Organic Carbon Burial in a Freshwater Marsh to Mangrove Transitional Area in Everglades National Park

Kailey R. Comparetto

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Organic Carbon Burial in a Freshwater Marsh to Mangrove Transitional Area in

Everglades National Park

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
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Date of Approval:
June 13, 2018

Keywords: Wetland, Peat, Salinity, Accretion, Sea level

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1. Introduction

The Everglades are an intricate network of ecosystems supporting various unique communities that provide many ecosystem services including coastal protection, water filtration and storage, and nutrient storage and cycling, specifically organic carbon (OC) sequestration (Walters et al., 1992; Craft and Richardson, 1993; Costanza et al., 2008). Halophytic mangroves and freshwater sawgrass marshes form regionally-dominant communities that bury OC in their soils. Wetland plant communities in the region often meet at abrupt ecotones, determined by salinity tolerance, where a blending of ecosystem characteristics encourages transition to the more biogeochemically favored community (Schuyler et al., 1993; Smith et al., 2013; Jiang et al., 2014). Rising sea level will inevitably increase salinity and inundation regimes, while the short and long-term effects on the carbon burial process remain unclear.

Freshwater peat deposits began accumulating in the southern Everglades between six and seven thousand years ago with deposits in the central Everglades forming around five thousand years ago (Willard and Bernhardt, 2011). The Everglades geology, characterized as a limestone depression, coupled with the high levels of precipitation due to the subtropical climate and rising sea level which created a barrier to flow, allowed for accumulation of peat (Gleason and Stone, 1994). Following progressive rises in sea level throughout the Holocene, the Everglades coastal area transitioned to a saline environment, encouraging the accumulation of mangrove and salt marsh peats (Willard and Bernhardt, 2011; Chambers et al., 2015; Yao and Liu, 2017). In 1946, it was
of highly vulnerable coastal landscape, placing this large store of carbon at risk of loss or
degradation. Even a relatively small loss of carbon stock in mangrove soils would equate
to a disproportionately large release of stored carbon back into the atmosphere.

Whereas wetlands are recognized for storing OC, there is significant variability in
their burial rates depending upon species characteristics and soil biogeochemistry.
Loomis and Craft (2010) found rates of OC sequestration greater in freshwater marshes
(Zizaniopsis milacea (Michx.) and other species) (124 ± 10 g C m⁻² yr⁻¹) than salt
marshes (Spartina alterniflora Loisel.) (40 ± 7 g C m⁻² yr⁻¹) along rivers in Georgia.
Whereas Bianchi et al. (2013) found rates for OC sequestration in mangrove (Avicennia
germinans) soils (253-270 g C m⁻² yr⁻¹) to be greater than those for saltmarsh (Spartina
alterniflora) soils (101-125 g C m⁻² yr⁻¹) in the northern Gulf of Mexico. Hansen and
Nestlerode (2014) compared accumulation rates of OC from mangroves (Rhizophora
mangle, Laguncularia racemosa, Avicennia germinans) in northwest Florida (78.9 ± 16.3
g C m⁻² yr⁻¹) to those from a freshwater sawgrass marsh (Cladium sp.) in southwest
Florida (47.4 ± 15.9 g C m⁻² yr⁻¹). Each study demonstrated differences in OC burial rates
based upon the characteristics of the ecosystem.

Whereas relatively slow increases in sea level led to the formation of Everglades
peat in the early to mid-Holocene, recent acceleration of sea-level rise (SLR) driven by
climate change (Wdowinski et al., 2016) could be detrimental to those same formation
processes. This is due to two primary factors: (1) increasing depths and periods of
inundation and (2) the increasing presence of seawater salinity in historically fresh or
oligohaline soils. First, coastal wetlands typically cycle through varying periods of tidal
inundation and subaerial exposure where inundation positively influences accretion by
conditions set up a real-world, ecosystem-scale experiment representing a SLR scenario of increased salinity and inundation in a previously exclusively freshwater system. Soil cores were collected to compare mangrove and marsh soil intervals of similar age, with similar environmental parameters. This research compared rates of OC burial along a transect of mangrove encroachment into sawgrass marsh that occurred over the last 100 years and contributes to better projections for how each system may respond to future SLR, from an OC burial perspective. The hypothesis is that mangrove forest soils bury OC at greater rates than sawgrass marsh based on findings from previous studies that attributed releases of OC from freshwater marsh communities to salinity exposure (Weston et al., 2011; Chambers et al., 2014). The null hypothesis is rates of OC burial are the same for mangrove and marsh soils.

2. Methods

2.1 Study site

The study site is located approximately 10 km upstream from the Gulf of Mexico on the Harney River in Everglades National Park and has a tidal range in excess of 2 m during spring tides (Figure 1A) (Smith III et al., 2013). Soil cores were collected across a 300 m transect that originated in the mangrove forest fringe, crossed transitional ecotones, and terminated into a freshwater marsh dominated by sawgrass (Cladium sp.) (Fig. 1A, 1B, 1C, and 1D). The fringe mangrove forest was dominated by red (Rhizophora mangle) and white (Lagunculariea racemosa) mangroves with few black (Avicennia germinans) mangroves present and little to no underbrush. Tree heights were 14-16 m tall with stem diameters ranging from 2-60 cm and tree density ranging from 5500-11,300 stems per hectare (Smoak et al., 2013). The transition zone was composed of red, white,
2.3 Core Dating

Soil accumulation rates were determined by measuring excess $^{210}\text{Pb}$ by using methods described by Smoak et al. (2013). Briefly, sectioned core intervals were freezedried, homogenized, and packed and sealed into gamma tubes. Gamma activities were measured using an intrinsic germanium well detector (Princeton Gamma-Tech Model: IGW-10023-15) coupled with a multichannel analyzer (Princeton Gamma-Tech system 8000). Pb-210 activity was measured by the 46.5keV peak and $^{226}\text{Ra}$ by its daughter, $^{214}\text{Pb}$, at the 351.9keV peak (Appleby et al. 1988). For $^{226}\text{Ra}$ measurements, packed samples were set aside for at least 21 days to allow for $^{222}\text{Rn}$ ingrowth establishing secular equilibrium between $^{226}\text{Ra}$ and its granddaughter $^{214}\text{Pb}$. Excess $^{210}\text{Pb}$ activity was calculated by subtracting the supported $^{210}\text{Pb}$ (i.e., $^{226}\text{Ra}$ activity) from the total $^{210}\text{Pb}$ activity. The Constant Rate of Supply (CRS) model was used to calculate soil accumulation rates and ages of soil intervals (Appleby & Oldfield, 1978; Smoak et al., 2013). The CRS model was chosen because it allows for variation of excess $^{210}\text{Pb}$; such increases/decreases are commonly seen in systems where sediment or soil supply varies due to climatic or anthropogenic influences (Diaz-Asencio et al., 2016). The CRS model was used under the assumption that rates of soil accumulation have varied but the supply of excess $^{210}\text{Pb}$ was constant over the entire $^{210}\text{Pb}$ record. The age-depth model yields ages for the base of each sectioned interval of the core. Since accretion has been observed to cause compaction of underlying soil layers at similar sites in the Everglades (Smoak et al., 2013; Breithaupt et al., 2014), interval depths of lower bulk densities were normalized to the density of bottom layers (Lynch et al., 1989). Both non-normalized and normalized accretion rates are provided herein. Pb-210 dates can sometimes be confirmed with an
pigment-specific spectra. Pigments are expressed in concentrations of nmol g$^{-1}$ of dry organic matter. For precision, repetitions were completed every 7-10 samples to ensure reproducibility and relative percent differences (RPD) were calculated. Replications were required to be 10% or less RPD for 3 major pigments. For accuracy, calculations were based upon individual standards of each pigment. In addition, a chlorophyll check standard was used to ensure accuracy. The internal standard normalizes for evaporation during extraction and sample preparation since the use of acetone can easily volatilize.

2.5 OC analysis and Stable Isotope Ratio ($\delta^{13}C$)

Cores were analyzed for total OC and $\delta^{13}C$ using methods found in Breithaupt et al. (2014). Briefly, samples were acidified to remove carbonate material prior to analysis and then were analyzed using a Flash Elemental Analyzer (Thermo Flash EA 1112) coupled to a Thermo Fisher Delta V isotope ratio mass spectrometer. Analytical precision was as follows: $C = 0.1\%$, $\delta^{13}C = 0.1\%$. Working standard for $\delta^{13}C$ was glucose, 10.7‰. A pair of standards were measured with every 20 samples. These standards were calibrated initially against international absolute standards LSVEC and NIST8542. If a sample was not available for analysis (TRN-5 3-4cm), OC was estimated using the formula

$$OC = 0.4371 \times (LOI\%^{0.9245})$$

which was derived from Everglades-specific data in Breithaupt et al. (2014). This estimation is valid for this site based on total average OC % for the end-member cores (MNG-1 and MRS-6) which were found to be 30% and 39%, respectively.

2.6 Decadal aggregation of site rates

The CRS model provides dates at the bottom of each sectioned core interval but does not provide a rate for every year over the last 100 years, making comparisons
3. Results

3.1 Pigments and aerial imagery

Historic aerial images dated 1940 and 2004 showed mangrove dominance at MNG-1 and marsh dominance at TRN-5 and MRS-6 (Fig. 1C) (Smith et al., 2013). Analysis of aerial photographs showed that sometime after 1952 but prior to 1964, TRN-2 and TRN-3 transitioned from sawgrass marsh to a mangrove dominated system (Figs. 3A and 3B). TRN-2 had no discernable pigment trend (Fig. 4). For TRN-3, overall chlorophyll-b and chlorophyll-a pigment concentrations, which are associated with macrophytes and primary producer abundance, respectively, decline down core (Fig. 4). Chlorophyll-b pigment concentrations ranged from 0.0 to 6.5 nmol g⁻¹ and were not detected prior to 1974 (Fig. 4).

3.2 Soil characteristics and dating

Mean DBD (± 1SD), OM % (±SD), OC% (±SD), and δ¹³C (±SD) values for each core are found in Table 3. Mean DBD ranged from 0.11 ± 0.02 to 0.21 ± .04 g cm⁻³. Mean OM% ranged from 62 ± 5 to 84 ± 3%. For each core, average total DBD and OM % showed a strong negative relationship ($R^2 = 0.97$, $F = 147.70$, $p = 0.0003$) (Fig. 5). All cores have a typical exponential decrease in specific excess $^{210}$Pb down core (Fig. 6). Mean OC% ranged from 30 ± 2 to 44 ± 6% (Table 3). Mean δ¹³C values ranged from -27.7 ± 0.8 to -27.1 ± 0.4% and were found to increase with depth (Table 3 and Fig. 7).

3.3 Calculated Rates

Rates of accretion, OM accumulation, and OC burial for the previous ten years (~2004-2014) and 100 years (~1904-2014) for each core are found in Table 4. Mean 10 and 100-year accretion, OM accumulation, and OC burial rates were greatest in mangrove cores.
hydroperiods that cycle through wet and dry periods, allowing soil pigments to oxidize and disappear from the soil record when exposed to oxygen, light, or increased temperatures (Ross et al., 2003; Waters et al., 2013). A more consistent hydroperiod and shadier areas associated with an established mangrove canopy would encourage increased preservation of soil pigments and explain the increases in pigment concentrations since the 1970s (Waters et al., 2009).

Aerial images confirmed that a vegetation transition took place before the 1970s, and further narrowed the time period to sometime after 1952, but before 1964, for cores TRN-2, TRN-3, and TRN-4 (Fig. 3A and 3B). Smith et al. (2013) quantified this migration as an ecotone shift 125 m inland during the period of 1940-2004 and while not significantly linked to SLR, two other studies have related mangrove expansion in this region to increases in salinity caused by sea level rise (Jiang et al., 2012; Yao, 2017). The recorded vegetation community shift indicates that this site has experienced a sustained increase to salinity from SLR during the last century (Sharpe and Baldwin, 2012).

For cores TRN-2, TRN-3, and TRN-4, a transition from marsh to mangrove within the soil record was expected. Using the mid-1960s as a reference point from the aerial images, the average δ¹³C value for the transition cores between the mid-1960s to 2014 was calculated to be -28 ± 0.5‰. This falls within the accepted range for mangrove litter of -28 to -30‰ which was calculated from all available data at the time (Kristensen et al., 2008). In addition, a decrease in δ¹³C values to within the accepted range for mangroves occurred earlier in core TRN-2 (1950s) than in TRN-4 (1970s), indicating that mangroves migrated into the transition zone over time, likely as a result of gradual sea level rise as recorded in other locations in the Everglades (Ross et al., 2000).
MNG-1, TRN-2, TRN-3, and TRN-4 accretion rates are similar to the average 100-year normalized accretion rate of 2.2 ± 0.1 mm yr\(^{-1}\) found by Breithaupt et al. (2017) for 13 sites dominated by mangroves throughout the Everglades. The mangrove fringe and transition area, where mangroves have become established as the dominant vegetation, are keeping pace with accretion rates from the Everglades’ coastal zone (Breithaupt et al., 2017). TRN-5 and TRN-6 accretion rates are less than freshwater marsh rates of accretion from the Everglades Water Conservation Area of 1.4 to 1.6 mm yr\(^{-1}\) (Craft and Richardson, 1998). Marsh accretion rates at this site are not keeping pace with those from the coastal zone or central Everglades (Breithaupt et al., 2017; Craft and Richardson, 1998). All accretion rates were less than the 100-year (1914-2014) and ten-year (2004-2014) regional rates of SLR of 2.4 mm yr\(^{-1}\) and 7.3 mm yr\(^{-1}\), based on the Key West, FL tide gauge data (station ID: 8724580) (NOAA National Ocean Service, 2018), suggesting that this site’s accretion may not be keeping pace with SLR, especially with the accelerated rates recorded over the last decade. Overall, mangroves are accreting at a faster pace than marshes on both time scales and may be more able to adapt to SLR (Craft and Richardson, 1993; Craft and Richardson, 1998; Smoak et al., 2013). However, if mangroves do not migrate quickly enough into the marsh area, this marsh may submerge and become an open water bay at some point in the future under continued SLR conditions as predicted by historical SLR reconstructions (Gillman et al., 2007; Doyle et al., 2010; Punwong et al., 2013; Urrego et al., 2013).

4.3 OC burial rates- site specific, regional, and global comparisons

Overall, 100-year OC burial rates decreased from 137 to 52 g m\(^{-2}\) yr\(^{-1}\) across the transect (Table 4, Fig 10). The 100-year OC burial rate for the mangrove-dominate
methanogenesis, leading to an overall increase in the carbon mineralization rate. A slight increase in salinity, like that found during Hurricane Wilma (Jiang et al. 2012), or that occurs from gradual SLR, may not show immediate negative effects aboveground; belowground however, it may equate to large losses in stored carbon and may contribute to the overall lower rates of marsh burial found during this study.

The 100-year mean burial rate from MNG-1 was greater than rates of burial in the transition cores, however only TRN-3 was found to be significantly different (Table 4, Fig. 10). The lower rates of burial were somewhat expected as 100-year rates from the transition zone cores factor in lower marsh rates of OC burial from deeper in the core. Decadal-aggregated rates of OC burial for intervals delineated as mangrove dominant found in the transition zone were also less than the fringe mangrove intervals' rates (Table 5). This difference could be attributed to location in the transect and variations between fringe and basin systems, like organic and mineral sediment contributions and transport between systems (Hatten et al. 1983; Sanders et al. 2010). Percent OM for the fringe core was 61%, an indication that OC burial may be attributed more to allochthonous sedimentation or storm surge deposits (Smoak et al., 2013) that supply additional phosphorous stimulating growth (Castañeda-Moya et al., 2010). The basin cores OM% ranged between 79% and 84%, which is related to high autochthonous production and burial (Table 3). Organic matter % values followed an inverse trend to DBD, with lower OM% equating to greater DBD (Fig. 5). Williams and Rosenheim (2015) suggested that greater bulk density values are related to higher organo-mineral associations and lead to greater stability of soil OC. Another possibility is that the transition area is burying carbon at a lower rate due to maturity of the system since more mature forests bury
Certain areas of the Everglades may be burying slightly less OC than other wetlands around the globe, depending on which rates are selected when calculating an estimated global burial rate.

4.4 Peat Collapse

Severe instances of accelerated OM decomposition and carbon release have been linked to peat-collapse events. Peat collapse can be caused by many factors, but if it were to occur at this site, saline-intrusion-induced accelerated decomposition would most likely be the cause as other peat-collapse events in the Everglades have been documented and attributed to increases in salinity (Wanless and Vlaswinkel, 2005). Freshwater marsh soils, like those of the Everglades, are especially susceptible to peat collapse due to their lower DBD and high OM composition. This is especially apparent at this site where DBD and OM% were very similar for the marsh and the basin mangroves in the transitional area, but rates of accretion and OC burial for mangroves were around two to three times that found by marshes, depending upon the time period. The lower rates of freshwater marsh OC burial found in this study suggest that this marsh may be experiencing accelerated decomposition of OM from saline intrusion that could lead to peat-collapse events; this would further release years of stored carbon and create open-water bays, like those that exist to the east of this site. Further, this would hinder the migration and establishment of mangroves, largely decreasing OC burial.

4.5 Implications for the future

When comparing OC burial and accretion rates by vegetation type, similar site locations and soil ages provide a more equal comparison. Compiled OC burial rates from coastal wetlands with different environmental characteristics have shown great variability
remained. Based on the estimated 500,000 ha of freshwater wetland in the Everglades (Craft and Richardson, 1993), a total habitat replacement by mangroves, using the aggregated OC burial rate of 148 g C m$^{-2}$ yr$^{-1}$, would equate to an additional 445 Gg of OC buried each year. However, this change would probably take hundreds to thousands of years to complete, based on rates of SLR. Conditionally, if mangrove accretion can keep pace with SLR and mangroves can expand their area by moving inland, there is the potential for an increase in rates of OC burial in the Everglades under a SLR scenario.

5. Conclusion

Rates of accretion and OC burial were compared temporally and spatially along a transect where mangroves have been encroaching into the marsh. For each comparison, the mangrove accretion and OC burial rates were greater than their marsh counterparts, though rates among mangroves varied, possibly due to differences in age and distance from salt water. While most of the Everglades has been a freshwater ecosystem, SLR has increased porewater salinities throughout, and will continue to do so as the rate of SLR continues to increase. This change in ecotones presents the potential for increased rates of OC burial in the Everglades on a long-term scale but will depend upon many factors, including mangrove accretion keeping pace with SLR, mature mangrove establishment inland, and carbon loss from freshwater carbon oxidation not exceeding new burial.
Table 3: Mean and standard deviation (SD) for soil characteristics.

<table>
<thead>
<tr>
<th>Core</th>
<th>Dry Bulk Density (g cm$^{-3}$)</th>
<th>Organic Matter (%)</th>
<th>Organic Carbon (%)</th>
<th>$\delta^{13}$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>MNG-1</td>
<td>0.21</td>
<td>.04</td>
<td>62%</td>
<td>5%</td>
</tr>
<tr>
<td>TRN-2</td>
<td>0.13</td>
<td>.03</td>
<td>82%</td>
<td>4%</td>
</tr>
<tr>
<td>TRN-3</td>
<td>0.11</td>
<td>.02</td>
<td>84%</td>
<td>1%</td>
</tr>
<tr>
<td>TRN-4</td>
<td>0.12</td>
<td>.02</td>
<td>84%</td>
<td>3%</td>
</tr>
<tr>
<td>TRN-5</td>
<td>0.11</td>
<td>.02</td>
<td>83%</td>
<td>2%</td>
</tr>
<tr>
<td>MRS-6</td>
<td>0.15</td>
<td>.03</td>
<td>79%</td>
<td>2%</td>
</tr>
</tbody>
</table>

Table 4: Calculated 10-yr and 100-yr rates for each core.

<table>
<thead>
<tr>
<th>Core</th>
<th>Organic Matter Accumulation (g m$^{-2}$ yr$^{-1}$)</th>
<th>Non-Normalized Accretion (mm yr$^{-1}$)</th>
<th>Normalized Accretion (mm yr$^{-1}$)</th>
<th>Organic Carbon Burial (g m$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10-yr Mean</td>
<td>100-yr Mean</td>
<td>10-yr Mean</td>
<td>100-yr Mean</td>
</tr>
<tr>
<td>MNG-1</td>
<td>551</td>
<td>295</td>
<td>4.9</td>
<td>2.5</td>
</tr>
<tr>
<td>TRN-2</td>
<td>387</td>
<td>244</td>
<td>4.5</td>
<td>2.3</td>
</tr>
<tr>
<td>TRN-3</td>
<td>246</td>
<td>197</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>TRN-4</td>
<td>382</td>
<td>210</td>
<td>3.8</td>
<td>2.2</td>
</tr>
<tr>
<td>TRN-5</td>
<td>144</td>
<td>87</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>MRS-6</td>
<td>164</td>
<td>100</td>
<td>2.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 1: Site location in Everglades National Park: A) Site location in southwest Everglades B) Soil core transect C) Photo of site in 2004 with 1940 aerial image overlay (Smith et al. 2013). Shows ecotone’s transition inland 125m over time. D) Photo of site’s sharp transition from mangrove to marsh (Smith et al. 2013).

Figure 2: Conceptual model of the study design. Red line represents the transition from marsh to mangrove material within the core. Yellow boxes represent the comparison of similarly aged mangrove and marsh soil with intervals of same age but different dominant vegetation type.
Figure 4: Depth and age profiles for sedimentary photosynthetic pigments for cores TRN-2 and TRN-3. Ages are $^{210}$Pb ages. Pigment concentration is nmol pigment g$^{-1}$ organic material.
Figure 6: Depth profiles of excess $^{210}$Pb for dated intervals (~100 years) of the six soil cores.
Figure 8: Average 10 and 100-yr rate of accretion (±SD) for each core.

Figure 9: Average 10 and 100-yr rate of organic matter accumulation (±SD) for each core.
References


