



Historical reconstruction of mangrove expansion in the Gulf of Mexico: Linking climate change with carbon sequestration in coastal wetlands

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ABSTRACT

There has been considerable interest in a recently recognized and important sink in the global carbon pool, commonly referred to as “blue carbon”. The major goal of this study was to determine the historical reconstruction of mangrove expansion (*Avicennia germinans*) into salt marshes (*Spartina alterniflora*) and its effects on carbon sequestration and soil chemistry in wetland soils of the northwestern Gulf of Mexico. We used bulk stable isotopic, chemical biomarker analyses, and aerial imagery analysis to identify changes in OC wetland sources, and radiotracers (¹³⁷Cs and ²¹⁰Pb) for chronology. Soil cores were collected at two sites at Port Aransas, Texas (USA), Harbor Island and Mud Island.

Stable isotopic values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of all soil samples ranged from -26.8 to -15.6‰ and 1.8 – 10.4‰ and showed a significant trend of increasing depletion for each isotope from bottom to surface soils. The most depleted $\delta^{13}\text{C}$ values were in surface soils at the Mud Island (Mangrove 2) location. Carbon sequestration rates were greater in mangroves and for the Mud Island Mangrove 1 and the Marsh 1 sites ranged from 253 to 270 and 101 – $125\text{ g C m}^{-2}\text{ yr}^{-1}$, respectively. Lignin storage rates were also greater for mangrove sites and for the Mud Island Mangrove 1 and the Marsh 1 ranged from 19.5 to 20.1 and 16.5 to $12.8\text{ g lignin m}^{-2}\text{ yr}^{-1}$, respectively. The Λ_8 and Λ_6 values for all cores ranged from 0.5 to 21.5 and 0.4 to 16.5 , respectively, and showed a significant increase from bottom to surface sediments. If regional changes in the Gulf of Mexico are to persist and much of the marsh vegetation was to be replaced by mangroves, there could be significant increases on the overall storage and sequestration of carbon in the coastal zone.

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1. Introduction

There has been considerable interest in a recently recognized and important sink in the global carbon pool, commonly referred to as “blue carbon”, or that which is associated with organic carbon (OC) burial in seagrass meadows and intertidal wetlands (mangroves and intertidal marshes) (Chmura et al., 2003; Duarte et al., 2005; McLeod et al., 2011; Hopkinson et al., 2012). In fact, the second largest release of carbon dioxide (CO_2) to the atmosphere,

after fossil fuel combustion, is from deforestation and land-use change, which accounts for 8–20% of the total emissions (IPCC, 2007; van der Werf et al., 2009). Consequently, Reduced Emissions from Deforestation and Degradation (REDD+) has been proposed internationally as way to help mitigate climate change effects (Donato et al., 2011). Therefore, the effects of current natural and human-induced alterations in the composition of wetland plant species, and their associated carbon sequestration capacity, needs further attention.

In coastal wetlands, a warming climate is expected to increase the spatial extent of C_3 carbon-rich woody mangroves at the expense of C_4 herbaceous salt marshes (Ross et al., 2000; Stevens et al., 2006; McKee and Rooth, 2008; Williamson et al., 2010). The response of plant communities to global change is expected to be discernible in such boundaries because of their rapid and extreme

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responses under such physiologically stressful conditions (Allen and Breshears, 1998). Salt marsh-mangrove ecotones, which occur in many geographic locations, provide locations to examine changes in carbon sequestration in such dynamic transitional regions (Lopez-Portillo and Ezcurra, 1989; Patterson and Mendelssohn, 1991; Stevens et al., 2006). While the literature is replete with studies suggesting that elevated CO₂ levels will promote the growth of C₃ plant species, there are only few that have examined plant competition under elevated CO₂ conditions in ecotonal communities where C₃ and C₄ species converge (e.g., McKee and Rooth, 2008).

Although previous work has focused on factors controlling zonation at the ecotone between *Avicennia* and *Spartina* spp. in the Gulf of Mexico (Patterson and Mendelssohn, 1991; Stevens et al., 2006), only recently has there been examination of how spatial changes in these taxa affect ecosystem properties (e.g., elevational changes and edaphic parameters) (Perry and Mendelssohn, 2009; Comeaux et al., 2012). The major goal of this study was to determine the historical reconstruction of mangrove expansion (*Avicennia germinans*) into salt marshes (*Spartina alterniflora*) and its effects on carbon sequestration and soil chemistry in wetland soils of the northwestern Gulf of Mexico.

We used bulk stable isotopic, chemical biomarker analyses, and aerial imagery analysis to identify changes in OC wetland sources, and radiotracers (¹³⁷Cs and ²¹⁰Pb) for chronology. This work is in part connected with a recent study by Comeaux et al. (2012), that focused more on the effects of mangrove transitions on resistance to accelerating eustatic sea level rise (ESLR) and/or relative sea level rise (RSL) rates, and wetland stability to wave attack in large storms (increased cyclonic storm frequency/intensity).

2. Materials and methods

2.1. Site description

Populations of *Avicennia germinans* and *Spartina alterniflora* growing in isolation of each and in overlapping locations (along with other salt tolerant plants, including in some cases *Spartina patens*), in similar geomorphological settings were selected as field sites in a back-barrier region near Port Aransas, Texas. The two sites at Port Aransas consisted of the Harbor Island (27°51' 50.25"N, 97°3' 35.36"W) and Mud Island (27°56' 32.24"N, 97°1' 38.14"W) locations, both situated along the Lydia Ann Channel, north of Mustang Island (Fig. 1) (Comeaux et al., 2012). Two different cores were taken at the Harbor Island Mangrove site (Mangrove 1 and 2), two cores at the Mud Island Mangrove (Mangrove 1 and 2), and two cores at the Mud Island Marsh site (Marsh 1 and 2), for a total of 6 cores. Harbor Island is a flood tidal delta (Sherrod and McMillan, 1981), entirely mangrove-dominated at present, but having had past reversals in mangrove versus marsh vegetation - associated with freezes in the 1980's. Sub-freezing conditions in December, 1983 resulted in a mortality rate of approximately 80–85% of mangrove populations in Texas (McMillan and Sherrod, 1986), with Harbor Island experiencing an 85% loss and Galveston a ≥95% loss (Sherrod and McMillan, 1985). Galveston populations were impacted to a greater extent and reduced to less than 5 percent of the original population after 1983 (Everitt and Judd, 1989; Everitt et al., 1996). Other studies have examined the impact of a freeze event in December 1989 on mangrove colony expansion (Everitt et al., 1996; Buskey et al., 1997). In general, the Port Aransas mangrove colonies were thick and flourishing when we sampling

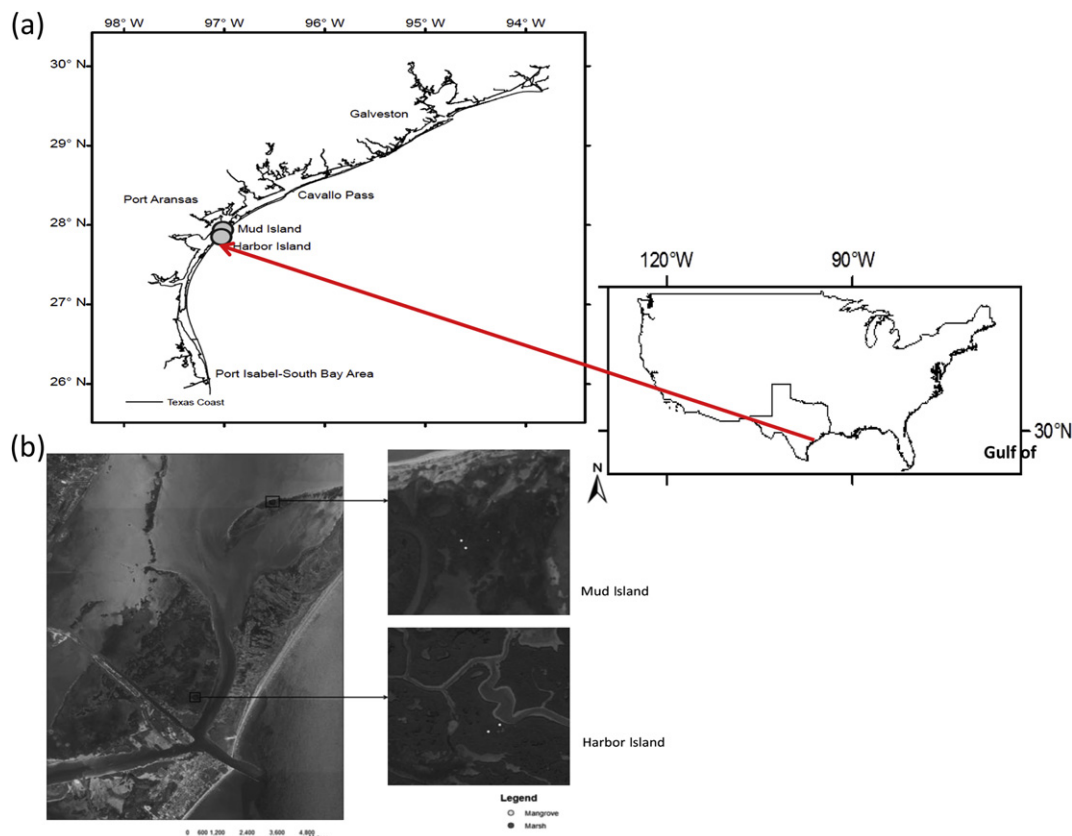


Fig. 1. Map of the two sites at Port Aransas, Texas (USA), at harbor island (27°51' 50.25"N, 97°3' 35.36"W) and Mud island (27°56' 32.24"N, 97°1' 38.14"W).

occurred in this study – with tree sizes reaching 1–2 m in height (Comeaux et al., 2012).

2.2. Soil sampling and processing

Peat auger cores (minimal compaction) from marsh and mangrove areas were collected for sampling of total organic carbon (TOC), total nitrogen (TN), stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), lignin-phenols, porosity, ^{210}Pb and ^{137}Cs radiotracer geochronology. Cores were cut on site and sub-sampled the same day in a field lab prior to freezing for analysis and storage.

2.3. Radionuclides and sediment accumulation

Total sediment accumulation in sediment cores from mangrove and marsh sites (mineral + organic) were measured using the radiotracers ^{210}Pb (half-life = 22.2 years) and ^{137}Cs (half-life = 30.1 years) to identify any difference in total accumulation rates that might result in differences in elevation, see Comeaux et al. (2012) for more details. Basically, radiotracers were measured by gamma spectrometry (planar and well geometry LEGE detectors) using freeze-dried sediment intervals from the cores. A best-fit linear regression of the natural log of excess ^{210}Pb ($^{210}\text{Pb}_{\text{ex}}$) with depth below any surface mixed layer of homogenous activity was used to determine the sediment accumulation for the past ca.100 years (Nittrouer and Sternberg, 1981). ^{137}Cs is the product of fallout from atmospheric testing of thermonuclear weapons that began in 1954. We used the depth of maximum ^{137}Cs fallout in the northern hemisphere (1963 according to Chmura and Kisters, 1994) and ^{210}Pb to estimate sedimentation rates for each site. ^{137}Cs rates were calculated by dividing the depth of the 1963 peak occurrence in the core by the number of years passed; errors were derived by extrapolating across the core interval represented by that particular year. Final accumulation rates were depth-corrected to a standard core porosity (60%) to expand or contract interval depths (to allow for inter-comparison of sites in linear terms; see Allison et al., 2007), and were converted from linear accumulation rates (consolidation-corrected cm yr^{-1}) to mass accumulation rates ($\text{g cm}^2 \text{ yr}^{-1}$).

2.4. Bulk isotope and elemental analysis

Total organic carbon, total nitrogen, and stable carbon and nitrogen isotopes were analyzed at the University of California, Davis Stable Isotope Facility. Measurements were made using an elemental analyzer (Carlo Erba EA-1108; CE Elantech, Lakewood, NJ) interfaced with an isotope ratio mass spectrometer (Delta Plus, Thermo Electron, Waltham, MA) operating in continuous flow mode. Carbon isotope ratios were calculated in δ notation as follows:

$$\delta = \left[\left(R_{\text{sample}} - R_{\text{STD}} \right) / R_{\text{STD}} \right] \times 10^3 \quad (1)$$

where, R_{STD} is the $^{13}\text{C}/^{12}\text{C}$ ratio of the V-PDB standard (Coplen, 1996) and R_{sample} is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample. The precision of duplicate measurements was $\pm 0.1\text{‰}$.

2.5. Lignin-phenols

Freeze-dried sediment containing 3–5 mg of OC were analyzed for lignin-phenols using the CuO method of Hedges and Ertel (1982), as modified by Goni and Hedges (1992). Sediments were transferred to stainless-steel reaction vials and digested with 330 mg (± 4 mg) CuO in 2N NaOH at 150 °C for 3 h. Reaction products were allowed to cool and then extracted with three successive 3 mL aliquots of diethyl ether (peroxides removed), filtered through combusted

glass-fiber, dried under N_2 , and converted to trimethylsilyl derivatives using bis-(trimethylsilyl)-trifluoroacetamide (BSTFA). Lignin-phenol derivatives were analyzed with an Agilent 5890 Gas Chromatograph/5973 Mass Spectrometric Detector (GC–MS).

Quantification was based upon the internal ARS standard and ethyl vanillin was added before extraction to account for extraction efficiency. New response factors were generated with each batch by using a mixed standard of the target compounds. The average standard deviations, based upon two replicates ($n = 2$), for the sum of lignin phenols is less than 9% while that for individual compounds ranged from 2 to 17%. Eleven lignin phenols, *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenol, *p*-hydroxycoumaric acid, vanillin, acetovanillone, *p*-hydroxybenzoic acid, syringaldehyde, vanillic acid, acetosyringone, syringic acid and ferulic acid, were quantified and used as molecular indicators for source and diagnostic state of vascular plant tissue. Lamda-6 (Λ_6) is defined as the sum of vanillyl (vanillin, acetovanillone, vanillic acid) and syringyl (syringaldehyde, acetosyringone, syringic acid) phenols, and Lamda-8 (Λ_8) includes the cinnamyl (*p*-coumaric and ferulic acid) phenols, both were per 100 mg OC^{-1} . Total cinnamyl/vanillyl and syringyl/vanillyl phenols represent C/V and S/V ratios, respectively, and were used in part, to determine plant lignin sources. Ratios of vanillic acid to vanillin (Ad/Al)v (Hedges et al., 1988), *p*-hydroxyl/(vanillyl + syringyl phenols) [$\text{P}/(\text{V} + \text{S})$] (Dittmar et al., 2001) were used as indices of lignin decay.

2.6. Carbon sequestration, lignin storage rate, and historical carbon and lignin pools

Mud Island Mangrove 1 and Marsh 1 sites were selected to examine historical changes in carbon and lignin storage. The calculation of organic carbon (kg C m^{-2}) and lignin (kg lignin m^{-2}) pool was modified from Bernal and Mitsch (2008) as follows:

$$\text{TOC}_{\text{layer}}(\text{g}) = \text{dry weight}_{\text{layer}}(\text{g}) \times \text{TOC}(\%) \times 0.01 \quad (2)$$

$$\text{TOC pool}_{\text{layer}}(\text{kg OC m}^{-2}) = 1000 \times \text{TOC}_{\text{layer}}(\text{g}) / A(\text{m}^2) \quad (3)$$

where,

$$\text{dry weight}_{\text{layer}}(\text{g}) = \text{density}(\text{g cm}^{-3}) \times A(\text{m}^2) \times 10000 \times \text{depth}_{\text{layer}}(\text{cm}) \quad (4)$$

density = 2.65 g cm^{-3} ; TOC is the percentage of the organic carbon; $\text{TOC}_{\text{layer}}$ is the mass of organic carbon in each layer; A, the area of the sample corer, was canceled out during the calculation. TOC sequestration (kg OC m^{-2}) was integrated from the TOC pool layer (kg OC m^{-2}) over a specific time period, based on the ^{210}Pb -derived sediment accumulation rate in Comeaux et al. (2012) to determine the carbon sequestration rates for the Mud Island cores.

Similarly, the lignin storage rate (kg lignin m^{-2}) was integrated from lignin pool layer (kg lignin m^{-2}) over specific time period based on the ^{210}Pb derived sediment accumulation rate in Comeaux et al. (2012) to determine the lignin sequestration rates for the Mud Island cores. The lignin pool layer (kg lignin m^{-2}) was determined as follows:

$$\begin{aligned} \text{Lignin pool}_{\text{layer}}(\text{kg lignin m}^{-2}) \\ = \text{density}(\text{g cm}^{-3}) \times \text{Depth}_{\text{layer}}(\text{cm}) \times \text{TOC}(\%) \\ \times \Lambda_8(\text{mg } 100 \text{ mg}^{-1} \text{ OC}) \times 0.001 \end{aligned} \quad (5)$$

2.7. Aerial imagery

The six core locations were located within a Geographic Information System (ArcGIS, ESRI, Redlands, California) according to their GPS coordinates. From a larger set of imagery, aerial photos then were acquired representing the years 1951, 1967, and 2008/2009. Analysis was limited to only those images where the two vegetation types, mangroves versus salt marshes, were clearly discernible. Subsequently, the percent cover of each vegetation or land cover type was found within a 10 m buffer around each point by digitizing and calculating areal coverage. Land-cover types in the area included *Avicennia germinans*-dominated mangrove, *Spartina alterniflora*-dominated salt marsh, unvegetated salt flat, high marsh, estuarine beach sands, and open water. The percent cover of land cover type was then plotted across time.

2.8. Statistical analyses

Origin 8.6 software was used to for statistical analyses. A One way-ANOVA was performed to examine for differences between variables at different sites and different depths. Statistically significant differences are discussed within the 95% confidence interval.

3. Results

3.1. Sediment accumulation and carbon sequestration rates

Excess ^{210}Pb activities in surficial sediments range from 6.8 to 8.6 dpm g^{-1} within Port Aransas sediments (Comeaux et al., 2012). Sediment accumulation rates for Mud Island (Mangrove 1) and Mud Island (Marsh 1), represented as linear accumulation rates (LAR) in cm yr^{-1} , ranged from 0.54 ± 0.15 to 0.74 ± 0.21 cm yr^{-1} and 0.18 ± 0.06 to 0.26 ± 0.04 cm yr^{-1} – based on both the 1963 ^{137}Cs peak and ^{210}Pb profiles (Table 1). Large scale accretion rates for Mud Island (Mangrove 1) and Mud Island (Marsh 1) were 49 ± 19 to 35 ± 14 tonnes of sediment $\text{ha}^{-1} \text{yr}^{-1}$ and 12 ± 6 to 17 ± 4 tonnes of sediment $\text{ha}^{-1} \text{yr}^{-1}$, respectively (See sample profiles of ^{210}Pb and ^{137}Cs in Comeaux et al. (2012)). Accumulation rates were not calculated for Harbor Island sediments because down-core variable activities make it difficult to select an exact point of maximum atmospheric peak or onset.

Carbon sequestration rates for the Mud Island Mangrove 1 and the Marsh 1 sites ranged from 253 to 270 and 101 to 125 $\text{gC m}^{-2} \text{yr}^{-1}$, respectively (Table 1). There were only some slight differences between the integrated rates based on the 1963 horizon, estimated from both ^{137}Cs and ^{210}Pb profiles. Carbon sequestration rates were significantly higher in mangrove than marsh sediments at Mud Island.

3.2. Porosity, soil strength, pore water salinity, pH, and Eh

Detailed analyses of edaphic properties (porosity, soil strength, pore water salinity, pH, and Eh) of soils at Mud and Harbor Island's mangrove and marsh sites, and the associated methods, are reported in Comeaux et al. (2012). Here we report some of the

general ranges of these parameters in these soils and discuss them later in the paper as they relate to carbon accumulation and decay rates in wetland soils.

Average porosities at Port Aransas are 0.48, 0.64, and 0.72 within wetland soil intervals of Harbor Island mangroves and Mud Island mangroves and marsh, respectively. Soil strength averaged 20.8 and 11.6 kPa in mangrove and marsh cores, respectively from Port Aransas Mud Island and 25.1 kPa in Harbor Island mangroves over wetland intervals. Below these depths values ranged from 11.7 to 30.8 kPa in Mud Island mangroves and marsh and 24.1 kPa in Harbor Island mangroves. Soil pore water salinity levels in Port Aransas ranged from approximately 60 (Mud Island marsh sediments) to 80 and 140 in Mud Island and Harbor Island mangrove sediments, respectively. Mangrove soil salinity levels remain consistently 10 to 30 higher than marsh salinities throughout the entire core depth. Port Aransas soil pH values range from approximately 7.0–9.0 in mangrove and 8.0 to 9.5 in marsh cores. Eh values at Port Aransas range from –248–270 mV: Mud Island marsh values range from –248 to 107 mV, while Mud Island mangrove values range from 27 to 158 mV compared to 75–270 mV in Harbor Island mangroves. Below 20 cm depth, redox values stabilize around zero to 150 mV (Mud Island) and 200–270 mV (Harbor Island).

3.3. Bulk TOC, TN, and stable isotopes

Percent TOC, TN, and C:N ratios at all sites and depths ranged from 0.1 to 11.37, 0.1 to 9.5, and 9.0 to 18.8, respectively (Fig. 2). There was a significant increasing trend in %TOC and TN from bottom to surface soils, with the highest values found in the surface at Mud Island (Marsh 2); the lowest values were found in soils from Harbor Island (Mangrove 1). The most significant change in %TOC, %TN, and C:N ratios occurred after each site had reached establishment as a wetland, or approximately post-1963. The highest C:N ratio was found in soils at Mud Island (Mangrove 1) at depth (10 cm), except for this one sub-surface peak, there was an increasing trend in C:N ratios from bottom to surface soils at all sites, that were related to changing sources of carbon from algae and marsh to woody plant material.

Stable isotopic values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of all soil samples ranged from –26.8 to –15.6‰ and 1.8–10.4‰ (Fig. 3). There was a significant trend of increasing depletion for each isotope from bottom to surface soils. The most depleted $\delta^{13}\text{C}$ values were in surface soils at the Mud Island (Mangrove 2) location. The greatest change in $\delta^{13}\text{C}$ values over depth was at the Harbor Island (Mangrove 2) site. The $\delta^{15}\text{N}$ values were most depleted in surface soils at the Mud Island (Mangrove 2) site.

3.4. Lignin-phenols as chemical biomarkers

Lignin storage rates for the Mud Island Mangrove 1 and the Marsh 1 ranged from 19.5 to 20.1 and 16.5 to 12.8 $\text{g lignin m}^{-2} \text{yr}^{-1}$, respectively (Table 1). The lignin storage rates were significantly higher in mangrove compared to marsh sediments at Mud Island. The Δ_8 and Δ_6 values for all cores ranged from 0.5 to 21.5 and 0.4 to 16.5, respectively, and showed a significant increase from bottom to

Table 1
Annual sediment accretion/accumulation rates, carbon sequestration rates, and lignin storage rates for the two sites in Port Aransas, Texas (USA), at Mud Island.

Station	Annual sediment accretion (cm yr^{-1})	Annual sediment accumulation (tonnes $\text{ha}^{-1} \text{yr}^{-1}$)	Carbon sequestration rate ($\text{gC m}^{-2} \text{yr}^{-1}$)	Lignin storage rate ($\text{g lignin m}^{-2} \text{yr}^{-1}$)
Mud Island (Mangrove 1 and 2)	0.74 ± 0.21 (^{137}Cs -1963)	49 ± 19 (^{137}Cs -1963)	270 ± 12 (^{137}Cs -1963)	20.1 ± 0.2 (^{137}Cs -1963)
	0.54 ± 0.15 (^{210}Pb)	35 ± 14 (^{210}Pb)	253 ± 11 (^{210}Pb -1963)	19.4 ± 0.6 (^{210}Pb -1963)
Mud Island (Marsh 1 and 2)	0.18 ± 0.06 (^{137}Cs -1963)	12 ± 6 (^{137}Cs -1963)	101 ± 23 (^{137}Cs -1963)	12.7 ± 3.9 (^{137}Cs -1963)
	0.26 ± 0.04 (^{210}Pb)	17 ± 4 (^{210}Pb)	125 ± 11 (^{210}Pb -1963)	16.5 ± 1.3 (^{210}Pb -1963)

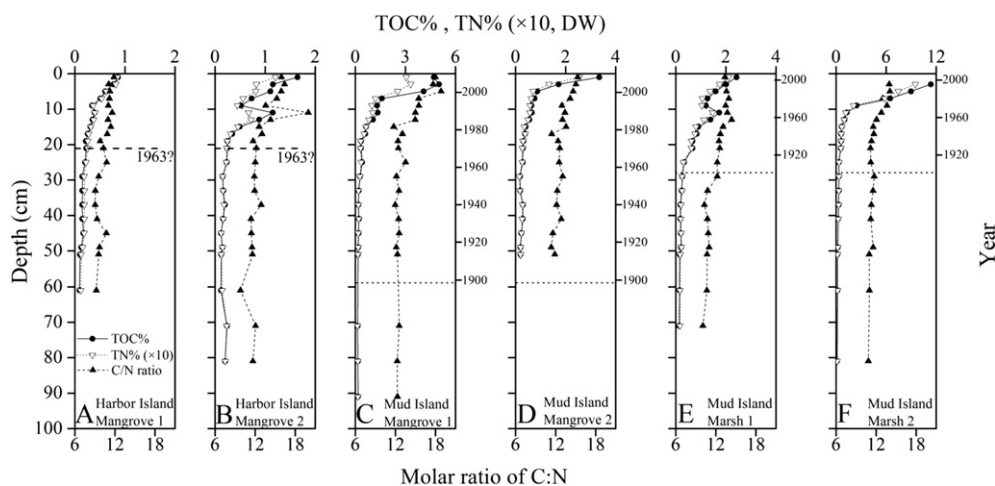


Fig. 2. Percent TOC, TN, and C:N ratios at the two sites in Port Aransas, Texas (USA), at harbor island and Mud island.

surface sediments (Fig. 4). The lack of significant difference between Δ_8 and Δ_6 values throughout the core depths suggests that the inputs of cinnamyl (*p*-coumaric and ferulic acid) phenols were not a significant component of the total Δ_8 in these soils. Similar to the bulk TOC and TN values, the most significant depth change in Δ_8 and Δ_6 values, occurred post-1963. The highest Δ_8 and Δ_6 values were found in Mud Island (Marsh 1) soils at a depth of 10 cm; the lowest values were found at the Harbor Island (Mangrove 1) location.

Both indices of lignin decay [(Ad/Al)*v*, P/(V + S)], showed significantly less variability than %TOC, %TN, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, Δ_8 , and Δ_6 , from the bottom to surface soils in all cores at the study sites (Fig. 5). The ranges of the (Ad/Al)*v* and P/(V + S) indices were from 0.1 to 0.6 and 0.1 to 0.5, respectively. The highest values of (Ad/Al)*v* occurred at 30 cm at the Harbor Island (Mangrove 1) site. The highest values of P/(V + S) occurred at Harbor Island (Mangrove 1), Harbor Island (Mangrove 2) and Mud Island (Mangrove 1) with subsurface peaks at 15, 40, and 70 cm, respectively. C/V and SV ratios were relatively stable throughout all cores (Fig. 6). However, sub-surface peaks in C/V ratios may suggest that there was more loss of cinnamyl phenols relative to vanillyl over time compared to syringyl phenols. In fact, the most significant decrease in C/V ratios was observed post-1963 at the Mud Island (Marsh 2) site (Fig. 6). Historical changes in carbon and lignin pools over the past 120 years in Mud Island soils, showed that there has been a significantly

greater increase in both of these pools at the mangrove site compared to the marsh site (Fig. 7).

3.5. Aerial imagery

Both average mangrove and salt marsh vegetation cover increased between 1951 and 1967, in the 10 m area surrounding each core location (Fig. 8). Unvegetated cover types (open water and salt flat) decreased in this time period, apparently due to large-scale geomorphic alteration in the back-barrier island environment. In the Mud Island area, the formerly aquatic substrate appeared to raise in elevation, possibly due to sediment overwash driven by a Category 4 hurricane at landfall, Hurricane Carla in 1961. In the Harbor Island area, the former salt flat appeared to have dropped in relative elevation, allowing wetland migration onto the former surface, following a common trend seen throughout the Texas Coastal Bend area during this time period (White et al., 2006).

However between 1967 and 2008, the mangrove and marsh core locations diverged. The Harbor Island Mangrove 1 and 2 locations and the Mud Island Mangrove 1 and 2 locations saw expansion of mangrove cover to 100% of the 10 m buffers. The Mud Island Marsh 1 and 2 saw marsh continue to expand, with little mangroves in the 10 m buffers by 2008. On average across all of the study locations, mangrove cover continued to expand, while salt marsh cover decreased (Fig. 8d).

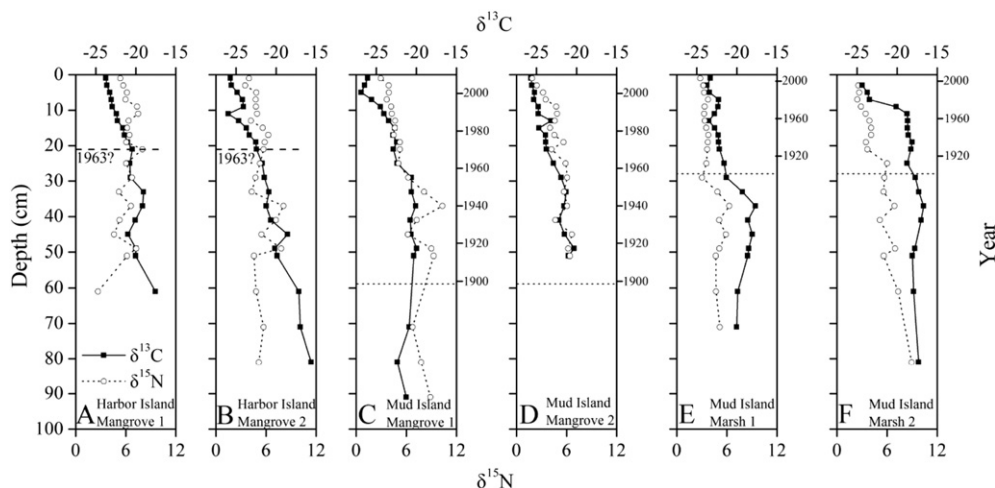


Fig. 3. Stable isotopic values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of all soil samples at the two sites in Port Aransas, Texas (USA), at harbor island and Mud island.

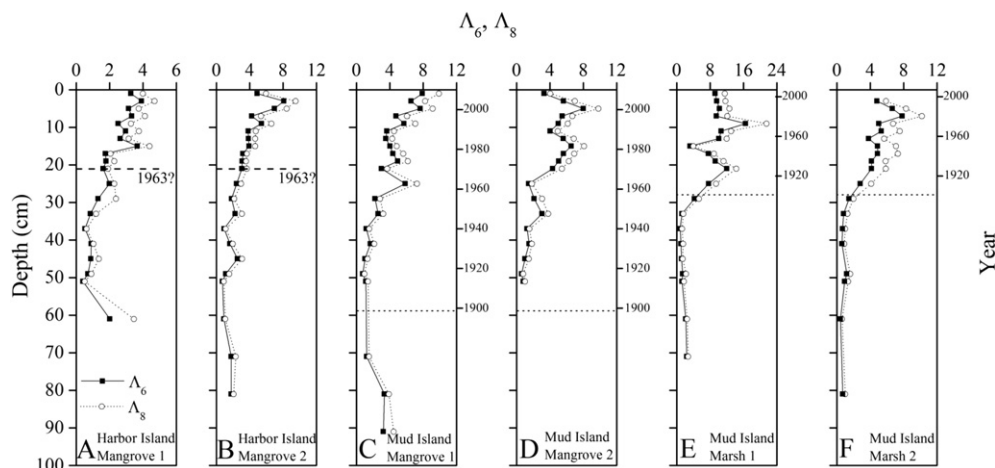


Fig. 4. The Δ_8 and Δ_6 values for all soil samples at the two sites in Port Aransas, Texas (USA), at harbor island and Mud island.

4. Discussion

4.1. Geochemical tracers of historical mangrove expansion

Mud and harbor island mangrove sites – Based on lignin-phenols, C:N ratios, and stable $\delta^{13}\text{C}$ values, there has been an increasing trend of mangroves compared to marsh wetlands along the southern Texas coast over the past 60 years. For example, the change in the range of $\delta^{13}\text{C}$ values from ca. -15 to -26‰ suggest a shift from C_4 to C_3 plants. It is well known that C_3 plants discriminate more against ^{13}C than C_4 plants through different metabolic pathways, which results in the $\delta^{13}\text{C}$ values of C_3 and C_4 to range from -35 to -20‰ and -19 to -9‰ , respectively (Fry, 2006; Kuzyakov, 2006). However, based on past satellite imagery, both Mud and Harbor Island also appear to have been dominated by unvegetated, but tidally-influenced surfaces around 1951, near the locations of our cores. This could implicate algae as well in these areas, though there is no obvious algal cover in the imagery. In fact, the $\delta^{13}\text{C}$ values of marsh benthic algae (-16 to -27.7‰) (Fry and Sherr, 1984; Neubauer, 2000) and coastal phytoplankton (-18 to -24‰) (Fry and Sherr, 1984; Currin et al., 1995) overlap with $\delta^{13}\text{C}$ values in wetland soils and need to be considered when examining coastal wetland plant community shifts. Another factor that needs to be considered here is how $\delta^{13}\text{C}$ values were affected by decomposition processes in these wetland soils. Although we did not directly examine the effects of decomposition, the $\delta^{13}\text{C}$ values of decomposing mangroves leaves has been shown to

become slightly depleted over time (ca. 2‰) (Fourqurean and Schrlau, 2003), which is significantly less than the observed shifts in our cores, though they may have in part contributed to the more depleted signal over time. Similar to $\delta^{13}\text{C}$ in mangrove leaves $\delta^{15}\text{N}$ also becomes more depleted with decay, which may have also contributed to the overall depletion of $\delta^{15}\text{N}$, particularly since 1963, in our mangrove cores. Sources of inorganic nitrogen for plants (e.g., NO_3^- , NH_4^+), microbial processes that both deplete and enrich soils, and physiological plant processes that discriminate against ^{15}N all contribute to $\delta^{15}\text{N}$ values in soils (McKee et al., 2002). The more depleted range of $\delta^{15}\text{N}$ in mangrove soils in southern Texas wetlands could have been in part due to epibionts, which in some tropical regions have been shown to have signatures from 5 to 6‰ (McKee et al., 2002), or perhaps greater utilization of NH_4^+ over NO_3^- , which through greater discrimination results in more depletion. Moreover, it has been shown that wetland sites further inshore and not directly fringing on the coast; although Mud Island and Harbor Island mangrove sites were in close proximity to the coast, they are tens to hundreds of meters from the shoreline. Mangroves not directly on the shoreline have been shown to exhibit greater NH_4^+ utilization over NO_3^- (McKee et al., 2002). We can only speculate about such effects at this time, further work is needed to better decipher these complex processes that control $\delta^{15}\text{N}$ in wetland soils.

Although algal inputs can interfere with separating $\delta^{13}\text{C}$ inputs from different wetlands sources, the increase in lignin-phenols and C:N ratios at about 1970 (Figs. 2 and 4) suggests that these changes

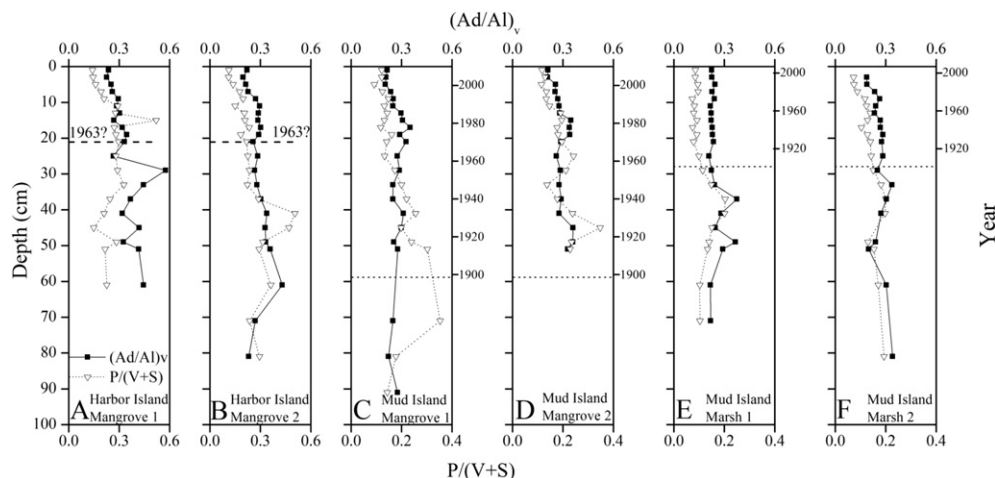


Fig. 5. Indices of lignin decay $[(\text{Ad}/\text{Al})_v \text{ and } \text{P}/(\text{V} + \text{S})]$ for all soil samples at the two sites in Port Aransas, Texas (USA), at harbor island and Mud island.

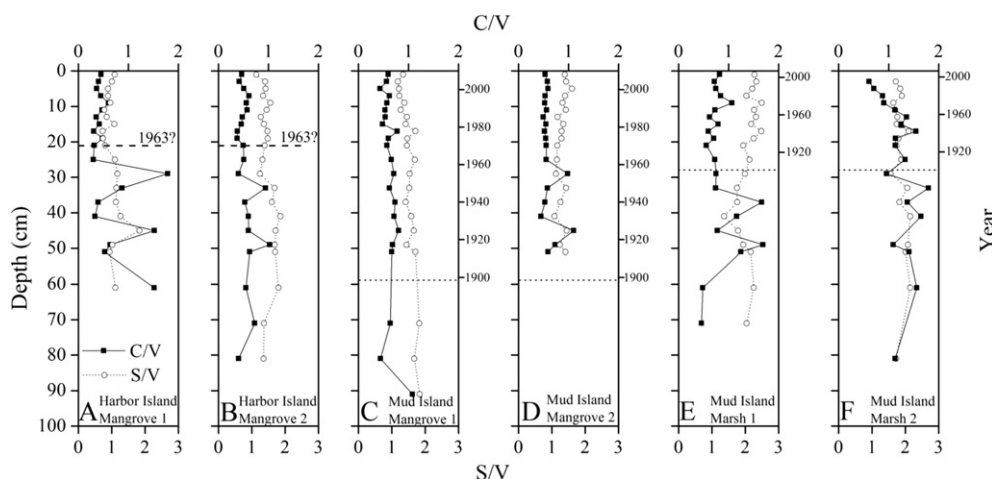


Fig. 6. Cinnamyl/vanillyl (C/V) and syringyl/vanillyl (S/V) ratios for all soil samples at the two sites in Port Aransas, Texas (USA), at harbor island and Mud island.

in $\delta^{13}\text{C}$ values were due to vascular plant changes, as well as changes from earlier unvegetated algal sources – as mentioned earlier. Moreover, the range of $\delta^{13}\text{C}$ in our surface soils are within the range expected for *Avicennia germinans* trees that are around with 1–2 m in height; this is based on the strong positive relationship ($r = 0.90$, $P < 0.01$) between plant height and $\delta^{13}\text{C}$ values in mangrove leaves (Lin and Sternberg, 1992). The much taller *A. germinans* (ca. 6 m) have $\delta^{13}\text{C}$ values that are approximately -28‰ . However, the C:N ratios in soils from the mangroves sites were significantly lower than the C:N ratio of *A. germinans* leaf litter (53) (Dittmar et al., 2001). Nevertheless, we expect an even more dramatic effect on carbon dynamics from more mature forests, these trees have only colonized and reached maturity in the last 23–29 years, since the freezes in the 1980's killed many of these Texas mangroves.

4.2. Carbon decay dynamics

The lower than expected C:N ratios in the mangrove soils at Mud and Harbor Islands was likely due to selective loss of carbon due to leaching/remineralization. The stabilization of C:N ratios in deeper horizons of soils suggest that much of the loss of both carbon and nitrogen occurs in the early stages of diagenesis in surface soils. This same pattern was shown for mangrove soils in Furo do Meio, Caete Estuary, Brazil (Dittmar et al., 2001). Here, they suggested that to have such low C:N ratios, it is necessary to have an estimated loss of $\sim 75\%$ carbon from leaf litter due to leaching and/or

remineralization in surface soils. Similar to what was found in the Caete Estuary, Brazil, the low C:N ratios also indicate that the contribution of woody material to the overall biomarker and stable isotopic signatures was minimal. Other edaphic parameters (e.g., Eh, pH, elevation, and salinity) measured at the Mud and Harbor Island mangroves sites were also shown to be conducive to enhanced remineralization of OC in these soils (Comeaux et al., 2012). The higher elevation, greater exchange of oxygen (via drainage and pneumatophores), higher pH and redox suggest that the surface soils of mangroves could at times have greater carbon turnover than in marshes. Although mangroves are generally lower in elevation than marshes (Rogers et al., 2005; Krauss et al., 2008) particularly in areas where they overlap, and that marshes are generally turning carbon over faster through a seasonal cycle the mangrove sites did have higher carbon sequestration rates compared to marshes on Mud Island. This fits with new results that show mangroves as important global sites for carbon storage – containing an estimated $1023 \text{ Mg C ha}^{-1}$ (Donato et al., 2011).

Relatively stable profiles of $\text{P}/(\text{V} + \text{S})$ and $(\text{Ad}/\text{Al})/\text{v}$ ratios in soils at the mangrove sites indicated that lignin was primarily decomposed via aromatic ring cleavage. Lignin decay usually occurs by propyl side-chain oxidation and/or demethylation of methoxyl groups (Bianchi and Canuel, 2011, and references therein). However, based on the stable profiles of $\text{P}/(\text{V} + \text{S})$ (an indicator of demethylation) and $(\text{Ad}/\text{Al})/\text{v}$ ratios it appears that aromatic ring cleavage was the primary means by which lignin was degraded in these soils; this also agrees with what was found at Caete Estuary,

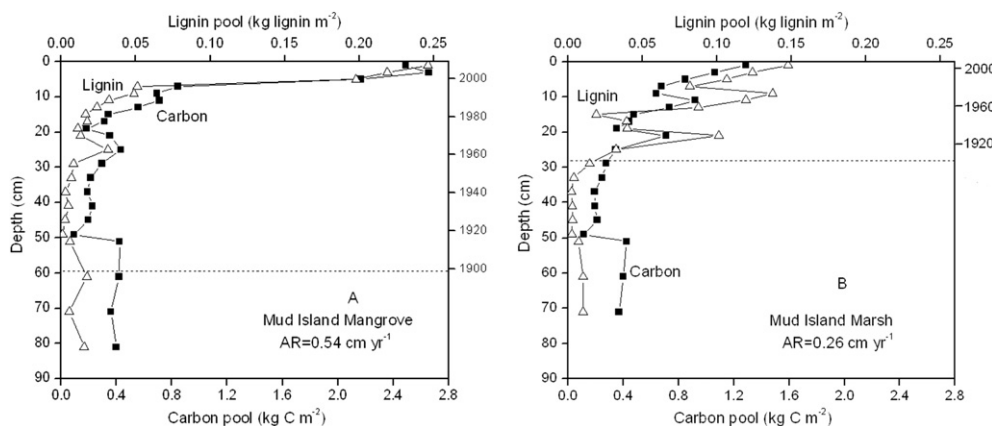


Fig. 7. Historical changes in carbon and lignin pools over the past 120 years in Mud island soils.

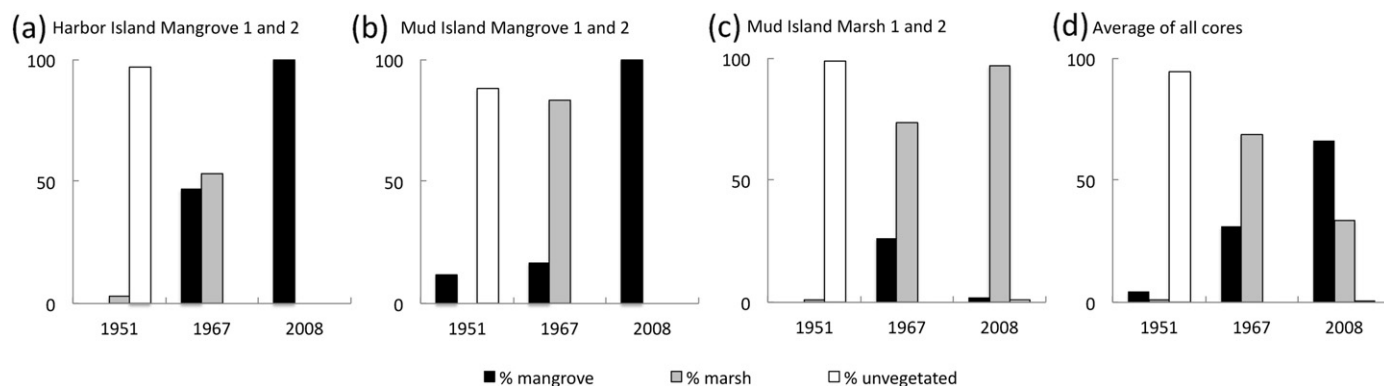


Fig. 8. Historical changes in vegetation percent cover at harbor island and Mud island in 1951, 1967, and 1981 based on satellite imagery.

Brazil (Dittmar et al., 2001). The greater decreases in C/V relative to S/V ratios post-1963, also agrees with trends found in mangrove soils at Caete Estuary, Brazil (Dittmar et al., 2001). This suggests that the more labile cinnamyl phenols, compared to syringyl and vanillyl phenols, resulted in selective loss of cinnamyl phenols. Cinnamyl phenols are more labile because of their ester-bound linkage in lignin and common association with carbohydrates (Hartley, 1973; Kirk et al., 1980; Bianchi et al., 2002). The lack of a significant difference in the Δ_8 and Δ_6 profiles also supports that cinnamyl phenols did not contribute significantly to the total lignin pool. Therefore, as mentioned earlier, while there may have been some leaching/remineralization of other carbon pools in these soils, lignin seemed to be relatively stable.

Mud Island marsh sites – The post-1970 mean $\delta^{13}\text{C}$ values in marsh site soils were significantly more enriched than all other mangrove sites, except between Mud Island (Marsh 1) and Harbor Island (Mangrove 1). The more enriched signal in marsh soils is expected considering that *Spartina alterniflora* litter typically has a $\delta^{13}\text{C}$ of ca. -13.6 to -13.1‰ (Ember et al., 1987; Yang et al., 2010). The fact that the marsh sites do not have a more distinct biomarker and stable isotopic signature is likely due to the proximity that mangroves were growing in and around these sites. In fact, the Mud Island Marsh 1 and 2 sites are within 60 m of the nearby Mud Island Mangrove 1 and 2 sites. Multiple mangrove trees were growing within the 10 m buffer of the Marsh 1 and 2 core locations in some years that we inspected. This proximity of the two vegetation types may lead to a biomarker-averaging of the litter deposited onto the soil surface in this aquatic environment. Moreover, it is also quite possible that these Marsh 1 and 2 sites had already been occupied by mangroves at various times in the past; in fact, the aerial image analysis details that both of these 10 m buffers had more mangroves in 1967 than they do today. Patterns in the lignin biomarker indices were also very similar between marsh and mangroves sites. Once again, this reflects relict inputs from mangroves material, however, similar decay dynamic of lignin [e.g., $\text{P}/(\text{V} + \text{S})$ and $(\text{Ad}/\text{Al})/\text{v}$ ratios] have shown similar patterns in *S. alterniflora* marshes that have never been previously occupied by mangroves (Benner et al., 1991).

The highest soil OC content was found at the Mud Island Marsh 2 site, which was not consistent with the Marsh 1 core. This Marsh 2 location also had the highest percentage cover of marsh at the 1951 and 1967 date of imagery analysis, and only recently showed a rapid drop in $\delta^{13}\text{C}$ after the ^{137}Cs peak after 1963, indicating that this core location may have been the most marsh-like over the historical time period. The Marsh 1 location more closely tracks the various mangrove core locations in each of these parameters. Many wetland soils have considerable heterogeneity in soil properties, as reflected in these differences. While mangroves were shown to

actually sequester more carbon than marshes in this study (see next section), some marshes have been shown to more effective in storing carbon through the association of macroaggregates (Zhang et al., 2010). This work showed that the highest carbon accumulation rate of $64.1 \text{ C kg}^{-1} \text{ soil yr}^{-1}$ in a *Spartina alterniflora* marsh was associated with macroaggregates. It is important to also note that in many cases there is more below-ground than above-ground biomass in salt marshes (Schubauer and Hopkinson, 1984). Although this paper is focused on the expansion of mangroves over marshes, there are many coastal regions that have had *S. alterniflora* introduced to rapidly replace other native C_3 species (e.g., *Suaeda salsa*), so *S. alterniflora* can also considered to be an invasive halophyte in other coastal regions (Zhang et al., 2010).

4.3. Carbon accumulation and sequestration rates

Significantly higher carbon sequestration in mangrove compared to marsh sites on Mud Island, are consistent with the recent reports on blue carbon sinks, which show that mangroves store more carbon than marshes on a global scale (Cai, 2011; Donato et al., 2011; Murray et al., 2011; McLeod et al., 2011; Hopkinson et al., 2012). Although the soil carbon pools in these two wetland habitats can be quite variable, however, the real difference in carbon sequestration between these two habitats is found when factoring in the amount of living biomass. For example, the living biomass of estuarine mangroves sequester $237\text{--}563 \text{ tonnes CO}_2 \text{ e ha}^{-1}$ compared to only $12\text{--}60 \text{ tonnes CO}_2 \text{ e ha}^{-1}$ for marshes (Murray et al., 2011). This is also consistent with earlier work that showed the typical standing crop of biomass for marshes and mangroves are 500 to $200 \text{ g dry wt m}^{-2}$ (Day et al., 1989) and $10,000$ to $40,000 \text{ g dry wt m}^{-2}$ (Twilley et al., 1992), respectively. The range of carbon sequestration rates for mangrove ($253\text{--}270 \text{ g C m}^{-2} \text{ yr}^{-1}$) and marsh ($101\text{--}125 \text{ g C m}^{-2} \text{ yr}^{-1}$) soils at Mud Island was within the mid-range observed ($25\text{--}504 \text{ g C m}^{-2} \text{ yr}^{-1}$) for a broad spectrum of isolated depressional and/or forested freshwater wetlands reported by Bernal and Mitsch (2012).

When examining the historical changes in carbon and lignin pools over the past 110 years in Mud Island soils, it is clear that there has been a significantly greater increase in both of these pools at the mangrove site compared to the marsh site (Fig. 7). While some of this up-core increase in the bulk carbon pool is related to diagenetic loss at the deeper depths, as mentioned earlier (e.g., leaching/remineralization), the aforementioned discussion on lignin decay proxies indicate that much of the change is more likely due to the build-up of a changing source of lignin-containing material (e.g., mangrove). If we accept that this greater increase in the Mud Island Mangrove core was due to mostly the changing

inputs of mangrove material over older marsh deposits, we see the largest increase occurring post-1970 to present. This is also supported by the most dramatic changes in $\delta^{13}\text{C}$, Δ_8 , and Δ_6 , which support a change in plant source inputs from a C_3 to C_4 over this time period.

4.4. Implications of climate change and changing wetlands

Recent work (Comeaux et al., 2012) along with the results from this study, suggested that the mangroves which have replaced marshes over the past ca. 100 years on portions of the lower Texas coast, have higher carbon sequestration rates and have increased accretion rates of coastal wetlands during this timeframe. The higher accretion rates in mangroves, may serve as more efficient barrier to RSL and hurricane events along the Texas coast (Comeaux et al., 2012). If the conversion of marshes to mangroves continues to expand further up the coast and into the central northern Gulf coastline of Louisiana, where 40% of the nation's coastal wetlands reside, the consequences of greater carbon sequestration may be quite serious. Recent work has shown that there has been expansion *Avicennia germinans* over *Spartina alterniflora* in certain regions of coastal Louisiana since the 1980s (Perry and Mendelssohn, 2009).

On the basis that visual and geochemical data support that mangroves have replaced marshes in these regions (Fig. 8), we can make some estimates on projected carbon storage changes for coastal wetlands in the Gulf of Mexico. If we were to take all of the coastal marshes (which would include *Spartina alterniflora* marshes) in the Gulf of Mexico, which comprise an area of approximately 2.5 million acres (EPA, 1992; USFWS, 2011), and replace them with *Avicennia germinans* we could estimate the change carbon sequestration rates that might occur over time. Of course, this would assume that all *A. germinans* over *S. alterniflora* have similar carbon sequestration rates that have been measured here, and that *Spartina patens* and *Juncus* spp. or other species are not part of the equation. The result would be a net increase of $1.29 \pm 0.32 \text{ Tg C yr}^{-1}$ in current carbon sequestration. This represents about 1% of all the carbon buried by all the “blue carbon” on the planet (100 Tg C yr^{-1}) (Hopkinson et al., 2012, and references therein). The additional accretion afforded by *A. germinans*, again assuming that our data is extrapolated to the entire Gulf, would further alter this summary change. The final result of such a scenario could be a net increase of $129 \pm 45 \text{ Tg C}$ in 100 years. Considering the loss of blue carbon habitats around the globe at rates that vary from 0.7 to 7% annually (Hopkinson et al., 2012, and references therein), such changes here in the Gulf and other possible regions where such changes may occur, may prove to have an ameliorating effect on regional atmospheric CO_2 increases and emphasize the importance of preserving and restoring blue carbon environments.

5. Conclusions

1. Based on lignin-phenols, C:N ratios, and stable $\delta^{13}\text{C}$ values, there has been an increasing trend of mangroves compared to marsh wetlands along the southern Texas coast over the past 60 years. These trends have important implications for how carbon is stored and sequestered in this region. It also impacts the effectiveness of wetlands as buffer zones for protection from storms because changing from marshes to mangroves not only changes the infrastructure to a woodland system but also raises the surface topography of the wetland which should enhance protection from storms.
2. While there may have been some leaching/remineralization of other carbon pools in these soils, lignin seemed to be relatively

stable during these vegetation changes over the observed time period. The higher percentage of lignin associated with woody materials in a mangrove versus a marsh wetland should slow down the overall decay dynamics on decadal to centennial scales. This is important in terms of the overall stability and residence time of stored carbon in these soils.

3. Significantly higher carbon sequestration in mangrove compared to marsh sites on Mud Island, are consistent with the recent reports on blue carbon sinks, which show that mangroves store more carbon than marshes on a global scale. Higher carbon sequestration, greater lignin inventories, and higher wetland surface topography will stabilize the rates of organic carbon turnover in these coastal regions of the Gulf of Mexico. Future work on changes in the overall sequestration of CO_2 on a regional scale is needed to further verify that such coastal margin changes are impacting local CO_2 fluxes.
4. If regional changes in the Gulf of Mexico are to persist and much of the marsh vegetation was to be replaced by mangroves, there would be a significant increase in the overall storage and sequestration of carbon in the coastal zone. If such changes were shown to be impacting local CO_2 fluxes in the Gulf, this could provide evidence for further management of local wetlands that could result in new mangrove planting programs to increase the rate of mangrove to marsh conversion and to change the value of the land in terms of carbon trading units.

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