ORGANIC CARBON FLUX AT THE MANGROVE SOIL-WATER COLUMN INTERFACE IN THE FLORIDA COASTAL EVERGLADES

A Thesis

by

MELISSA MARIE ROMIGH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2005

Major Subject: Wildlife and Fisheries Sciences

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Approved as to style and content by:

_____	_____
Stephen Davis (Chair of Committee)	Luis Cifuentes (Member)
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ABSTRACT

Organic Carbon Flux at the Mangrove Soil-Water Column Interface in the Florida Coastal Everglades. (May 2005)

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Chair of Advisory Committee: Dr. Stephen Davis

Coastal outwelling of organic carbon from mangrove wetlands contributes to near-shore productivity and influences biogeochemical cycling of elements. I used a flume to measure fluxes of dissolved organic carbon (DOC) between a mangrove forest and adjacent tidal creek along Shark River, Florida. Shark River's hydrology is influenced by diurnal tides and seasonal rainfall and wind patterns. Samplings were made over multiple tidal cycles in 2003 to include dry, wet, and transitional seasons. Surface water [DOC], temperature, salinity, conductivity and pH were significantly different among all sampling periods. [DOC] was highest during the dry season (May), followed by the wet (October) and transitional (December) seasons. Net DOC export was measured in October and December, inferring the mangrove forest is a source of DOC to the adjacent tidal creek during these periods. This trend may be explained by high rates of rainfall, freshwater inflow and subsequent flushing of wetland soils during this period of the year.

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I would like to acknowledge many people for their guidance and support throughout my master's program. I would especially like to thank my advisor, Dr. Steve Davis, for his generous contribution of time, commitment and direction. Throughout my master's program, he encouraged me to develop challenging research skills, constantly stimulated my analytical thinking and assisted me in the scientific writing process. I am grateful for the contribution from my committee members and wish to thank Drs. Robert Twilley, Luis Cifuentes and Dan Roelke for their constructive support and encouragement.

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A special thank-you and much gratitude go to my parents, Jack and Patty Romigh, who provided me with the discipline and drive to excel in higher education. Friends and family have all inspired me to pursue the path of knowledge and respect the community and environment we live in.

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INTRODUCTION

Background Information

The dissolved organic carbon (DOC) pool in the oceans is one of the largest exchangeable organic reservoirs on the planet and the transfer of organic matter (OM) from land to sea is a key link in the global carbon cycle (Hedges 1992, Smith and Hollibaugh 1993). A major step in defining this link is determining the rates and direction of carbon flux between wetlands and adjacent coastal waters, as these ecosystems can serve as both sources and sinks for carbon (Mitsch and Gosselink 2000). Particulate and dissolved organic matter (POM and DOM) from mangrove wetlands can be an important source of energy and nutrition to heterotrophic communities of surrounding estuarine and marine ecosystems (Odum and Heald 1975). Mangroves provide food, shelter and nursery habitat for a wide assortment of wildlife that spend all or critical periods of their life cycle in these environments (Robertson 1986, Primavera 1998, Ley and McIvor 2002).

Beginning with the outwelling hypothesis in the 1960s, researchers have attempted a range of sampling techniques to identify and quantify sources and sinks of carbon and other nutrients in the estuarine and coastal environment (Twilley 1985, 1988, Lee 1990, Dittmar and Lara 2001a). However, the role and extent that mangroves play in the coastal microparticulate and dissolved carbon budgets is still not clear (Dittmar and Lara 2001a). Results from previous research in the Everglades have shown that the export of DOC to the adjacent ocean may be one of the dominant outputs of material

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from a mangrove wetland, accounting for greater than 80% of total organic carbon (TOC) export in some cases (Furukawa et al. 1997, Machiwa and Hallberg 2002). It has been documented that the extent of tidal export depends on amplitude and frequency of tidal inundation, and may also be related to freshwater inflow, rainfall or seasonal and inter-annual fluctuation in sea level (Wolanski et al. 1980, Twilley 1985, 1995, Davis et al. 2001a, Dittmar and Lara 2001b). Macro-invertebrates can also be an important factor in regulating the magnitude of organic carbon export from mangroves, as evident in Australia (Robertson 1986, Camilleri 1992).

A flume sampling method was developed to evaluate how tidally inundated wetlands process nutrients specifically at the wetland soil-water column interface and has since been utilized in determining both carbon and nutrient fluxes in various wetland systems, including mangroves (Wolaver et al. 1985, Childers and Day 1988, Whiting et al. 1989, Rivera-Monroy et al. 1995, Davis et al. 2001a). The present study utilized this flume method to consider possible short-term variability in fluxes over consecutive days by quantifying organic carbon flux between the wetland soil and inundating water column over multiple replicate tides. Literature on OM export is not consistent about whether seasonal trends are present in OM flux in mangroves (Dittmar and Lara 2001a, Dittmar et al. 2001, Davis et al. 2001a, Sutula 2003). The present study will also quantify seasonal variability related to freshwater inflow to understand the importance of seasonal freshwater inflow patterns in regulating carbon dynamics in mangrove forests of the Florida Coastal Everglades.

Litter, mainly leaves and twigs, produced in the canopy of mangroves represents a significant source of the OM and nutrients available for outwelling to adjacent coastal

waters (Odum and Heald 1972, Twilley 1995, Davis et al. 2003). Leaching of mangrove litterfall is a rapid decomposition process and provides an important source of labile organic material to the water column (Cundell et al. 1979, Benner and Hodson 1985, Robertson 1988, Davis et al. 2003). The efficiency of microbial conversion of the leachable portion of mangrove leaves is 30-36%, making a significant amount of mangrove detritus potentially available to higher trophic levels in the aquatic food web (Benner and Hodson 1985).

While leaf litter is typically the main component of mangrove litterfall (40-95%) (Day et al. 1996, Clough et al. 2000, Twilley and Rivera-Monroy, unpublished data), twigs and branches may also comprise a significant fraction of the total litterfall (Clough et al. 2000) and be an important source of leachable organic material. Approximately one half of the OM of mangrove leaves are leachable water-soluble compounds (tannins and sugars) with the remainder consisting of more slowly degrading plant structural polymers (lignocellulose; Cundell et al. 1979, Benner and Hodson 1985). Mangrove wood has a much higher lignocellulose content (83%) than leaves, rendering it a potentially smaller contributor to the labile DOC pool.

Previous leaching experiments of wetland leaf litter have focused on the change in leaf mass lost, bacterial growth and remaining leaf nutrient content (Chale 1993, Mann and Wetzel 1996). Rapid loss of labile OM from leaf litter in the initial decay phase has been shown due to leaching of soluble organic compounds, with gradual decrease in weight loss due to microbial breakdown thereafter (Valiela et al. 1985, Chale 1993). Both short term (hours-days) and long term (weeks-months) decomposition studies have addressed changes in nutritional content of the leaf litter (Chale 1993, Davis et al. 2003).

However, there is a lack of information on carbon available from different mangrove species and litter types (i.e. leaf, wood, reproductive structures). Further, there are few studies that budget carbon loss associated with this initial phase of decomposition for different mangrove species in a forest.

The use of isotopes has been used to trace the source and fate of mangrove OM in many estuarine environments (Zieman et al. 1984, Dittmar et al. 2001, Jaffe et al. 2001). Typically, mangrove-derived OM has $\delta^{13}C$ values between -27‰ and -32‰, while marine phytoplankton have more enriched $\delta^{13}C$ values between -15‰ and -22‰. C:N ratios have been used as an indicator of nutritional value of organic matter, and a decrease in the C:N ratio from senescent leaves to partially decomposed leaves of Rhizophora mangle has been observed (Newell 1984). Rather than comparing freshness of the litter types with nitrogen analysis, I expected to identify the stable carbon isotope signature of OM leached from several mangrove species to support the hypothesis that the OM export from mangrove wetlands in Shark River, Florida is terrestrially-derived.

From a laboratory litter leaching study, I report the amount DOC leached from leaf and wood litter during the initial 24-hour decay period of three species of mangrove, *Laguncularia racemosa* (white mangrove), *Rhizophora mangle* (red mangrove) and *Avicennia germinans* (black mangrove) and one freshwater sedge, *Cladium jamaicense* to compare differences in available leachable DOC to the mangrove zone of an estuarine environment. The stable carbon isotope ratios of the dry litter are also reported to compare the signature of these OM sources to the $\delta^{13}C$ values of related coastal waters reported in other mangrove studies. These data may be used to construct a portion of the

mangrove forest carbon budget related to the organic carbon available for export from litterfall through the initial decay process.

Few past studies have quantified mangrove-water column interactions directly, and there have been even fewer mangrove carbon exchange studies in the Everglades (Twilley 1985, Davis et al. 2001a, 2001b, Sutula et al. 2003) where landscape-scale hydrologic restoration efforts have begun. Research utilizing *in situ* techniques to quantify carbon fluxes at the mangrove soil-water column interface is needed to solidify our understanding of carbon cycling in these coastal wetlands.

Nature of the Problem

Restoration of the Everglades is mandated by federal and state law. The Federal Settlement Agreement of 1991 and Everglades Forever Act of 1994 established the need to reduce phosphorus in runoff waters and increase flows of freshwater through the Everglades to restore natural hydroperiods. There are many different modeling approaches to assess Everglades hydrology and ecology, and to predict the positive and negative impacts of such a large scale hydrologic restoration (Sklar et al. 2001, Bolster and Saiers 2002).

A result of increased freshwater flow through the Everglades will likely be increased water depth and hydroperiod, which are important environmental controls on vegetation patterns in this low nutrient environment. At the level of the mangrove soil, a change in the flow and the content of source water can alter microbial processes in the soil and thus influence the rate of organic carbon turnover in the soils. Further, soil accretion rates may be reduced as a result of higher freshwater flushing rates and reduced

sediment inputs from the Everglades. This would negatively affect the ability of the mangrove to maintain elevation over the long term. Within the mangrove itself, aboveground and belowground plant biomass and production may be reduced in the short-term in response to less saline conditions. Salinity is also important in regulating plant zonation patterns, and competitive exclusion of the inland extent of mangroves by freshwater plant species may occur under low salinity conditions. This study will provide a basis for understanding the temporal variability and the importance of freshwater flow on organic carbon exchange in mangroves.

Solution and Rationale

To better understand the temporal variability in mangrove carbon dynamics and begin to address how it may be affected by freshwater inputs, this study focused on quantifying the flux of organic carbon between the water column and mangrove soil in a tidally influenced riverine mangrove wetland in Shark River, Florida. There is evidence that net export of DOM reaches the same order of magnitude as litter export in some mangrove areas (Twilley 1985). Therefore, this study expected to identify both the particulate and dissolved fractions of OM import and export. The study area was located in a riverine mangrove forest, which, due to high flushing rates, was expected to be a net source of DOC and TOC to the water column and tidal river for part of the year, in response to intra-annual variations in freshwater inputs and litter production. The study was designed to incorporate sampling periods during the characteristic wet season, dry season and 'Norte' season (an intermediate between wet and dry seasons, characterized by cold fronts moving through the region).

In addition to the field study, a laboratory litter leaching experiment was conducted to determine DOC leaching rates for different litter types of three mangrove species. The DOC leaching rates combined with litterfall data from the study site were used to create a small DOC budget indicating the amount of DOC potentially available for export from the initial 24-hour leaching of mangrove litter. This research is also part of a larger effort seeking to elucidate net ecosystem exchanges of carbon in the mangroves of the Florida Everglades. Findings from this study will contribute to a better understanding of the short-term influence of season and water source (Everglades vs. Gulf of Mexico) on mangrove carbon cycling along the Florida Coast.

METHODS

Site Description

Everglades National Park is located in southern Florida and comprises 610,483 hectares, of which 189,644 hectares are mangrove forest (Lewis et al. 1985). Average annual rainfall in the region is 138 cm, with distinct wet (approximately 60% average annual rainfall from June to September) and dry (approximately 25% average annual rainfall from November to April) seasons (Figure 1) (Duever et al. 1994). Shark River is a mangrove dominated tidal river along the southwest coast of Everglades National Park and is one of the largest estuaries in South Florida. Discharge of freshwater from Shark River Slough to the estuary follows patterns of seasonal and inter-annual rainfall (Chen and Twilley 1999). Tides in Shark River are predominantly diurnal with a mean amplitude of 1.1 m.

The flume study was conducted in a riverine mangrove forest along a tidal creek connected to Shark River (Figure 2), approximately 1.8 km inland from the mouth of the estuary (25°21.852 N, 81°04.667 W). The width of the tidal creek at the site of the flume is approximately 2 m. The surrounding mangrove forest is tidally inundated and dominated by the white, red and black mangroves.

DOC Sampling Techniques

This study was designed to characterize temporal variability in DOC concentrations and flux from the coastal Everglades mangroves. Flux measurements were made during 2003 covering three seasons within a Shark River mangrove forest: dry

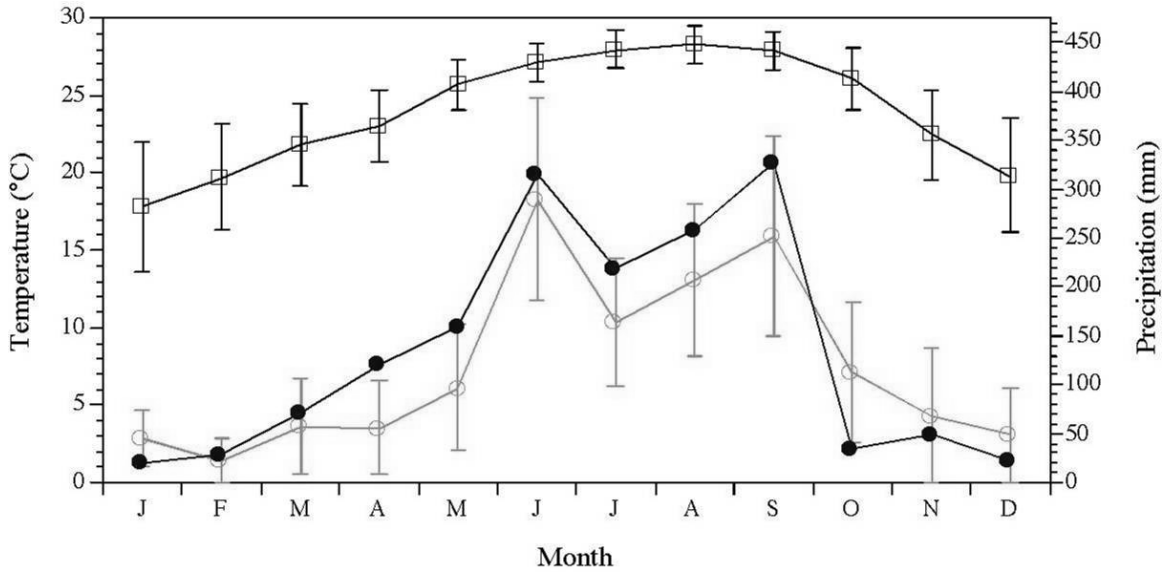

Figure 1. Seasonal pattern of temperature and precipitation in Southwest Florida from 1994-2003. Long-term pattern of temperature (○) and precipitation (□) represented as mean (±SD) values for 1994-2003. Precipitation for 2003 alone represented as monthly values (●). Data collected by United States Geological Survey.

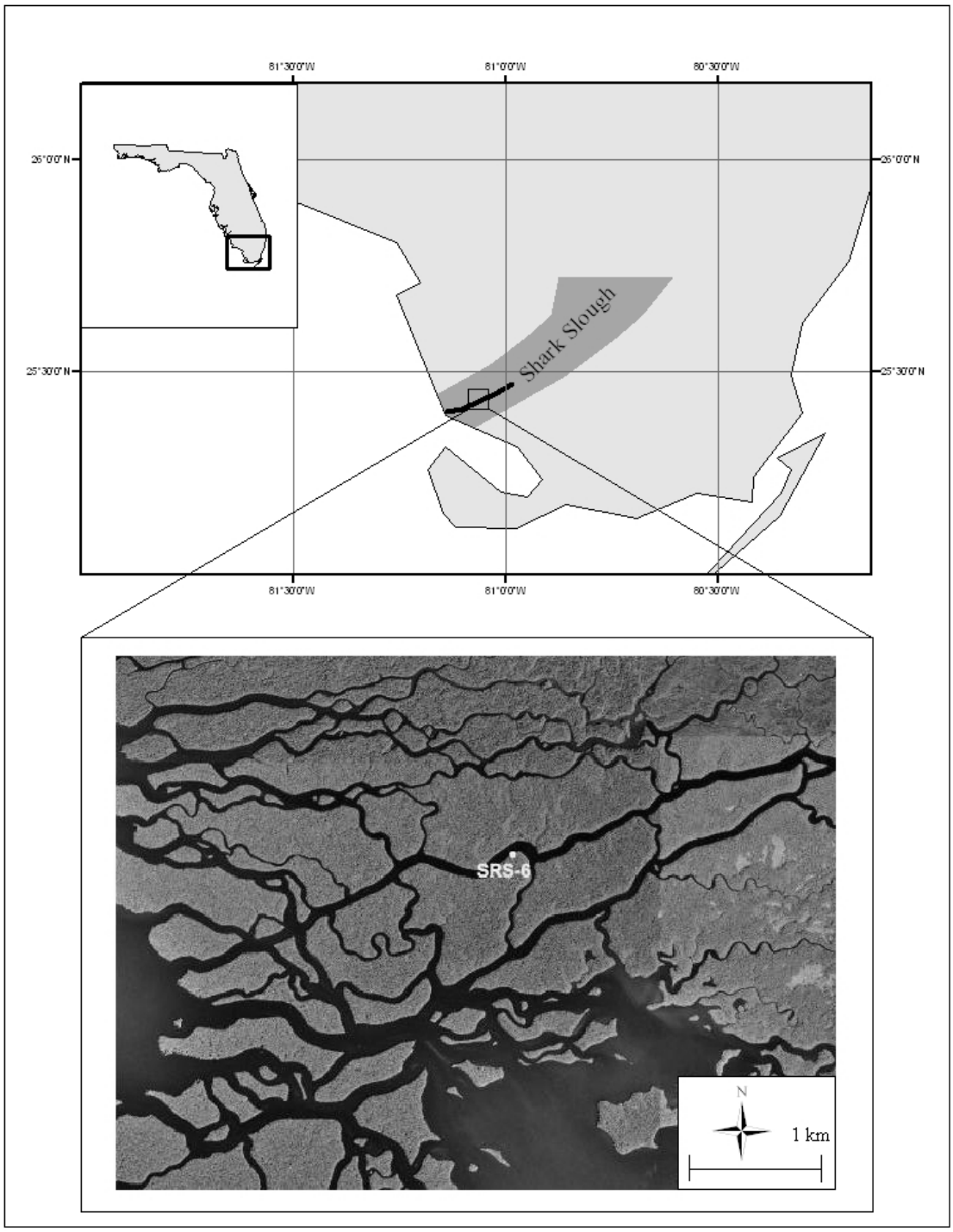

Figure 2. Map of South Florida and the experimental flume study site (SRS-6) along Shark River within Everglades National Park.

(May), wet (October) and the transitional 'Norte' season (December). Exchange patterns over multiple tidal cycles (4-6 tides per sampling), were examined during each season.

A flume was used to measure organic carbon exchange between the mangrove soil and inundating water column. The experimental flume was located approximately 30 m inland from Shark River, in a fringe mangrove along a small tidal creek (2.5 m width and 1 m depth) draining the area. The flume was open to flow at both ends and measured approximately 2 m wide and 12.5 m in length, extending from the tidal creek into the basin mangrove forest (Figure 3). The flume walls were positioned perpendicular to the tidal creek and parallel to the direction of flow of the flooding tidal water, so as to mimic natural flooding patterns in the enclosed area of wetland. Panels on the flumes, consisting of clear, corrugated fiberglass, were removed after each sampling to prevent long-term panel effects such as shading, edge scouring, and detritus accumulation (Childers and Day 1988).

During each sampling period, an ISCO autosampler was placed at each end of the flume and programmed to collect a 1-liter water sample every 30 minutes from a single point inside the flume. Samples were collected simultaneously from each end of the flume during replicate flood and ebb half tides. Samples were retrieved every 12 hours, packed in ice and transported to the field laboratory for processing.

The temperature, salinity, pH, conductivity and dissolved oxygen concentration of the tidal creek water were also recorded simultaneously using a Hydrolab mini-sonde. This study was conducted at a monitoring station for the Florida Coastal Everglades Long Term Ecological Research (FCE-LTER) program where continuous data on surface water level, salinity and concentrations of total nitrogen and total phosphorus are collected.

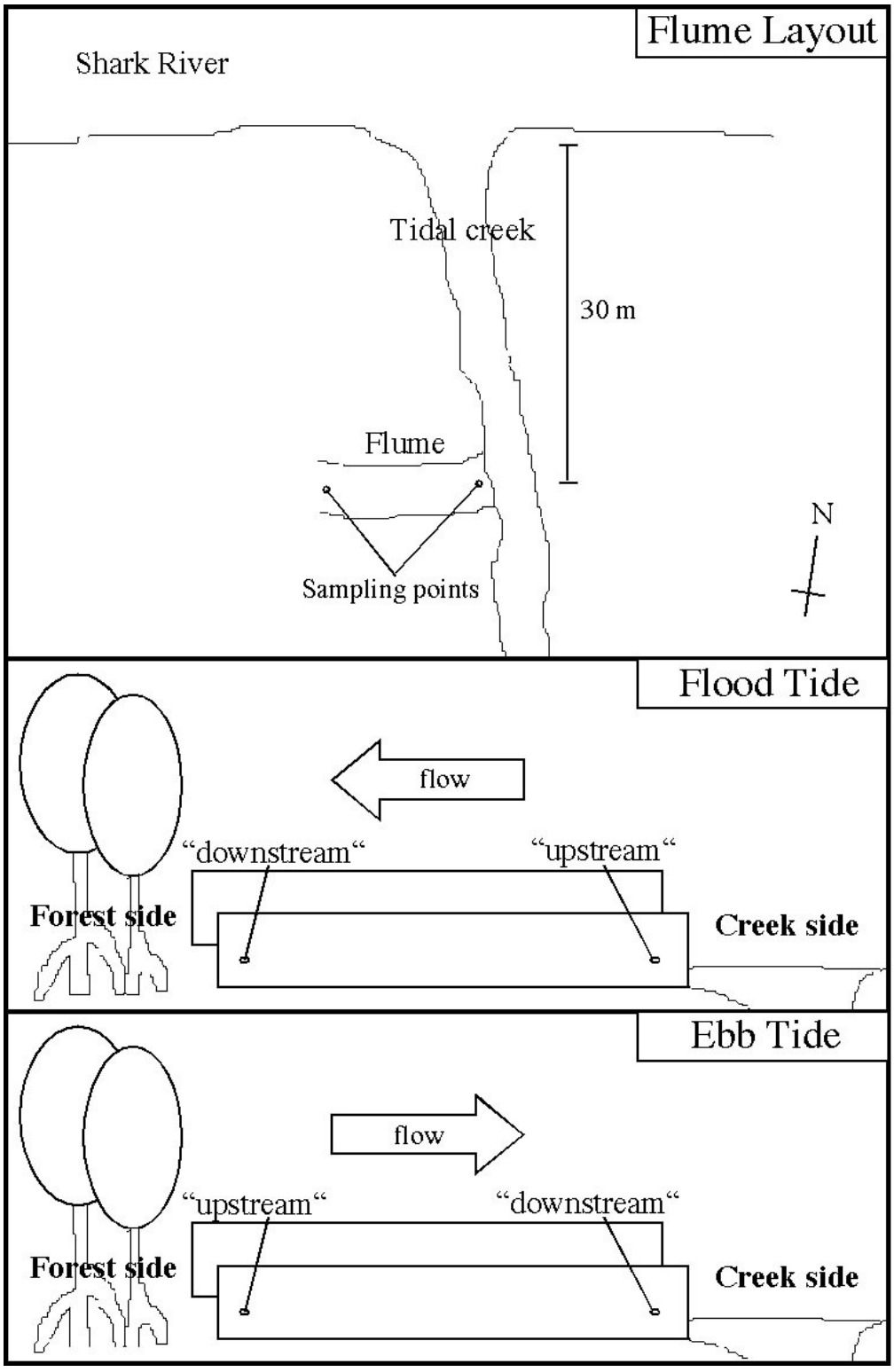

Figure 3. Map of experimental flume layout including Shark River and sampling points. Flood and ebb tide diagrams illustrate the change in "upstream/downstream" designation of the two flume sampling points.

Microtopography within the flume was surveyed in August 2003 to build a detailed map of elevation, which was used in estimating volumetric changes in the flume.

DOC Laboratory Analyses

DOC samples were filtered through pre-rinsed (triplicate 5 mL rinses with de-ionized water), pre-combusted (4 hours at 500°C) and pre-weighed 47 mm Whatman GF/F papers. Filtration was performed within 24 hours of collection and both filtered and unfiltered samples were refrigerated at 4 °C in 125 ml bottles. Particulate matter trapped on the filter was dried at 70°C for 24 hours and weighed for total suspended sediment (TSS) calculation, then combusted (500°C for 4 h) to determine losses on ignition.

DOC and TOC concentrations in filtered and unfiltered samples were assayed by high temperature catalytic oxidation (HTCO) and infrared detection using a Shimadzu TOC-5000. Carbon concentrations were determined against potassium hydrogen phthalate standards. Samples were measured in triplicate with a fixed c.v. of 2%; otherwise, further replicates were automatically carried out by the instrument. Duplicate samples were analyzed periodically to check for reproducibility of results and to evaluate the precision of measurements. Fluxes of organic carbon were calculated from the measurements of water level and concentration change within the flume following the methods of Childers and Day (1988) and later modified by Rivera-Monroy et al. (1995).

Flux Calculations and Statistical Analyses

I used formulas described in Childers and Day (1988) to calculate fluxes of organic carbon (Appendix A). One formula was modified by Rivera-Monroy et al. (1995) to obtain net areal fluxes of regularly flooded fringe mangroves when a constant area of the experimental flume was inundated. I also utilized this equation and calculated net areal fluxes for half tides (flood and ebb) only when both ends of the flume were inundated (Equation 1). Net fluxes were obtained by adding flood and ebb fluxes for each tide.

$$\text{Net areal flux } (\text{g m}^{-2}\ \text{h}^{-1}) = \frac{\text{total flux}_{\text{upstream}} - \text{total flux}_{\text{downstream}}}{\text{flume area x total time}} \quad (1)$$

Using a hypsometric approach, I inferred fluxes of water from changes in water level collected at 30-minute intervals during several whole-tides. Direct measurements of water level within the flume over the course of one complete tidal inundation were correlated with the continuous water level recorder data supplied by the FCE-LTER station at the bank of Shark River (SRS-6). This correlation was used to calculate water level within the flume for all additional sampling periods. To best correlate water level in a system with asymmetrical tides, I developed separate correlation curves for flood- and ebb-tides (adjusted R^2 values of 0.999 and 0.997 for ebb- and flood-tide correlations, respectively).

Paired t-tests between upstream and downstream DOC concentrations over each half tide were used to determine if fluxes of organic carbon within the flume were

significant ($p<0.05$). No difference in concentration between upstream and downstream pairs was interpreted as no net flux over a given half-tide (net area flux = 0 μmoles C $m^{-2}h^{-1}$). For example, higher concentrations during flood tide at the streamside end (upstream) indicated a net uptake of carbon by the wetland, while lower concentrations at the streamside end indicated a nutrient release. Net areal fluxes were calculated only when water was present at both ends of the flume and a significant difference was observed.

Seasonal differences in temperature, salinity, conductivity, pH, dissolved oxygen and organic carbon concentration were analyzed using a one-way ANOVA and LSD post-hoc analysis to test between sampling seasons ($p<0.05$). Seasonal differences in TSS concentrations were analyzed using a one-way ANOVA and Dunnett's T3 post-hoc analysis ($p<0.05$).

Mangrove Litter Analysis Techniques

Senescent leaves and wood litter from each of the white, red and black mangroves were collected from the surrounding riverine fringe mangrove forest along Shark River. One freshwater sedge, *Cladium jamaicense*, was collected approximately two kilometers upstream as an upstream OM source comparison. Three replicate samples of each litter type were refrigerated separately in plastic bags at 4°C for one week before analysis. Litter was dried at 60 °C for 72 h and 3.000 g of each sample was weighed for incubation. Each litter sample was incubated in 150 mL of deionized water in 250 mL clear glass bottles for a 24-hour period.

Leachate samples collected from each bottle were filtered through Whatman GF/F glass fiber filters and divided into two separate 60 mL HDPE sample containers (one each for DOC content and stable carbon isotope analysis). The samples to be used for isotope analysis were acidified, each with 1 mL 10% HCl, and both sets of water samples were then refrigerated until analyzed. DOC analysis was performed using a Shimadzu TOC-5000 total organic carbon analyzer. Isotope analysis was performed using an elemental analyzer for dry tissue samples and a new method by Cifuentes et al. (*in prep*.) with a TOC analyzer interfaced with an IRMS analyzer in order to determine $\delta^{13}C$ of the organic carbon in liquid samples.

Using SPSS, single factor analyses of variance were used to determine significant difference in DOC leachate content between litter type and species ($p<0.05$). Tree species composition and average monthly litterfall estimates (January 2001 to June 2003) for a Shark River mangrove forest were used to calculate the proportion of mangrove species present and litterfall composition at the study site (Twilley and Rivera-Monroy, unpublished data). I estimated the amount of DOC available from initial (24 h) leaching of mangrove litter at the soil-water column interface using a summation formula (Equation 2; Appendix A). This formula combined the DOC leaching rates obtained during the leaching experiment with actual litterfall composition from the study site.

$$\text{DOC (g m}^{-2}\text{ yr}^{-1}) = \sum (LL_x * R_{l,x}) + (WL_x * R_{w,x}) \quad (2)$$

where LL is leaf litter produced (g m^{-2} yr^{-1}), WL is wood litter produced (g m^{-2} yr^{-1}) and R is the DOC leaching potential of leaf or wood litter (g DOC/g dry tissue) of a particular species, x.

RESULTS

DOC Concentrations and Physical Parameters

Water temperature in the flume ranged from 17.9 to 30.6 °C and was significantly different between all sampling seasons (ANOVA, $p<0.05$). Highest temperatures occurred in May, followed by October and then December [Figure 4(a)]. Salinity in the flume ranged overall from 6.4 to 29.8 ppt. Lowest salinities were observed in the wet season when freshwater flow was greatest (October), followed by December, and highest salinities in the dry season (May) [Figure 4(b)]. A tidal salinity pattern of increased salinities during flood tide and decreased salinities during ebb tide was observed for all tides sampled. The percent saturation of dissolved oxygen in the water column was significantly highest during May and lowest during October (ANOVA, $p<0.05$). Dissolved oxygen content of the inundating water column also followed a tidal pattern of decreasing % saturation with increasing duration of inundation, indicating oxygen depletion of the water column due to respiration. The pH of the inundating water column was between 7.3 and 7.6 during all sampling seasons.

Mean concentration of both TSS and DOC were significantly different between sampling seasons (ANOVA, $p<0.05$). TSS concentrations ranged from 1 to 192 mg l^{-1}. Significantly higher mean TSS concentrations occurred in May (112 mg l^{-1}), while concentrations were very low in both October (22 mg l^{-1}) and December (24 mg l^{-1}) [Figure 4(c)]. DOC concentrations were significantly different between seasons (ANOVA, $p<0.05$) and ranged from 1.7 to 17.9 mg l^{-1}. Overall, DOC was highest in May and lowest in October [Figure 4(d)]. DOC concentrations during ebb tide were

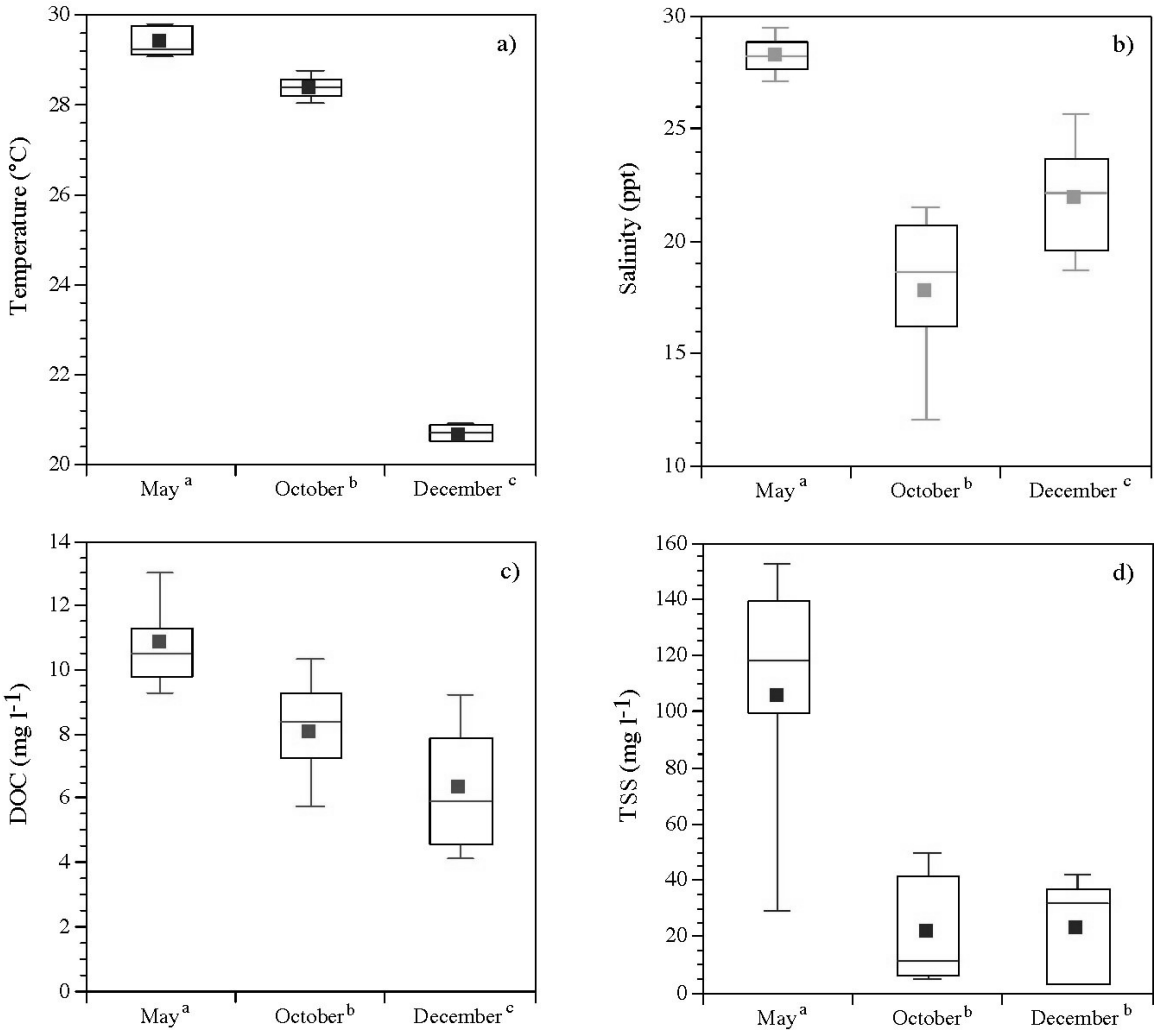

Figure 4. Seasonal patterns of (a) temperature, (b) salinity, (c) DOC concentration and (d) TSS concentration of water during tidal inundation of the flume at the study site. Sampling periods followed by different letters were significantly different from one another (ANOVA, $p<0.05$).

higher than flood tide during May, while ebb tide concentrations were lower than flood tide during October (Figure 5). During December, average DOC concentrations were similar for both ebb and flood tide, though highly variable between the flood tides sampled. Significant changes in DOC concentration within the flume were observed for one-half of the tides sampled.

Fluxes

DOC exchange occurred both vertically between the wetland soil and inundating water column and horizontally between the tidal creek, fringe and basin mangrove forests. Total exchanges of DOC were much greater between the tidal creek and fringe forest than between the fringe and basin forests (Figure 6). There was a net import of DOC to the fringe forest from both the basin forest and the tidal creek during the dry season. The highest significant import rate of DOC (0.3227 g m^{-2} h^{-1}) occurred in the dry season. The average import rate of DOC to the mangrove soil during the dry season was 0.0908 g m^{-2} h^{-1}, based on significant fluxes during the sampling period. On average, 86% of the DOC imported to the fringe mangrove occurred during flood tide. There was a net export of DOC from the fringe forest to both the tidal creek and basin forest during the wet season. The highest export rate of DOC to the inundating water column (0.5784 g m^{-2} h^{-1}) occurred in the wet season. The average export rate of DOC to the inundating water column during the wet season was 0.0606 g m^{-2} h^{-1}, based on significant fluxes during the sampling period. On average, 65% of the DOC exported from the fringe mangrove occurred during ebb tide. Difficulty in the field due to equipment malfunction and low tidal inundation at the site

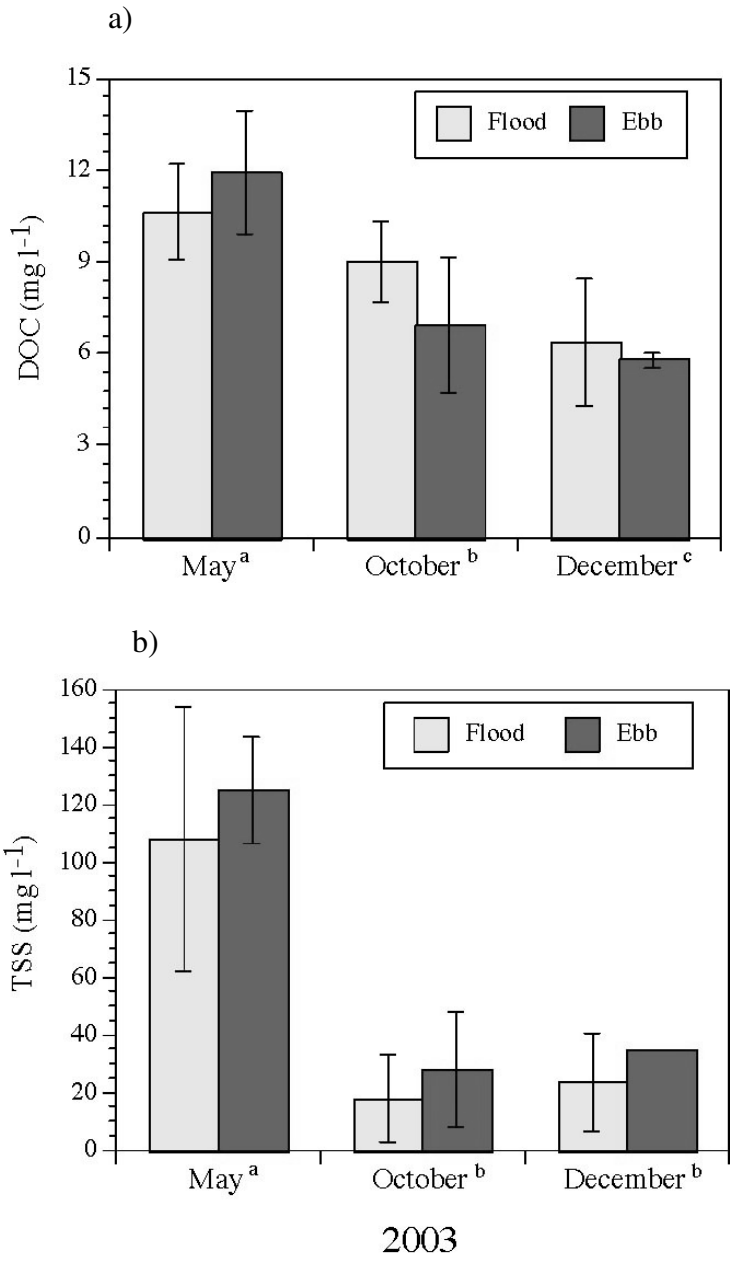

Figure 5. Seasonal flood- vs. ebb-tide mean (± SD) concentrations of (a) TSS and (b) DOC. Sampling periods followed by different letters are significantly different (ANOVA, $p<0.05$).

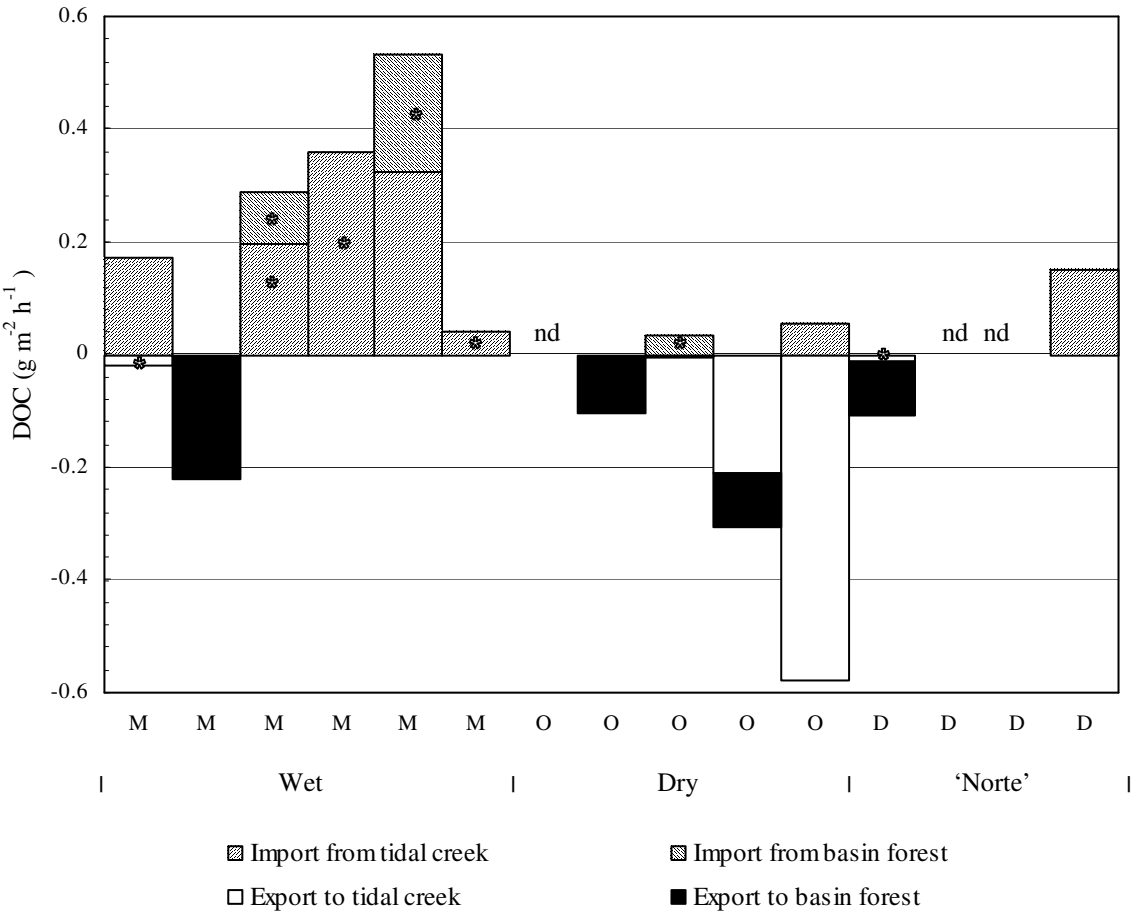

Figure 6. Net fluxes of whole tides for DOC in the experimental flume. Positive flux is import to the mangrove soil; negative flux is export to the inundating water column. * Flux not significantly different ($p>0.05$). nd, No data.

only allowed for the calculation of two tidal fluxes in December. These tides indicate both import and export of DOC with an average DOC import rate of 0.0265 g m^{-2} h^{-1} during the 'Norte' season.

Twelve and 60% of the paired t-tests performed on DOC content for the half-tides were significantly different from zero ($p<0.05$). Three tides during the 'Norte' season did not have both upstream and downstream paired samples. Therefore, I could not determine fluxes for these tides. To calculate an average yearly DOC flux, I used the average DOC flux rate of significant tides (-0.0403 g m^{-2} h^{-1}), the average tidal inundation period (2 h) and the estimated number of tides at the site during 2003 (696 tides). The result of this was a net annual export of DOC from the fringe mangrove to both the tidal creek and basin mangrove forest (-56 g DOC m^{-2} yr^{-1}).

Mangrove Litterfall Leaching Rates

There was a significant difference in the mass of carbon leached over a 24-hour period between mangrove leaves vs. twigs, and all litter types lost a significant amount of mass (ANOVA, $p < 0.05$). Mangrove leaves of all three species leached significantly more carbon than wood litter (ANOVA, $p<0.001$). A comparison of leaching between species shows that the black and red mangroves leached the greatest mass of DOC per gram dry mass, followed by the white mangrove and the least by the sawgrass (ANOVA, $p<0.05$; Figure 7).

During this initial 24-hour decay phase, leaf litter leached on average 0.0502 g DOC/g dry tissue. Wood litter and sawgrass leached less than 15% of this amount (0.0073 and 0.0064 g DOC/g dry tissue, respectively). This translates to 5% of the dry

mass of leaves and less than 1% of the dry mass of wood litter and the sawgrass being lost as DOC in the first 24 hours of litter decomposition.

Stable carbon isotope ratios of the mangrove dry litter tissue samples ranged from -26.08 to -28.1 (Table 1), which are consistent with other $\delta^{13}C$ values reported for mangrove carbon (Lin and Sternberg 1992, Dittmar et al. 2001). The sawgrass had a similar stable carbon isotope ratio (-28.07). Distinction between species and litter type could therefore not be made based solely on the $\delta^{13}C$ data.

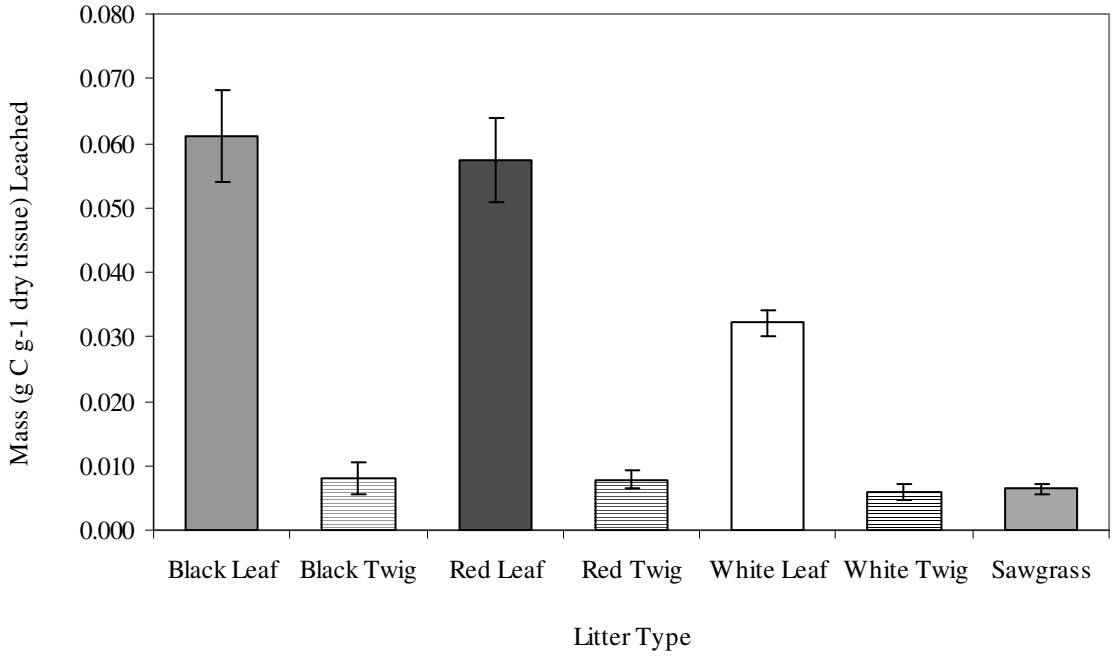

Figure 7. Comparison of DOC leached by different litter types in the 24-hour leaching experiment.

Table 1. $\delta^{13}C$ values and amount of DOC leached over a 24-hour period for three mangrove species and one freshwater marsh sedge.

Litter Type	Dry Litter $\delta^{13}C$
Black Leaf	-26.5
Red Leaf	-27.19
White Leaf	-28.1
Black Twig	-26.4
Red Twig	-26.08
White Twig	-27.32
Sawgrass	-28.07

Mean (SD) mass of leached DOC. Letters represent groups of significantly different leached DOC mass (ANOVA, $p<0.001$).

CONCLUSION

DOC Flux

The magnitude and direction of material fluxes in estuarine systems involve processes occurring at different spatial and temporal scales. Small scale processes occurring directly at wetland exchange interfaces (i.e. water-soil, water-atmosphere or soil-atmosphere) are influenced by short-term variability in environmental conditions (i.e. material concentration, wind and rain events, duration of inundation, flushing time). Larger spatial scales broadening in area from tidal creeks draining these exchange interfaces to the landscape-scale of the entire estuary increasingly incorporate more general processes of estuarine mixing and long-term climate patterns in controlling carbon and nutrient exchange.

Water flux estimates and paired upstream/downstream measurements of dissolved organic carbon concentration were used to quantify the flux of DOC between the mangrove soil and inundating water column of a fringe riverine mangrove wetland. Sampling over repeated tides within a season allowed for the examination of the short-term variability in flux that occurs in the natural environment. I measured vertical flux and found an indication of DOC import to the mangrove soil during the dry season (May), export to the inundating water column during the wet season (October) and import to the mangrove soil during the 'Norte' season (December) in 2003.

Particulate organic carbon (POC) export can represent a significant amount of the organic matter leaving mangrove systems, though it most often varies with season. Export of POC measured in an Australian riverine mangrove forest was 420 g C m^{-2} yr^{-1}

(Boto and Bunt 1981) whereas studies in Florida have measured 64 g C m^{-2} yr^{-1} (Twilley 1985) and 186 g C m^{-2} yr^{-1} (Heald 1971). For all sampling periods in this study, DOC accounted for >95% of the TOC in the water column. However, nets were not used in this study to capture leaf-size particulate matter, which may make up a significant portion of export from mangrove forests (Boto and Bunt 1981, Twilley 1985). Several other mangrove studies have also measured a high DOC fraction of TOC in the water column. Twilley (1985) estimated that up to 75% of all carbon exchanged in a basin mangrove forest in Florida was DOC, Davis et al. (2001b) estimated >90% of the TOC in mangrove island enclosures was DOC and Sutula et al. (2003) found that in Taylor River, Florida approximately 98% of TOC was in DOC form.

Due to the sampling technique and asymmetrical tidal patterns, water samples could only be collected in the mangrove flume during high tide, and only during those high tides when the mangrove forest was inundated. Samples at the beginning and end of a high tide may have been influenced by the resuspension of particulates produced by stronger currents flowing across the soil surface. However, no significant difference in organic carbon content was detected between filtered and unfiltered samples, indicating very low POC in the water column and little influence of particulate resuspension on the water samples.

Concentrations of DOC in this fringe riverine mangrove system were slightly higher than reported values for other mangrove systems (Table 2). Actual DOC concentrations were highest during the dry season, possibly due to the occurrence of peak litterfall production in May, but freshwater inflow and tidal amplitude were at their lowest. Tidal amplitude and freshwater inflow to the system play a factor in regulating

Table 2. Comparison of DOC and TOC concentrations of various wetland studies.

Location	Wetland Type	Source	TOC	DOC
Florida	Riverine mangrove	This study		1.7-17.9
Florida	Freshwater & mangrove	Sutula et al. (2003)		8.4-19.2
Zanzibar	Fringe mangrove	Machiwa and Hallberg (2002)		0.78-1.28
Florida	Mangrove creek	Davis et al. (2001a)		8.4-21.6
Florida	Dwarf mangrove	Davis et al. (2001b)	10.8-18	8.4-18
Brazil	Riverine mangrove	Dittmar and Lara (2001)	7.20	4.32
Australia	Fringe mangrove	Furukawa et al. (1997)	2.67	2.21
Bahamas	Fringe mangrove	Moran et al. (1991)		2.3
Louisiana	Freshwater marsh	Childers and Day (1988)		10.8-29.1
Louisiana	Brackish marsh	Childers and Day (1988)		6.8-48.7
Louisiana	Saltmarsh	Childers and Day (1988)		2.5-12.6
Australia	Fringe mangrove	Boto and Wellington (1988)		1-2
Florida	Basin mangrove	Twilley (1985)	9.4-21	

DOC and TOC concentrations reported in mg l^{-1}.

DOC flux from wetland soils by influencing the amount of time the soil has to interact with the inundating water column and by regulating the amount of water discharged through the interface. Increased freshwater input has been shown to increase DOC flux from estuaries to adjacent coastal waters, sometimes by as much as 300% (Miller 1999). The greater the tidal amplitude and freshwater inflow, the longer the wetland is submerged and the more water flows through the system. Vertical flux data in this study indicate that the highest export of DOC from the wetland soil to the inundating water column occurred during the wet season. Tidal amplitude and freshwater inflow are correlated in this study, as tides reached a minimum amplitude of 2.3 feet during the dry season, a maximum of 2.9 feet during the wet season and 2.6 feet during the 'Norte' season. These flux results indicate DOC flux from the wetland is controlled to a greater extent by freshwater discharge rather than DOC concentration.

Flux estimates from the riverine fringe mangrove forest in this study were similar in magnitude to findings of previous mangrove carbon flux studies (Table 3). Seasonal fluxes indicated net import of DOC to the wetland soil during the dry season and export of DOC to the inundating water column during the wet season, with an overall net DOC export of 56 g DOC m^{-2} yr^{-1} from the mangrove wetland to the adjacent tidal creek. A flux study in a fringe mangrove forest in Australia using a 'eulerian' approach was unable to detect net flux of dissolved materials, including DOC (Boto and Wellington 1988). Previous estimates of total carbon export from mangroves range from 2 to 400 g C m^{-2} yr^{-1} with an average of about 200 g C m^{-2} yr^{-1}, while salt marshes typically export about half this amount (Twilley 1998).

Table 3. Estimates of net annual TOC and DOC flux from mangrove wetlands.

Location	TOC	DOC	Method	Source
Florida		-56	mangrove flume	This Study
Florida	-7.1		mangrove creek	Sutula et al. 2003
Florida		3.04	mangrove creek flume	Davis et al. 2001a
Florida		- 381	mangrove enclosures	Davis et al. 2001b
Florida	-64		basin mangrove	Twilley 1985
Australia		7.3	mangrove channel	Boto & Wellington 1988
World Average	-210		mangroves (review)	Twilley 1998

TOC and DOC flux reported in g C m^{-2} yr^{-1}.

Generally, terrestrially derived DOM undergoes conservative mixing down the estuarine gradient, forming an inverse linear relationship between salinity and concentration. A previous study by Jaffe et al. (2004) indicated that fluxes of DOC are controlled to a great extent by discharge rather than concentration, indicating lower DOC concentration with increasing freshwater input. The wet and 'Norte' season data indicate an inverse linear relationship of salinity vs. DOC and support previous findings of conservative mixing of DOC within the Shark River estuary (Figure 8; Jaffe et al. 2004). Consistent high salinities (25-30 ppt) due to depleted freshwater input to Shark River during May coupled with high variation in DOC concentration indicate similar import and export processes occurring at the wetland soil-water column interface even during the dry season. Riverine mangrove forests generally have higher flushing than fringe, basin and shrub forests (Lugo and Snedaker 1974), which may help explain why flux results from this study are higher than in other mangrove systems.

Mangrove Litterfall

The production of mangrove litter and its consequent degradation and consumption in the coastal environment is considered to be a major pathway of energy transfer through mangrove systems (Odum and Heald 1975). Main sources of DOM to the southwest coastal Everglades are from freshwater marsh plant biomass, mangrove forests and marine organisms (Jaffe et al. 2004).

The magnitude of litterfall in this riverine mangrove forest (12640 kg ha^{-1} yr^{-1}) is consistent with findings in other riverine mangrove forests, and higher than reported for basin and fringe mangrove forests (Lugo et al. 1988, Day et al. 1996). Litterfall

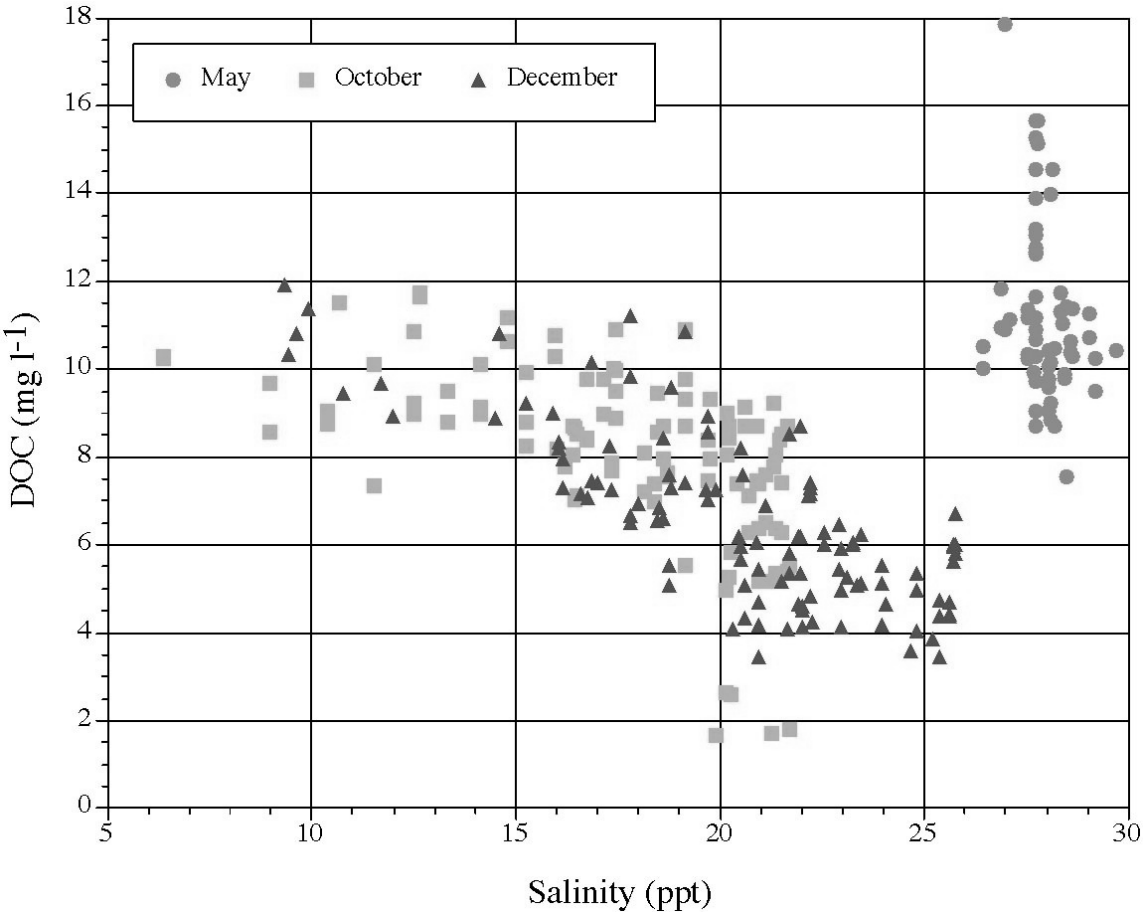

Figure 8. Salinity vs. DOC concentration plot of water samples during study sampling periods.

composition varies greatly throughout the year, with leaf litterfall representing 40-94% and wood litterfall ranging from 1-33% of the total litterfall (Twilley and Rivera-Monroy, unpublished data). Net primary productivity of mangrove forests is generally high compared to upland forests of the same latitude (Twilley et al. 1992, Saenger and Snedaker 1993). *Laguncularia racemosa* (1063 trees ha^{-1}) and *Rhizophora mangle* (900 trees ha^{-1}) are the dominant mangrove species present at the study site, with *Avicennia germinans* interspersed (125 trees ha^{-1}) (Twilley and Rivera-Monroy, unpublished data). Based on these tree densities, *L. racemosa* (51%) and *R. mangle* (43%) contribute the highest amount of litterfall available for leaching. However, *R. mangle* leaves leach significantly more DOC than *L. racemosa* and therefore provide 55% of the DOC potentially leached into the water column during the initial decay phase while *L. racemosa* provides only 37%. Due to higher litterfall and initial DOC leaching rates, leaf litter represents a much greater source of leachable DOC than wood material from this riverine mangrove forest. Comparisons made in a deciduous forest also found that fresh leaf litter is a more important source of DOC to the forest floor than labile substrates (glucose and cellulose), forest floor materials or wood litter (Park et al. 2002). The mangrove leaf litter was also a more significant source of labile DOC than the marsh grass *C. jamaicense*, which leached DOC in an amount similar to mangrove wood litter.

Litterfall studies in both mangrove and upland tropical forests have suggested that environmental conditions including low tides, lack of precipitation and high evapotranspiration due to high temperature may promote leaf senescence and higher litterfall rates during dry seasons (Duke et al. 1981, Day et al. 1996, Wright and Cornejo 1990). This higher available litter fall may lead to greater leaching and in turn cause

higher DOC concentrations of the inundating water column during the dry season. However, there is indication that DOC is imported to the mangrove soil during this period. It is possible that this imported DOC is flushed out of the soil during the wet season or that mangrove uptake from the soil serve to control the import of DOC to the soil during periods of high concentration.

Using tree densities combined with average monthly leaf and wood litterfall data, the total amount of DOC potentially leached during initial decay at the soil-water column interface is 450 kg DOC ha^{-1} yr^{-1} (Table 4). This amount of DOC is around 4% of the dry weight of total litterfall, and assumes no significant grazing by herbivores. However, this excludes litterfall of reproductive structures, which have the potential to leach additional DOC. Based on a net annual export of 56 g DOC m^{-2} yr^{-1}, the initial 24-hour litterfall leaching phase could provide 43% of the DOC exported from the forest.

In addition to higher litterfall rates, riverine mangrove forests generally have a significantly higher inundation frequency and duration, leading to greater in situ decomposition than basin and fringe mangrove forests. This high turnover and export of OM leads to more extensive energy flow pathways to surrounding coastal communities (Twilley 1985, Lugo et al. 1988). This study provided an interesting comparison of leaching rates of litterfall between species and litter types in a riverine mangrove forest. Combining litterfall rate, composition and a leaching experiment yielded quantitative information on the extent to which the initial decay phase of litterfall may provide the source of DOC measured as export from this system.

Table 4. Litterfall estimates and DOC available from the initial 24-hour leaching of litter from three mangrove species in South Florida.

Mangrove	Leaf litter ($g\ m^{-2}\ yr^{-1}$) *	Wood litter ($g\ m^{-2}\ yr^{-1}$) *	DOC (leaf + wood) ($g\ m^{-2}\ yr^{-1}$)	DOC (leaf + wood) ($kg\ ha^{-1}\ yr^{-1}$)
L. racemosa	507.6	35.8	16.50	165.0
R. mangle	429.7	30.3	24.86	248.6
A. germinans	59.7	4.2	3.68	36.8
Total	997	70.3	45.04	450.4

* Twilley and Rivera-Monroy, unpublished data.

Overall Conclusion

The present study documents the ability to determine carbon flux at the wetland soil-water column interface using a flume and provides support to the argument that productive, riverine mangrove forests are sources of DOC to surrounding coastal waters. The flux of DOC at the mangrove soil-water column interface is seasonal, based on rainfall and freshwater inflow to the system. There is short-term variation in organic carbon flux, with both import and export of DOC within seasons. Overall, however, there is a trend of import of DOC to the mangrove soil during the dry season and export to the inundating water column during the wet season. Seasonal fluxes of DOC were used in calculating a net annual export of 56 g DOC m^{-2} yr^{-1} at the mangrove soil-water column interface. Import of DOC to the mangrove during the dry season and export during the wet season indicates that freshwater inflow has a strong influence on the direction of organic carbon flux to this mangrove forest. Periods of rainfall and increased freshwater inflow facilitate export of DOC at the soil-water column interface. It is unclear, however, whether atmospheric carbon fluxes mimic these patterns. It is also unclear whether an increase in freshwater flow to the Everglades would affect DOC export, or whether the mangrove forests would suffer from inability to accumulate peat at a rate comparable to rising sea level.

Based on 24-hour litterfall leaching rates, initial leaching of mangrove leaf and wood litter may provide 43% of the DOC exported from the forest. Due to both higher litter fall rates and higher DOC leaching rates, mangrove leaf litter is a greater immediate source of this DOC to the mangrove environment than mangrove wood litter or freshwater marsh sedge. Upstream, however, freshwater marsh sedge is the dominant

vegetation and may represent the significant source of DOM in the freshwater zone of the Everglades. Different mangrove species leach differing amounts of DOC, and vegetation species composition determines the ultimate potential amount of DOC available for leaching to a system.

This study only addressed a one-year period and does not have the power to identify long-term trends in organic carbon flux from this system. Ongoing study would help determine the effect of long-term hydrologic influences (drought or mandated increases in freshwater flow) on carbon cycling in mangroves. Combining the quantitative flux data from the mangrove soil-water column interface with atmospheric flux data will allow a more accurate depiction of the carbon budget in mangrove forests.

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APPENDIX A

Calculations

1. Dissolved Organic Carbon Flux

Dissolved organic carbon flux calculations in this study were based on volumetric flux calculations from Childers and Day (1988) and Rivera-Monroy et al. (1995).
Note upstream/downstream designation of flume samples.
Flood tide: upstream = creek side of flume; downstream = forest side of flume
Ebb tide: upstream = forest side of flume; downstream = creek side of flume

Steps 1.1 through 1.8 were calculated in order using Microsoft Excel.

1.1 Water level correlations from water level at LTER water level recorder
A. Flume water level (m) (flood tide) = $-40.822386 + 0.005262x^2 + 0.00000475831922x^3$
† Adjusted $R^2 = 0.997$
B. Flume water level (m) (ebb tide) = $-79.788354 + 1.022432x + 0.00000436898977x^3$
† Adjusted $R^2 = 0.999$

1.2 Flume volume (m^3) = flume water level * flume $area_{x,y,z}$ (m^2)

1.3 Instantaneous volume flux ($m^3\ s^{-1}$) = $dV/dt = (V_t - V_{t-1})/t$
* *Calculated for both upstream and downstream ends of the flume.*
** *Timestep (t) for this study was 1800s.*
*** *An increase in volume in the flume is a positive volume flux.*

1.4 Instantaneous DOC Flux ($g\ s^{-1}$) = dDOC/dt = dV/dt * [DOC]
* *Calculated for both upstream and downstream ends of the flume.*

1.5 Incremental DOC (g) = average instantaneous DOC flux * t
= [(instantaneous $flux_t$ + instantaneous $flux_{t-1}$)/2] * t
* *Calculated for both upstream and downstream ends of the flume.*
** *Timestep (t) for this study was 1800s.*

1.6 Total Flux (g) of DOC for entire half-tide
A. Total Flux (g) (flood tide) = Σ Incremental DOC Flux
* *Calculated for both upstream and downstream ends of the flume.*
B. Total Flux (g) (ebb tide) = Σ Incremental DOC Flux
* *Calculated for both upstream and downstream ends of the flume.*

1.7 Net Flux (g h^{-1}) of DOC
A. Net Flux (g h^{-1}) (flood tide)
= (Σ Incremental DOC $Flux_{upstream}$ - Σ Incremental DOC $Flux_{downstream}$)/t (h)
B. Net Flux (g h^{-1}) (ebb tide)
= (Σ Incremental DOC $Flux_{upstream}$ - Σ Incremental DOC $Flux_{downstream}$)/t (h)

$$\text{1.8 Net area flux (g } m^{-2} h^{-1}) = \frac{\text{total flux}_{upstream} - \text{total flux}_{downstream}}{\text{flume area x total time}} \quad (1)$$

2. DOC Leached from Mangrove Litter During Initial 24-hour Leaching Period

Mangrove litterfall rates were measured at the study site, SRS-6, by Twilley and Rivera-Monroy (unpublished data). Litter leaching rates were calculated based on a 24-hour leaching period. This summation formula utilizes actual litterfall rates from the study site and litterfall composition to determine the amount of DOC made available by different litter types to the water column during the initial 24-hours of decomposition at the wetland soil-water column interface.

Table 5. Mangrove litterfall estimates at SRS-6.

Month*	Total Litterfall	Total Leaf Litter	White Leaf Litter	Red Leaf Litter	Black Leaf Litter	Total Wood Litter	White Wood Litter	Red Wood Litter	Black Wood Litter
J	1.0044	0.7793	0.3967	0.3359	0.0467	0.1165	0.0593	0.0502	0.0070
F	1.9042	1.6464	0.8382	0.7096	0.0986	0.0829	0.0422	0.0357	0.0050
M	2.7900	2.3020	1.1719	0.9922	0.1379	0.2602	0.1325	0.112	0.0156
A	2.8734	2.1442	1.0916	0.9241	0.1284	0.3335	0.1698	0.1437	0.0200
M	2.9743	2.6025	1.3249	1.1217	0.1559	0.0982	0.0500	0.0423	0.0059
J	5.5157	4.8641	2.4763	2.0964	0.2914	0.1571	0.0800	0.0677	0.0094
J	4.9152	3.9240	1.9977	1.6912	0.2350	0.1404	0.0715	0.0605	0.0084
A	3.8333	2.9305	1.4919	1.2630	0.1755	0.1378	0.0702	0.0594	0.0083
S	9.1991	6.9773	3.5521	3.0072	0.4179	0.2197	0.1119	0.0947	0.0132
O	3.6792	2.0496	1.0434	0.8834	0.1228	02715	0.1382	0.1170	0.0163
N	1.8433	1.2509	0.6368	0.5391	0.0749	0.2690	0.1370	0.1159	0.0161
D	1.0746	0.6929	0.3528	0.2987	0.0415	0.1934	0.0934	0.0791	0.0110
Average	2.8695	2.6803	1.3645	1.1552	0.1606	0.1892	0.0963	0.0815	0.0113

Litterfall estimates (g m^{-2} d^{-1}) at SRS-6 from January 2001-June 2003.

$$\text{DOC (g } m^{-2} h^{-1}) = \Sigma (LL_x * R_{l,x}) + (WL_x * R_{w,x}) \quad (2)$$

* LL is leaf litter produced by a species (g m^{-2} yr^{-1}), WL is wood litter produced by a species (g m^{-2} yr^{-1}) and R is the DOC leaching potential of leaf or wood litter (g DOC/g dry tissue) of a particular species, x.

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Tidal and intra-annual variability in fluxes of carbon between a mangrove forest and tidal creek in Florida. Student Research Symposium in Conservation, Ecology and Evolutionary Biology, College Station, Texas. 21 February 2004.

Carbon exchange between an Everglades riverine mangrove wetland and adjacent tidal creek. Long-Term Ecological Research All Scientists' Meeting, Seattle, Washington. Contributed poster. 19-20 September 2003.

Benthic macro-invertebrate communities and habitat characteristics of created and natural marshes in Galveston Bay, Texas. Society of Wetland Scientists' Annual Meeting, New Orleans, Louisiana. 10 June 2003.

Structural comparisons of created and natural wetlands in Galveston Bay, Texas. Wildlife and Fisheries Department Lunchtime Seminar, College Station, Texas. 11 April 2003.