2002).

The majority of studies that test functional trajectories of TOC or organic matter (OM) in restored and created salt marshes do not see OC reach functional equivalence. In studies that ranged from one- to 42-year-old marshes, only two reached equivalence with their natural wetland references in terms of SOC (Simenstad and Thom 1996, Zedler and Calloway 1999; Craft 2001, Havens et al. 2002, Morgan and Short 2002, Craft et al. 2003). They were 25 (Craft

et al. 2003) and 42 (Craft 2001) years old. These authors concluded that it takes a long time for restored salt marshes to develop SOC pool equivalence and acknowledged that such equivalence may never be reached.

Predictions from salt marsh studies may be valuable for understanding trajectories of constructed mangrove forests because both are intertidal systems that take a long time to reach equivalence. Sediment OM in a 6-year and 14-year-old mangrove forests in Southwest Florida remained at 18 to 32% of reference forest values (McKee and Faulkner 2000). SL 15 mangrove sediment TOC was well below that of references. The lack of a TOC trajectory for mangrove sediments contrasts to findings in salt marsh studies and indicate that not reaching equivalence is a possibility. In all salt marsh studies except one (Simenstad and Thom 1996) a trajectory of increasing OC/OM was documented (Zedler and Calloway 1999; Craft 2001; Craft et al. 2002; Havens et al. 2002; Morgan and Short 2002; Craft et al. 2003). Even a young constructed salt marsh in North Carolina increased its sediment TOC by over 100% in 1.3 years (Cammen 1975).

Predictions from salt marshes studies do not work for constructed and restored seagrass beds. OM content of restored sediments was higher than one reference and lower than another throughout the first 8 years in the only other known study of seagrass functional trajectories (on the New Hampshire coast, Evans and Short 2005). In SL 15 seagrass sediments, TOC was functionally equivalent in 2 out of 3 depths within a year.

There are several reasons why OC in seagrass sediments reach functional equivalence before OC in mangrove forests and in salt marshes. The first reason is elevation. In several studies of restored and constructed salt marshes, soil development was correlated to marsh elevation so that OC/OM was higher at lower elevations (Lindau and Hossner 1981; Moy and Levin 1991; Craft et al. 2002). OC equivalence occurs faster at lower elevations because they are

inundated for longer periods of time (always in the case of seagrass beds), which can create more highly reducing conditions that slow OM decomposition. More contact with water also means more contact with, and accumulation of, the dissolved organic carbon (DOC), particulate organic carbon (POC), and nutrients that water transports. Nutrients and OC stimulate bacterial production in sediments, nutrients stimulate autotrophic production of OC, and POC settles becoming part of sediment OM (Gacia et al. 2002).

The second reason seagrass sediments reach OC functional equivalence first is parent material. In most constructed salt marshes, in the SL 15 mangrove system, and in the Southwest Florida restored mangroves, the parent material was dredge spoil that is practically devoid of OM. As previously discussed, dredge spoil was not the only material found in SL 15 seagrass sediments. There was also OM-rich material originating from old vegetated sediments that were disturbed during construction, in 5-10 cm depths. At time zero OC is therefore greater in seagrass sediments. In the New Hampshire seagrass study, the sediment material was not spoil but a previously vegetated, estuarine "A horizon" that had been devoid of seagrasses for 12 years (Evans and Short 2005). Like in the 5-10 cm depth of the SL 15 seagrass sediments, it is likely OC was present before restoration began.

The third reason seagrass sediments reach equivalence before mangrove and salt marsh sediments is the different OC amounts among the three coastal systems. OC content varies greatly, even among nearby reference sites (Craft et al. 1999), but generally seagrass sediments have the lowest OC and mangrove sediments the highest. Reported range in seagrass %OC is 0.15 to 1.3 (Evans and Short 2005; Vichkovitten and Holmer 2005). Reported range in salt marsh %OC is 1.7 to 13.5 (Moy and Levin 1991; Simenstad and Thom 1996; Zedler and Calloway 1999; Morgan and Short 2002). Reported range in mangrove %OC is 2.3 to 37

(McKee and Faulkner 2000; Alongi et al. 2001; Jennerjohn and Ittekkot 2002; Alongi et al. 2004; Bouillon et al. 2004; Otero et al. 2006). The functional equivalence "bar" is therefore lowest for seagrass sediments, which was true in this study where reference sediments' mean %OC was 1.4 in mangroves and only 0.74 in seagrass. Lower than reported %OC values in this study's reference mangrove sediments are likely due to their position around spoil islands—mangrove reference sites, just as SL 15, began development in dredge spoil.

No known functional trajectory studies have measured OC pools with short turnover times like ExOC and MBC. These OC pools were the only pools to approach equivalence in mangrove sediments. Because these pools are more active (Buyanovsky et al 1994; Rochette and Gregorich 1998), they are likely to develop faster in sediments. Constructed and reference sediments in this study had MBC that was about equal to greater than MBC in a North Sea tidal flat, a Brazilian mangrove forest, and an arctic salt marsh (Joergensen and Mueller 1995; Otero et al. 2006; Buckeridge and Jefferies 2007). Those other studies are the only known to measure MBC via fumigation extraction in a marine environment. MBC measured by fumigation-extraction has been found to correlate well with MBC measured by phospholipids fatty acid (PLFA) analysis but not by DNA analysis or substrate-induced respiration (Bailey et al. 2002; Leckie et al. 2004). A relationship between fumigated and extracted C and total PLFA concentrations has been developed by Bailey et al. (2002).

$$CFE_{flush} = 2.4(PLFA_{total}) + 46.2 \qquad (3\text{-}2)$$

In equation 3-2, CFE is the uncorrected flush of OC (ug C g^{-1} soil) resulting from fumigation and $PLFA_{total}$ (nmol g^{-1} soil) is the total amount PLFA extracted from the soil. Multiplying the results by the 2.22 CFE to MBC correction factor, MBC from this study was compared to MBC in studies that used the PLFA method. Converted measurements of PLFA yielded MBC values

that were the same order of magnitude as our constructed system sediments—MBC was 193 to 715 mg C kg^{-1} in a European seagrass bed (Boschker et al. 2000), 289 to 769 mg C kg^{-1} in a California salt marsh (Cordova-Kreylos et al. 2006), and 182 mg C kg^{-1} in an Australian seagrass bed (Moriarty et al. 1985). Note that this conversion equation came from sandy soils, not marine sediments, so values are not exact but are estimates for comparison purposes.

Organic carbon lability

The magnitude of OC pools is not the only factor that affects C storage, so further data exploration is needed to assess whether SL 15 stores sediment C as well as other seagrass beds and mangroves forests. SL 15 sediments must not only have OC pools equal to or greater than references to function as a significant C store, they must also have their OC stored in long term pools, where it can be sequestered away from the atmospheric C pool for decades, centuries, and even millennia. Relative amounts of the OC pool are important because the pool containing the most OC affects the overall storage abilities of a system. A system with most of its OC in non-reactive, recalcitrant pools is going to store C longer than a system with most of its OC in active pools like microbial biomass (Buyanovsky et al. 1994).

The constructed system generally stored more OC in short-term pools than references. In all sediments except constructed mangrove sediments, ExOC made up less than 1% of the TOC pool (Fig. 3-9), but the percentage of the TOC pool made up by MBC was greater in constructed than in reference sediments. In SL 15 mangrove sediments, 53 to 63% of their TOC was MBC, while in reference sediments 11 to 15% of TOC was MBC (Fig. 3-9). This trend was the same in mangrove surface layers. In SL 15 seagrass 0-10 cm sediments, 24 to 38% of their TOC was MBC, while in references 17 to 20% of TOC was MBC (Fig. 3-9). SL 15 accreted layers and reference 0-5 cm depths had similar percentages that ranged from 19 to 27% (Fig. 3-9). Sediments in this study had more TOC stored as MBC than in other coastal systems, which

generally had less than 10% of their MBC as TOC (Boschker et al. 2000; Bouillon et al. 2004; Cordova-Kreylos et al. 2006). OC limitation is a possible reason for high microbial biomass. The low C:N ratios of constructed and reference sediments suggest a C limitation (Sterner and Elser 2002). When microbes are C limited they tend to sequester C in their cells instead of respiring C for energy (Anderson 2003). This mechanism is supported by another study with high MBC percentages (23 to 50% of TOC), as its sediments also had low TOC (<1.0%) (Joergensen and Mueller 1995).

Constructed sediments do not store OC as well as reference sediments because the lability of SL 15 OC was greater than references at all depths except for seagrass floc and accreted layers. Lability is a proxy for the decomposability of OC—the greater the lability, the faster OC is decomposed releasing C back to the atmosphere. It is therefore unlikely that labile OC would be stored in sediments for long periods of time. One study of macro organic matter (MOM), a precursor of sediment OM, in constructed marshes showed that younger marshes had more labile MOM than older marshes indicating they were less likely to sequester OC in the long term (Craft et al. 2003)

Organic carbon accumulation

Rates of OC accumulation are another factor that determines how well constructed systems function as OC stores. Pool sizes measure how much C systems are keeping from the atmosphere, lability indicates how long C is likely sequestered, and accumulation rates measure how much C is being actively taken from the atmosphere (via plant production). Salt marsh studies found equal and even greater OC accumulation rates in constructed marshes (Cammen 1975; Craft et al. 1999; Craft et al. 2003). In this study, OC accumulation rates in constructed seagrass sediments were similar to those in other studies, but rates of constructed mangrove sediments were much lower than other studies unless the algal mat was included (Table 7, Fig. 3-

9). Negative rates in mangrove sediments were due to a decrease bulk density throughout the year while TOC concentrations remained constant, but if the algal mat becomes more permanent (i.e. buried) its OC will more than compensate for negative rates. Positive rates in seagrass sediments were driven by the accreting layer. It is unknown whether the accreted layer in seagrass sediments of SL 15 will continue to accumulate material at the same rates as in the first year. Continued accumulation depends on how much the accreted layer formation was due to a physical response to an uneven benthic surface after construction and how much was due to macroalgae and seagrasses trapping particles from the water column.

Conclusion

Mangrove sediments are farther from being equivalent C stores than seagrass sediments. Mangrove sediments have only begun to reach equivalence in active pools (ExOC and MBC) and contain a relatively small amount of TOC, while seagrass sediments have equivalent TOC at most depths (Fig. 3-9). The difference between constructed and reference OC lability is also much greater in mangrove than in seagrass sediments, and OC accumulation rates in mangrove sediments are negative (if the algal mat is excluded). However, if constructed mangrove sediments do begin to follow a functional trajectory, their potential OC storage is greater than constructed seagrass sediments because mangrove reference sediments have larger TOC pools, less OC stored as MBC (Fig. 3-9), and lower OC lability than seagrass reference sediments. Overall, due to potential OC limitations, low TOC values for their ecosystem type, and nitrogen eutrophication (Morris and Bradley 1999; Sigua and Tweedle 2003) IRL coastal ecosystems are probably not as effective at storing C as their counterparts elsewhere.

The C storage capabilities of coastal ecosystems make them a great contender for use as C offsets. One year is not enough time to discern whether these systems will become significant C stores. More studies should investigate constructed coastal ecosystems as potential C sinks by

measuring functional trajectories, OC lability, and OC accumulation rates. If constructed systems are similar to natural systems, then constructing coastal ecosystems may become an accepted way to offset CO_2 emissions, which would encourage more restoration.

Table 3-1. Mean (± SE) bulk density, % shell pieces, pH, and Eh (redox potential) of the sediments according to depth and site. The bulk density and % shell data were averaged over the July and November 2006 sampling periods (n=24 for SL 15 and n=18 for references). The pH and Eh data were measured in September 2006 (n=3).

System	Depth	Bulk density ($g\ cm^{-3}$)		Shells >1mm (%)		pH		Eh (mV)	
		SL 15	Reference	SL 15	Reference	SL 15	Reference	SL 15	Reference
Mangrove	Algal mat/ Litter	1.03 (0.2)	0.41 (0.1)	0	0	NA	NA	NA	NA
	0-5 cm	1.62 (0.03)	0.95 (0.04)	24 (2)	21 (5)	8.3 (0.04)	7.6 (0.07)	-71 (90)	-130 (40)
	5-10 cm	1.48 (0.03)	0.93 (0.05)	30 (2)	14 (2)	8.2 (0.03)	7.5 (0.03)	-5.7 (100)	-160 (8)
Seagrass	Floc	0.32 (0.04)	0.54 (0.09)	0	0	NA	NA	NA	NA
	Accreted	0.91 (0.05)		6.0 (1)		8.2 (0.04)		-98 (50)	
	0-5 cm	1.51 (0.04)	0.89 (0.04)	20 (3)	0.33 (0.1)	8.3 (0.04)	8.0 (0.18)	-230 (4)	-150 (30)
	5-10 cm	1.48 (0.04)	1.03 (0.03)	19 (5)	0.49 (0.2)	8.2 (0.03)	8.3 (0.07)	-180 (60)	-240 (8)
	10-15 cm		1.20 (0.02)		0.48 (0.1)		8.3 (0.14)		-320 (40)

Table 3-2. Results of factorial ANOVAs comparing SL 15 and references. Sediments and surface layers of the mangrove and seagrass systems were each run individually. BD=Bulk Density, ExOC=Extractable organic carbon, MBC=Microbial biomass carbon, TOC=Total organic carbon, and TN=Total nitrogen. Concentration (conc) parameters are reported in mg kg-1 dry soil, and storage parameters are reported in g m-2.

ANOVA	Effect	BD	TOC (conc)	(storage)	TN (conc)	C:N	ExOC (conc)	(storage)	MBC (conc)	(storage)	Lability
Sediment											
Mangrove	Site	***	***	***	***	**	***	***	**	***	*
	Month	NS	NS	NS	NS	NS	NS	NS	***	***	NS
	Depth	*	NS	NS	NS	NS	**	**	**	***	**
	Site*Month	NS	NS	NS	NS	NS	NS	NS	*	*	NS
	Site*Depth	NS	NS	NS	*	NS	*	NS	NS	NS	NS
	Month*Depth	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Seagrass	Site	***	**	**	***	NS	***	***	***	***	***
	Month	NS	NS	NS	**	NS	***	***	***	***	NS
	Depth	***	***	***	***	NS	***	***	***	***	***
	Site*Month	NS	NS	NS	NS	NS	NS	NS	NS	**	NS
	Site*Depth	***	*	NS	*	NS	***	**	NS	***	***
	Month*Depth	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Surface layers											
Mangrove algae/litter	Site	*	***	***	**	**	NS	NS	NS	NS	**
	Month	NS	NS	*	NS	NS	NS	NS	NS	NS	NS
	Site*Month	NS	NS	NS	NS	*	NS	NS	NS	NS	*
Seagrass floc	Site	*	NS	NS	NS	NS	*	NS	NS	NS	NS
	Month	NS	NS	NS	NS	*	NS	NS	**	NS	NS
	Site*Month	NS	NS	NS	*	**	NS	NS	NS	NS	NS

For significance NS=not significant, * p = or <0.05, **p < 0.01, ***p < 0.0001. Please see Appendix A for a table listing how these data were transformed prior to running the factorial ANOVA.

Table 3-3. Results of the repeated measures ANOVAs for SL 15 mangrove and seagrass sediments (0-5 cm, 5-10 cm, and seagrass accreted) and surface layers (algal mat and floc).

ANOVA	Effect	BD ($g\ cm^{-3}$)	ExOC ($mg\ kg^{-1}$)	MBC ($mg\ kg^{-1}$)	TOC (%)	TN (%)	C:N (molar ratio)	Lability ($mg\ O_2\ g^{-1}OC\ hr^{-1}$)
Mangrove								
0-10	Month	***	NS	***	NS	*	*	NS
	Depth	**	NS	NS	NS	**	NS	*
Algal mat	Month	NS	NS	**	NS	*	NS	*
Seagrass								
0-10	Month	NS	***	***	**	NS	NS	NS
	Depth	NS	NS	NS	NS	NS	NS	*
Accreted	Month	NS	NS	*	NS	*	NS	NS
Floc	Month	*	*	***	*	*	*	*

For significance NS=not significant, * $p < 0.05$, ** $p < 0.01$, *** $p < 0.0001$. Please see Appendix A for a table listing how these data were transformed prior to running the repeated measures ANOVA.

Table 3-4. Mean (± SE) organic carbon concentrations (%) and storage (g m^{-2}), nitrogen concentrations, and carbon to nitrogen molar ratios of SL 15 (n=4) and reference (n=3) mangrove and seagrass sediments according to depth and month. TOC=total organic carbon and TN=total nitrogen.

Month and system	Depth	TOC (%)		TOC (g m^{-2})		TN (%)		C:N (molar ratio)	
		SL 15	Reference	SL 15	Reference	SL 15	Reference	SL 15	Reference
July mangrove	Algal mat/ litter	2.49 (0.7)	11.9 (3)	170 (20)	670 (50)	0.26 (0.07)	1.1 (0.3)	8.2 (.22)	9.3 (0.29)
	0-5 cm	0.13 (0.04)	1.3 (0.1)	110 (30)	610 (50)	0.018 (0.005)	0.096 (0.02)	5.0 (0.99)	9.6 (2.5)
	5-10 cm	0.11 (0.03)	1.4 (0.4)	77 (20)	620 (90)	0.010 (0.003)	0.11 (0.03)	8.0 (1.7)	9.2 (1.3)
Nov. mangrove	Algal mat/ litter	3.27 (0.7)	18.0 (3)	310 (60)	1300 (400)	0.37 (0.1)	0.79 (0.1)	8.1 (0.92)	21 (5.4)
	0-5 cm	0.17 (0.02)	1.3 (0.3)	140 (10)	600 (90)	0.024 (0.004)	0.12 (0.02)	5.5 (0.33)	7.0 (1.1)
	5-10 cm	0.14 (0.03)	1.7 (0.5)	110 (30)	760 (200)	0.013 (0.001)	0.14 (0.03)	6.2 (0.77)	8.8 (0.9)
July seagrass	Floc	1.8 (0.4)	2.7 (1)	60 (20)	84 (40)	0.20 (0.06)	0.39 (0.1)	8.2 (0.95)	5.7 (0.55)
	Accreted	0.9 (0.01)		260 (50)		0.096 (0.01)		7.6 (1.1)	
	0-5 cm	2260 (0.07)	0.91 (0.6)	170 (40)	440 (20)	0.023 (0.008)	0.12 (0.01)	6.9 (0.27)	6.7 (0.16)
	5-10 cm	0.27 (0.1)	0.65 (0.8)	200 (80)	330 (20)	0.027 (0.01)	0.084 (0.01)	7.0 (0.98)	6.6 (0.19)
	10-15 cm		0.63 (1.0)		370 (40)		0.077 (0.01)		7.0 (0.21)
Nov. seagrass	Floc	5.0 (1)	3.7 (0.3)	130 (30)	96 (10)	0.62 (0.1)	0.30 (0.04)	6.8 (0.08)	10.8 (0.65)
	Accreted	1.0 (0.1)		340 (40)		0.13 (0.02)		6.1 (0.38)	
	0-5 cm	0.25 (0.05)	0.97 (0.1)	180 (30)	390 (30)	0.027 (0.006)	0.15 (0.02)	6.7 (0.76)	5.4 (0.22)
	5-10 cm	0.41 (0.1))	0.65 (0.6)	280 (60)	340 (10)	0.041 (0.01)	0.10 (0.01)	7.3 (1.1)	5.6 (0.35)
	10-15 cm		0.62 (0.3)		370 (1)		0.089 (0.009)		6.1 (0.36)

Table 3-5. Mean (± SE) concentration (mg kg^{-1}) and storage (g m^{-2}) of two relatively labile types of organic carbon in SL 15 (n=12) and reference (n=9) mangrove and seagrass sediments according to depth and month. ExOC=extractable organic carbon and MBC=microbial biomass carbon.

Month and system	Depth	ExOC (mg kg^{-1} dry soil)		MBC (mg kg^{-1} dry soil)		ExOC (g m^{-2})		MBC (g m^{-2})	
		SL 15	Reference	SL 15	SL 15	Reference	Reference	SL 15	Reference
July mangrove	Algal Mat/ litter	830 (200)	1800 (1000)	8500 (2000)	14000 (5000)	6.7 (2.0)	8.8 (3)	57 (5)	75 (9)
	0-5 cm	47 (4)	130 (30)	740 (20)	1900 (100)	3.8 (0.3)	6.3 (1)	60 (2)	87 (4)
	5-10 cm	38 (3)	86 (7)	690 (10)	1600 (100)	2.8 (0.3)	3.9 (0.5)	51 (2)	69 (4)
Nov. mangrove	Algal Mat/ Litter	600 (100)	750 (200)	12000 (3000)	7200 (1000)	5.7 (1.0)	4.7 (2)	110 (30)	49 (20)
	0-5 cm	52 (7)	76 (5)	900 (30)	1800 (100)	4.2 (0.5)	3.5 (0.2)	75 (4)	83 (3)
	5-10 cm	32 (3)	80 (4)	820 (20)	1800 (200)	2.4 (0.2)	3.8 (0.2)	61 (2)	80 (3)
July seagrass	Floc	100 (9)	89 (10)	18000 (100)	16000 (500)	0.33 (0.08)	0.26 (0.02)	55 (10)	48 (3)
	Accreted	77 (6)		1700 (100)		2.1 (0.1)		47 (4)	
	0-5 cm	29 (2)	53 (4)	840 (40)	2100 (100)	2.2 (0.1)	2.4 (0.1)	64 (2)	100 (4)
	5-10 cm	24 (1)	25 (1)	800 (40)	1340 (80)	1.8 (0.1)	1.4 (0.1)	59 (2)	67 (3)
	10-15 cm		24 (3)		1100 (70)		1.2 (0.04)		67 (3)
Nov. seagrass	Floc	130 (11)	91 (6)	24000 (1100)	23000 (3000)	0.37 (0.03)	0.24 (0.0)	65 (4)	60 (9)
	Accreted	100 (6)		2300 (100)		3.4 (0.3)		75 (5)	
	0-5 cm	31 (2)	62 (5)	990 (30)	2600 (200)	2.3 (0.1)	2.5 (0.1)	74 (3)	100 (2)
	5-10 cm	36 (2)	39 (5)	1000 (40)	1400 (100)	2.6 (0.2)	2.0 (0.3)	73 (3)	71 (5)
	10-15 cm		28 (1)		1300 (40)		1.7 (0.07)		74 (2)

Table 3-6. Mean (± SE) organic carbon lability of organic carbon in SL 15 (n=4) and reference (n=3) sites according to depth and month.

System and month	Depth	Lability ($mg\ O_2\ g^{-1}OC\ hr^{-1}$)	
		SL 15	Reference
July mangrove	Algal mat/ litter	1120 (300)	760 (290)
	0-5 cm	1480 (580)	520 (170)
	5-10 cm	360 (120)	332 (130)
Nov. mangrove	Algal mat/ litter	2230 (540)	320 (100)
	0-5 cm	1210 (250)	355 (21)
	5-10 cm	572 (350)	198 (48)
July seagrass	Floc	631 (73)	782 (320)
	Accreted	387 (45)	
	0-5 cm	1170 (120)	527 (34)
	5-10 cm	856 (120)	677 (48)
	10-15 cm		469 (29)
Nov. seagrass	Floc	333 (79)	421 (120)
	Accreted	555 (52)	
	0-5 cm	1280 (110)	492 (25)
	5-10 cm	800 (69)	625 (38)
	10-15 cm		626 (40)

Table 3-7. Organic carbon accumulation rates in mangrove and seagrass systems in this and other studies.

System	Rate (g OC m^{-2} y^{-1})	Location and remarks	Source[a]
Seagrass	195	Florida, USA	This study
	40-65	Mexico	1
	19-191	Spain	2
	182	Spain	3
Mangrove	-189	Florida, USA; sediment of 1-year - old planted system	This study
	120	Florida, USA; above system with algal mat included	This study
	180	Australia	4
	168-841	China	5
	105-159	Florida, USA	6
	191-328[1]	Florida, USA	7
	101-127	Malaysia	8
	33-104	Mexico	1
	184-281	Thailand	9

[a] 1, Gonneea et al. 2004; 2, Romero et al. 1994; 3, Gacia et al 2002; 4, Brunskill et al. 2002; 5, Alongi et al. 2005; 6, Callaway et al. 1997; 7, Cahoon and Lynch 1997; 8, Alongi et al. 2004; 9, Alongi et al. 2001

[1]This author reported organic matter accumulation rates, so rates were divided by 2 to obtain these numbers.

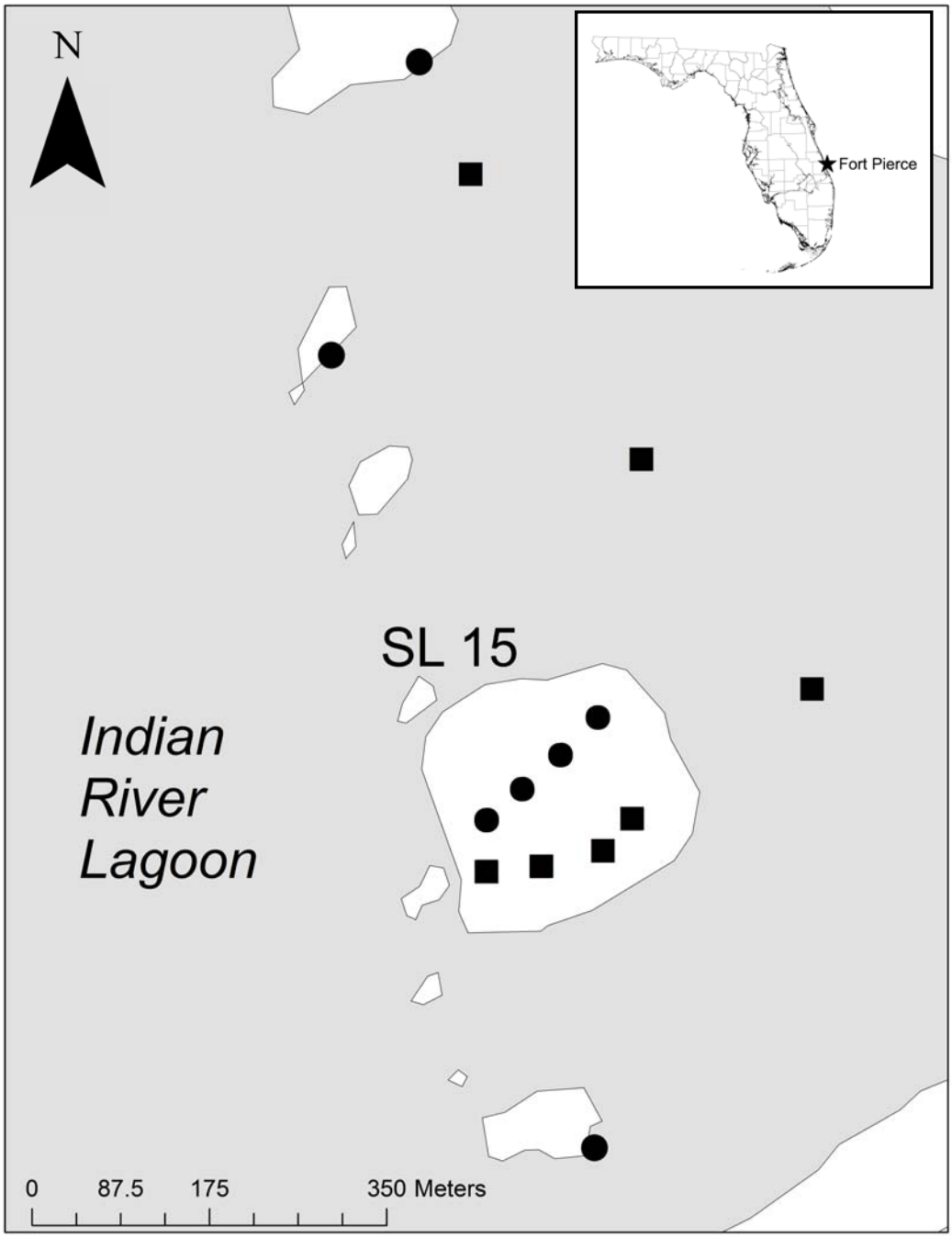


Figure 3-1. The study area in the Indian River Lagoon, next to Fort Pierce, Florida (inset). SL 15 is the large island in the center. Circles are mangrove system plots and squares are seagrass system plots. Symbols outside of SL 15 are the reference sites, which have one plot each.

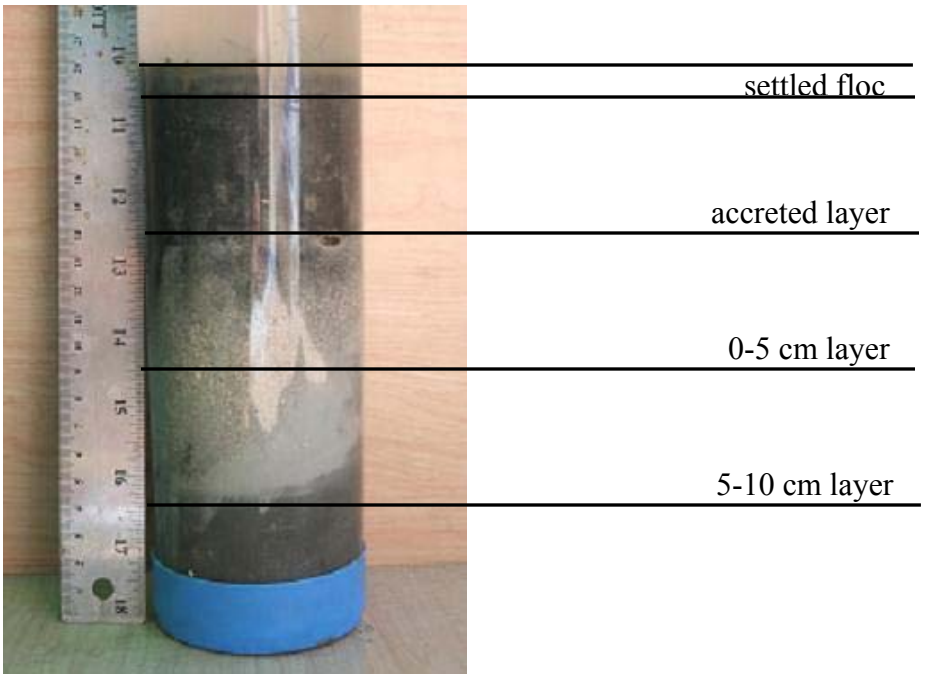


Figure 3-2. Core from SL 15 seagrass system illustrating the surface layer (floc) and different sediment depths (accreted layer, 0-5 cm, 5-10 cm). Note the difference in color between the accreted layer and 0-5 cm depth.

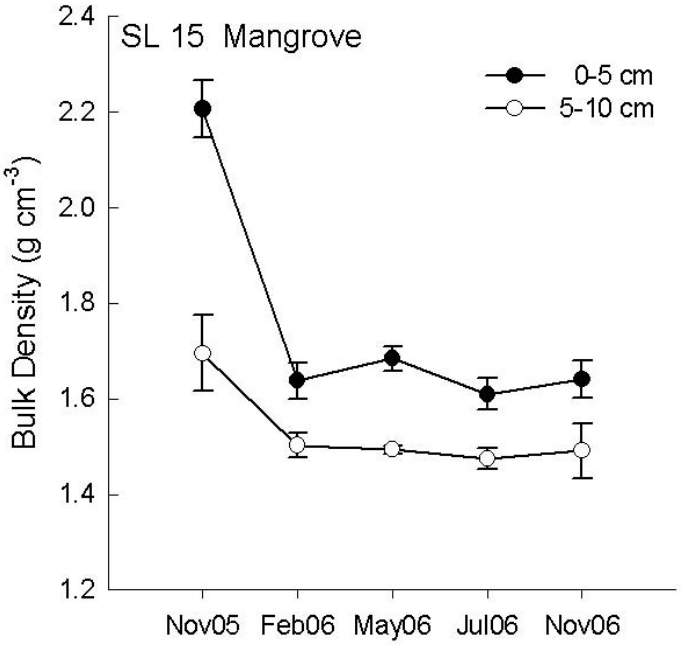


Figure 3-3. The functional trajectory the bulk density of SL 15 mangrove sediments followed over the first year after construction. The symbols are the mean values for each sampling date (n=12) and error bars are ± SE.

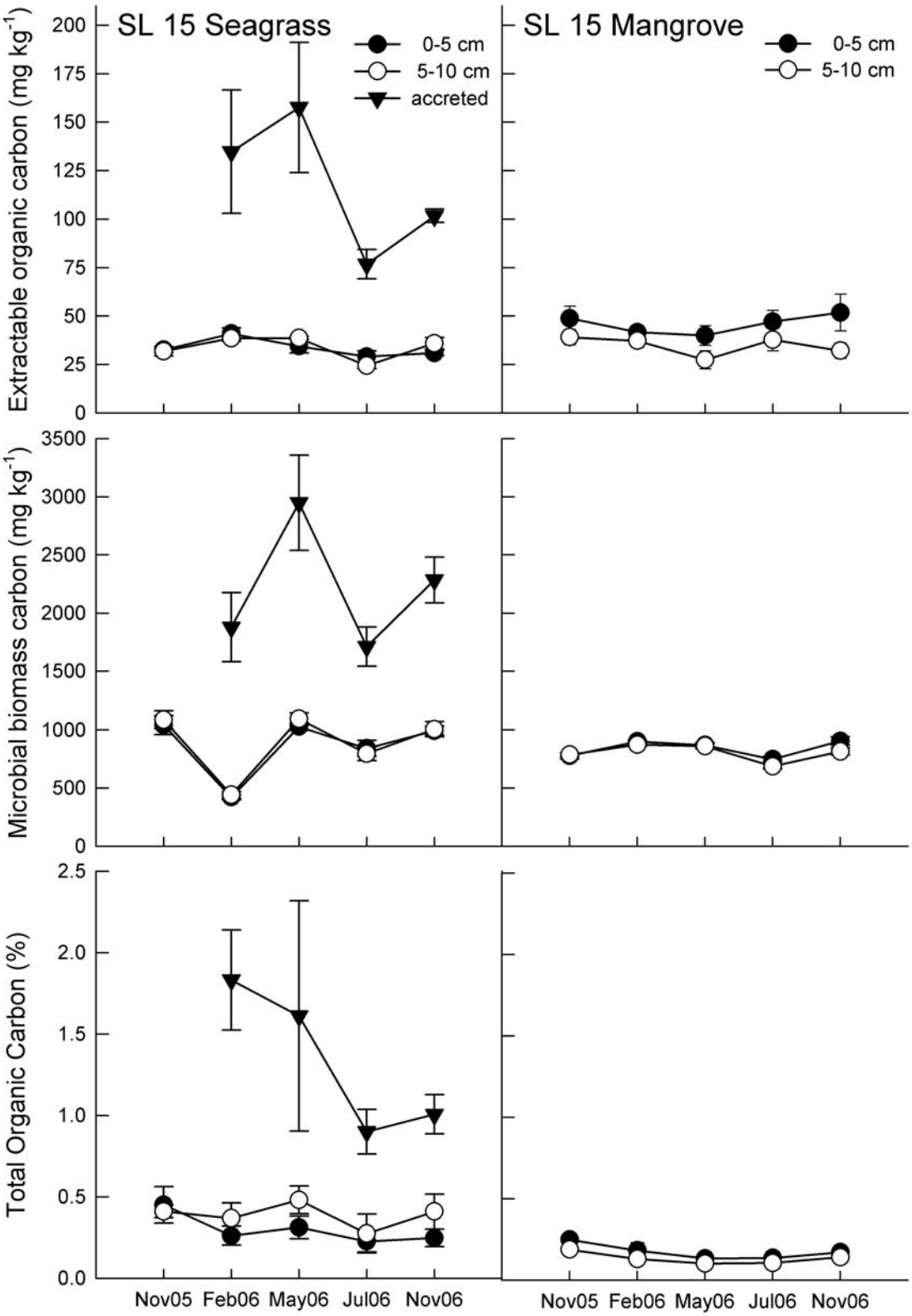


Figure 3-4. The changes in organic carbon parameters over the first year after construction in SL 15 seagrass and mangrove sediments. The symbols are the mean values for each sampling date (n=12 for ExOC and MBC and n=4 for TOC) and error bars are ± SE.

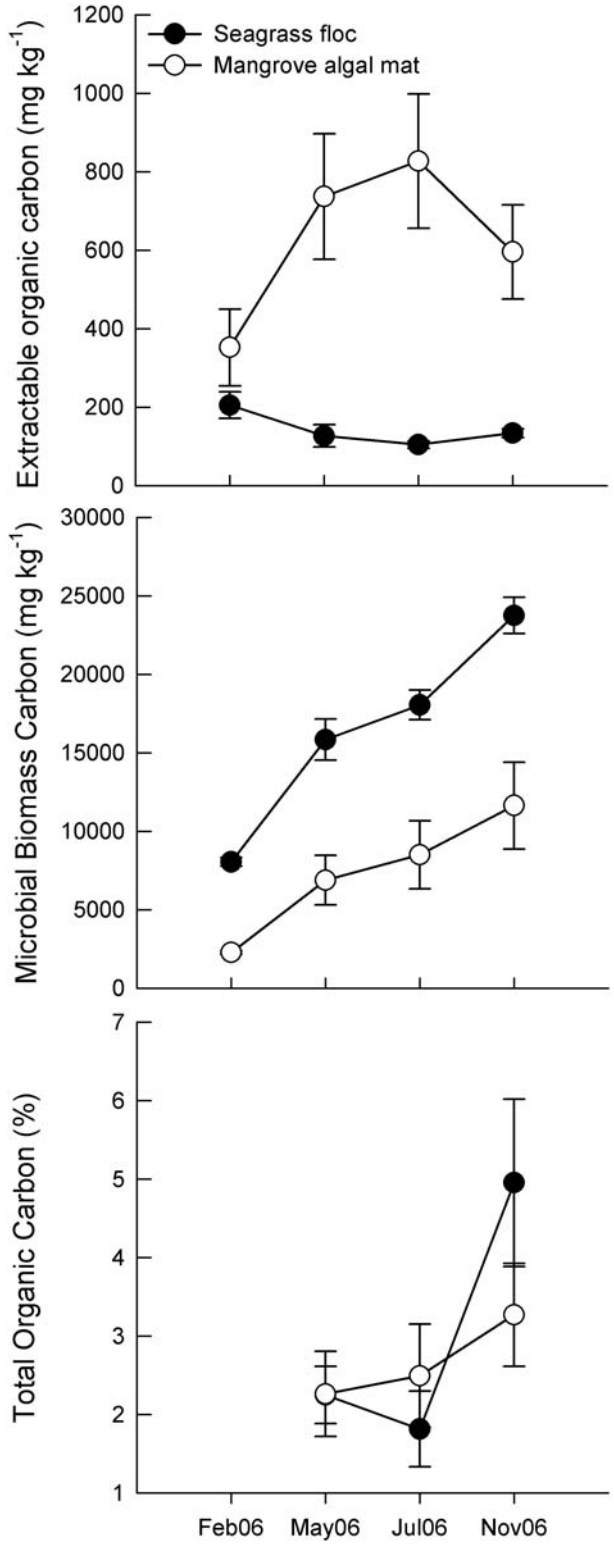


Figure 3-5. The changes in organic carbon parameters over the first year after construction in SL 15 seagrass and mangrove surface layers. The symbols are the mean values for each sampling date (n=4) and error bars are ± SE.

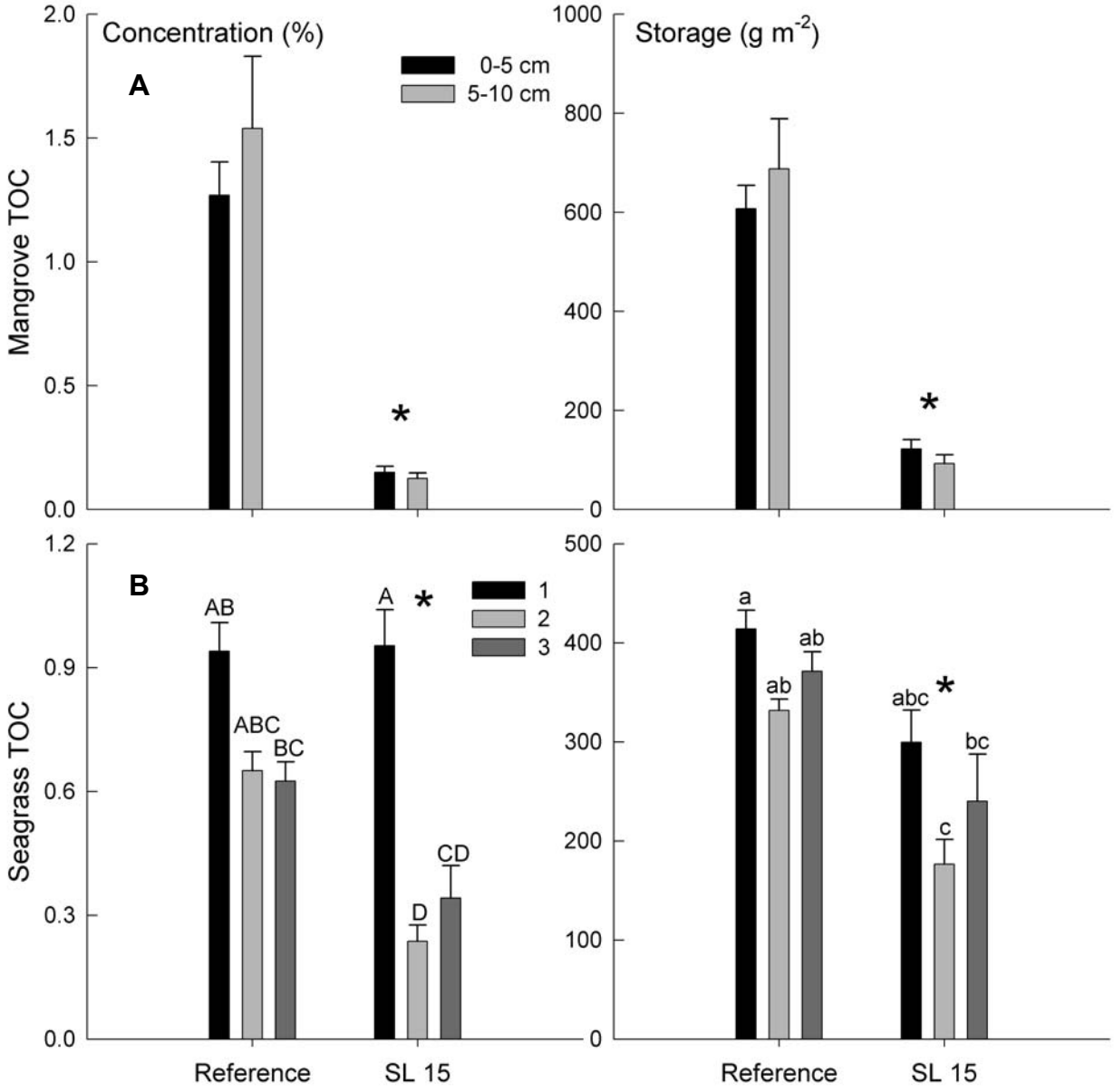


Figure 3-6. Comparisons between total organic carbon (TOC) in reference and SL 15 mangrove (top) and seagrass (bottom) sediments. The bars are mean TOC averaged over month (July and November 2006) for each depth of sediment (n=4 for SL 15 and n=3 for reference). Error bars are ± SE. Depths in the seagrass systems are as follows: 1= SL 15 accreted and reference 0-5, 2= SL 15 0-5 and reference 5-10, 3= SL 15 5-10 and reference 10-15. An asterisk indicates a significant site effect (Table 3-5). Capital letters are results of a Tukey test performed after a significant site x depth interaction, and lowercase letters are results of a Tukey performed after an unsignificant site x depth interaction, but a significant one-way ANOVA. Bars that share letters are not significantly different.

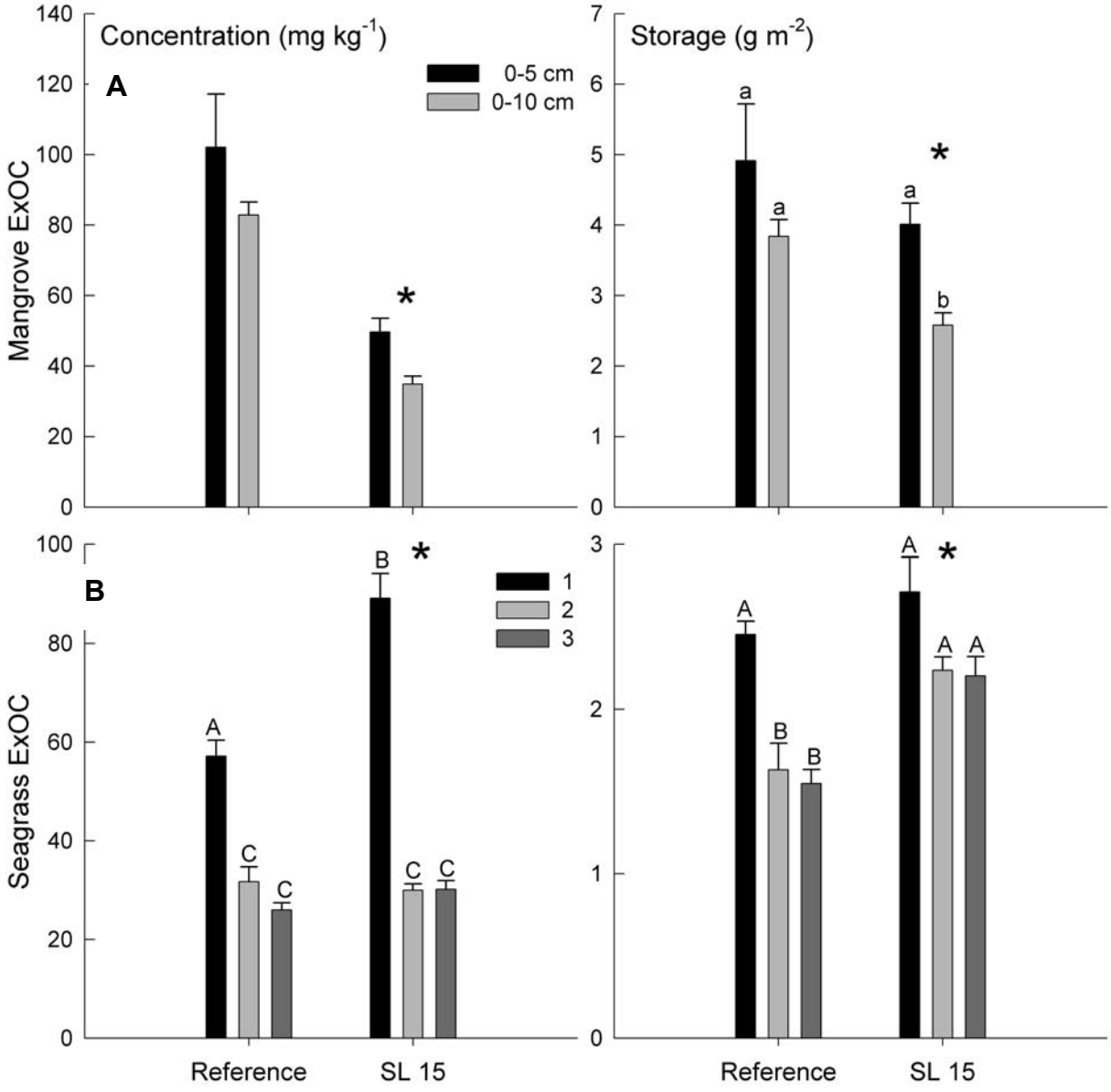


Figure 3-7. Comparisons between extractable organic carbon (ExOC) in reference and SL 15 mangrove (top) and seagrass (bottom) sediments. The bars are mean ExOC averaged over month (July and November 2006) for each depth of sediment (n=12 for SL 15 and n=9 for reference). Error bars are ± SE. Depths in the seagrass systems are as follows: 1= SL 15 accreted and reference 0-5, 2= SL 15 0-5 and reference 5-10, 3= SL 15 5-10 and reference 10-15. An asterisk indicates a significant site effect (Table 3-5). Capital letters are results of a Tukey test performed after a significant site x depth interaction, and lowercase letters are results of a Tukey performed after an unsignificant site x depth interaction, but a significant one way ANOVA. Bars that share letters are not significantly different.

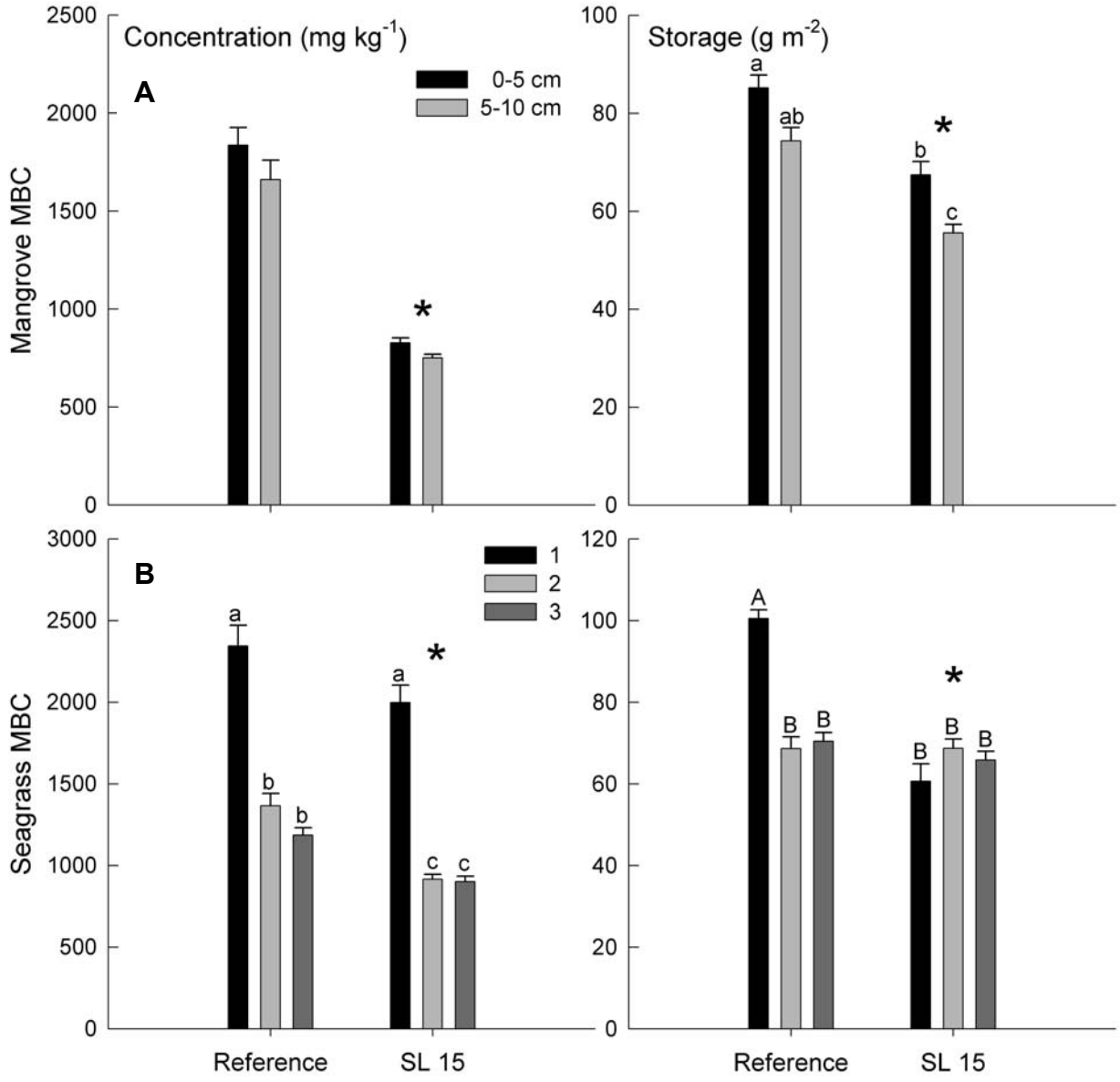


Figure 3-8. Comparisons between microbial biomass carbon (MBC) in reference and SL 15 mangrove (top) and seagrass (bottom) sediments. The bars are mean MBC averaged over month (July and November 2006) for each depth of sediment (n=12 for SL 15 and n=9 for reference). Error bars are ± SE. Depths in the seagrass systems are as follows: 1= SL 15 accreted and reference 0-5, 2= SL 15 0-5 and reference 5-10, 3= SL 15 5-10 and reference 10-15. An asterisk indicates a significant site effect (Table 3-5). Capital letters are results of a Tukey test performed after a significant site x depth interaction, and lowercase letters are results of a Tukey performed after an unsignificant site x depth interaction, but a significant one way ANOVA. Bars that share letters are not significantly different.

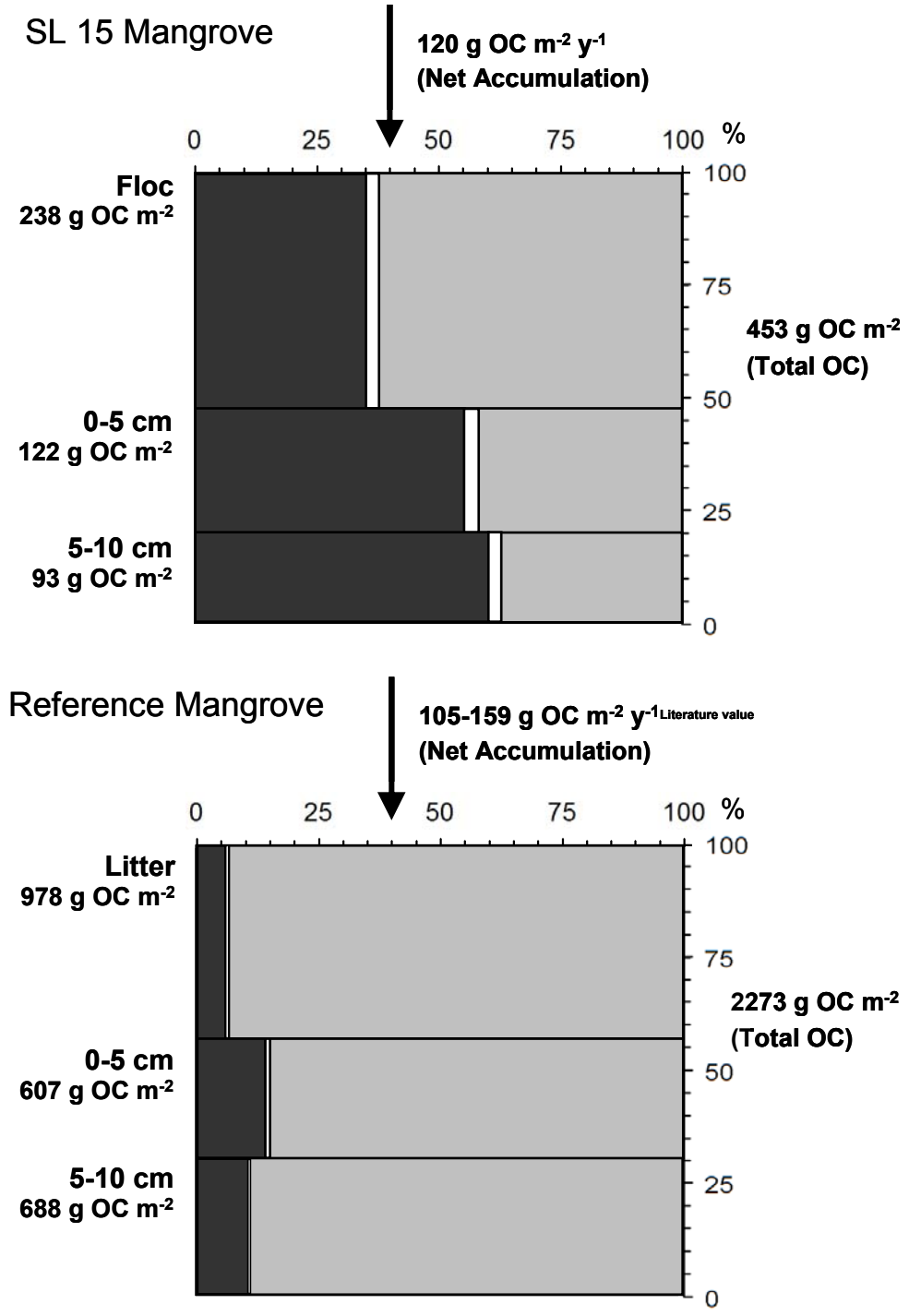


Figure 3-9. Organic carbon (OC) pools in SL 15 and reference mangrove and seagrass sediments. Beside each box is the total amount of OC in the depths analyzed. OC accumulation rates were calculated in this study for SL 15 sediments (includes algal mat for SL 15 mangrove) but are literature values for reference sediments (Callaway et al. 1997 for mangrove and Gonnoeea et al. 2004 for seagrass). Boxes show the percentage distribution of the total OC in each depth and OC pool—MBC (dark grey), ExOC (white), and other (light grey).

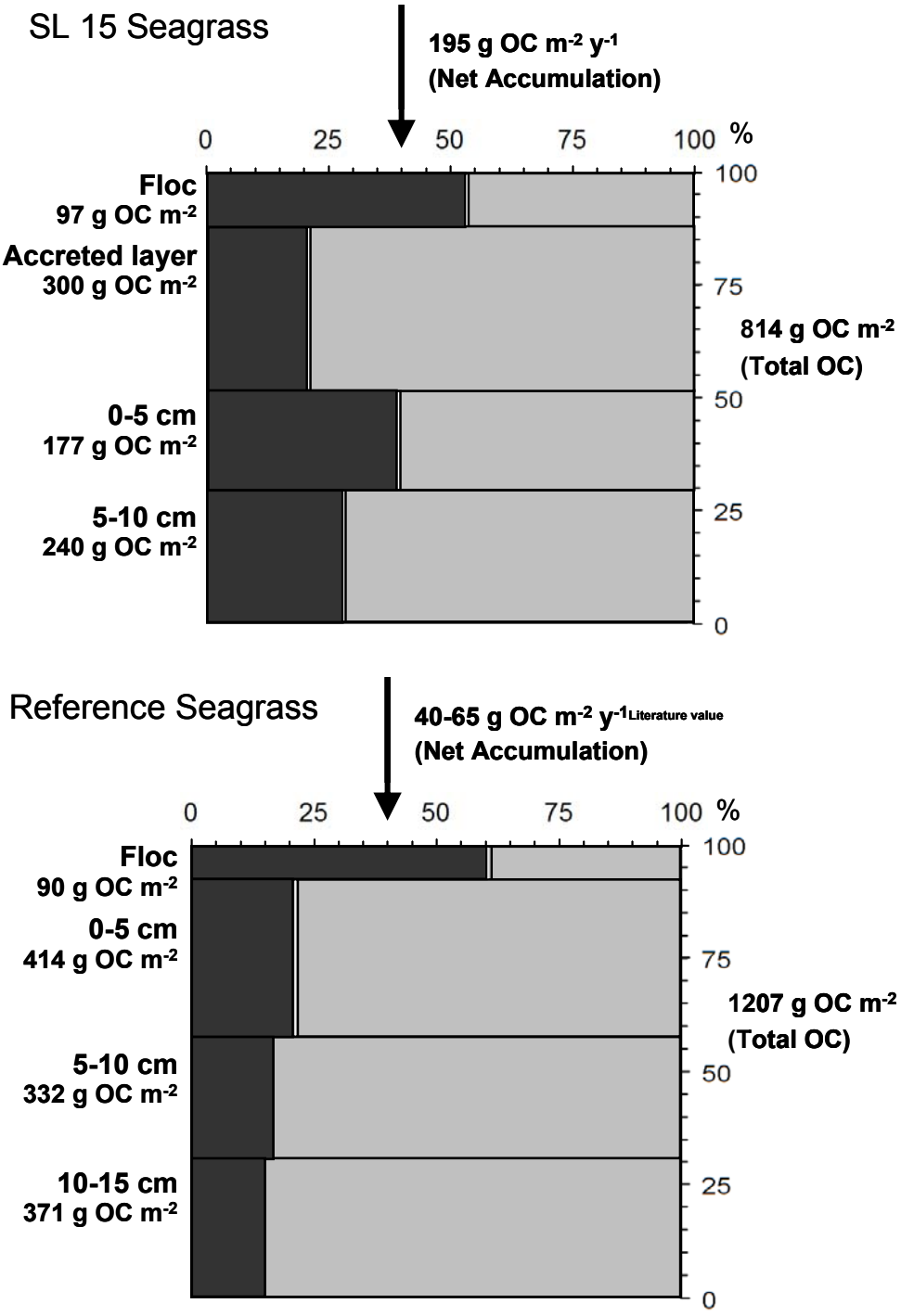


Figure 3-9. Continued

CHAPTER 4
SOURCES OF SEDIMENT ORGANIC CARBON IN A CONSTRUCTED MANGROVE AND SEAGRASS SYSTEM

Introduction

Sediments can accumulate organic carbon (OC) from *in situ* vegetation, drift macroalgae, plankton, and water column terrestrial- and marine-derived detritus. Understanding sources of OC in soils and sediments is important to our understanding of local and global C cycles (Hedges 1992). The source of OC influences the quality and stability of OC in sediments. OC sources, like temperature and oxygen availability, affect decomposition rates (Chapin et al. 2002), which in turn affect OC sequestration. Certain ecosystems, like macrophyte-dominated coastal systems, accumulate and store large amounts of OC in their sediments. These salt marshes, mangrove forests, and seagrass beds are sinks for CO_2 and therefore mitigate climate change by keeping C out of the atmosphere. Worldwide, salt marshes and mangroves store at least 44.6 Pg C in their sediments (Chmura et al. 2003), equivalent to 2% of the global soil C pool (Lal et al. 1995). Seagrass beds, which make up only 0.15% of global marine area, account for 15% of the global marine OC storage (Hemminga and Duarte 2000). Determining the vegetation that are the main OC sources to coastal sediments helps researchers predict how changing environmental conditions may affect the future of these significant C stores.

Coastal ecosystems are experiencing great losses worldwide (Valiela et al. 2001; Alongi 2002; Green and Short, 2003). The loss of vegetated coastal ecosystems has caused at least a 25% decrease in their global C sequestration capacity (Duarte et al. 2005). Constructing coastal ecosystems may restore a portion of the lost C sink (Connor et al. 2001). Knowing OC sources of constructed coastal systems can indicate whether these constructed systems can become effective at storing OC. For example, a constructed mangrove system whose principle sedimentary OC (SOC) source is relatively labile macroalgae will not store as much C for as

long amount of time as a well-established mangrove system whose main OC sources are the more recalcitrant leaves and roots of mangroves.

There are a myriad of methods researchers utilize to determine OC sources. The most widely used method measures bulk stable isotopes (usually ^{13}C and ^{15}N) in possible sources and sediments. Bulk analyses measure isotopic signatures of entire OC pools in sediments or of whole plant parts. Sources are then determined by a simple comparison of source and sediment isotopic signatures (Haines 1976; Hemminga et al. 1994; Jennerjahn and Ittekkot 2002; Thimdee et al. 2003) or by mixing models (Dauby 1989; Kennedy et al. 2004; Papadimitriou et al. 2005; Zhou et al. 2006;). Other parameters are used with isotopic signatures to determine sources using ternary diagrams of N:C ratios plotted against $\delta^{13}C$ (Gonnoeea et al. 2004; Miserocchi et al. 2007) or more complex mixing models using $\delta^{13}C$ and biomass or %OC as parameters (Chmura et al. 1987; Middelburg et al. 1997; Bouillon et al. 2003;). Sources must have consistently distinct stable isotopic signatures for this method to be useful (Papadimitriou et al. 2005). Lipids are also used as biomarkers to determine OC sources (Wang et al. 2003). The lipids, generally sterols, fatty acids, or hydrocarbons, vary in specificity as some can identify groups of organisms such as vascular plants or algae while others may be specific to one genera or species (Canuel et al. 1997). Finer resolution of sources is possible when the isotopic signatures of lipids are measured in compound specific stable isotope analyses (Canuel et al. 1997; Bull et al. 1999; Hernandez et al. 2001; Mead et al. 2005). Some lesser-used methods involve comparing relative amounts of certain OC structures in the soil, either visually as in petrographic analysis (Lallier-Verges et al. 1998; Marchland et al. 2003) or chemically as in nuclear magnetic resonance spectroscopy (Golding et al. 2004).

Stable isotopes of bulk compositions have successfully identified the main SOC sources in subtropical and tropical coastal ecosystems dominated by mangroves and seagrasses because potential sources in these ecosystems have a wide range of $\delta^{13}C$ (Hemminga et al. 1994; Jennerjahn and Ittekkot 2002; Gonnoeea et al. 2004; Kennedy et al. 2004; Papadimitriou et al. 2005; Smit et al. 2005; Zhou et al. 2006). Mangroves have the most depleted $\delta^{13}C$ because Rubisco carboxylase discriminates against isotopically heavy C during C_3 photosynthesis (Hemminga and Mateo 1996; Hemminga and Duarte 2000). Seagrasses have the most enriched $\delta^{13}C$, despite C_3 characteristics, because of diffusional constraints on C uptake in an aquatic environment (Hemminga and Mateo 1996). Isotopic signatures of other potential sources such as plankton and epiphytes generally fall between mangrove and seagrass values (Kennedy et al. 2004; Papadimitriou et al. 2005).

In this study, we determine: 1) significant sources to the SOC in a constructed mangrove and seagrass system, 2) how sources change over time in a constructed system, and 3) how sources differ between the constructed system and nearby mangrove and seagrass reference sediments. We hypothesized that SOC sources in the constructed system will initially be macroalgae or seston, while SOC sources in the reference systems will be vascular plants like mangroves and seagrasses.

Methods

Study Site

SL 15 (Fig. 4-1) is a mitigation site located in the subtropical portion of the Indian River Lagoon (IRL) adjacent to Fort Pierce, Florida. The IRL is a long, shallow, and microtidal water body that lies in both temperate and subtropical climates. SL 15 is one of many spoil islands created in the Indian River Lagoon during the construction of the Atlantic Intracoastal Waterway. These islands sit several meters above sea level and are populated by many exotics,

such as Australian Pine (*Casuvina casuvina*) and Brazilian Pepper (*Shinus terebinthifolius*), in their interiors and by native red, black, and white mangroves (*Rhizophora mangle*, *Avicennia germinans*, and *Laguncularia racemosa*) around their edges. To mitigate destruction of a nearby mangrove forest and seagrass bed, seagrass and mangrove systems were created on SL 15. These systems were created by burning and removing interior vegetation and removing dredge spoil down to several different elevations. The seagrass bed, which remains submerged during low tide, is at the lowest elevation, the mangrove forest, which is exposed at low tide, is at the middle elevation, and at the highest elevation, above sea level, is a maritime forest. The mangrove fringe of SL 15 was left intact except for a few flushing channels. In between the constructed seagrass and mangrove systems a thin *Spartina alterniflora* buffer was planted. The mangrove forest was planted with *R. mangle*, and maritime forests were planted with *Coccoloba uvifera*, *Borrichia frutescens*, *Rapanea guinensis*, *Conocarpus erectus*, and *Distichlis spicata*, but seagrasses were left to colonize naturally. Natural systems near SL 15 include its original mangrove forest fringe, surrounding seagrass beds, and mangrove fringes of adjacent spoil islands, which are at least 40 years old.

Litter Bags

Plant material from *Syringodeum filiforme*, *Thalassia testudinum*, *Halodule beaudettei*, *Acanthophora spicifera*, *Sargassum* spp, *A. germinans*, and *R. mangle* were collected in July 2006. Living seagrass fronds were taken from the beds around SL 15, which is similar to the material ripped off by wind and wave events (Moore and Fairweather 2006). Clumps of live macroalgae were taken from the subtidal areas in and around SL 15. Yellow mangrove leaves, the kind about to fall, were taken from trees on the edge of SL 15 and surrounding islands. Plant material was transported back to the laboratory and rinsed. Epiphytes were removed from seagrass fronds and macroalgae. Plant material was then air dried for several weeks before being

weighed by species into 2-3 g (only 1 g for *A. spicifera*) allotments and placed intact into 13 cm x 13 cm litter bags of nylon mesh with 0.5 x 0.25 mm holes.

This litter bag study is a "common garden" study where we investigated the relative decomposition rates of the potential sources to SOC, so all litter bags were placed in the same area of the SL 15 mangrove system. On September 8, 2006, litter bags were placed on the sediment surface, pinned down with metal stakes, and overlaid with large wire mesh to prevent them from washing away. Three litter bags from each plant species were randomly collected at 2, 4, 8, 16, and 32 weeks. Sediment and algae were rinsed from the litter bags in the laboratory before the bags were air dried for several weeks. Once dry, the bags were opened, and plant material in each bag was weighed.

Source Sampling

Plants were sampled on SL 15 in January, July, October, and November 2006 and at reference sites in July and November 2006. Sampled plants included all potential sources to SOC found in and around SL 15 and reference sites and fell into 3 main groups: Subtidal, which include seagrasses (*S. filiforme*, *T. testudinum*, *H. beaudettei*, *Halophila johnsonii*) and macroalgae (epiphytes on seagrasses, *Acanthophora spicifera*, *Caulerpa sertulariodes*, *Sargassum* spp., *Ulva* spp., *Chaetomorpha linum*, *Rosenviga intricata*, *Hypnea cervicornis*, *Gracilaria tikvahiae*, and *Enteromorpha* spp.); Intertidal, which included mangroves (*Avicennia germinans*, *Rhizophora mangle*, *Laguncularia racemosa*), *Sueda linearis*, and *Spartina alterniflora*; and Terrestrial (*Schinus terebenthifolias*, *Casuarina equisetifolia*, *Coccoloba uvifera*, and *Triplasis purpurea*). Not all plants were collected at all sampling dates because some plants, particularly species of macroalgae were not present throughout the year. Vascular plant samples were a composite of 3-5 live, healthy leaves or fronds from greater than three individuals collected across the sampling area (i.e. SL 15 or reference sites). Macroalgae

samples were composites of different clumps collected from across the sampling area. Epiphyte samples were composites of algal material scraped from seagrass fronds in the laboratory. Roots of seagrasses and mangroves were taken from sediment cores for analysis; they were not identified to species. Roots of *A. germinans*, *R. mangle*, and *S. alterniflora* were collected in the field as well. At the laboratory, seagrass fronds were scraped clean, and seagrasses, roots, and macroalgae were rinsed. All plants were dried at 60ºC for three days before being initial ground on a Wiley mill (if necessary) and then ground to a fine powder using a ball mill.

Seston was collected in May, September, October, and November 2006 and February 2007. For each seston sample, 500 mL of water was collected from the middle of the water column in the subtidal area of SL 15. Three samples each were taken on a flood and an ebb tide except in February 2007, where only ebb tide samples were collected. Water samples were kept on ice and transported to the laboratory where they were filtered through precombusted Whatman GF/F glass fiber filters. Blanks of 500 mL of deionized water were also filtered for each sampling event. Filters were then freeze-dried for 24 hours.

Sediment Sampling

Four, 2 m x 2 m plots were established in the mangrove forest and in the seagrass bed on SL 15 (Fig. 4-1). Three, 7 cm in diameter sediment cores from each of these plots were retrieved in November 2005, January (mangrove only), February (seagrass only), May, July, and November 2006. Cores were taken from different areas of the plots each time to ensure an area was not re-sampled. For references, three randomly-selected plots were established in natural mangrove forests and seagrass beds within 1 km of SL 15. These plots were sampled in July and November 2006 using the same procedure as for SL 15 plots. Sediment cores were sectioned in the field and stored in plastic bags on ice for transport and then in a 4ºC refrigerator. SL 15 cores were initially divided into 0-5 cm and 5-10 cm sediment depths. In subsequent samplings,

material had accumulated on top of the seagrass section, which was collected and analyzed separately from the original sediment depths as an accreted layer. Surface layers—floc from seagrass systems, algal mats from the SL 15 mangrove system, and litter layers from the reference mangrove system—were collected from each core and were composited by plot. Differences in color and texture were used to separate accreted and surface layers from original depths except for floc, which was the fraction of the accreted layer that poured off (Fig. 4-2).

Laboratory Analyses

Rocks, roots, and detritus were removed from each sample prior to homogenization. Samples were then freeze-dried for 48 hours. Freeze-dried sediment samples were composited by plot and sieved through a 1 mm mesh to remove large shell pieces and carbonate rock, which were weighed so their mass could be accounted for in calculations. Sediment and surface layer samples were then ball-milled to a fine powder in stainless steel canisters.

TOC, TN, and $\delta^{13}C$ were measured in sediment, surface layers, seston filters, and plant samples. TOC and TN were used to calculate C:N ratios on a molar basis. Inorganic carbon (IC) was removed from sediment, surface layer, and seston samples via vapor acidification (Hedges and Stern 1983; Harris et al. 2001; Gonneea et al. 2004). Sediment and surface layer samples were weighed out into 9 x 5 mm or 10 x 10 mm silver capsules (Thermo Scientific, Waltham MA and CE Elantech, Lakewood, NJ), which were arranged in plastic well plates and moistened with deionized water before acidification. Three holes (7 mm in diameter) were cut from each seston filter with a hole punch and arranged in plastic well plates. The filled well plates were then placed in a glass desiccator with a beaker of concentrated HCl (12 *M*) for 24 hours before being dried at 60ºC for another 24 hours. Seston filter samples were then put into 10 x 10 mm silver capsules. Plant samples were weighed into 9 x 5 mm tin capsules (Costech Analytical Technologies, Valencia, CA). All samples were combusted on an elemental analyzer (ECS

4010, Costech) in line with an isotope ratio mass spectrometer (ThermoFinnigan MAT Delta Plus XL, Thermo Scientific, Waltham MA) for %OC and $\delta^{13}C$. Plants were analyzed for %TN simultaneously. Peach leaves (NIST 1547) were used for EA calibration, with sucrose and an internal soil standard used as check standards. Sucrose and Peach leaves were used as internal standards for mass spectrometry measurements. C isotopes were reported in per mil notation based on deviations from the Pee Dee Dolomite standard. Tests were run on sand samples with various carbonate percentages and total weights to assess the efficacy of the vapor acidification method and determine the maximum sample mass that still ensured complete removal of IC. Furthermore, $\delta^{13}C$ values were used to confirm complete removal of IC because the presence of carbonate greatly raised $\delta^{13}C$ values. If incomplete IC removal was suspected, samples were rerun at a lower total mass. The $\delta^{13}C$ of filter blanks were accounted for in the calculation of seston $\delta^{13}C$. Unacidified sediment, surface layer, and seston samples were run separately in tin capsules (Costech) on an elemental analyzer (Flash EA 1112 Series, Thermo Scientific, Waltham, MA) for TN. Acetinilide was used for calibration standards, while peach leaves (NIST 1547) and an internal soil standard were used for quality control.

Data Analyses

Individual plant $\delta^{13}C$ and C:N were averaged across sites and sampling dates. Values of certain species were also averaged together into plant groups of seagrass, macroalgae, mangroves, or C_3 terrestrial. Differences in $\delta^{13}C$ between sampling date and tide phase (ebb or flood) were tested on seston samples using one-way analyses of variance (ANOVAs) in JMP Version 6. For all sources, C:N ratios are reported, even though N:C ratios are used in graphs, so data can be easily compared across studies. Litter mass loss for each species was modeled using a first-order exponential decay curve.

$$M_t = M_0 * e^{(-kt)} \quad (4\text{-}1)$$

In equation 4-1, M_0 is the initial litter mass, M_t is the litter mass at time t, and k is the decay constant. The decay constant for each species was estimated using nonlinear models in JMP Version 6 (SAS Institute, Cary, NC).

To investigate whether $\delta^{13}C$, TOC, or C:N changed through time in SL 15 sediments and surface layers, repeated measures ANOVAs were run for both mangrove and seagrass areas. A spatial power covariance structure was used to account for unequal spacing between time points. Subjects were the plots on SL 15, and the repeated factor was time. For the 0-5 and 5-10 cm depths in each system, the ANOVAs were run with depth as a main effect and a time*depth interaction term. The floc, algal mat, and accreted layers were each run separately in ANOVAs where time was the only effect. These analyses were run using the mixed procedure in SAS Version 8 (SAS Institute, Cary, NC).

Comparisons between SL 15 and the reference sites were analyzed using one factorial ANOVA each for the mangrove and seagrass sediments and one factorial ANOVA each for the mangrove and seagrass surface layers (algal mat/litter and floc). Sediment ANOVAs consisted of three fixed factors—site, month, and depth. Surface layer ANOVAs consisted of only the site and month factors. All two way interactions were tested. SL 15 plot and reference site data were pooled into two site treatments, SL 15 and reference. Months used in these analyses were July and November 2006, the sampling dates for which both SL 15 and reference data were available. For seagrass sediment analysis, SL 15 and reference depths were assigned to 3 categories in order to make comparisons: SL 15 accreted and reference 0-5 cm were depth 1, SL 15 5-10 cm and reference 0-5 cm were depth 2, and SL 15 5-10 cm and reference 10-15 cm were depth 3. Factorial ANOVAs were run on JMP Version 6 (SAS Institute, Cary, NC).

A portion of the above analyses were performed on data transformed to meet the normality requirement (see Appendix A for details). Post hoc multiple comparisons were carried out on significant effects using the Tukey test. Significance was decided using an alpha level of 0.05.

Ternary diagrams (Dittmar et al. 2001; Goni et al. 2003, Gonnoeea et al. 2004) were used to determine the main SOC sources. Because ternary diagrams can only have three end members, field observations and the position of mean sediment $\delta^{13}C$ relative to mean potential source $\delta^{13}C$ on a $\delta^{13}C$ line (Fig. 4-3) were used to choose the three most likely end members for each constructed and reference sediment and for the mangrove litter layer and seagrass floc. N:C of the three end members and sediments were plotted against $\delta^{13}C$. N:C ratios are used instead of C:N ratios because with the larger number in the denominator, they are more statistically robust (Goni et al. 2003). End members' N:C and $\delta^{13}C$ were averaged for all sampling dates and species within that group (e.g.: mangroves), but for plants where multiple parts were measured, only leaf/frond values were used. The three end members create a triangle that is expanded according to the standard deviations of the end members to account for natural variability and analytical error. Sediment samples that fall in the middle of the triangle are assumed to be a mixture of all three sources, samples that fall along a line connecting two end-members are considered a mixture of those two sources, and samples that fall around the vertex of an end member are assumed to have OM from mainly that source. Samples that fall outside of the expanded triangle have OC contributions from additional sources or have undergone changes during diagenesis.

Results

Source Characteristics

$\delta^{13}C$ and C:N varied among plant groups. Generally, the lowest $\delta^{13}C$ and greatest C:N were found in mangrove leaves and roots and C_3 terrestrial plant leaves (Table 4-1). The greatest

$\delta^{13}C$ and a relatively low C:N were found in seagrass fronds. *S. alterniflora* had a low $\delta^{13}C$ and high C:N. Seston had low $\delta^{13}C$ and low C:N. Seston samples had greater $\delta^{13}C$ in fall than in winter (ANOVA, df=4, p=0.0002) but did not differ between ebb and flood tides (ANOVA, df=1, p=0.54). Compared to variation among plant groups, variation of $\delta^{13}C$ within plant groups was usually low with mangrove tissues of all species varying by less than 2.5‰ and seagrass tissues (except *H. johnsonii*) by less than 3.4‰. The exception was the macroalgae group, whose $\delta^{13}C$ varied by 15‰. Macroalgae had high variability with C:N ratios as well. Plant tissue type influenced C:N ratios with greater C:N in roots than in leaves for both mangroves and seagrasses.

Plants also differed in their decay rates, even within groups (Table 4-2). The greatest decay constants, and fastest rates of decay, were for a macroalgae (*A. spicifera*) and a seagrass (*S. filiforme*). The slowest decay rates were for a seagrass (*H. beaudettei*) and a mangrove (*R. mangle*).

Sediments and Surface Layers

$\delta^{13}C$ of SL 15 sediments and surface layers, with the exception of the 0-10 cm seagrass sediments, changed significantly over time (month effect, $p<0.034$, Table 4-3, Fig. 4-4). Mangrove sediments and seagrass accreted layers had $\delta^{13}C$ that increased towards the mean $\delta^{13}C$ of their respective references over the first year after construction (Fig. 4-4). The mangrove algal mat's $\delta^{13}C$ also increased but moved away from reference values (Fig. 4-4). Most of the layers did not have changing %OC or C:N ratios throughout the year. C:N ratios changed significantly without direction in mangrove sediments and seagrass floc (Chapter 3). TOC significantly changed in seagrass 0-10 cm sediments and floc, but only with direction in floc, where it increased over time (Chapter 3). The $\delta^{13}C$, TOC, or C:N values did not differ among sediment depths (Table 4-3, Chapter 3).

SL 15 seagrass sediments had lower $\delta^{13}C$ than reference seagrass sediments (site effect, $p<0.0001$, Tables 4-3 and 4-4), but SL 15 mangrove sediments had $\delta^{13}C$ similar to reference mangrove sediments ($p=0.40$, Tables 4-3 and 4-4). SL 15 floc was more depleted than reference floc in July but more enriched than reference floc in November (month x site interaction, $p<0.0001$, Table 4-3 and 4-4). SL 15 algal mat was more enriched than reference litter in both months, but the difference was greater in November (month x site interaction, $p<0.0001$, Table 4-3 and 4-4). TOC (%) was generally lower in SL 15 sediments than references with the exception of the SL 15 seagrass accreted layer and floc, which had similar TOC to the reference's 0-5 cm depth and floc, respectively (Chapter 3). C:N ratios were similar in seagrass sediments and floc but were lower in SL 15 mangrove sediments and surface layers than in respective mangrove references (Chapter 3).

Source Determination

Putting source (plants and seston) and sediment $\delta^{13}C$ data together indicates potential sources to the various sediments and surface layers (Fig. 4-3). Using observations from the field and Fig. 4-3, the three ternary diagram end members for SL 15 mangrove sediment were seston, algal mat, and terrestrial plants (Fig. 4-5a). Seston, litter, and mangroves were the end members for reference mangrove sediments (Fig. 4-5b). Seston, seagrass, and macroalgae were the end members for SL 15 and reference seagrass sediments and floc (Fig. 4-6 and 4-7b). Seston, seagrass, and mangroves were the end members for reference mangrove litter (Fig. 4-7a). SL 15 algal mats did not need a diagram because they are their own source as primary producers. Ternary diagrams explained 74% of SL 15 mangrove sediment samples, 92% of reference mangrove sediment samples, 71% of SL 15 seagrass sediment samples, 33% of reference seagrass sediment samples, 100% of reference mangrove litter samples, and 89% of seagrass floc

samples (Fig. 4-5 through 4-7). All of the samples that fell outside the ternary plots, regardless of site or depth, did not fit because their N:C ratios were greater than that of the sources.

The majority of SL 15 mangrove sediment samples fell near the seston end member. Some samples fell in the middle of the triangle and others fell close to the terrestrial end member (Fig. 4-5a). Most reference mangrove sediment samples fell between seston and litter end members (Fig. 4-5b). In terms of $\delta^{13}C$, but not in terms of N:C, most SL 15 and reference seagrass sediment samples were within the range of macroalgal sources (Fig. 4-6). SL 15 seagrass sediment samples fell far from the seagrass end member (Fig. 4-6a). SL 15 seagrass 0-10 cm and accreted depths did not differ in their sources. Most reference seagrass samples fell outside the diagram due to high N:C ratios (Fig. 4-6b). Examining only $\delta^{13}C$, reference seagrass sediments were more enriched than macroalgae and seston but more depleted than seagrass (Fig. 4-3). Reference mangrove litter layer samples from July fell between seston and seagrass end members but November samples fell in the middle or at the mangrove vertex (Fig. 4-7a). Reference seagrass floc samples fell between seston and macroalgae end members in July but outside the diagram in November (Fig. 4-7b). SL 15 seagrass floc fell between seston and seagrass regardless of sampling data (Fig. 4-7b.)

Discussion

Source Characteristics

$\delta^{13}C$ of the main potential sources in the studied part of the Indian River Lagoon were within the range of literature from similar estuarine studies (Table 4-5). Our sources' C:N values were also within reported literature values of 30 to 99 for mangrove leaves and roots (Lallier-Verges et al. 1998; Thimdee et al. 2003; Gonnoeea et al. 2004; Muzuka and Shunula 2006), of 15 to 21 for seagrass fronds (Thimdee et al. 2003; Gonnoeea et al. 2004; Machas et al. 2006), of

5.8 to 9.3 for seston (Gonnoeea et al. 2004; Zhou et al. 2006), and of 7 to 30 for macroalgae (Kristensen 1994; Thimdee et al. 2003).

$\delta^{13}C$ of plants vary within different tissues (Vizzini et al. 2003; Papadimitriou et al. 2005;), within a single species (Hemminga and Mateo 1996), across sites (Kennedy et al. 2004), seasons (Vizzini et al. 2003), and years (Anderson and Fourqurean 2003; Fourqurean et al. 2005). Variations are most pronounced in seagrasses (Thimdee et al. 2003) and macroalgae. In submerged vegetation variation is due to the relative uses of dissolved CO_2 and bicarbonate, the source of inorganic C in the water, temperature, irradiance, and subsequent photosynthesis rates (Lin et al. 1991; Hemminga and Mateo 1996). Seston $\delta^{13}C$ can also vary temporally, spatially, and between ebb and flood tides (Hemminga et al. 1994). These variations in source $\delta^{13}C$ make it necessary to measure all potential sources' $\delta^{13}C$ for each study area, instead of relying on literature values, and ideally, measure significant sources across tissues, sites, and seasons. $\delta^{13}C$ variations within individual sources and plant groups in this study were generally smaller than differences among main sources, so the variations most likely do not affect our source determinations. Furthermore, where $\delta^{13}C$ did overlap among main sources their C:N ratios set them apart, as with seston and mangroves, or they were not both end members for the same ternary diagram.

There is some concern about whether $\delta^{13}C$ of plant tissues changes during diagenesis because large changes in $\delta^{13}C$ could lead to misleading source determinations. Studies that measured fresh and senescent mangrove leaves and seagrass found small (generally >1‰) differences (Thimdee et al. 2003; Gonnoeea et al. 2004). Decomposition studies found significant but minor (0.55 to 2‰) changes in seagrass, mangrove, and macroalgae $\delta^{13}C$ during diagenesis (Fenton and Ritz 1988; Fourqurean and Schrlau 2003), but others found no significant

changes (Machas et al. 2006). Where $\delta^{13}C$ did change in decomposition studies of multiple species, the initial differences in $\delta^{13}C$ between species were still clear. Unfortunately, we did not measure changes in $\delta^{13}C$ of our plant tissues during decomposition. Given the small magnitude of changes found in other studies, and the large differences in $\delta^{13}C$ between groups of potential sources, diagenetic changes in $\delta^{13}C$ are unlikely to cause misidentification of the main SOC sources in this study. Changes in C:N during decomposition also occur and can be greater in magnitude than $\delta^{13}C$ changes (Fourqurean and Schrlau 2003). Studies of mangrove, seagrass, and macroalgal decomposition have found decreases and increases in C:N ratios that were dependent upon species or tissue (Twilley et al. 1986; Bourgues et al. 1996; Fourqurean and Schrlau 2003); others found no change in C:N ratios (Machas et al. 2006).

Decay constants of seagrasses on SL 15 were within literature values, which ranged from 0.002 to 0.12 day^{-1} (Mateo and Romero 1996; Machas et al. 2006; Moore and Fairweather 2006). *T. testudinum* had a greater decay constant and therefore faster decomposition in this study than in Florida bay (Fourqurean and Schrlau 2003). Mangrove decay constants were also within literature values that ranged from 0.0048 to 0.022 day^{1} (Fourqurean and Schrlau 2003; Ake-Castillo et al. 2006; Ramos e Silva et al. 2006). *R. mangle*'s decay constant in this study fell on the low end of *R. mangle* reported values. Estimated macroalgae decay constants ranged widely from 1 to 0.014 (Foreman and Smith 1984; Mews et al. 2006). The decay constant of *Sargassum spp.* in our study was at the low end of the range, probably because *Sargassum* has more structural components than most other macroalgae. Surprisingly, differences among decay constants in this study did not fall along plant groups. We expected mangroves to have the lowest decay constants and macroalgae to have the highest with seagrass falling in between (Kristensen 1994; Bourgues et al. 1996; Fourqurean and Schrlau 2003). However, *S. filiforme*

decomposed as fast as the macroalgae and *T. testudinum*'s decomposition was at the rate of *A. germinans*. These results indicate that in terms of decomposition, species identity matters more than the group to which a species belongs. For source determination, these results specify which species of an end member group are more likely to contribute to SOC because the slower a species decomposes, the better chance its OC will be buried in sediments.

Sediments and Surface Layers

Changes in SL 15 SOC $\delta^{13}C$ over the course of a year indicate new SOC sources are adding to the sediment TOC pool or, without a change in TOC, decomposition of old source OC while new source OC accumulates. These changes were greater in upper sections of both mangrove (0-5 cm) and seagrass (accreted layer) sediments because the inputs of new OC reach the top of sediments first. Bioturbation then brings new OC inputs deeper into the profile. Bioturbating organisms were observed in mangrove, but not in seagrass sediments, which may explain why $\delta^{13}C$ of deeper mangrove sediments changed over time but deeper seagrass sediments did not. Surface layers had the greatest $\delta^{13}C$ changes through the year.

All changes were positive so that the new SOC sources to SL 15 after construction must be more enriched than old OC sources. Old OC sources were relatively depleted in $\delta^{13}C$ as they were most likely the terrestrial plants that inhabited SL 15 pre-construction. In mangrove sediments, the new source was most likely the algal mat and in seagrass accreted layers and floc the new sources were macroalgae or seagrass (Fig. 4-3). Enrichment of algal mat $\delta^{13}C$ is due to changing inorganic C sources, as unlike other sediments and layers, the algal mat is its own producer of OC. As the algal mats grow, so does their influence on the biogeochemistry of their environment. Photosynthesis and respiration within the algal mat changes the pH of the water around it (Kayombo et al. 2002). At night respiration decreases the pH, which can cause $CaCO_3$ in the sediment below the algal mat to dissolve. $CaCO_3$ dissolves into various carbonate species

(CO_3^{-2}, HCO_3^{-1}), which inherit the high $\delta^{13}C$ of $CaCO_3$ (≈ 0) (Lin et al. 1991). These carbonate species then may be utilized by algae as inorganic C sources during daytime photosynthesis.

$\delta^{13}C$ in the literature ranges from -29.4‰ to -20.6‰ for mangrove sediments (Bouillon et al. 2003; Thimdee et al. 2003; Gonneea et al. 2004) and from -10.3‰ to -26.6‰ for seagrass sediments (Hemminga et al. 1994; Kennedy et al. 2004; Papadimitriou et al. 2005). Sediment $\delta^{13}C$ in this study are for the most part within literature values. SL 15 and reference mangrove sediments span the range of literature values from -27.5‰ to -19.4‰. SL 15 and reference seagrass sediments are at the lower end of the literature values with $\delta^{13}C$ ranging from -23.2‰ to -19.4‰. Differences in $\delta^{13}C$ among SL 15 and reference sediments and surface layers suggest their SOC sources differ. Observations of the distribution of primary producers around the sites also suggest sources differ, even between SL 15 and reference mangrove sites, whose $\delta^{13}C$ were not significantly different.

Source Determination

The ternary diagram indicated that seston was the dominant source for SL 15 mangrove sediments with some OC being contributed by terrestrial plants and the algal mat (Fig. 4-5a). Terrestrial sources most likely contributed to SOC before and during construction. During construction, we observed terrestrial plant parts that were not fully removed by burning and clearing being mixed into spoil within SL 15's intertidal zone. The algal mat's influence as a source was supported by $\delta^{13}C$ enrichment of mangrove sediments over the first year. Mangroves were not included as a source in the ternary diagrams because SL 15 mangroves were young (>2 years old) and mangrove litter was very sparse. Seston was also a dominant source for reference mangrove sediments according to the ternary diagram, but in this instance it shared this designation with the litter layer (Fig. 4-5b). According to Fig. 4-3, mangroves also contributed to SOC because mean sediment $\delta^{13}C$ was more depleted than mean seston and litter values.

Seston and macroalgae were the dominant OC sources in SL 15 seagrass sediments according to the ternary diagram (Fig. 4-6a). Seagrasses, which had colonized most of SL 15 at generally low densities by July 2006 (Fischler 2007), were not yet important SOC sources. Seston and macroalgae as main SOC sources were further supported by observations—drift macroalgae was frequently found buried in the accreted layer section of cores throughout the study where it seemed to trap particles from the water, driving accretion. High N:C (low C:N) ratios of seagrass reference sediments interfered with determining sources via the ternary diagram (Fig. 4-6b). Samples outside of the diagram can indicate an unknown source of SOC, but that is unlikely as almost all plants encountered were measured and none had high N:C (low C:N) ratios (Table 4-1). According to $\delta^{13}C$ only, seston and seagrass are probably both sources because reference seagrass SOC $\delta^{13}C$ falls in the middle of those end members. The contribution of macroalgae is unknown though due to its intermediate $\delta^{13}C$. Mangroves were not chosen as a potential source for seagrass sediments as mangrove litter was observed infrequently on seagrass sediments. Therefore mangrove's influence to SOC was believed to be mediated through seston.

Sources to the reference mangrove litter layer change with season as the ternary diagram indicates that seagrass and seston are the dominant sources in July but mangroves are the dominant sources in November (Fig. 4-7a). Conclusions from the ternary diagram match field observations. The litter layer was primarily seagrass wrack in July but was primarily partially-decomposed mangrove leaves in November. Since the litter layer is one of the main sources to reference mangrove SOC, seagrass and mangroves are therefore also sources to mangrove SOC through the litter. Sources to seagrass floc varied seasonally for references but not SL 15. Seston was a dominant floc OC source for all seasons and sites according to the ternary mixing

diagram (Fig. 4-7b). Macroalgae was also a dominant source for November reference floc samples.

Ternary diagrams indicated that seston is a dominant source to almost all sediments and surface layers regardless of site. Seston is not the only source, however, because all sediments and surface layers are more enriched in ^{13}C than seston (Fig. 4-3). A review of source determination studies in mangrove and seagrass sediments found that seston was a dominant source at 47% of sites (Chapter 2). OC in sediments of young mangrove forests were dominated by algal and seston sources, just as the constructed sediments were in this study (Marchland et al. 2003; Alongi et al. 2004). In sediments with low %OC, as in this study (Chapter 3), the dominant macrophytes such as mangroves or seagrass seemed less likely to be significant OC sources (Gonnoeea et al. 2004; Kennedy et al. 2004). Middelburg et al. (1997) showed a significant relationship of decreasing $\delta^{13}C$ (more depleted than *in situ* macrophyte $\delta^{13}C$) with decreasing %SOC. These trends may be because when seston settles onto sediments, it does so with inorganic particles, which dilute SOC, lowering the %OC.

Seston comes from a variety of sources as it is made up of phytoplankton, zooplankton, bacteria, and detritus (Fig. 4-8). Its high $\delta^{13}C$ in this study is indicative of a mangrove or terrestrial origin. Its high N:C (low C:N), however, indicates a mixture of phytoplanktom, which have C:N ratios from 7.7 to 10.1 (Holligan et al. 1984), and bacterioplankton, which have C:N ratios from 2.6 to 4.3 (Lee and Fuhrman 1987). Other estuarine studies similarly had seston with low $\delta^{13}C$ and low C:N ratios (Hemminga et al. 1994; Cifuentes et al. 1996; Zhou et al. 2006). Cifuentes et al. (1996) demonstrated that bacteria in the water column were likely immobilizing N in the process of decomposing terrestrial-derived organic matter, which could lead to incorporation of that nitrogen into organic matter during humification and a lower C:N ratio.

Low C:N ratios of many sediment samples are concerning because it may have lead us to overstate the importance of seston as a source because it is the only source with equally low C:N ratios. Just as microbial activity likely lowered C:N ratios in seston (Cifuentes et al. 1996), it could lower C:N ratios in sediments. Decreasing sediment C:N ratios during diagenesis has also occurred in other source determination studies (Thimdee et al. 2003; Gonnoeea et al. 2004; Kennedy et al. 2004). Changes due to bacteria are likely because a high percentage of TOC in these sediments is microbial biomass (11 to 63%; Chapter 3). Decreases in source C:N ratios during decomposition may also explain the relatively low C:N ratios of the sediments compared with living source material. Unfortunately, C:N ratios during decomposition were not measured in this study. Results of studies that measured decomposition in similar systems were equivocal (see source characteristics section). Another reason for low C:N ratios is the eutrophication of the IRL, which has greatly increased the availability of inorganic N sources (Sigua and Tweedale 2003). Due to the influence of factors other than source identity in determining sediment C:N ratios, caution is emphasized in interpreting ternary diagram results.

Conclusion

In all sediments, seston was a dominant source and diagenesis of organic matter within sediments lowered sediment C:N ratios (Fig. 4-9). Because the other main sources differed between SL 15 and reference sediments (Fig. 4-9), their abilities to sequester SOC probably differ too. The litter bag decomposition study suggests which SOC sources are likely to be sequestered in sediments the longest. This information allows us to predict how OC storage will differ in sediments of SL 15 and reference sites. Since seston is an OC source for all sediments, the fact that its decomposition was not measured should not greatly affect these predictions. Because fast-decaying macroalgae OC dominates in SL 15 seagrass sediments, they are unlikely to store OC for as long as reference seagrass sediments. A year after construction, SL 15's

seagrass sediments therefore do not store C as well as references. OC in both SL 15 and reference mangrove sediments are a mixture of seston and vascular plants (terrestrial plants in SL 15 and mangrove/seagrass via litter in references). Since terrestrial plants most likely have decay rates similar to mangroves and slower than most seagrass species, it is possible that the length of OC storage in SL 15 and reference mangrove sediments are currently similar. The labile algal mat, however, has the potential of becoming a main source in constructed mangrove sediments because it caused sediment $\delta^{13}C$ enrichment throughout the year, which may ultimately shorten the length of constructed mangrove OC storage.

Table 4-1. $\delta^{13}C$ (‰) and C:N ratios for all potential sources of organic carbon to mangrove and seagrass sediments in SL 15 and reference sites averaged over various collection times and plant parts (unless otherwise noted). Values in parentheses are ± SE; where no standard error is listed, the value is for a single composite sample.

Location	Species	$\delta^{13}C$ (‰)	C:N
Subtidal	Seagrass	-11.54 (0.84)	
	Leaves	-10.95 (1.3)	14 (0.52)
	Roots	-12.42 (0.78)	31 (2.5)
	Syringodium filiforme	-9.23 (0.86)	14 (0.5)
	Thalassia testudinum	-9.83 (1.2)	13 (0.9)
	Halodule beaudettei	-12.62	11
	Halophila johnsonii	-20.07	16
	Epiphytes	-16.20 (1.9)	11 (0.6)
	Macroalgae	-21.00 (0.98)	18 (1.6)
	Acanthophora spicifera	-17.11 (0.78)	12 (0.3)
	Caulerpa sertulariodes	-18.36	14
	Sargassum spp.	-17.48 (0.29)	28 (0.9)
	Daysa baillouviana	-32.06	15
	Ulva spp.	-20.64	14
	Chaetomorpha linum	-25.29	25
	SL subtidal macroalgae	-21.75 (0.86)	16 (2)
	Rosenviga intricata	-20.94 (1.1)	16 (0.8)
	Hypnea cervicornis	-19.69 (1.2)	21 (0.1)
	Gracilaria tikvahiae	-22.50 (1.4)	11 (0.4)
	Enteromorpha spp.	-25.24	19
	Seston	-26.29 (0.47)	6.5 (0.2)
	May 2006	-27.30 (0.44)	7 (0.5)
	September 2006	-25.78 (2.2)	6 (0.5)
	October 2006	-24.23 (0.21)	6 (0.2)
	November 2006	-24.58 (1.3)	6.5 (0.7)
	February 2007	-30.10 (0.84)	7.5 (1)
Intertidal	*Spartina alterniflora*	-12.94 (0.30)	
	Leaves	-13.37 (0.27)	27 (2)
	Roots	-12.30 (0.04)	42 (11)
	Sueda linearis	-29.22	14
	Mangrove	-26.95 (0.24)	
	Leaves	-27.27 (0.32)	27 (1.4)
	Roots	-26.18 (0.20)	58 (3.7)
	Avicennia germinans	-27.46 (0.53)	
	Leaves	-27.77 (0.49)	22 (1.7)
	Roots	-25.26	55
	Rhizophora mangle	-27.17 (0.36)	
	Leaves	-27.32 (0.47)	31 (1.7)
	Roots	-26.34 (0.30)	55 (9)
	Laguncularia racemosa	-26.31 (0.84)	26 (3.0)
Terrestrial	C_3 terrestrial	-27.54 (0.44)	33 (4)
	Schinus terebenthifolius (leaves)	-28.30	31
	Casuarina equisetifolia (needles)	-26.33	34
	Coccoloba uvifera (leaves)	-27.77 (0.32)	32 (11)
	Borrichia frutescens	-27.86 (0.60)	21 (0.9)
	Distichlis spicata	-13.67 (0.86)	27 (2.6)

Table 4-2. Decay constants (± SE) and turnover times calculated from a nonlinear regression (exponential decay) of litter bag experiment data.

Species	k (day^{-1})	Turnover time (days)
Haludule beaudettei	0.0049 (0.0006)	203
Thalassia testudinum	0.0099 (0.001)	101
Syringodium filiforme	0.046 (0.006)	22
Acanthophora spicifera	0.070 (0.006)	14
Sargassum spp.	0.019 (0.001)	53
Avicennia germinans	0.0093 (0.0004)	109
Rhizophora mangle	0.0047 (0.0004)	213

Table 4-3. Results of ANOVAs comparing $\delta^{13}C$ values in SL 15 and reference mangrove and seagrass sediments and surface layers (right) and of repeated measures ANOVAs of $\delta^{13}C$ values in SL 15 sediments and surface layers (left).

ANOVA	Effect	$\delta^{13}C$
Repeated measures		
Mangrove 0-10	Month	*
	Depth	NS
	Month*Depth	NS
Mangrove algal mat	Month	**
Seagrass 0-10	Month	NS
	Depth	NS
	Month*Depth	NS
Seagrass accreted	Month	*
Seagrass floc	Month	*

ANOVA	Effect	$\delta^{13}C$
Sediment comparison		
Mangrove	Site	NS
	Month	NS
	Depth	NS
	Site*Month	NS
	Site*Depth	NS
	Month*Depth	NS
Seagrass	Site	***
	Month	NS
	Depth	NS
	Site*Month	NS
	Site*Depth	NS
	Month*Depth	NS
Surface Comparison		
Mangrove algal mat/litter	Site	***
	Month	NS
	Site*Month	***
Seagrass floc	Site	**
	Month	***
	Site*Month	***

For significance NS=not significant, * $p < 0.05$, ** $p < 0.01$, *** $p < 0.0001$. Please see Appendix A for a table listing how these data were transformed prior to running the 3-way ANOVA.

Table 4-4. Mean $\delta^{13}C$ and C:N (± SE) for sediments and surface layers of SL 15 and reference mangrove and seagrass systems.

System and month	Depth	$\delta^{13}C$		C:N (molar)	
		SL 15	Reference	SL 15	Reference
July mangrove	Algal Mat/ Litter	-15.72 (0.46)	-18.21 (0.63)	8.2 (0.2)	9.3 (0.3)
	0-5 cm	-23.57 (1.03)	-24.12 (0.91)	5.0 (1)	9.6 (3)
	5-10 cm	-23.70 (0.50)	-22.17 (1.40)	8.0 (2)	9.2 (1)
Nov. mangrove	Algal Mat/ Litter	-11.96 (0.47)	-24.43 (1.56)	8.1 (0.9)	21 (5)
	0-5 cm	-21.96 (0.18)	-23.42 (0.70)	5.5 (0.3)	7.0 (1.1)
	5-10 cm	-24.11 (0.46)	-24.10 (0.31)	6.2 (0.8)	8.8 (0.9)
July seagrass	Floc	-21.05 (0.14)	-18.93 (0.27)	8.2 (1)	5.7 (0.6)
	Accreted	-21.00 (0.44)		7.6 (1)	
	0-5 cm	-21.03 (0.35)	-18.97 (0.29)	6.9 (0.3)	6.7 (0.2)
	5-10 cm	-20.93 (0.60)	-19.11 (0.20)	7.0 (1)	6.6 (0.2)
	10-15 cm		-18.79 (0.33)		1.0 (0.2)
Nov. seagrass	Floc	-19.50 (0.15)	-24.46 (0.56)	6.8 (0.1)	10.8 (0.6)
	Accreted	-20.06 (0.20)		6.1 (0.4)	
	0-5 cm	-21.55 (0.41)	-17.87 (0.21)	6.7 (0.8)	5.4 (0.2)
	5-10 cm	-20.80 (0.48)	-18.80 (0.46)	7.3 (1)	5.6 (0.4)
	10-15 cm		-19.10 (0.48)		6.1 (0.4)

Table 4-5. Mean $\delta^{13}C$ or $\delta^{13}C$ ranges of means for sources in this study and in the literature. Means are averaged across and ranges are across plant parts, species, and sites for this study and where applicable in the literature. The sources listed here are the main SOC sources that were used in this study's ternary diagrams.

Source	$\delta^{13}C$ (‰) This study	$\delta^{13}C$ (‰) Other studies	Data source[a]
Seagrass	Mean: -11.54	-10.0	1
	Range: -20.07 to -9.23	-19.7 to -10.7	2
		-13.3 to -5.8	3
		-12.4	4
		-12.2	5
		-16.1 to -11.9	6
		-10.5	7
		-23 to -3, -10 (mode)	8
		-10.4 to -7.2	9
		-14.6 to -8.8	10
		-12.7 to -11.4	11
Mangrove	Mean: -26.95	-27.0	12
	Range: -27.77 to -25.26	-28.3 to -24.1	2
		-29.0 to -27.0	13
		-28.4 to -27.9	3
		-28.8	7
		-28.2	14
		-27.9	15
		-30.1 to -28.3	16
		-29.7 to -25.9	17
Macroalgae	Mean: -21.00	-31.7 to -16.6	11
	Range: -32.06 to -17.11	-21.5 to -15.0	18
		-26.0 to -20.9	15
		-15.61	7
Seston	Mean: -26.29	-22.0 to -21.0	12
	Range: -30.10 to -24.23	-23.0 to -20.5	13
		-18.4	1
		-23.3 to -13.7[b]	2
		-27.6 to -12.1	3
		-22.1	4
		-24.7	5
		-25.32 to -22.06[b]	6
		-20.6	7
		-22.6[b]	19
		-28.1 to -20.8[b]	20
		-26.4[b]	21
Terrestrial (C_3)	Mean: -27.54	-28 to -25	22
	Range: -28.30 to -26.33	-30 to -25	23
		-26	24

[a]1, Canuel et al. 1997; 2, Hemminga et al. 1994; 3, Kennedy et al. 2004; 4, Papadimitriou et al. 2005; 5, Gacia et al. 2002; 6, Gonnoeea et al. 2004; 7, Thimdee et al. 2003; 8, Hemminga and Mateo 1996; 9, Anderson and Fourqurean 2003; 10, Vizzini et al. 2003; 11, Smit et al. 2005; 12, Jennerjahn and Ittekkot 2002; 13, Bouillon et al. 2003; 14, Bouillon et al. 2004; 15, Bouillon et al. 2002; 16, Lallier-Verges et al. 1998; 17, Muzuka and Shunula 2006; 18, Fenton and Ritz 1988; 19, Zhou et al. 2006; 20, Dittmar et al. 2001; 21, Cifuentes et al. 1996; 22, Miserocchi et al. 2007; 23, Kang et al. 2007; 24, Ogrinc et al. 2005

[b]Called particulate organic matter (POM) or suspended particulate matter (SPM) by the authors

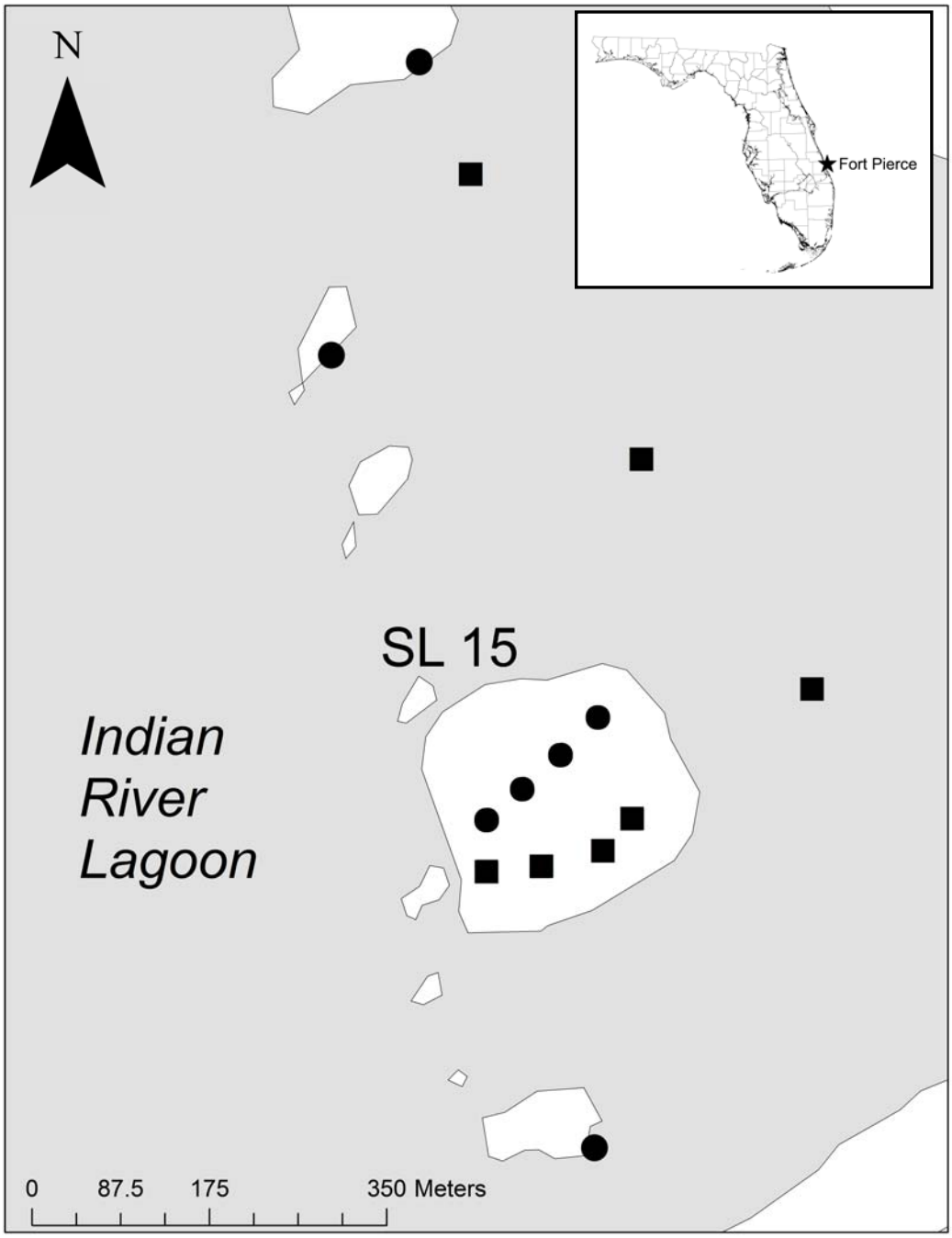


Figure 4-1. The study area in the Indian River Lagoon, next to Fort Pierce, Florida (inset). SL 15 is the large island in the center. Circles are mangrove system plots and squares are seagrass system plots. Symbols outside of SL 15 are the reference sites, which have one plot each.

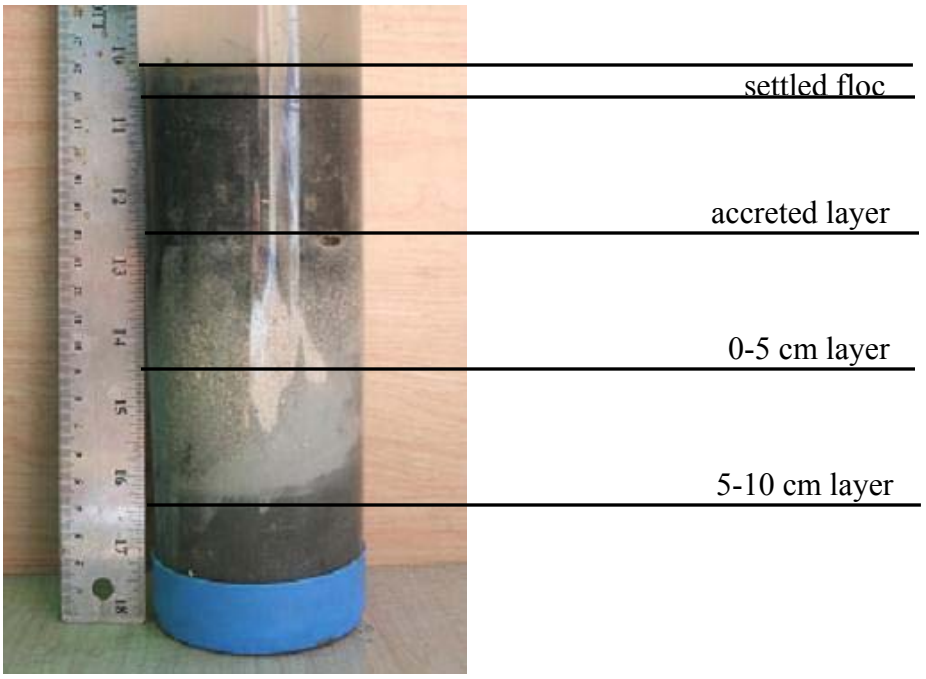


Figure 4-2. Core from SL 15 seagrass system illustrating the surface layer (floc) and different sediment depths (accreted layer, 0-5 cm, and 5-10 cm). Note the difference in color between the accreted layer and 0-5 cm depth.

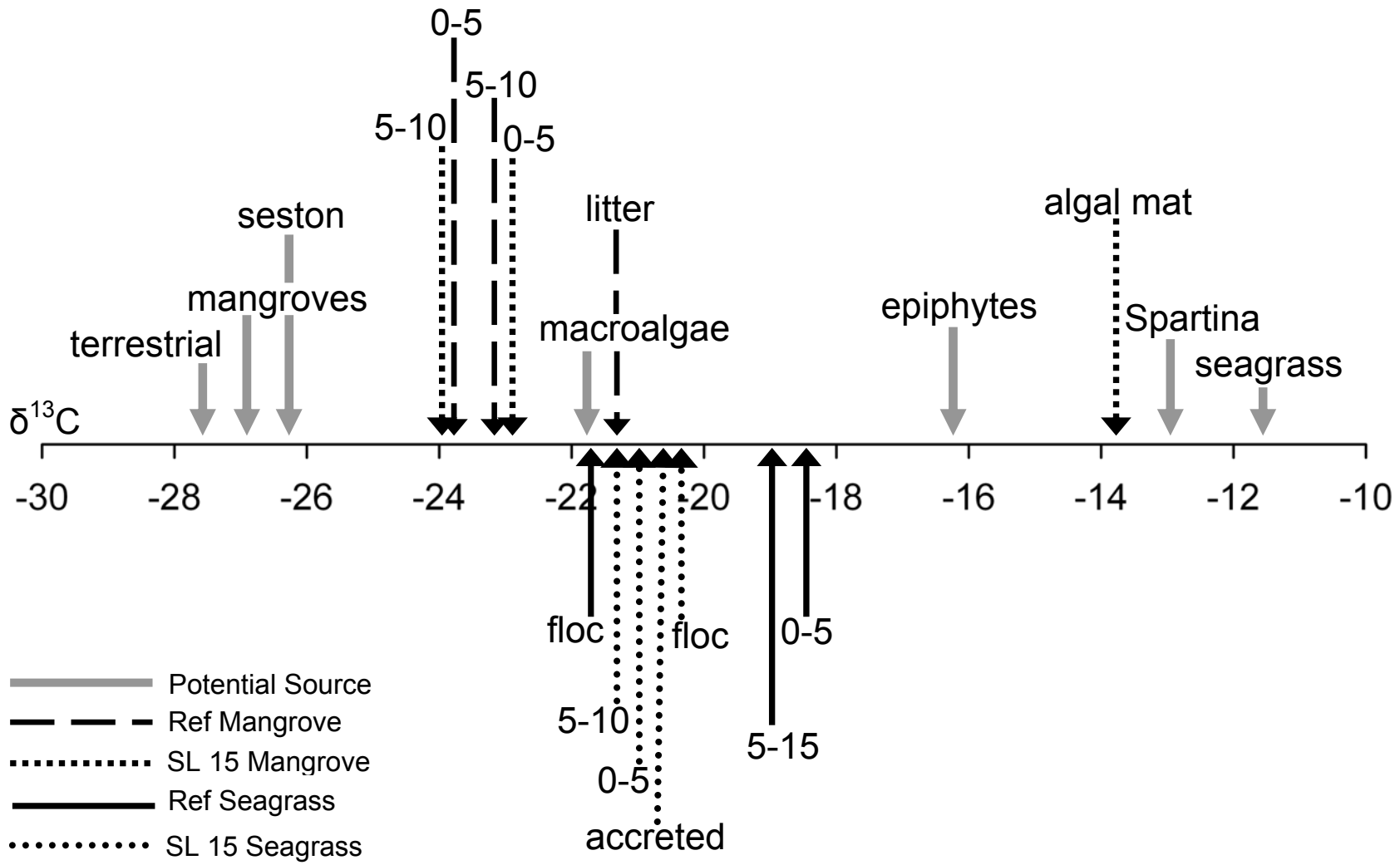


Figure 4-3. $\delta^{13}C$ averaged over July and November 2006 for SL 15 and reference sediments and surface layers compared to mean $\delta^{13}C$ of potential sources.

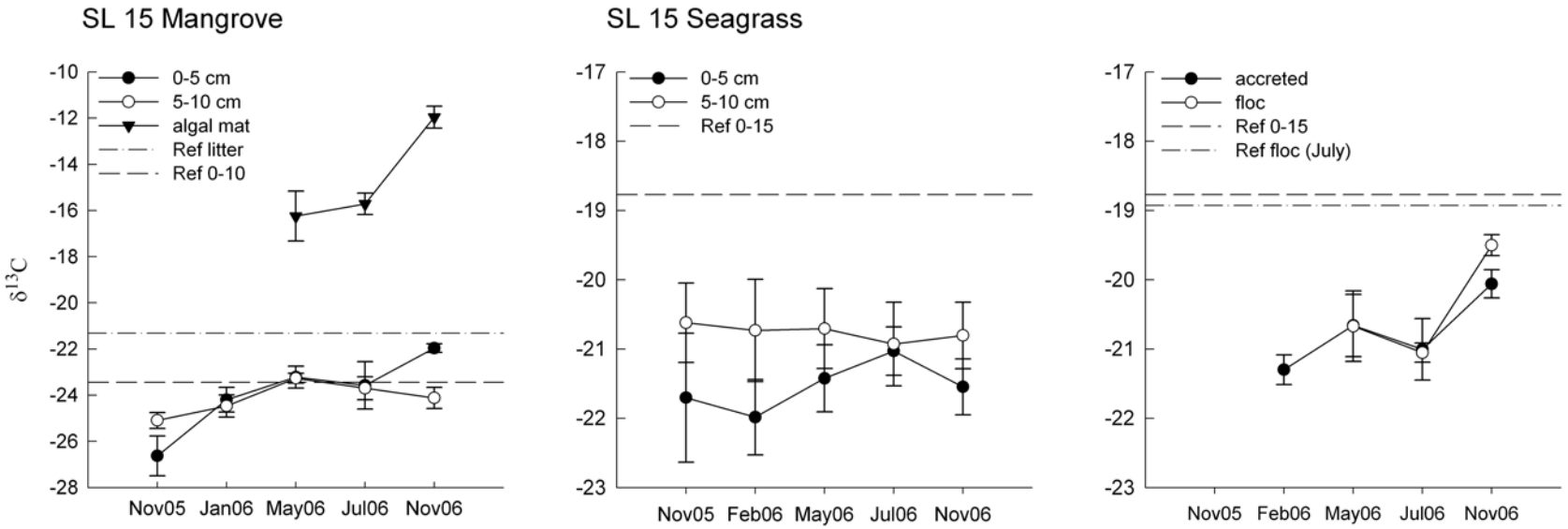


Figure 4-4. Mean $\delta^{13}C$ of SL 15 sediments and surface layers over the first year after construction. Error bars are ±SE. Reference lines are $\delta^{13}C$ averaged over depth (for sediments) and month (except for reference floc) for the respective reference systems.

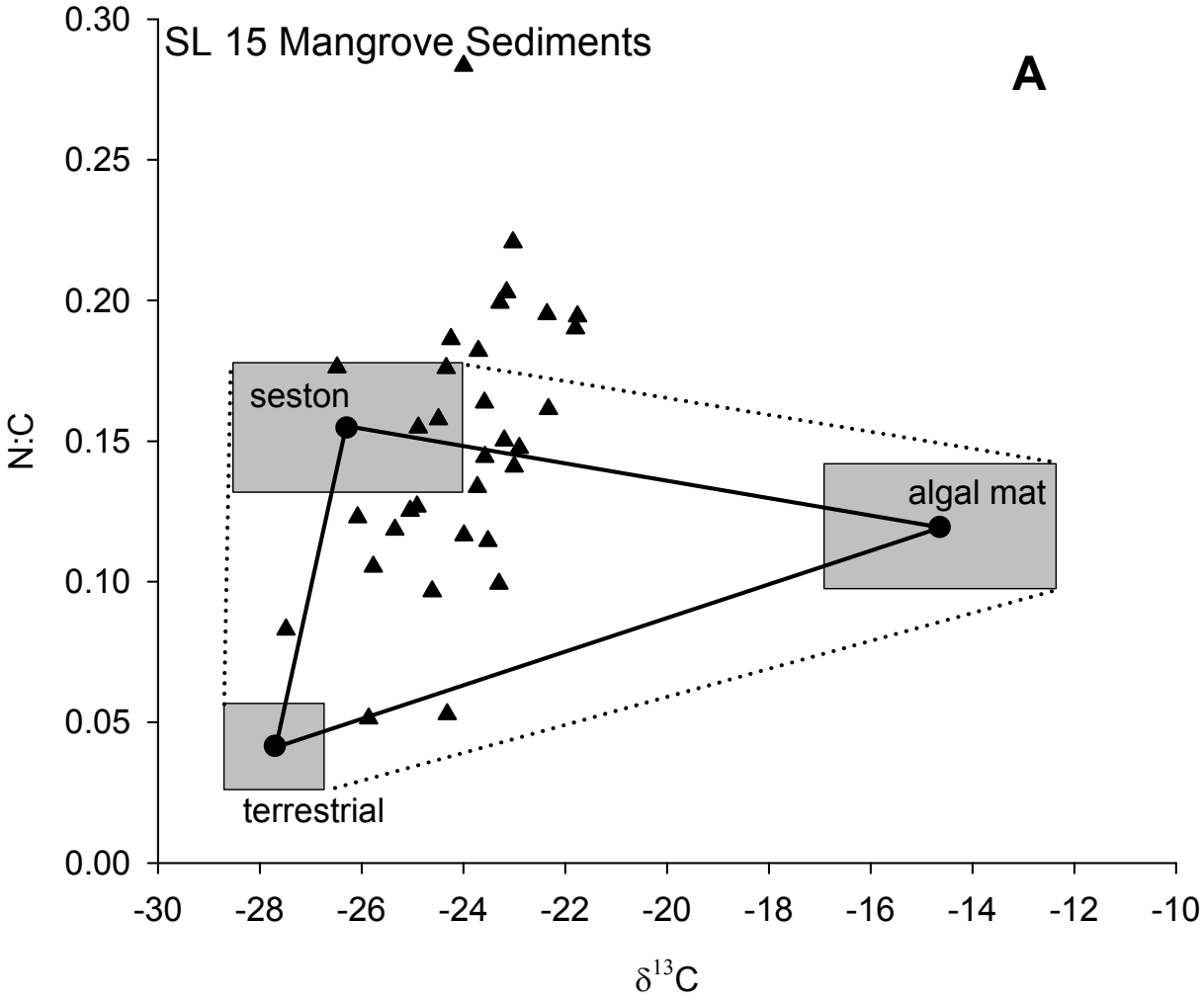


Figure 4-5. N:C vs. δ13C in ternary mixing diagrams of three potential OC sources and mangrove sediments. Circles are the mean end member values and boxes are ± standard deviation of N:C and δ13C. Triangles are mangrove sediment values for SL 15 (A) and the reference (B).

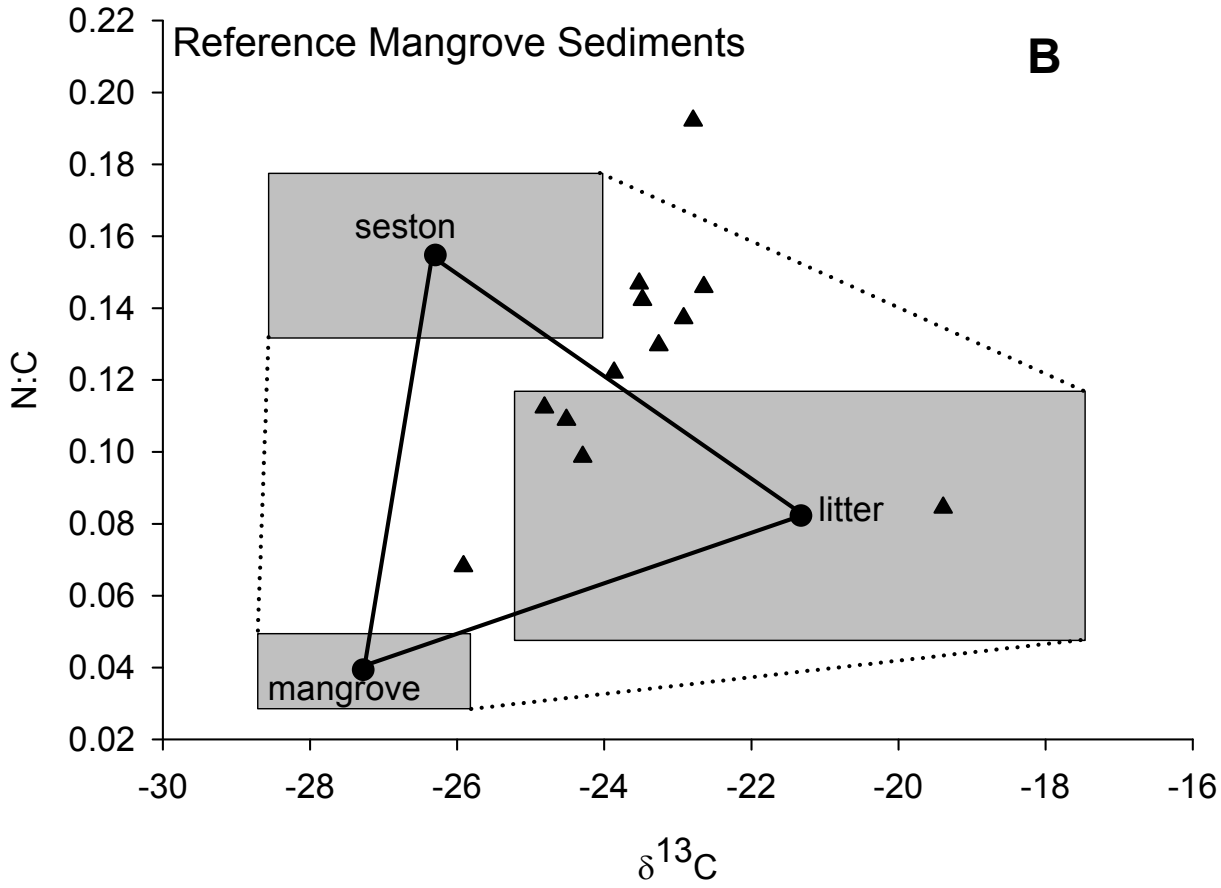


Figure 4-5. Continued

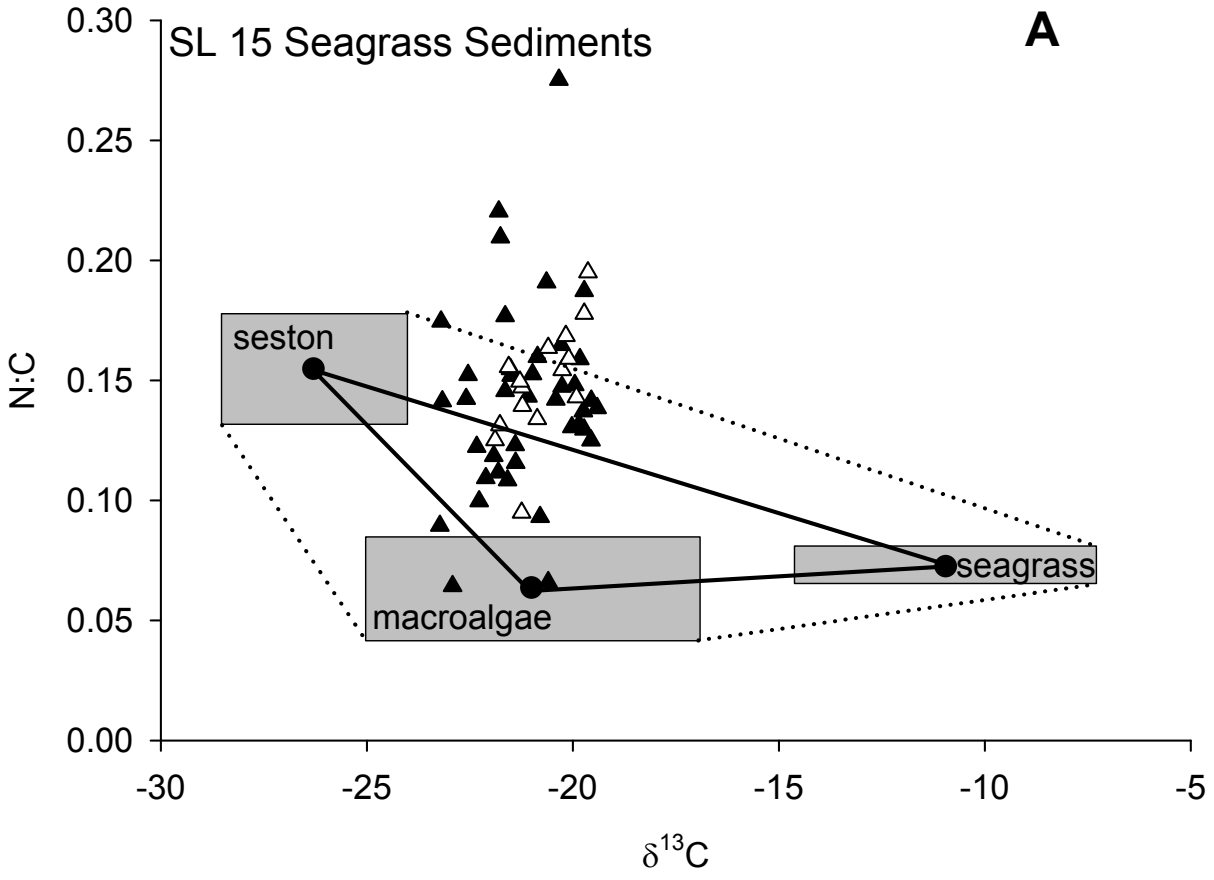


Figure 4-6. N:C vs. δ13C in ternary mixing diagrams of three potential OC sources and seagrass sediments. Circles are the mean end member values and boxes are ± standard deviation of N:C and δ13C. Filled triangles are 0-10 cm sediment values for SL 15 (A) and 0-15 cm sediment values for reference (B). Open triangles are accreted layer values for SL 15 (A).

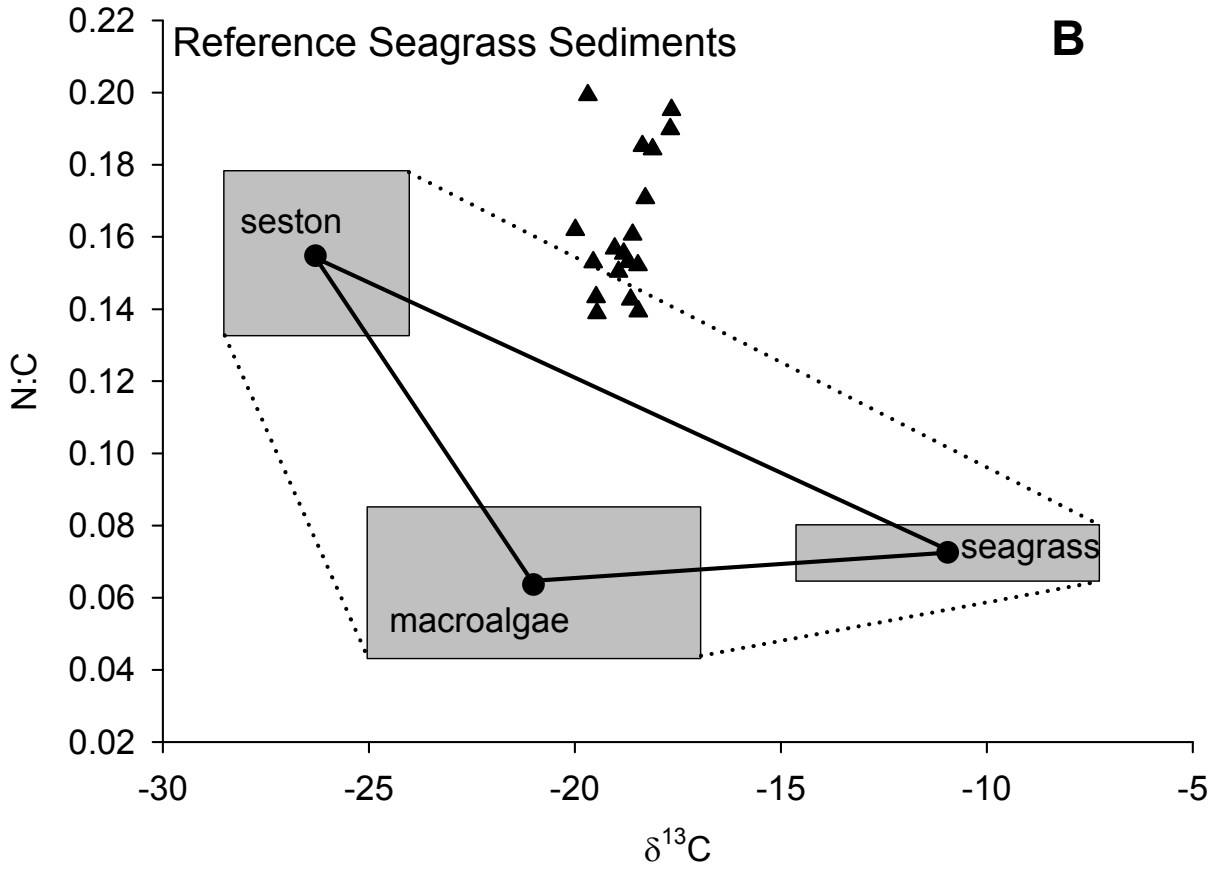


Figure 4-6. Continued

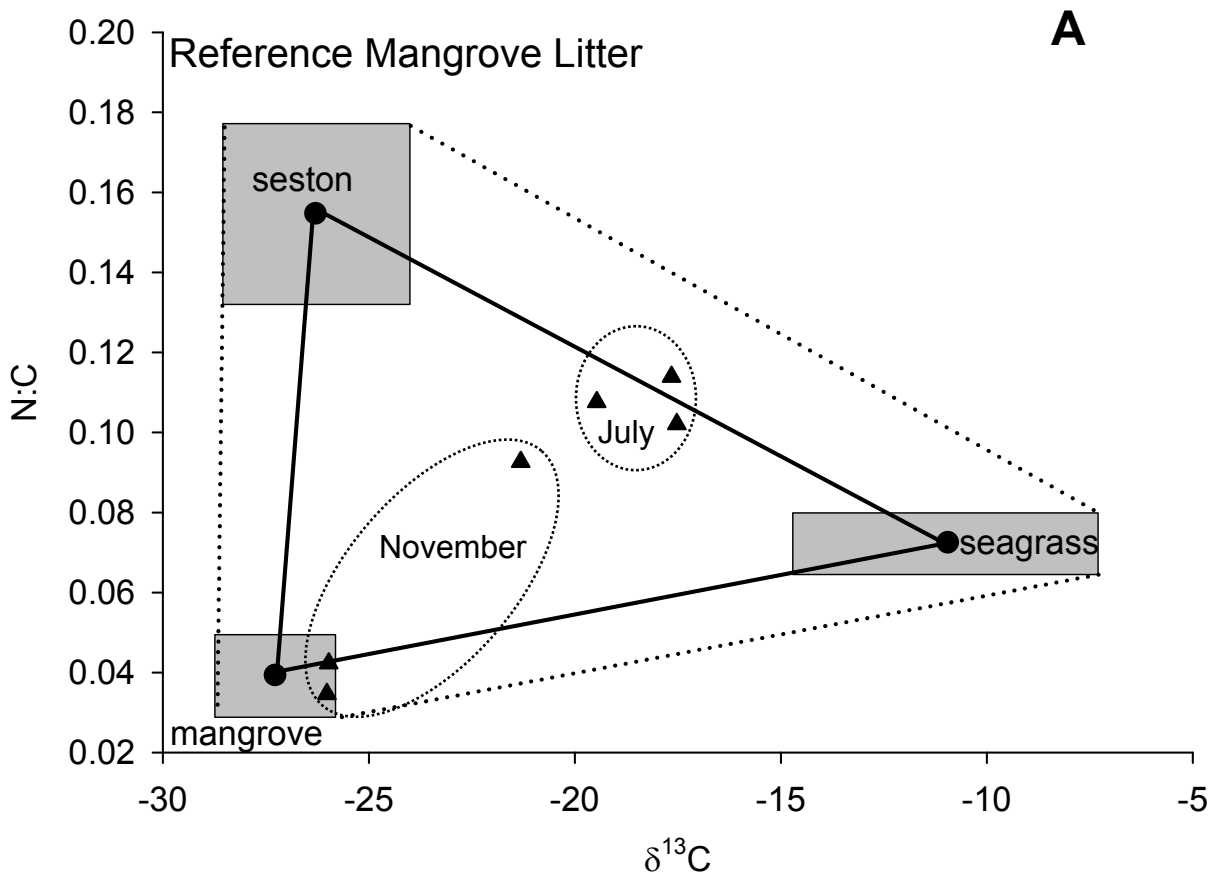


Figure 4-7. N:C vs. δ13C in ternary mixing diagrams of three potential OC sources and surface layers. Circles are the mean end member values and boxes are ± standard deviation of N:C and δ13C. Filled triangles are reference litter layer values (A) and SL 15 floc values (B). Open triangles are reference floc values (B).

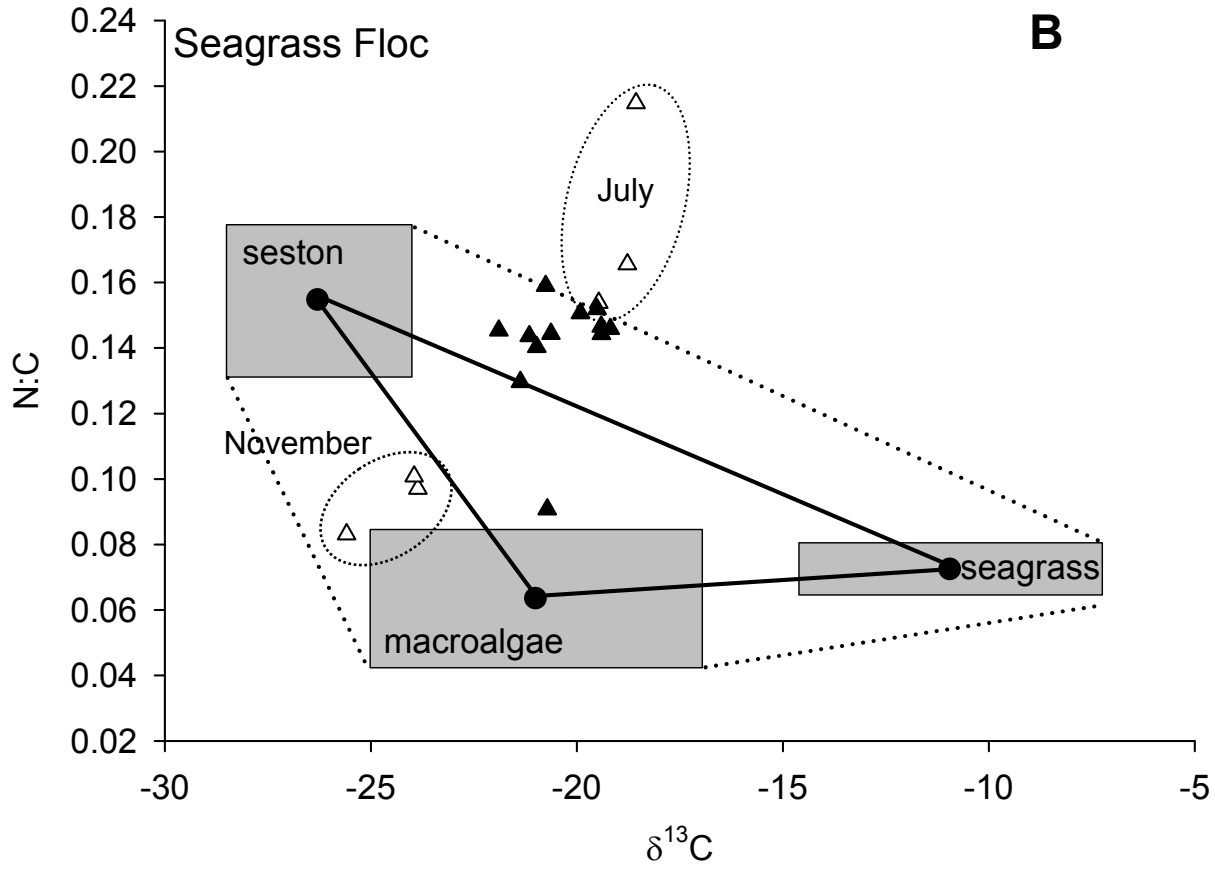


Figure 4-7. Continued

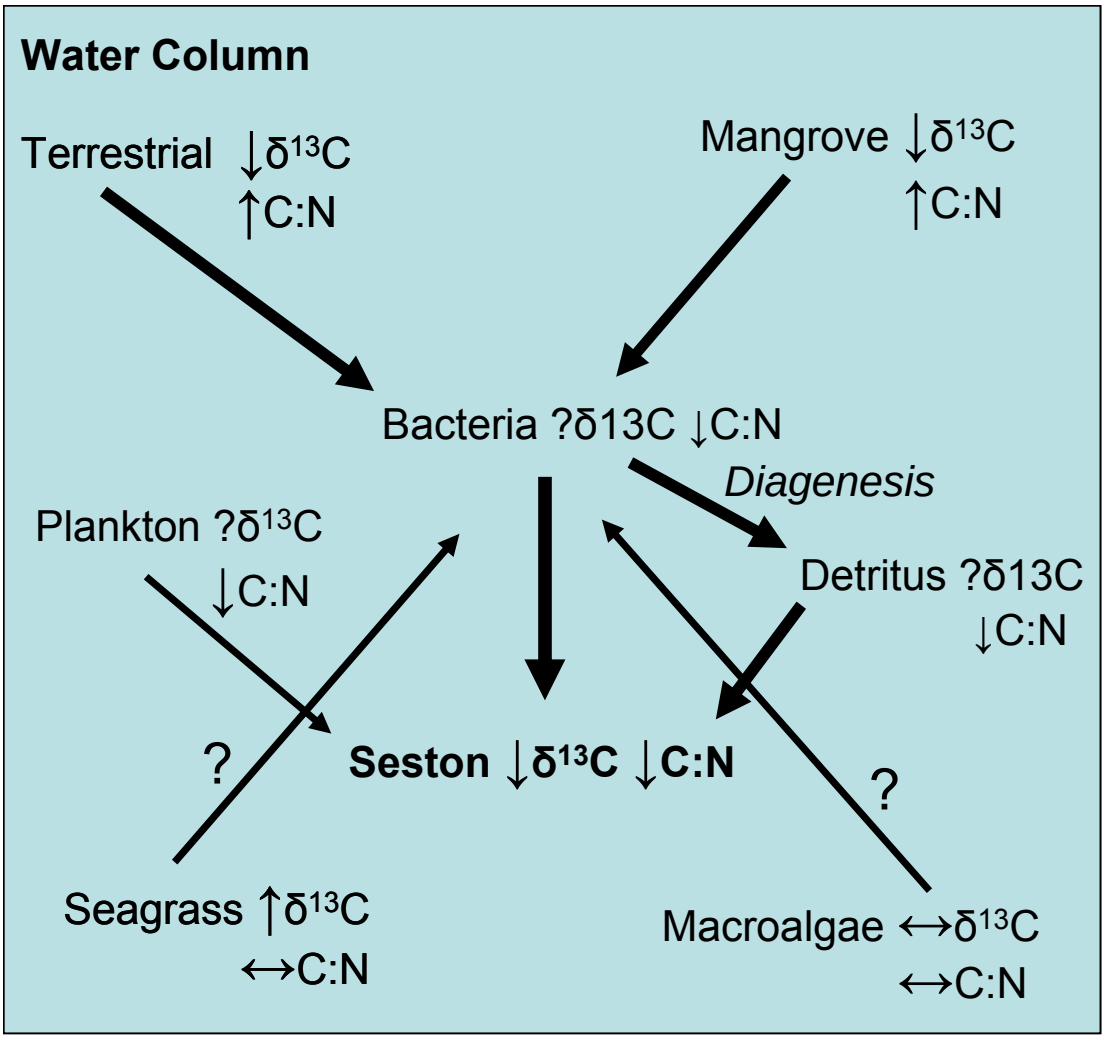
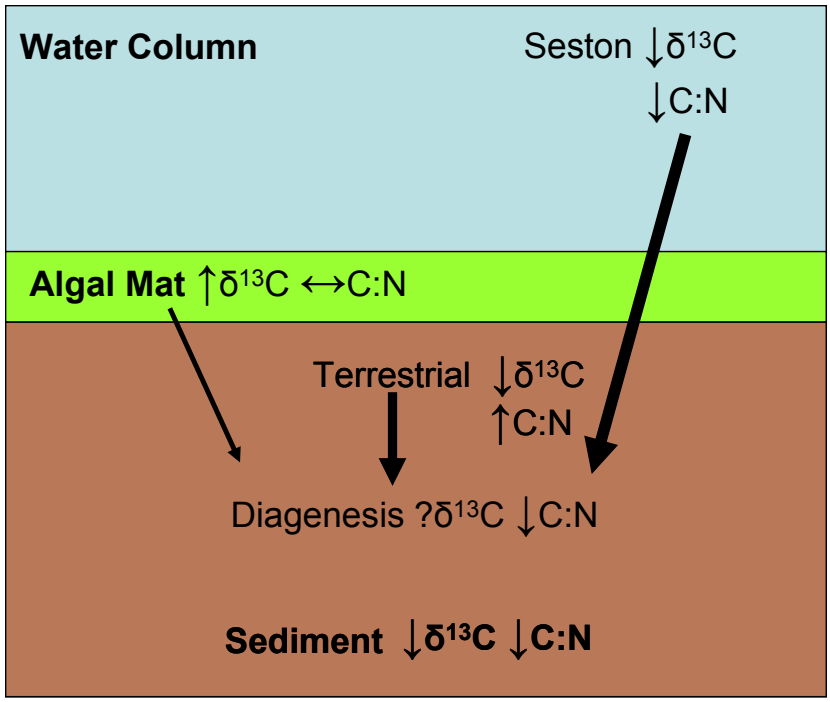


Figure 4-8. A theoretical diagram of organic carbon sources that may constitute seston and how they affect seston $\delta^{13}C$ and C:N. Arrow sizes indicate the possible relative contributions of each source. ↓ indicates depleted $\delta^{13}C$ and low C:N, ↑ indicates enriched $\delta^{13}C$ and high C:N, and ↔ indicates mid-range $\delta^{13}C$ and C:N.

SL 15 Mangrove



Ref Mangrove

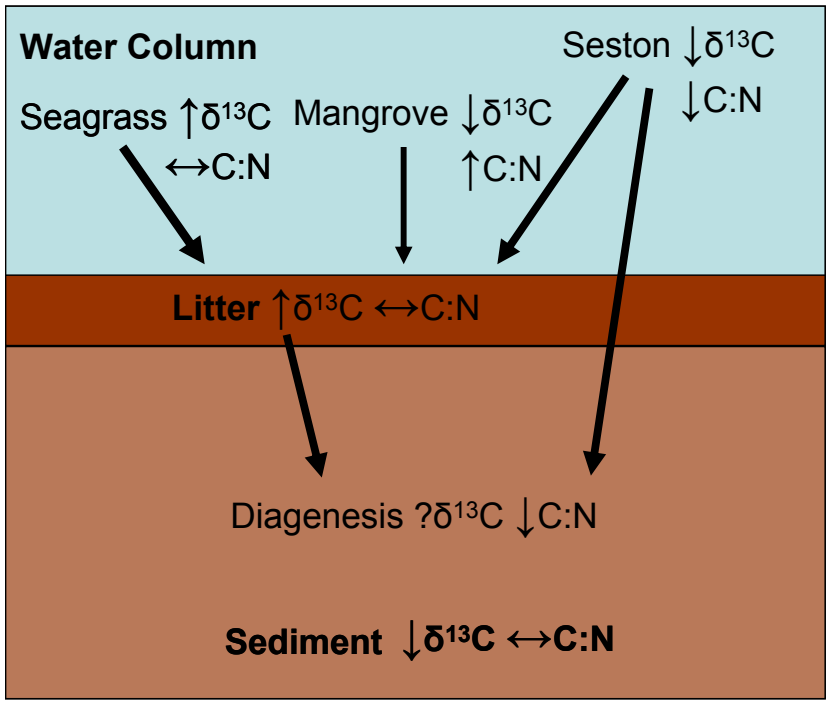
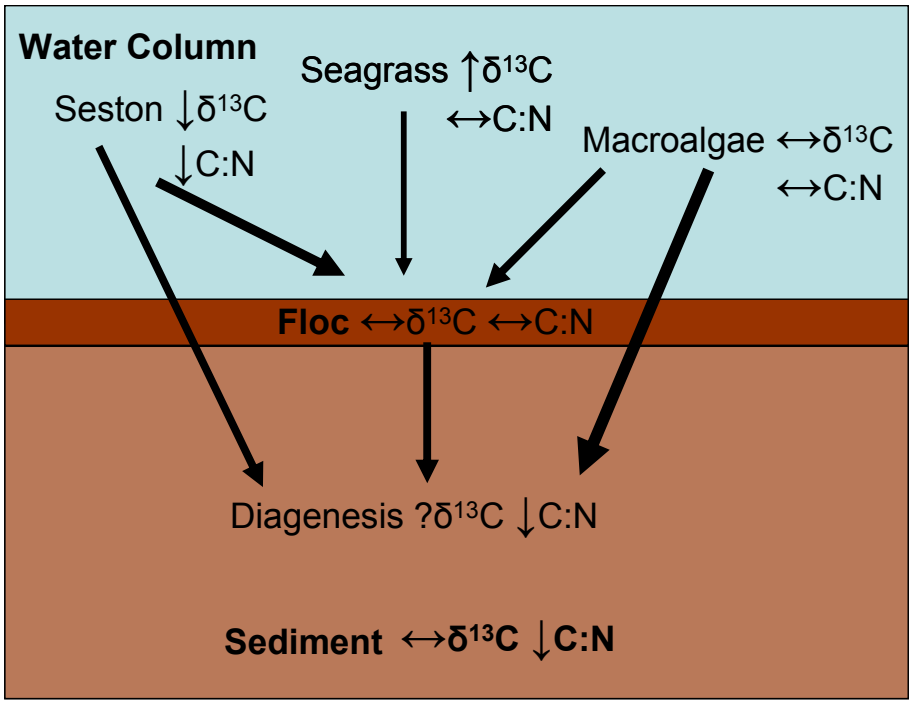


Figure 4-9. Main sources and how they affect surface layer and sediment $\delta^{13}C$ and C:N. Arrow sizes indicate the relative contributions of each source. ↓ indicates depleted $\delta^{13}C$ and low C:N, ↑ indicates enriched $\delta^{13}C$ and high C:N, and ↔ indicates mid-range $\delta^{13}C$ and C:N.

SL 15 Seagrass



Ref Seagrass

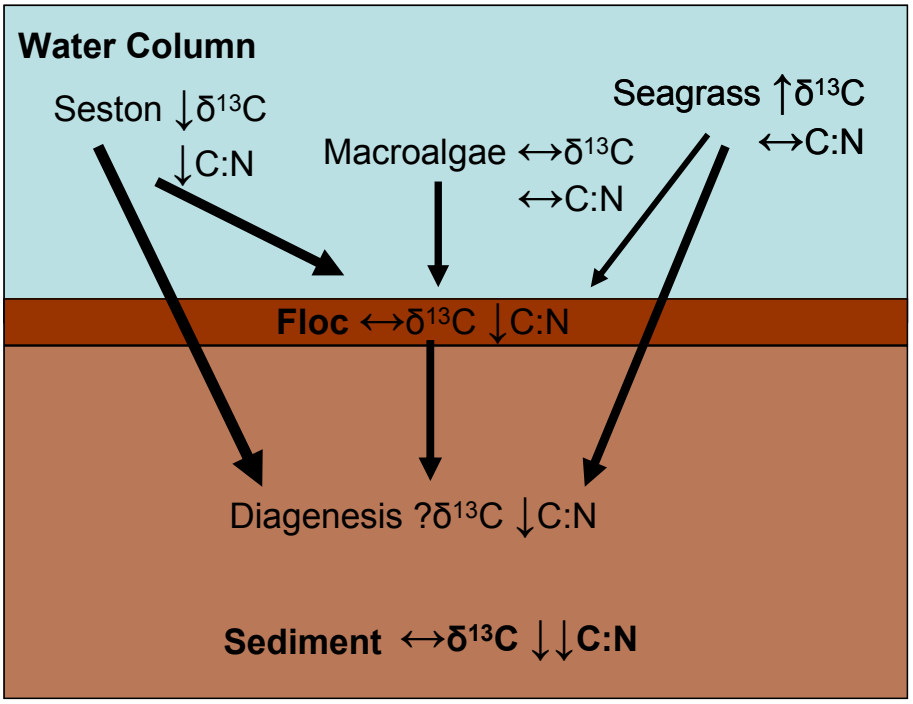


Figure 4-9. Continued.

CHAPTER 5
SYNTHESIS

Coastal ecosystems including salt marshes, seagrass beds, and mangrove forests are more effective carbon (C) sinks than terrestrial systems and freshwater wetlands (Chapter 2). These ecosystems store large amounts of OC and actively accumulate OC at high rates; about 44.6 Pg C is stored and about 120 Tg C y^{-1} accumulates in salt marsh and mangrove sediments globally (Jennerjahn and Ittekkot 2002; Chmura et al. 2003). Many coastal ecosystems have been degraded or lost due to anthropogenic disturbances (Valiela et al. 2001; Kennish 2002; Zedler 2004). Destruction of coastal ecosystems increases atmospheric CO_2 concentrations because their organic C (OC) stores are often mineralized as a result and their future OC sequestration capacity is lost (Duarte et al. 2005; Bridgham et al. 2006). Generally in the United States, the destruction of coastal ecosystems must be mitigated by restoring or creating coastal ecosystems elsewhere. Whether mitigation of seagrass and mangrove systems restores the C sink capacity is currently not well-studied.

In the present study, functional trajectories of sediment OC (SOC) parameters in a constructed mangrove and seagrass system in the Indian River Lagoon, Florida were measured. Sediment OC (SOC) parameters in constructed systems were also compared to mature reference systems to indicate if constructed sediments had reached functional equivalence in terms of OC storage. The objectives of this study were: 1) to determine short term trajectories of SOC pools in a constructed mangrove forest and seagrass bed; 2) to compare SOC pools in the constructed system with those in reference systems; 3) to compare the lability of SOC in the constructed and reference systems; 4) to determine and compare significant sources to the total SOC pool in the constructed and reference systems. The hypotheses were: 1) in the short term, storage in the three OC pools studied would increase in the constructed systems, but would not reach the level

of storage in the references' OC pools; 2) OC lability would be greater in sediments of constructed systems than in reference sediments; 3) SOC sources in constructed systems would be macroalgae or plankton, while SOC sources in reference systems would be vascular plants, like mangroves and seagrass. Key findings addressing each objective and the validity of the hypotheses are presented below.

Objective One: Short Term Trajectories of Sediment Organic Carbon Pools

Contrary to the hypothesis, functional trajectories were not followed by OC parameters in the constructed site sediments. Instead of steady increases, SOC parameters either remained unchanged or increased and decreased throughout the year, driven by seasonal changes in the water column. The only sediment functional trajectory was followed by the mangrove system's bulk density, which decreased throughout the year but remained above reference levels. Functional trajectories were somewhat followed by surface layers as both microbial biomass C (MBC) and total OC (TOC) increased. Due to their proximity to OC inputs, it is logical that OC should increase in the surface layers before they increase in sediments. However, whether increases in surface layer OC were due to a recovering function or an annual pattern could not be discerned. For example, the increase in floc MBC and TOC followed the same trend as total suspended solids, a water quality parameter. Overall, one year was not sufficient time to map OC functional trajectories in the constructed mangrove and seagrass system. The lack of a functional trajectory did not preclude the OC parameters from being functionally equivalent to reference values.

Objective Two: Comparisons of Sediment Organic Carbon Pools

The hypothesis that SOC pools would be smaller in constructed systems was by and large correct for mangrove sediments but not for seagrass sediments (Fig. 5-1 and 5-2). Floc and accreted layers of constructed seagrass sediments reached or exceeded functional equivalence for

all three OC pools—TOC, Extractable OC (ExOC), and MBC. The 0-10 cm depths, also reached equivalence for ExOC pools. On a storage (areal) basis, equivalence was also reached by mangrove 0-5 cm depths for ExOC and MBC and seagrass 0-10 cm depths for MBC. This equivalence was only on a storage basis because it was driven by greater bulk densities in the constructed sediments. Seagrass sediments reached SOC pool equivalence more than mangrove sediments due to their constant inundation, parent material, and lower equivalence goal (reference seagrass sediments had less TOC and ExOC than reference mangrove sediments).

SOC pool sizes were not the only factors that indicated if constructed systems had attained functionally equivalent OC storage—information about OC accumulation rates and OC lability was also needed. OC accumulation rates in the constructed mangrove and seagrass systems were similar to literature values if accumulation in surface layers was considered. It was unknown if the constructed systems could sustain these accumulation rates over the long term or if the rates reflected an immediate response in SOC after construction. Larger proportions of the TOC pool were MBC in constructed 0-10 cm sediments indicating greater SOC lability and therefore less SOC storage in constructed systems.

Objective Three: Comparisons of Sediment Organic Carbon Lability

Generally, constructed systems SOC was more labile than reference system SOC for both mangrove and seagrass sediments (Fig. 5-1 and 5-2). Lability was only similar between constructed and reference systems in the upper portion of seagrass sediments and in seagrass floc. These results confirm hypothesis two. Greater lability of OC in the constructed system indicates that the constructed system does not function as well as reference systems in terms of OC storage. Even when SOC pool sizes are similar to references', as in the 5-10 cm depth of constructed seagrass sediments, greater OC lability indicates that OC storage is not functionally equivalent. The more labile OC is, the more likely it will be mineralized by microbes and

respired to CO_2 instead of being stored in sediments long term. Differences in OC lability were partially due to differing C limitations and to differences in SOC sources between constructed and reference systems.

Objective Four: Comparisons of Sediment Organic Carbon Sources

Sources to the SOC pool differed between constructed and reference systems, but not to the extent that was hypothesized (Fig. 5-1 and 5-2). Ternary diagrams suggested that seston from the water column was a main SOC source for all systems—constructed and natural. The true importance of seston, however, was unclear because the low sediment C:N ratios that led to the conclusion that seston was a main source, can also result from diagenetic transformations. In mangrove sediments, both systems had lignin-containing higher plants as other main sources—terrestrial plants in the constructed system and mangroves/seagrass via litter in the reference systems. The effect of sources on OC storage in mangrove sediments was therefore similar; but there was an indication that the labile algal mat was becoming an increasingly important source in constructive sediments, which would shorten OC storage times. Sources in reference seagrass sediments were unclear. It was apparent though, that a greater amount of SOC was derived from macroalgae in the constructed system than in the reference system. Litter bag studies demonstrated that macroalgae generally have the fastest decomposition rates of all aquatic macrophytes, indicating that the macroalgae-derived OC would not be stored in constructed sediments for long amounts of time.

Conclusion

Overall, neither mangrove nor seagrass sediments of the constructed system are functionally equivalent to their respective references in regards to OC storage (Fig. 5-1 and 5-2). Recovery indices indicate how close various parameters are to equivalence with references.

$$RI = \log\left(X_{constructed} / X_{reference}\right) \quad (5\text{-}1)$$

In Equation 5-1, RI is the recovery index, $X_{constructed}$ is the value of the parameter in the constructed system, and $X_{reference}$ is the value of the parameter in the reference system. RI's equal to zero indicate equivalence, less than zero indicate that equivalence has not been reached, and greater than zero indicate equivalence has been surpassed. The constructed seagrass system is closer to equivalence than the constructed mangrove system (Fig.5-3). Upper depths of constructed seagrass sediments had similar SOC pools and lability to upper depths of reference seagrass sediments, causing the seagrass sediments to be closer to equivalence. As the mangroves and seagrasses within the constructed systems mature, it is likely that their SOC will become less algae-derived, leading to lower OC lability and better OC storage. Dominance of seston as a source in all systems means that a switch in less significant sources may take time to register in the sediments. Ultimately, if the OC pools and lability in reference systems are any indication (Fig. 5-1 and 5-2) and if functional trajectories are followed in the future, the constructed mangrove system will become more effective at OC storage than the constructed seagrass system.

This study adds to the body of research on functional trajectories. It is one of two known studies on seagrass trajectories and the only known study of mangrove trajectories. More importantly, it is the first known study to examine the trajectory of OC storage in depth. If constructed and restored coastal ecosystems store and accumulate OC as well as their established counterparts, corporations and governments could construct coastal systems in exchange for C credits. This action can replace lost systems and restore many of the ecologically important functions these systems provide. Conclusions based on this study are limited because it only followed constructed systems during the first year of recovery. The constructed mangrove and

seagrass system in this study accumulated SOC at rates similar to rates in mature systems over the first year. If these rates are sustained and more OC is stored in long-term, recalcitrant pools, then the constructed systems will be effective C sinks. Longer term studies are needed to fully assess the effectiveness of constructing coastal ecosystems for OC storage.

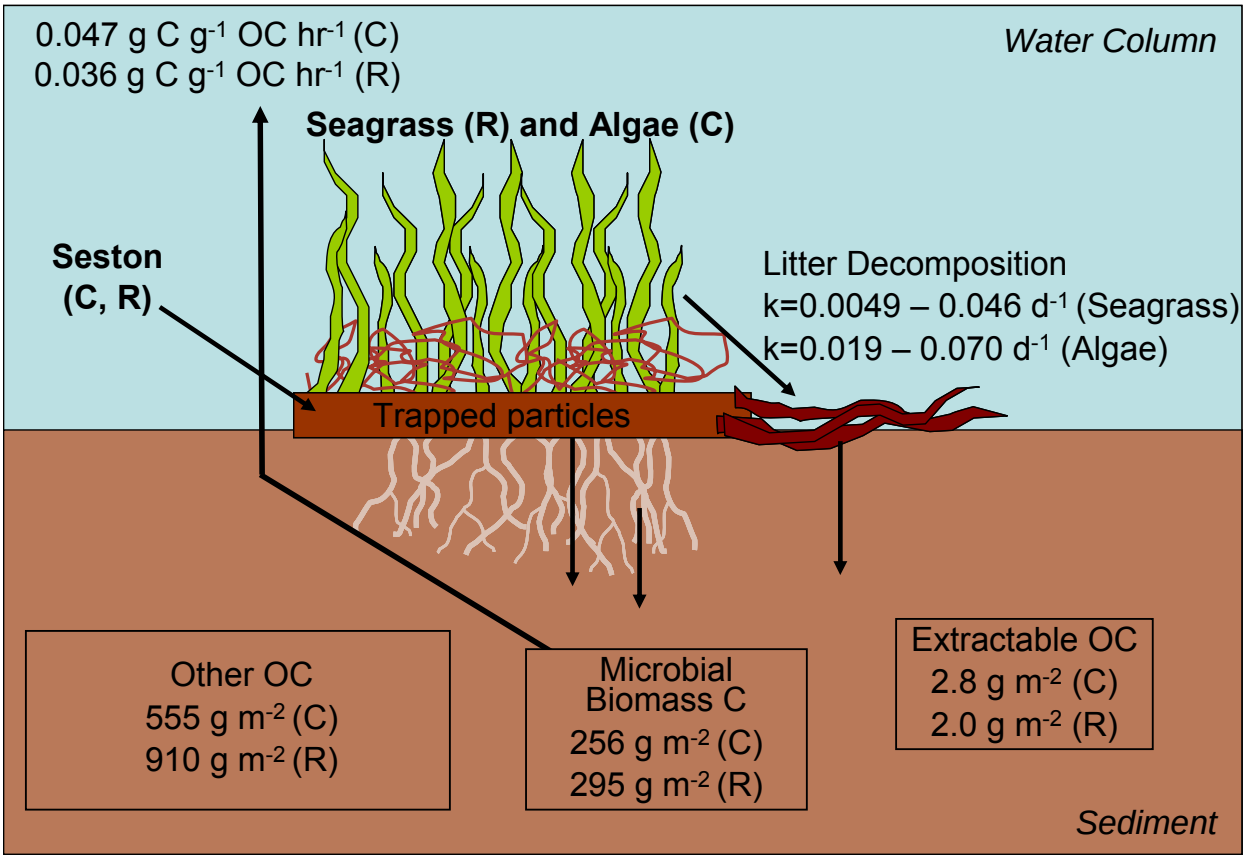


Figure 5-1. A modified seagrass bed carbon cycle showing values from this study in constructed (C) and reference (R) systems. Organic carbon (OC) pools are the sum of sediment and surface layer means (July and November data). Rates of microbial carbon respiration are the mean of all depths (sediment and surface layers) in July and November, adjusted from an O_2 uptake rate to a carbon release rate by an assumed 1 O_2 to 6 C molar ratio. Bolded words are the main contributors to sediment OC pools.

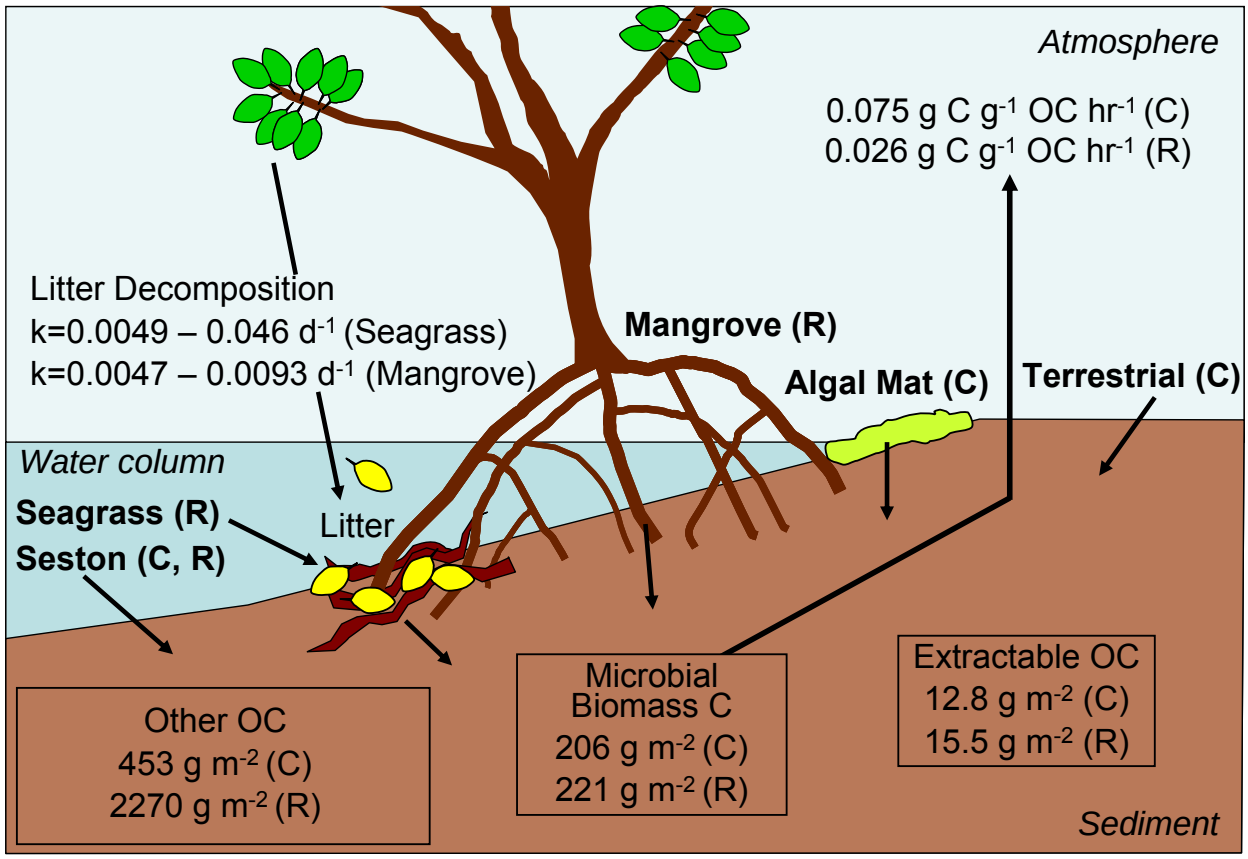


Figure 5-2. A modified mangrove forest carbon cycle showing values from this study in constructed (C) and reference (R) systems. Organic carbon (OC) pools are the sum of sediment and surface layer means (July and November data). Rates of microbial carbon respiration are the mean of all depths (sediment and surface layers) in July and November, adjusted from an O_2 uptake rate to a carbon release rate by an assumed 1 O_2 to 6 C molar ratio. Bolded words are the main contributors to sediment OC pools.

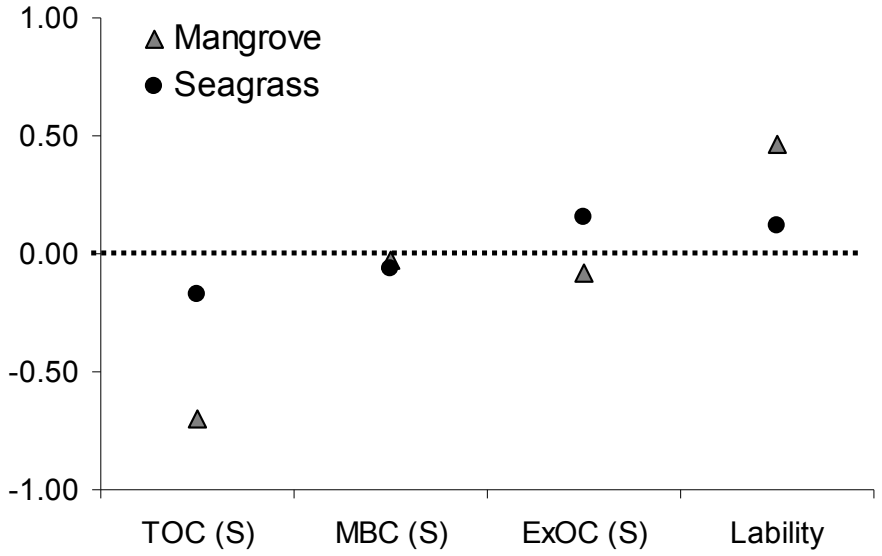


Figure 5-3. Recovery indices of three organic carbon (OC) pools and OC lability parameters for constructed mangrove and seagrass systems. For each system, OC pools are summed for all sediment depths and surface layers and lability is the average of all depths and surface layers. TOC=total organic carbon, MBC=microbial biomass carbon, ExOC=extractable organic carbon, and (S) indicates that these OC pool parameters were calculated on a storage basis.

APPENDIX A
STATISTICAL TRANSFORMATIONS

Table A-1. How data were transformed to meet the normality assumption prior to running ANOVAs. For parameters, TOC=total organic carbon, TN= total nitrogen, C:N= carbon to nitrogen ratio, ExOC=extractable organic carbon, and MBC=microbial biomass carbon. For transformations, NT= not transformed, Sqrt=square root, and a C (as in X-C) indicates that a constant was subtracted or added to a parameter before it was transformed via square root, log, arcsine, etc.

Chapter	ANOVA	Depths	Parameter	Transformation
3	Mangrove factorial	Sediments 0-10	Bulk density	NT
			TOC (conc)	Log 10 (Arcsin)
			TOC (storage)	Log 10
			TN (conc)	Log 10 (Arcsin)
			C:N	Sqrt
			ExOC (conc)	Log e
			ExOC (storage)	Log e
			MBC (conc)	Sqrt (MBC-C)
			MBC (storage)	Log e
			Lability	Log 10
	Seagrass factorial	Sediments 1-3	Bulk density	NT
			TOC (conc)	NT
			TOC (storage)	NT
			TN (conc)	NT
			C:N	Log e
			ExOC (conc)	Log e (ExOC-C)
			ExOC (storage)	Log 10
			MBC (conc)	Sqrt (MBC-C)
			MBC (storage)	NT
			Lability	Log 10
	Mangrove factorial	Surface layers	Bulk density	Sqrt
			TOC (conc)	Log 10 (Arcsin)
			TOC (storage)	Log 10
			TN (conc)	Log 10 (Arcsin)
			C:N	Log e (C:N-C)
			ExOC (conc)	Log e (ExOC-C)
			ExOC (storage)	Log 10
			MBC (conc)	Sqrt
			MBC (storage)	Sqrt
			Lability	Log e
	Seagrass factorial	Surface layers	Bulk density	NT
			TOC (conc)	Arcsin (sqrt)
			TOC (storage)	NT
			TN (conc)	Sqrt
			C:N	Sqrt
			ExOC (conc)	Sqrt
			ExOC (storage)	Sqrt
			MBC (conc)	Sqrt
			MBC (storage)	Log e
			Lability	NT
	Mangrove repeated Measures	Sediments 0-10	Bulk density	Log e
			TOC (conc)	Sqrt
			ExOC (conc)	NT

Table A-1. Continued

Chapter	ANOVA	Depths	Parameter	Transformation
3			TN (conc)	Sqrt
			C:N	Log e
			Lability	Sqrt
		Algal mat	Bulk density	NT
			TOC (conc)	NT
			ExOC (conc)	NT
			MBC (conc)	Sqrt (MBC-C)
			TN (conc)	Log e (TN-C)
			C:N	Log e
			Lability	Log e
	Seagrass repeated Measures	Sediments 0-10	Bulk density	Log e
			TOC (conc)	Sqrt
			ExOC (conc)	NT
			MBC (conc)	NT
			TN (conc)	Sqrt
			C:N	Sqrt
			Lability	
		Sediments accreted	Bulk density	NT
			TOC (conc)	Log e
			ExOC (conc)	Sqrt (ExOC-C)
			MBC (conc)	Sqrt
			TN (conc)	Log e
			C:N	Log e (C:N-C)
			Lability	NT
		Floc	Bulk density	Log 10
			TOC (conc)	NT
			ExOC (conc)	Sqrt (ExOC-C)
			MBC (conc)	NT
			TN (conc)	NT
			C:N	Log e (C:N-C)
			Lability	NT
4	Mangrove factorial	Sediments 0-10	$\Delta^{13}c$	NT
	Seagrass factorial	Sediments 1-3	$\Delta^{13}c$	NT
	Mangrove factorial	Surface layers	$\Delta^{13}c$	NT
	Seagrass factorial	Surface layers	$\Delta^{13}c$	Log 10 ($\delta^{13}C$*-1)
	Mangrove repeated measures	Sediments 0-10	$\Delta^{13}c$	NT
		Algal mat	$\Delta^{13}c$	NT
	Seagrass repeated measures	Sediments 0-10	$\Delta^{13}c$	NT
		Sediments accreted	$\Delta^{13}c$	NT
		Floc	$\Delta^{13}c$	NT

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BIOGRAPHICAL SKETCH

Caitlin Hicks was born in Framingham, Massachusetts and grew up in Western Massachusetts. She spent her summer vacations on Cape Cod where she learned to love nature among the Cape's beaches, salt marshes, and forests. She attended Middlebury College in Vermont where she enjoyed views of the Green Mountains and Adirondacks every day. She pursued a joint major in biology and environmental studies, graduating in May 2004. During college, she spent a challenging but immensely rewarding semester at the Ecosystem Center of the Woods Hole Marine Biology Laboratory where she came to appreciate the cycling of elements within ecosystems. Upon graduation, Caitlin worked as a research assistant for Dr. Steward Pickett at the Institute of Ecosystem Studies in Millbrook, New York. While at that job, she ran a laboratory, worked on GIS projects, and enjoyed arduous field work in Kruger National Park, South Africa. In August 2005, seeking a change from the northeast climate, biota, and culture she had grown up with, Caitlin moved to Gainesville, Florida to begin her masters work with Dr. Reddy in the University of Florida's Soil and Water Science Department. For her masters work, Caitlin was given the freedom to pick her own project, so she chose to work in a coastal environment, like the ones she loved as a child, and on carbon, her favorite element. Caitlin is now beginning her PhD in the Botany Department at the University of Florida working with Dr. Ted Schuur. She has switched field sites but not elements and will now study carbon in Alaska.