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Carbon dynamics in a marsh-influenced marine-dominated ecosystem

Heidi O'Hora
Union College - Schenectady, NY

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CARBON DYNAMICS IN A MARSH-INFLUENCED MARINE-DOMINATED ESTUARINE ECOSYSTEM

Heidi E. O’Hora

advised by
David P. Gillikin

Submitted in partial fulfillment of the requirements for
Bachelor of Science in the Department of Geology

UNION COLLEGE
June 2019
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ABSTRACT

A combination of global climate change, local anthropogenic pressures, and naturally occurring processes have impacted biogeochemical cycling in coastal systems. Here, a coastal estuarine ecosystem in North Carolina is studied in order to determine spatial relations, seasonal changes, and overall fluxes of carbon, as well as the influences of these factors on the biogeochemistry of the system as a whole. Partial pressure of carbon dioxide (pCO$_2$), percent dissolved oxygen (DO), particulate organic carbon (POC), total dissolved inorganic carbon (DIC), total alkalinity (TA), and carbon isotopes of organic and inorganic carbon—amongst additional data—were collected from numerous study locations in the Cape Lookout region of North Carolina in April 2017, October 2017, April 2018, June 2018, and October 2018. Carbon isotopes of POC ranging between -30 and -17.79‰ coupled with a decreasing trend in C/N values moving down-estuary indicate that the organic carbon in the system is mainly sourced from upland vascular plant and agricultural inputs, with a small influence from in-estuary Spartina marsh grasses. The majority of the estuary was oversaturated with CO$_2$ compared to the atmosphere during all seasons, with the marsh-creek Smyrna Creek consistently exhibiting the most extreme pCO$_2$ values, peaking at 14606 µatm in the head of the creek in June 2018. Some estuarine sites were occasionally undersaturated in CO$_2$, likely from local phytoplankton blooms occurring during spring and summer. Carbon flux from these three creeks into Jarrett Bay is evident, as is further flux of CO$_2$ through the sound and out into the ocean where the CO$_2$-saturated estuarine waters combine with the less CO$_2$-rich marine waters to produce ocean values of ~625 µatm. TA values throughout the system range from 1872–2342 µmol kg$^{-1}$, excluding Smyrna and Williston marsh-creeks which exhibited anomalous TA in several different seasons. Omitting these two creeks, the remainder of the system shows an increasing spatial TA trend moving down-estuary over the salinity gradient with the lowest values in Jarrett Bay and the highest values in the ocean. Due to seasonal mixing trends, DIC concentration increased down-estuary in the Summer and Spring and decreased over the salinity gradient in the Fall; however, the head of Smyrna Creek typically exhibited notably high DIC compared to the rest of the system, as CO$_2$ is the main contributor to DIC within the salt marsh. Plotting DIC against TA indicates that inorganic carbon likely originates from a combination of sulfate reduction, denitrification, CO$_2$ invasion, and aerobic respiration. Calculations of air–sea CO$_2$ flux indicate that the estuarine waters as a whole are a significant source of CO$_2$ to the atmosphere with an average air–sea CO$_2$ flux of 13.4 mmol m$^{-2}$ day$^{-1}$. 
ACKNOWLEDGEMENTS

I wish to extend my gratitude to several individuals who have provided me with guidance, support, and inspiration throughout my academic and research experience.

First and foremost, I would like to sincerely thank my advisor David Gillikin for not only being an excellent mentor, but for instilling in me a strong passion for research, teaching, and personal development. Under his guidance, I have learned many invaluable skills and lessons, accomplished several exciting research projects, and grown significantly as both a scientist and as an individual. His inspiration is an asset I will take with me always.

I also wish to thank Professor Donald Rodbell for his untiring avidity for teaching and for the field the paleoclimatology. He has continuously inspired me throughout my academic experience and has helped me to discover my own passion for paleoclimatology research.

I would further like to thank the rest of the Union College Geology Department faculty for their continuous support, motivation, and guidance. I have been extremely fortunate to have been part of a department that so consciously aims to encourage and assist one another.

To my colleagues Hayley Bennett and Elizabeth Cilia, Professor David Goodwin and his students from Denison University, and my advisor David Gillikin—thanks for all of your help collecting samples and data for my thesis in both the field and the lab. This project would not have been possible without you all.

I would like to thank Professor Anouk Verheyden-Gillikin and Madelyn Miller for their valuable assistance in processing my samples in the Union College Stable Isotope Lab.

Thank you to my family for making my undergraduate education and research experience at Union College possible. I am forever grateful for your ceaseless support and confidence in me.

Finally, thanks to the organizations that provided funding to make my research possible, including the Union College Field Fund for funding my research trip to North Carolina, and the Nation Science Foundation for funding Union College’s stable isotope ratio mass spectrometer and peripherals (NSF-MRI #1229258).
INTRODUCTION

As the changing climate and its implications continually raise concerns around the globe, comprehension of the global carbon cycle and all of its constituents is becoming increasingly important. One commonly overlooked but critical system in this cycle is the coastal marine environment. The coastal system accounts for ~7.5% of the total ocean area with the continental shelf contributing ~7.2% and estuaries only ~0.3% (Cai, 2011). Despite the very small percentage of estuary area relative to total ocean area, the CO₂ degassing flux of estuaries is a highly significant contributor to the global CO₂ flux (Cai, 2011); however, past studies attempting to model carbon cycling of the ocean and atmosphere have ignored the CO₂ flux of coastal marine systems (Sarmiento and Gruber, 2002; Cai et al., 2003). Regarding the past research that has been conducted on the biogeochemistry of estuaries, it is relevant to note that the majority of this effort has focused on the analysis of river-dominated estuaries as opposed to marine-dominated estuaries (Jiang et al., 2008; Cai, 2011). This lack of research into marine-dominated estuaries may lead to incorrect assumptions and estimations regarding large-scale estuarine processes and fluxes due to a weighting of available data toward river-dominated estuaries. Therefore, it is crucial to study more marine-dominated estuaries and to subsequently compare this data with that from river-dominated estuaries in order to determine more accurate large-scale biogeochemical flux patterns and estimates.

Furthermore, both the interactions between estuaries and their adjacent continental shelves and the interactions between these shelves and the atmosphere are not well-constrained in terms of carbon cycling and fluxes (Cai, 2011). Due to the possible implications of these processes on the global biogeochemical scale, it is critical to emphasize and analyze these topics in order to expand understanding of the carbon cycle (Wang and Cai, 2004). This paper aims to clearly describe the concepts of estuarine carbon cycling by distinguishing between different forms of estuaries and their related fluxes, with a focus on a marine-dominated estuary to ultimately emphasize the significance of the coastal marine system in global biogeochemistry.

**Figure 1.** [a] Total surface area of each of the three constituents in the ocean system (open oceans, estuaries, continental shelves). [b] Estimated air–sea CO₂ fluxes from each of these three sub-systems (from Cai, 2011).
1. TYPES OF ESTUARIES
Coastal marine environments are complex and important systems made up of several sub-systems including estuaries and continental shelves. While a single universal definition of an estuary does not exist, one of the most frequently cited definitions states that an estuary is “a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which seawater is measurably diluted with freshwater derived from land drainage” (Cameron and Pritchard, 1963; Jiang et al., 2008). Under this description, both river mouths and coastal brackish lagoons may be considered estuaries (Jiang et al., 2008). Distinguishing between these two categories of estuarine systems is crucial to understanding the processes of carbon cycling in coastal marine environments and to applying this knowledge on the global scale. River mouths are therefore classified as river-dominated estuaries, whereas coastal brackish lagoons that do not receive significant upland freshwater inputs are categorized as marine-dominated estuaries (Jiang et al., 2008). Understanding the differences and similarities between these two systems is the first step toward understanding estuarine carbon cycling.

1.1 River-dominated estuaries
Systems in which significant upland freshwater is transported to the mouth of a river at the point which it meets the ocean are considered to be river-dominated estuaries (Jiang et al., 2008). The substantial flow of freshwater in this type of estuary impacts several different biogeochemical factors including salinity, CO₂ degassing rates, pCO₂, and DIC (Jiang et al., 2008). Regular flushing of river-dominated estuaries promotes mixing of freshwater and seawater and decreases estuarine water residence time. Periods of increased river discharge during times of high-flow influence river-dominated estuaries with an influx of freshwater that lowers the surface water salinity (Jiang et al., 2008). Flushing rates also affect the amount of riverine CO₂ that is present in the total CO₂ flux out of the river-dominated estuary into the atmosphere. Rate of flow is positively correlated with riverine CO₂ concentration; thus, high-transit rivers contribute more significantly to the overall degassing of CO₂ out of the related estuary than do low-transit rivers (Borges et al., 2006). The total CO₂ efflux out of river-dominated estuaries is consistently recognized as being greater than the CO₂ efflux out of non-riverine estuaries (Ortega et al., 2005; Fagan and Mackenzie, 2007; Jiang et al., 2008). Similarly, pCO₂ is also typically higher in river-dominated estuaries due to the significance of upland freshwater inflow as a source of CO₂ to the system (Raymond et al., 2000; Borges et al., 2006; Jiang et al., 2008). The inflowing river carries CO₂-supersaturated waters into the estuarine zone which also contributes to the total pCO₂ of the system via in situ processes (Abril and Borges, 2004; Jiang et al., 2008). Therefore, pCO₂ of river-dominated estuaries is a function of both river discharge and estuarine processes; high discharge brings increased amounts of CO₂ into the estuary while simultaneously promoting flushing of the system, whereas periods of low discharge are associated with
a more significant CO$_2$ contribution by processes occurring exclusively within the estuarine zone (Jiang et al., 2008). The DIC concentration of a river-dominated estuary is also generally higher than that of a marine-dominated estuary because the total DIC in an estuary is determined by mixing of the DIC in the ocean and freshwater endmembers. In river-dominated estuaries, the freshwater endmember is a significant contributor to total estuarine DIC, as is the ocean endmember (Jiang et al., 2008). This is not the case for marine-dominated estuaries, which differ in both morphology and biogeochemistry from river-dominated estuaries.

### 1.2 Marine-dominated estuaries

In contrast to the estuaries fed by significant riverine inflow, marine-dominated estuaries (also commonly called marsh-dominated estuaries) receive minimal freshwater inputs other than precipitation and groundwater, creating the characteristic brackish lagoon environment of such systems (Jiang et al., 2008). The lack of substantial freshwater inflow into marine-dominated estuaries relative to river-dominated estuaries affects the biogeochemistry of this type of system. As the name suggests, marine-dominated estuaries are typically influenced more significantly by the ocean endmember than by the freshwater endmember (Jiang et al., 2008). During periods of low-flow, river-dominated estuaries may resemble marine-dominated estuaries because low freshwater discharge into an estuary allows for the marine influence to become relatively more visible (Jiang et al., 2008). Eliminating regular riverine inputs removes a major source of CO$_2$ and DIC to the estuary; thus, marine-dominated estuaries generally exhibit lower pCO$_2$ and DIC values than river-dominated estuaries (Jiang et al., 2008). This lack of river-borne influxes of CO$_2$ is likely responsible for the lower CO$_2$ degassing rates typically observed in marine-dominated estuaries. A study by Jiang et al. (2008) found a strong correlation between flux differences in the two types of estuaries compared with calculated river-borne CO$_2$ fluxes, supporting the above statement that marine-dominated estuaries generally exhibit relatively less degassing than river-dominated estuaries.

The concept of excess DIC—the total amount of DIC sourced from estuarine zone inputs—also contributes to degassing fluxes (Jiang et al., 2008). Although marine-dominated estuaries typically exhibit relatively low total DIC, they often have high excess DIC due to direct CO$_2$ inputs from surrounding marshland and long residence times within the estuarine zone (Cai et al., 1999; Neubauer and Anderson, 2003; Wang and Cai, 2004; Jiang et al., 2008). Intertidal salt marshes are frequently found adjacent to or surrounding marine-dominated estuaries (Jiang et al., 2008). These ecosystems are characterized by high levels of productivity and decomposition which contribute significant quantities of CO$_2$ to the estuarine zone via tidal oscillation and marsh sediment porewater drainage (Jahnke et al., 2003; Neubauer and Anderson, 2003). The resultant large amounts of excess DIC in these estuaries are responsible for much of the CO$_2$ degassing that occurs in such

2. ESTUARINE CARBON CYCLE

Estuaries play a critical role in the global carbon cycle, contributing to both the atmospheric and oceanic cycles of carbon (Cai and Wang, 1998; Cai et al., 2003). Numerous past studies have suggested that although estuaries account for only 0.3% of global ocean surface area, the global estuarine CO$_2$ degassing flux is comparable in magnitude to the atmospheric CO$_2$ uptake by the continental shelf (Borges, 2005; Borges et al., 2005; Cai et al. 2006; Chen and Borges, 2009; Cai, 2011). Furthermore, estuaries have been identified as significant sources of DIC transport to the adjacent continental shelf with a particular emphasis on the importance of marsh-influenced marine-dominated estuaries in this operation (Wang and Cai, 2004). Again, the cruciality of focusing more research on the processes occurring within marine-dominated estuaries is emphasized. It is also critical that studies attempting to model the global carbon cycle begin to consider the biogeochemical fluxes that characterize the interactions between marshes, estuaries, coastal marine waters, and the atmosphere.

2.1 Carbon sources

Estuaries regularly receive significant inputs of carbon from a variety of sources. The dominating origins of the carbon differ between river-dominated and marine-dominated estuaries (Cai and Wang, 1998; Jiang et al., 2008). The characteristic high freshwater inflow of river-dominated estuaries is responsible for the majority of the carbon carried into these systems. Jiang et al. (2008) observe that estuarine pCO$_2$ levels and river discharge are positively correlated, indicating that riverine inflow is a significant source of CO$_2$ to the estuarine zone of river-dominated estuaries. Extensive microbial decomposition of organic material present in the sediments and waters of rivers produces abundant CO$_2$ that supersaturates the river waters before they enter the estuarine zone (Cole and Caroaco, 2001; Abril and Borges, 2004; Jiang et al., 2008). Additionally, the presence of high concentrations of humic substances occurring in some rivers further contributes to the supersaturation of CO$_2$ (Cai and Wang, 1998; Jiang et al., 2008). These CO$_2$-rich waters are injected into the estuarine zones of the river-dominated estuaries at which point they mix with the DIC from the marine endmember and the in-estuary decompositional processes (Jiang et al., 2008).

In contrast, marine-dominated estuaries do not receive significant carbon inputs from far-traveled, CO$_2$-rich river waters; rather, these systems rely on estuarine zone processes and intertidal marshland inputs for their DIC (Jiang et al., 2008). Similarly to riverine processes, respiration and microbial decomposition of organic matter occurs within the soils and waters of the estuarine zone of marine-dominated estuaries, producing CO$_2$. This process is amplified in these systems due to the importance of intertidal mixing in marine-dominated estuaries and the significant exchange that occurs accordingly between an estuary and its adjacent marshes (Jiang et al., 2008). These
marshes are extremely productive ecosystems with the potential to sequester significant amounts of carbon from the atmosphere (Cai et al., 2003; Cai, 2011). Marsh plants directly remove CO$_2$ from the atmosphere through photosynthesis and then eventually die, directly contributing their biomass into the marsh waters where decomposition will take place (Cai, 2011). Cycles of tidal ebb and flow flood the salt marsh and then subsequently draw large amounts of organic detritus, marsh porewaters, DOC, and DIC out into the estuarine zone (Middelburg et al., 1996; Cai and Wang, 1998; Jahnke et al., 2003; Neubauer and Anderson, 2003; Jiang et al., 2008). Here, further decomposition of the biomass takes place, producing CO$_2$. Porewaters also release CO$_2$ into the estuarine waters as the previously trapped DIC is transported out of the marsh (Cai and Wang, 1998; Chen and Borges, 2008). This combination of autochthonous and allochthonous organic carbon inputs fosters the net heterotrophy of this type of system and accounts for the observed excess in DIC (Cai et al., 2003; Wang and Cai, 2004; Chen and Borges, 2008; Cai, 2011).

2.2 Atmospheric flux
The waters of both river- and marine-dominated estuaries have been identified as sources of CO$_2$ to the atmosphere (Jiang et al., 2008). This is due to the heterographic status of these ecosystems in which excess CO$_2$ collects and then is naturally released as an air–water flux (Wang and Cai, 2004; Cai, 2011). Numerous studies have been conducted on the carbon flux in different estuaries around the globe, producing results that vary in magnitude but form the consensus that estuarine waters exhibit positive degassing of CO$_2$ into the atmosphere. Chen and Borges (2008) compiled an inclusive list of air–water CO$_2$ fluxes obtained by other researchers at many different estuaries. These CO$_2$ efflux values range from 2.2 mol C m$^{-2}$ yr$^{-1}$ at Randers Fjord in Denmark (Gazeau et al., 2005) to 76.0 mol C m$^{-2}$ yr$^{-1}$ at the Douro estuary in Portugal (Frankignoulle et al., 1998) with an average value of 32.1 mol C m$^{-2}$ yr$^{-1}$ (Chen and Borges, 2008). This large range in air–water CO$_2$ flux values depicts the variability in estuarine carbon capacity and cycling, likely caused by differing estuary types, surrounding environments, amount of inflow, mixing dynamics, relative location, etc. Identifying and understanding these differences are crucial steps to applying these individual flux data on a global biogeochemical scale.

Further research into marine-dominated estuaries is necessary to constrain the estimates regarding global estuarine CO$_2$ efflux. Existing data on air–water CO$_2$ flux from estuaries is biased toward river-dominated estuaries, which are recognized to typically have higher flux than marine-dominated estuaries (Jiang et al., 2008). Therefore, previous estimates of global-scale air–water CO$_2$ flux are likely overestimated and would benefit from refinement via a more balanced dataset. For example, Borges (2005) and Borges et al. (2005) approximate global estuarine CO$_2$ efflux to be ~0.40 Pg C yr$^{-1}$. This estimate is based off of flux data collected predominantly from river-dominated
estuaries but uses a global estuary surface area value that includes both river- and marine-dominated estuaries (Jiang et al., 2008; Borges, 2005; Borges et al., 2005). Cai (2011) attempts to refine this estimate by using air–water CO\textsubscript{2} flux values reported in Jiang et al. (2008) for a river-dominated estuary and two marine-dominated estuaries. By differentiating between these two types of systems and their relative fluxes, the global air–water CO\textsubscript{2} flux estimate is decreased by ~25% to a value of ~0.25 Pg C yr\textsuperscript{-1} (Cai, 2011). This estimate could be refined even further by separately averaging air–water CO\textsubscript{2} flux values from numerous river-dominated and marine-dominated estuaries and then combining these values to generate a weighted average that may then be related to the global estuary surface area.

2.3 Continental shelf flux

In addition to the carbon flux between estuaries and the atmosphere, there exists an observable movement of estuarine DIC out onto the continental shelf region of the coastal ocean (Wang and Cai, 2004; Chen and Borges, 2008). This transport of material from marshlands and estuaries out into coastal waters was originally coined the “outwelling hypothesis” and has been the subject of many studies for several decades (Wang and Cai, 2004). This outwelling hypothesis has evolved from the basic idea that biomass and nutrients are drawn out of marshes and deposited in estuaries and the coastal ocean where they work as fertilizers (Teal, 1962; Odum, 1968) to the more recent understanding of the coastal marine environment as a complex and multifaceted system in which the flux of DIC plays an important role (Childers, 1995; Wang and Cai, 2004). The movement of DIC through the coastal system provides substantial insight into the biogeochemical interactions between estuaries and the continental shelf as well as implicatory discernment of global carbon cycling (Gattuso et al., 1998; Tsunogai et al., 1999; Cai et al., 2000; Frankignoulle and Borges, 2001; Wang and Cai, 2004). The basic but significant finding of research into the modern outwelling hypothesis reveals that estuaries are major sources of DIC for the adjacent coastal waters (Winter et al., 1996; Cai and Wang, 1998; Cai et al., 2000; Raymond et al., 2000; Neubauer and Anderson, 2003; Wang and Cai, 2004). Wang and Cai (2004) reported that the Duplin River estuary on Sapelo Island, Georgia, transports 109 g C m\textsuperscript{-2} yr\textsuperscript{-1} out into the adjacent continental shelf. They then extrapolate this value to represent the flux from all marsh-influenced estuaries in the southeastern U.S. to obtain an estimated total annual DIC export of 0.7E+12 g C. If this estimate is fair, this flux may be regarded as comparable in magnitude to that of riverine DIC flux (Wang and Cai, 2004).

Research into air–water CO\textsubscript{2} fluxes of the continental shelf has also undergone substantial scrutiny and development (Chen and Borges, 2008). Scientific controversy exists regarding whether the continental shelf acts as a source or a sink of atmospheric CO\textsubscript{2} (Chen and Borges, 2008; Cai, 2011). Chen and Borges (2008) conclude that the quantity of studies reporting a negative air–water CO\textsubscript{2} flux outweighs the number of studies that
suggest positive CO$_2$ degassing from the shelf, and, therefore, they agree with the former opinion. They then combine all available past CO$_2$ flux data to calculate the estimated global average annual CO$_2$ uptake by the continental shelf to be \( \sim 0.35 \) Pg C yr$^{-1}$ (Chen and Borges, 2008). Chen and Borges (2008) also note the relative lack of data for low-latitude continental shelves and suggest that estimates may be refined by increasing this dataset.

In contrast, Cai (2011) interprets the existing data on continental shelf air–water CO$_2$ flux to indicate that shelves falling within the latitudinal range of 30° to 90° represent sinks of atmospheric CO$_2$ with a total uptake flux of 0.35 Pg C yr$^{-1}$, while shelves located between the latitudes of 0° and 30° act as sources of atmospheric CO$_2$ and release a total flux of 0.10 Pg C yr$^{-1}$. When combined, this interpretation estimates the net global CO$_2$ uptake flux of the continental shelf to be 0.24 Tg C yr$^{-1}$ (Cai, 2011). Cai (2011) then reports that this number is supported by the findings of Laruelle et al. (2010), who employed a different method of scaling but obtained a similar value. The predominant conclusion regarding this flux appears to consider continental shelves as sinks of CO$_2$ on the global-scale, although by varying amounts of uptake (Cai et al., 2003; Chen and Borges, 2008; Cai, 2011). If this is the case, it is possible that shelves work as a one-way pump, absorbing CO$_2$ from the atmosphere and then transporting it out into the open ocean (Cai et al., 2003). However, based on the variations observed in these two interpretations of the continental shelf carbon cycle, it is clear that further research needs to focus on this topic and work to better constrain the global air–water CO$_2$ flux estimates.

### 3. PROJECT SUMMARY

Although the coastal marine system accounts for only a small fraction of the total ocean surface area, the processes of carbon cycling occurring within this system are applicable on the global-scale. High degassing of CO$_2$ out of both river- and marine-dominated estuaries is clearly observable, indicating that these systems cannot be overlooked in the carbon cycle. Flux of DIC through these systems and out onto the continental shelf initiates further activity in the coastal carbon cycle and ultimately allows for atmospheric CO$_2$ uptake by the shelf. This process is likely to impact both atmospheric and oceanic biogeochemistry by moving carbon through the system accordingly. Both estuaries and continental shelves exhibit the potential for important climatic implications, such as the possibility of the shelf behaving as a mechanism for sequestering and re-directing atmospheric CO$_2$ as DIC in the deep ocean. This study aims to analyze the cycling dynamics of organic and inorganic carbon throughout the waters of a marsh-influence marine-dominated estuary in an attempt to contribute to the discussion of coastal system carbon fluxes.

### METHODS AND MATERIALS

This project employed both field and laboratory techniques, consisting of extensive field sampling of various biogeochemical parameters within a marsh-
influenced marine-dominated estuary and subsequent data analysis in the lab.

1. FIELD METHODS

1.1 Study area

The Cape Lookout region of North Carolina is situated in the central area of the state’s Outer Banks near the coastal townships of Smyrna and Marshallberg (Fig. 2). Both river- and marine-dominated estuaries are common features in this coastal region. This study focuses on a marine-dominated estuary transect spanning from within the marshlands of Jarrett Bay and throughout the estuarine system into the coastal marine waters at Cape Lookout. Samples were collected from three small tidal creeks originating in the salt marsh; Jarrett Bay into which these creeks flow; Core Sound, the lagoon located between the North Carolinian coast and adjacent barrier islands; and the area of ocean closest to the mouth of the sound at Cape Lookout. The salt marsh is dominated by the C4 cordgrass *Spartina alterniflora* while the lands surrounding the estuary are heavily influenced by extensive agriculture and anthropogenic development. Production by *Spartina alterniflora* in marsh systems has been estimated to range between 1281 and 762 g dry wt m$^{-2}$ yr$^{-1}$ (Darby and Turner, 2008). Several different species of algae, mollusks, and aquatic vertebrates were identified within the estuary, illustrating the diversity of life present in this system.

1.2 Sampling techniques

Samples were collected during five different sampling trips, two of which occurred in 2017 and three in 2018. The 2017 trips included one Spring trip (April 9–10) and one Fall trip (October 22). The three 2018 sample collections occurred in Spring (April 20), Summer (June 23–27), and Fall (October 18–20). At each sampling site during each trip, various techniques were employed to collected data. A handheld GPS was used to record specific coordinates of each site. Wind speed, air temperature, humidity, dew point, and barometric pressure were measured with a handheld Kestrel 5500 weather meter. Surface water was evaluated with either a YSI ProDSS or a YSI professionalPlus and a ProODO multiparameter digital water quality sampler to determine water temperature, marine barometric pressure, dissolved oxygen concentration and saturation, salinity, pH, and FNU/NTU.

Figure 2. Map of the study area with [a] showing the relative location of the Cape Lookout region along the east coast of the United States (pink star), and [b] providing a zoomed-in view of the estuary with all sample sites along the transect defined by pink markers. Map modified from Google.
Specifically, the oxygen saturation level was measured using an optical electrode calibrated on saturated air, exhibiting a ±1% accuracy. Sample pH was determined with a Glass Bulb Combination Electrode with an accuracy of ±0.2 pH units. Samples for later laboratory determinations of total alkalinity were collected at each site by initial filtration of duplicate 50 mL of surface water through pre-combusted (4 hours at 450°C) Whatman GF/F filters and subsequent filtration through 0.2 μm polyethersulfone syringe filters (Sartorius, 16532-Q) into HDPE bottles in which the samples were stored until titration analysis in the lab. Water sample filtration was also performed through two sizes (25 mm and 47 mm) of pre-combusted (4 hours at 450°C), pre-weighed Whatman GF/F glass-fiber filters with 0.7 μm nominal pore size. Samples of 100–1000 mL were filtered through the smaller filters, and 350–3000 mL of water were filtered through the 47 mm filters (site-specific sample sizes determined by maximum amount of water readily able to be filtered until material accumulated on the filter was sufficient for analysis). After filtration, the filters were air-dried and saved for subsequent lab analysis of particulate organic matter δ13C and δ15N (25 mm filters) and total suspended matter (47 mm filters). Chlorophyll a samples were collected by filtering 350–3000 mL of water over MF-Millipore 47 mm mixed cellulose esters (MCE) membrane filters (0.45 μm pore size), which were then stored in 15 mL polypropylene tubes in a cool box until return to the field-laboratory. Samples for water oxygen isotopes were taken by directly filling 15 mL polypropylene tubes with surface waters. Dissolved inorganic carbon isotopes (δ13C_DIC) were sampled by gently filling 12 mL Labco Exetainers with surface water, which were then poisoned with HgCl2 and capped without headspace. Dissolved CO2 concentrations were measured on site following Abril et al. (2015). Briefly, three syringes were filled with 30 mL surface water and 30 mL air, and a fourth syringe was filled with only air. All syringes had three-way valves, which were closed. Syringes were shaken by hand for 10 minutes. After which, the headspace was injected into an infrared gas analyzer (PP Systems EGM4, which was recently calibrated; average repeatability ± 2%). The pCO2 was calculated based on Henry’s law using the concentration measured in the headspace and accounting for the initial pCO2 in the air used for equilibration water temperature in both the surface water and in the syringe water after shaking.

2. LAB METHODS

2.1 Analytical techniques

Total alkalinity was measured on duplicate filtered samples for all sites using an automated electro-titrator (MetrOhm 888 Titrand and 869 autosampler) on 50 mL samples diluted by the titrant 0.1 M HCl. The reproducibility of these measurements was estimated to be ±6 μmol kg⁻¹ replicate analyses of an in-house Na2CO3 standard (N = 25). The 25 mm filters were prepared for isotopic analysis following the methods of Lorrain et al. (2003) with 12 hours of oven-drying at 55°C and subsequent decarbonation with HCl fumes for 4 hours, followed by a
was added to a helium preflushed Exetainer containing ~40 µL H₃PO₄ to convert all DIC species to CO₂. After overnight equilibration, the CO₂ was analyzed for δ¹³C values on a Thermo Gas Bench coupled to a Thermo Advantage isotope ratio mass spectrometer (GB-IRMS). The obtained δ¹³C data were corrected for the isotopic equilibration between gaseous and dissolved CO₂ as described in Gillikin and Bouillon (2007), and measurements were calibrated with certified reference materials LSVEC, NBS-19, and NBS-19. Reproducibility of δ¹³C measurements was 0.1‰ or better (see also Cheng et al. 2019).

Water oxygen isotopes (δ¹⁸Oₗ) were measured by equilibration with CO₂ using the aforementioned GB-IRMS. 0.5 mL of sample was transferred into 12 mL Exetainer, flushed with a 0.5% CO₂/helium mixed gas, and were equilibrated at 27°C in a thermostated tray for <24 hours. Three in-house water standards (Long Island sea water δ¹⁸O₀ = -0.60‰; Schenectady tap water δ¹⁸O₀ = -9.10‰; and Peruvian Andes lake water δ¹⁸O₀ = -16.52‰, all normalized to the VSMOW/SLAP scale) were measured along with samples to correct δ¹⁸O₀ values; reproducibility was ~0.02‰ based on repeated analysis of the tap water standard.

2.2 Computational techniques

[DIC], DIC species, and air–sea CO₂ flux were calculated using the application CO₂calc v4.0.9, designed by Robbins et al. (2010) with the preferred parameters of GEOSECS constants (NBS scale); K₁, K₂ from Mehrback et al. (1973); KHSO₄ from Dickson (1990); NBS pH scale; and air–sea
flux from Ho et al. (2006). Air–sea CO₂ flux was initially calculated using individual wind speeds measured in the field at each sampling site, and then subsequently recalculated using a single average annual wind speed value reported by windfinder.com for the Cape Lookout station. TA and DIC concentration values for all sites were normalized to salinity in order to accurately compare these measurements to determine source processes. Salinity-normalized TA was calculated using

$$T_{A_n} = T_{A_x} - \alpha(sal_x - sal_n)$$

where $T_{A_n}$ is the salinity-normalized TA; $T_{A_x}$ is the sample TA; $sal_x$ is the salinity of the given sample; $sal_n$ is the salinity to which the data are normalized (this study used the value 29 PSU); and $\alpha$ is the slope of the conservative mixing curve of TA, determined from the TA values at the two most extreme salinity values (Bouillon et al., 2007). DIC was normalized to salinity using a similar equation, with $D_{IC_n}$ and $D_{IC_x}$ substituted in for $T_{A_n}$ and $T_{A_x}$.

RESULTS

1. SALINITY

This marsh-dominated estuary exhibited a spatial salinity gradient that increased from the lowest values within Smyrna Creek (1.17–27.59 PSU) to intermediate values in the bay and sound (24.5–35.51 PSU) to highest values in the ocean (31.99–36.13 PSU). Temporally, Summer estuarine samples regularly exhibited the most extreme salinities compared to Fall and Spring samples, with the lowest seasonal values in the marsh-creeks and bay and the highest seasonal values in Core Sound and the ocean. Fall of 2017 (F17) and Spring of 2017 (SP17) showed the smallest variations in salinities between the freshwater and marine endmembers, with salinity values ranging by 7.17 PSU and 12.88 PSU, respectively. The estuarine salinity gradient for the Summer of 2018 (SU18) ranged by a total of 32.96 PSU. Salinities measured in Fall (F18) and Spring of 2018 (SP18) varied more substantially than the 2017 samples, but less than the SU18 samples (total range of 18.71 PSU in F18 and 25.32 PSU in SP18). All sites sampled within the sound and ocean exhibited the highest salinities in the Summer and lowest in the Fall. Smyrna Creek showed the opposite trend, with highest values in the Fall and lowest in the Summer. Jarrett Bay was unique, exhibiting its highest salinities during Spring, with varying lowest-salinity seasons.

2. DISSOLVED OXYGEN

The estuarine waters were generally fully saturated (100 ± 20%) with dissolved oxygen (DO), although a few sample sites near the freshwater endmember exhibited more extreme seasonal over- or under-saturation of DO (Fig. 3). By defining over-saturation of DO as >120%, both Williston and Wade Creek showed DO over-saturation in SU18 (180.9% and 146.2%, respectively). Slight over-saturation was also observed in and around Jarrett Bay in SP18 (DO ranging from 122.5–128%). DO under-saturation (values <80%) was seen in Smyrna Creek in F17 (68.2%), SU18 (41.3%), and F18 (53.3%).
3. TOTAL ALKALINITY

The TA throughout the estuary exhibited a positive correlation with salinity, revealing that TA increased toward the marine endmember of the system (Fig. 4). Smyrna Creek and Williston Creek exhibited anomalous TA values in at least one season; all other sites in the estuary yielded TA values ranging from 1872–2342 µmol kg\(^{-1}\) during all seasons. In SU18, both Smyrna and Williston Creeks showed noticeably low TA values that corresponded to low salinities. Smyrna Creek (salinity 1.17–6.4 PSU) had a TA of 1109–1177 µmol kg\(^{-1}\) while Williston creek (salinity 11.73 PSU) exhibited a TA of 1507 µmol kg\(^{-1}\). In contrast, unusually high TA was observed in Smyrna Creek in both SP18 and F18, as well as relatively low salinities during these two seasons. In SP18, the TA
of Smyrna Creek (salinity 9.51 PSU) was 2190 µmol kg⁻¹, and in F18, Smyrna (salinity 14.69 PSU) TA yielded a value of 2584 µmol kg⁻¹. Smyrna Creek exhibited unremarkable salinity and TA values in SP17 and F17, conforming to the observed positive trend between salinity and TA. The highest TA values in the system (excluding the F18 Smyrna Creek anomaly) occurred in the ocean samples, ranging from 2217–2342 µmol kg⁻¹ in all seasons.

4. CARBON

4.1 Particulate organic carbon

POC in the estuary was analyzed for amount, isotopic composition, and Chl a values. In general, the concentration of POC created a slightly hump-shaped trend, increasing from low to intermediate salinities then decreasing from intermediate to high salinities; however, several values measured in SU18 stand out from this observed trend (Fig. 5). Firstly, Williston Creek exhibited remarkably high POC of 4.59–8.92 mg L⁻¹. Secondly, Westmouth Bay—a small bay situated between two islands towards the marine endmember of the estuarine system—exhibited POC of 3.63 mg L⁻¹, which is unusually high for a site near the marine side of the estuary. Excluding these two values, in all seasons POC concentration values throughout the entire system ranged from 0.11–2.46 mg L⁻¹. The carbon isotopes of the estuarine POC were also measured and depicted an increasing trend from the creeks and bay towards the sound and ocean (Fig. 6). All δ¹³CPOC values for all sites and seasons fell between -30 and -17.79‰. Chl a measurements ranged from 2.29–14.62 µg

Figure 5. Particulate organic carbon concentration for all sites and seasons over the salinity gradient.

Figure 6. Carbon isotopic signatures of the POC from all sites and seasons over the salinity gradient.

Figure 7. Carbon to nitrogen ratio of the total suspended material from all sites and seasons over the salinity gradient.
L⁻¹, with values generally increasing up-estuary. The ratios of POC to Chl a for all sites were consistently >100 (109–303).

4.2 Carbon to nitrogen ratio

The C/N ratios of the total suspended matter for all sites and seasons plotted together fall within the range of 5.82–10.84 and exhibit a negative trend along the salinity gradient, with the highest C/N ratios in Smyrna and Williston Creeks (Fig. 7). The Spring season regularly had the lowest C/N values on average compared to the other seasons, excluding the high value of 9.79 in SP18 Smyrna Creek. F18 exhibited a unique seasonal trend of slightly increasing C/N values in the direction of the ocean, not accounting for Smyrna Creek which had the highest F18 C/N ratio of 10.84. This one seasonal trend opposes the observed overall decreasing trend throughout the estuary.

4.3 Carbon dioxide

In this estuary, CO₂ is over-saturated compared to the atmospheric level of 411 ppm in all but six samples (Fig. 8). Two of these samples—Williston Creek Bridge in SU18 and Wade Creek in SP18—exhibited remarkable under-saturation of CO₂, with pCO₂ values of 226 µatm and 283 µatm, respectively. Shell Point was consistently under-saturated in the Fall season, albeit only intermediately so, with pCO₂ values of 351 µatm in F17 and 331 µatm in F18. The remaining two under-saturated sites both occurred in SP18 and

Figure 8. CO₂ saturation at all sample sites during different seasons. Dashed line represents current atmospheric CO₂ concentration of 410 µatm. The two arrow-shaped bars indicate pCO₂ values that exceed the maximum value on the y-axis.
exhibited pCO$_2$ values that were very close to atmospheric levels (Jarrett Bay pCO$_2$ of 403 µatm and Williston Creek Bridge pCO$_2$ of 407 µatm). In contrast, Smyrna Creek showed extreme over-saturation of CO$_2$, with levels peaking at 14606 µatm in SU18. Excluding Smyrna Creek, the rest of the system yielded pCO$_2$ levels ranging from 226–1286 µatm, with a median value of 632 µatm. No distinct spatial or seasonal trends are observable, aside from the notably high pCO$_2$ values in Smyrna Creek in all seasons, with peak values in the Summer.

4.4 Dissolved inorganic carbon

Estuarine DIC was analyzed for both concentration and isotopic composition. Regarding concentration, DIC exhibited distinguishable seasonal trends over the salinity gradient (Fig. 9). Both F17 and F18 exhibited negative DIC trends moving toward the marine endmember of the estuary. In F17, the least saline site (upstream Smyrna Creek) yielded an abnormally low DIC value of 1.917 mmol kg$^{-1}$, while the downstream site had a DIC concentration of 2.169 mmol kg$^{-1}$, and the ocean sample exhibited 2.212 mmol kg$^{-1}$ of DIC. In F18, the freshwater endmember (again upstream Smyrna Creek) showed an anomalously high value of 2.908 mmol kg$^{-1}$, while in the bay the DIC concentration was 2.136, and the marine endmember exhibited DIC of 1.984 mmol kg$^{-1}$. The remaining three sampling seasons (SP17, SP18, and SU18) all showed increasing DIC along the salinity gradient—aside from the again anomalous upstream Smyrna Creek—with the downstream Smyrna Creek site representing the freshwater endmember, and the ocean sample being the marine endmember. Along this salinity gradient, DIC increased from 1.971–2.207 mmol kg$^{-1}$ in SP17, from 1.985–2.112 mmol kg$^{-1}$ in SP18, and from 1.232–2.109 mmol kg$^{-1}$ in SU18. An increased marsh-creek influence on the system was evident for SU18, due to the three noticeably low-salinity, low-DIC Summer samples corresponding to Smyrna and Williston Creeks.
Isotopic analysis of the DIC exhibits a strong positive trend in $\delta^{13}\text{C}_{\text{DIC}}$ progressing from the creeks and bay toward the marine endmember of the estuary (Fig. 10). $\delta^{13}\text{C}_{\text{DIC}}$ values ranged from -19.42–0.25‰ throughout, although the majority of the samples showed $\delta^{13}\text{C}_{\text{DIC}}$ between -5.57–0.25‰. The lowest $\delta^{13}\text{C}_{\text{DIC}}$ values in the system were observed in Smyrna Creek during all seasons, with the minimum values in the Summer (-9.19‰ in F17; -9.79‰ in SP18; -19.42‰ in SU18; -10.85‰ in F18).

4.5 Air–sea CO$_2$ flux

Calculations revealed that the majority of the sites within this estuary had positive daily air–sea CO$_2$ flux values, with eight sites exhibiting small negative fluxes during particular seasons (positive flux values indicate net movement of CO$_2$ out of the waters and into the atmosphere; negative values indicate sequestration of CO$_2$ from the atmosphere by the waters) (Fig. 11). These eight sites include F17 Shell Point (flux of -3.77 mmol m$^{-2}$ d$^{-1}$), SP18 Williston Creek Bridge (-1.24 mmol m$^{-2}$ d$^{-1}$), SP18 Wade Creek (-10 mmol m$^{-2}$ d$^{-1}$), SP18 Jarrett Bay (-1.69 mmol m$^{-2}$ d$^{-1}$), SP18 Ocean (-2.82 mmol m$^{-2}$ d$^{-1}$), SU18 Williston Creek Bridge (-13.42 mmol m$^{-2}$ d$^{-1}$), F18 Three Poles (-1.04 mmol m$^{-2}$ d$^{-1}$), and F18 Shell Point (-7.57 mmol m$^{-2}$ d$^{-1}$). All other sites had positive air–sea CO$_2$ flux values, with upstream Smyrna Creek consistently exhibiting the largest fluxes out of all sites during every season. The most extreme air–sea CO$_2$ flux in Smyrna Creek was 1087 mmol m$^{-2}$ d$^{-1}$, occurring during the Summer season. Excluding Smyrna, all

![Figure 11](image-url)

**Figure 11.** Air–sea CO$_2$ flux from all sample sites during different seasons. Positive values represent flux of CO$_2$ from the waters into the atmosphere, and negative values indicate sequestration of atmospheric CO$_2$ by the waters.
remaining positive flux values throughout the system ranged from 0.97–59.24 mmol m⁻² d⁻¹. The average area-weighted daily air–sea CO₂ flux of the entire system over all seasons was 13.4 mmol m⁻² d⁻¹, and total area-weighted annual estuarine air–sea CO₂ flux was 21.14 Gg CO₂ yr⁻¹ (both values calculated with weighted averages based on the surface areas of four distinctive estuarine regions: Smyrna Creek, Jarrett Bay plus Wade and Williston Creeks, Core Sound, and a small section of ocean directly outside of the mouth of the sound).

**DISCUSSION**

The waters of this North Carolinian marsh-influenced marine-dominated estuary are a significant source of CO₂ to the atmosphere. Several various sources contribute to the observed levels of organic and inorganic carbon in the system. Ultimately, the carbon will exit the estuarine water column through burial, transport out onto the continental shelf, and atmospheric degassing.

**1. ORGANIC CARBON**

**1.1 Sources of POC in the water column**

Estuarine POC is considered to consist of organic detritus, organic materials absorbed by clays suspended in the water column, and/or living organisms; however, the majority of estuarine POC is made up of the non-living components (Imberger et al., 1983). Through analysis of δ¹³CPOCH, the primary source of POC to this estuarine system was determined to be vascular plants situated around and upland of the estuary, with lesser POC contributions originating from the *Spartina alterniflora* marsh grass. Phytoplankton biomass was eliminated as a significant contributor of POC to the system based on POC/Chl a ratio values of >100 for all measured sites as POC/Chl a for living phytoplankton is usually between 30–100 (Abril et al., 2002; Bouillon et al., 2007). *Spartina alterniflora* was initially considered to be a possible source of estuarine POC due to its abundance and proximity to the estuary; upon evaluation of the δ¹³CPOCH, this cordgrass was eliminated as the main POC contributor, although it was likely responsible for minor contributions. POC directly sourced from *Spartina alterniflora* alone is expected to exhibit δ¹³C values of approximately -14‰ to -11‰ (Peterson et al., 1980). In contrast, POC from upland/vascular plant inputs should yield δ¹³C values between -22‰ and -34‰ (Peterson et al., 1980). The δ¹³CPOCH values for this estuary ranged between -30‰ and -17.79‰, with the majority of the values being < -22‰, thus mainly falling within the range of vascular plant isotopic signatures and revealing this source as the predominate estuarine POC contributor (Fig. 6). The existence of several δ¹³CPOCH values exceeding -22‰ indicate a secondary source of POC with a higher isotopic signature; ie. *Spartina alterniflora*. However, the lack of δ¹³CPOCH values >-17.79‰ suggests that this source provided relatively minor POC contributions to the estuary in comparison to the upland/vascular plant source.

Using C/N ratios of the TSM at each site as a proxy for terrestrial input—with higher C/N values indicating increased
allochthonous inputs—the notion of upland plants as the dominant POC source is further promoted. In general (excluding the unusual F18 seasonal trend), C/N increased moving progressively up-estuary, with the highest values observed in the marsh-creeks (as great as 10.84 in F18 Smyrna Creek) (Fig. 7). Such a trend is indicative of substantial terrestrial inputs and corresponding minor allochthonous influence in the marsh-creeks and adjacent up-estuary regions. This strong terrestrial input signal is likely caused by the substantial POC contributions from upland/vascular plants, and the minimal autochthonous influence corresponds to the minor amount of POC contribution sourced from the *Spartina alterniflora*. Temporally, the terrestrial POC inputs decreased in the Spring season, during which the C/N ratios throughout the estuary were at their lowest values. This seasonal observation likely indicates decreased productivity and/or stream flow during the Spring.

**1.2 Mixing of POC throughout the system**

The general negative seasonal trend in C/N corresponds to a hump-shaped trend (increasing from low to intermediate salinities then decreasing from intermediate to high salinities) in POC concentration over the full salinity gradient (Fig. 7; Fig. 5). These trends suggest conservative mixing of the POC—originally deposited in the marsh-creeks from terrestrial sources—throughout the entire system. The highest salinity sites (near/in the ocean) correspond to the lowest C/N ratios and POC concentrations because these areas are the furthest away from the region of direct terrestrial POC influx. Stream flow and weak ebb currents carry and distribute this POC toward the marine endmember of the estuary. However, the typically higher C/N ratios and POC concentrations up-estuary compared to the marine endmember indicate that the POC is influxed and/or recycled at a rate faster than the rate of estuarine water exchange, disallowing for a horizontal or purely positive mixing trend across the increasing salinity gradient. Recycling of terrestrial material in the marsh-creeks of this estuary is likely because the estuarine tidal circulation has only a very weak influence on these creeks (~30 cm), thus allowing for the hydrologic conditions of the creeks to dominate and promote POC recycling as well as substantial water–air exchanges (Houghton and Woodwell, 1980; Sigleo et al., 1982; Imberger et al., 1983; Matson and Brinson, 1990).

The highest POC concentration values were observed at intermediate salinities (~14–28 PSU), creating the hump-shaped POC trend and revealing the presence of the estuarine turbidity maximum (ETM) (Fig. 5). The ETM is the zone of the estuary in which the most highly energetic water conditions exist, promoting selective trapping of flocculated particles of organic material (Wolanski and Gibbs, 1995; Winterwerp et al., 2006). In all sampling seasons but SU18 and SP18, the ETM was determined to be located in the region spanning from upstream Smyrna Creek into and through Jarrett Bay, as POC concentration was highest in this area compared to the rest of the estuary, and the salinity of this region ranged between the
intermediate values of 14–28 PSU. In SU18, the ETM was present in Jarrett Bay only, causing high POC concentration in this moderately saline bay (24.5–28.3 PSU). Smyrna and Williston marsh creeks exhibited very low salinities (1.17–11.73 PSU) and varying POC concentrations, indicating that the ETM was not present in these creeks during this season. The ETM in the SP18 season spanned from the downstream section of Smyrna Creek through Jarrett Bay, with this region showing relatively high POC concentration and intermediate salinity (21.52–27.85 PSU). The upstream section of Smyrna Creek was determined to lay beyond the bounds of the ETM, as it exhibited a low salinity of 9.51 PSU and accompanying low POC concentration compared to the downstream/bay region.

1.3 Spatial anomalies

In the SU18 season, Williston Creek, and Westmouth Bay both exhibited POC concentrations that do not follow the observed POC trend (Fig. 5). The Williston Creek SU18 samples possessed remarkably high POC concentration values ranging from 4.59 mg L\(^{-1}\) downstream to 8.92 mg L\(^{-1}\) upstream. The POC samples from all other sites and seasons had concentrations of \(\leq 2.46\) mg L\(^{-1}\), excluding the anomalistic SU18 Westmouth Bay which had a POC concentration lower than that of Williston Creek, although higher than average. The sheer magnitude of the Williston Creek POC concentration values compared to all of the other samples indicates the likely existence of a unique process occurring in this creek during SU18. After coupling this high POC concentration with corresponding over-saturation of DO (180.9%) and under-saturation of CO\(_2\) (226 \(\mu\)atm) in Williston Creek, it seems likely that a phytoplankton bloom was occurring in this marsh-creek during the SU18 sampling period, with the biomass contributing to the abundance of POC and the related increased photosynthesis drawing down CO\(_2\) and producing substantial DO.

Westmouth Bay exhibited a notably high POC concentration of 3.63 mg L\(^{-1}\) in SU18 (Fig. 5). This bay is situated toward the marine endmember of the estuary near the south end of Core Sound, nestled between Harkers Island and Browns Island (Fig. 2). Unlike Williston Creek—in which high POC concentration was also observed—the levels of DO and CO\(_2\) in the waters of Westmouth Bay were unremarkable and not indicative of a phytoplankton bloom. However, the C/N ratio in this bay of 9.73 was high compared to other sites near the marine endmember of the estuary (Fig. 7). The high POC and C/N therefore likely suggest the presence of relatively large amounts of terrestrial material in Westmouth Bay. As this site is situated between two islands, it is possible that terrestrial POC from these islands was being washed into the bay, contributing to the high POC and C/N values. Alternatively, terrestrially sourced POC may be transported to this site through typical estuarine mixing processes, but then trapped and recycled inside the bay, producing high POC concentration and C/N.
1.4 Seasonal anomalies

The typical seasonal trend in C/N values moving down-estuary over the salinity gradient is negative, with the exception of the F18 seasonal trend which is distinctly positive (Fig. 7). The upstream Smyrna Creek sample taken in F18 exhibits the only C/N value that does not follow the positive F18 trend—at 10.84, it is noticeably high and resembles the upstream Smyrna Creek samples from other seasons with negative overall trends. Excluding this one data point, the remainder of the C/N values increase with increasing salinity. Such a pattern is unusual because a process of conservative mixing of POC originating in the marsh-creeks and traveling down-estuary is expected and was seen in all other seasons. This positive trend for F18 may indicate reduced estuarine mixing and/or increased influence of authigenic POC throughout the estuary. However, it does not appear that the source of the estuarine POC in F18 differed distinctly from the other seasons, as the carbon isotopic signatures of the POC for all seasons follow a very similar positive trend across the salinity gradient (Fig. 6).

The SU18 C/N trend is also slightly unusual in that it is generally negative but with a visible stacking of six data points with extremely similar salinity values and variable C/N values (Fig. 7). The C/N values for these six sites range from 6.94–9.73, while the salinities are very close, with values between 33.96–35.02 PSU. These six points include sites that range in location over almost the entirety of the estuarine sound, from Three Poles at the mouth of Jarrett Bay down to the Hook where the sound meets the ocean. The minimal variation in salinities over this large span of area is a seasonal characteristic of the Summer and is the reason for the apparent stacking of these six data points despite their greatly differing C/N values. Were these sites to exhibit salinity values similar to those observed at the same locations during the Spring and Fall seasons, the stacking effect would disappear, and the expected negative trend would be visible.

2. INORGANIC CARBON

2.1 Sources of CO₂ in the water column

The concentration of dissolved CO₂ in the estuarine water column was higher than the current atmospheric value of 411 ppm in all but six samples (Fig. 8). The highest pCO₂ values were obtained in Smyrna Creek in all seasons, with the very highest value observed in Summer 2018 (14606 µatm). These high values indicate that this creek is likely not affected by tidal influence, allowing for the accumulation of CO₂ in the narrow, shallow marsh-creek. Peak values in the Summer reveal that CO₂-producing processes are most active during this season. The occasional undersaturation of CO₂ in the waters of Wade and Williston marsh-creeks indicates that CO₂-uptake processes (such as the photosynthesis associated with a phytoplankton bloom) may occur in some regions of the estuary without affecting the whole system. The overall prevalence of CO₂ super-saturation in the estuary is evidence of net heterotrophy—consumption of organic matter exceeding primary production—of the system.
In order to determine the dominant CO₂-producing and -uptaking processes at work in the estuarine waters, the carbon isotopic ratios of the DIC from each sample site were analyzed and compared to both salinity and pCO₂ (Fig. 10; Fig. 12). Both of these comparisons yielded similar trends, with \( \delta^{13}C_{\text{DIC}} \) decreasing as salinity decreased and pCO₂ increased (both of which indicate progression toward the freshwater endmember of the estuary). High salinity, low pCO₂ waters exhibited \( \delta^{13}C_{\text{DIC}} \) values close to 0‰, indicating that photosynthesis and water-atmosphere equilibrium were the dominant processes contributing to the CO₂ concentration in the waters near the marine endmember of the estuary. In contrast, waters with lower salinity and higher pCO₂ exhibited lower \( \delta^{13}C_{\text{DIC}} \) values reaching close to -12‰. This decrease in \( \delta^{13}C_{\text{DIC}} \) is indicative of an increasing influence of respiration on the CO₂ in the up-estuary water column. Moreover, CO₂ and DO concentration exhibit an inverse relationship, further promoting the presence of photosynthesis and respiration processes significantly contributing to the CO₂ within the estuary (Fig. 13).

### 2.2 Sources of TA and DIC

In order to determine the sources of TA and DIC in this estuarine system, these two variables were normalized to salinity and plotted against each other along with the known slopes for several biogeochemical processes that affect TA and DIC (Fig. 14). The TA and DIC data collected from all sites and seasons were also plotted, with a linear regression line representing the general overall trend of the data. This regression line exhibited a slope of 0.47, falling between the slopes of CO₂ invasion (slope = 0) and denitrification (slope = 0.8). Aerobic respiration and sulfate (SO₄²⁻) reduction had the next closest slopes to the trendline, with values of -0.2 and 1, respectively. These four
processes were thus determined to be the most significant contributors of TA and DIC to this particular system. Calcium carbonate (CaCO$_3$) dissolution exhibited a slope of 2 but was eliminated as a significant TA/DIC source due to a lack of evidence of this process in the estuary backed up by several past studies that have shown this process to have a negligible contribution of TA and DIC in intertidal sediments (Green et al., 1993; Middelburg et al., 1996; Hellings et al., 2000). Iron and manganese reduction were also eliminated as substantial source processes of TA and DIC due to their distinctly steep slopes (8 and 4.4, respectively) compared to that of the regression line. Furthermore, iron reduction is typically a very minor process in intertidal sediments such as those in this estuary, as the microorganisms residing in the sediments are unable to reduce most of the iron in the sediments, especially in environments in which SO$_4^{2-}$ reduction is a dominant process, such as this estuary (Lovley and Phillips, 1986). Manganese reduction was negligible in this estuary likely due to the high sensitivity of this process to specific estuarine conditions including pH, DO concentration, and bicarbonate (HCO$_3^-$) concentration (Wollast et al., 1979).

CO$_2$ invasion, denitrification, SO$_4^{2-}$ reduction, and aerobic respiration were determined to be the four major sources of

Figure 14. Relationship between salinity normalized TA and DIC concentrations for all sites and seasons, with the dashed line representing the linear regression of all the data. Solid lines show slopes of several different DIC- and TA-affecting processes known to occur in coastal ecosystems.
TA and DIC to this system, although the exact amount of influence of each process cannot be quantitatively distinguished. However, each process acts in a different way to contribute to the system. CO2 invasion is the only process that contributes DIC to the system without affecting TA, as this process is simply the movement of atmospheric CO2 into the estuarine waters in an effort to obtain air–water equilibrium (Fig. 14). Denitrification occurs in the sediments of estuarine ecosystems where denitrifying bacteria reside. This process is described by the reaction

\[
\text{CH}_2\text{O} + 0.8\text{NO}_3^- + 0.8\text{H}^+ \rightarrow \text{CO}_2 + 0.4\text{N}_2 + 1.4\text{H}_2\text{O}
\]

in which nitrate (NO3\(^-\)) is reduced and released into the water column as gaseous molecular nitrogen (N2). In this process, 0.8 H\(^+\) ions are used up for every one molecule of CO2 produced. By consuming H\(^+\) and creating CO2, TA and DIC are both added to the system in a 0.8:1 ratio, creating the observed slope of 0.8 (Fig. 14). Dissimilatory SO4\(^{2-}\) reduction by microbial organisms also occurs in intertidal sediments, following the reaction

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{S} + \text{H}_2\text{O}
\]

in which SO4\(^{2-}\) is converted into hydrogen sulfide (H2S) through an anaerobic respiration process. This reaction is similar to that of denitrification in that both processes involve the consumption of CH2O and H\(^+\) ions in order to produce water and CO2, in addition to a third gaseous product (either N2 or H2S). The slope of 1 exhibited by the SO4\(^{2-}\) reduction trendline indicates that this process yields a simultaneous increase of TA and DIC in a 1:1 ratio, with each consumed H\(^+\) ion correlating to the production of a single molecule of CO2 (Fig. 14). In addition to the similarity of this slope to the slope of the data regression line, a prevalent sulfuric odor observed during sampling in the marsh-creeks was further evidence for the active reduction of SO4\(^{2-}\) in the sediments of this estuary. Although anaerobic respiration must have been occurring to drive the SO4\(^{2-}\) reduction, aerobic respiration was also identified as a significant process operating in the estuary. This process occurs in both the water column and intertidal sediments as microorganisms including bacteria, phytoplankton, and protozoa employ the reaction

\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 138\text{O}_2 + 16\text{HCO}_3^- \rightarrow 16\text{NO}_3^- + \text{H}_3\text{PO}_4 + 122\text{CO}_2 + 138\text{H}_2\text{O}
\]

to convert oxygen into cellular energy. This chemical equation shows how organic matter ((CH2O)\(_{106}(NH_3)_{16}H_3PO_4\)) performs oxic respiration whilst consuming bicarbonate (HCO3\(^-\)) to ultimately produce CO2, water, and nutrients—a process that releases H\(^+\) ions which lead to the decrease in TA. The creation of CO2 contributes to the increase in DIC that is characteristic of the aerobic respiration process. Coupling the decreasing TA with the increasing DIC and applying Redfield stoichiometry yields the TA to DIC ratio of 17:106, or a slope of -0.2 (Fig. 14). The presence of aerobic respiration in the estuary is further revealed by the inverse relationship between CO2 and DO, as well as by the decreasing \(\delta^{13}_{C}\text{DIC}\) values in the up-estuary region.
These four TA- and/or DIC-contributing processes cannot be quantitatively differentiated based on the available data, but they may be spatially distinguished to a degree. CO₂ invasion occurs throughout the entire system as the estuarine waters are constantly seeking to achieve equilibrium CO₂ concentration with the atmosphere. SO₄²⁻ reduction and denitrification occur predominantly within the up-estuary sediments where reducing bacteria are abundant, and SO₄²⁻ and NO₃⁻ are able to accumulate due to organic marsh matter decomposition, sediment leaching, allochthonous nutrient fluxes, and marsh-plant root oxidation and nutrient release (Stribling and Cornwell, 2001). The strong odor of sulfur in the up-estuary marsh-creeks indicates the release of gaseous H₂S in this area in response to the bacterial reduction of the SO₄²⁻. The similarity between this process and the denitrification reaction suggests that denitrification is likely to mainly occur in the same type of environment (marsh-creek sediments). Carbon isotopes of DIC reveal that aerobic respiration decreases moving down-estuary toward the marine endmember, indicating the highest DIC contributions from this source in the marsh-creeks and bay, with minimal contributions in the sound and ocean where CO₂ invasion dominates and drives the δ¹³C_DIC values close to 0‰ (Fig. 10).

2.3 Mixing of DIC throughout the system

The concentration of DIC along the salinity gradient was analyzed to determine seasonal mixing trends within the estuary (Fig. 9). Marsh-influenced marine-dominated estuaries generally exhibit high excess DIC (DIC sourced directly from estuarine zone inputs) in the up-estuary region due to significant DIC contributions from surrounding productive marshland and organic marsh matter decomposition (Cai et al., 1999; Neubauer and Anderson, 2003; Wang and Cai, 2004; Jiang et al., 2008). When flow into the estuary is high and/or decomposition rates are low, this up-estuary enrichment of DIC is not generally observable, and a positive trend in DIC along the salinity gradient occurs, indicating full-system mixing (Cai, 2011). During periods of low flow and/or high decomposition, a distinct signal of DIC enrichment is visible near the freshwater endmember of the estuary, and the data typically exhibit an overall negative trend moving down-estuary due to an increased influence from the marshes and related poor mixing of the full system (Cai, 2011). The Cape Lookout estuary exhibited positive DIC trendlines during Summer and Spring and negative trendlines in the Fall (Fig. 9). These seasonal patterns suggest that conservative full-system mixing was active in the Summer and Spring, while the estuarine waters were not thoroughly mixed in the Fall. These findings are supported by the fact that flow into this estuary is highest in the Spring and Summer, and the Fall is characterized by low flow and high rates of decomposition. A study of two marine-dominated estuaries in Georgia performed by Jiang et al. (2008) yielded very similar findings, with increasing DIC trends over the salinity gradient in the Summer and Spring and decreasing trends in the Fall.
The upstream section of Smyrna Creek was sampled for DIC concentration in F18, SU18, SP18, and F17. Due to the shallow, narrow nature of Smyrna Creek and the inability of the tidal influence to reach very far upstream, anomalistically high DIC concentration values were expected for these four samples. This prediction was substantiated by the F18, SU18, and SP18 Smyrna Creek DIC samples, which were all at least 17% higher than the next sample along the salinity gradient (Fig. 9). The F17 sample, however, did not conform to this prediction as it exhibited significantly lower DIC than the next sample along the salinity gradient. This finding was highly unusual, and the cause of this anomaly is still unknown.

3. AIR–SEA CO₂ FLUX

3.1 Site-specific fluxes and trends

The majority of the samples yielded positive air–sea CO₂ flux values, indicating that the system as a whole was acting as a source of CO₂ to the atmosphere (Fig. 11). Several samples exhibited small negative fluxes, the greatest of which was -13.42 mmol m⁻² d⁻¹ at Williston Creek Bridge in SU18. Williston Creek has formerly been identified as the site of a phytoplankton bloom, exhibiting notably low pCO₂ coupled with very high DO (Fig. 8; Fig. 13). Because this site was under-saturated with CO₂ compared to the atmosphere in SU18 due to the high rates of photosynthesis, CO₂ invasion outweighed CO₂ degassing rates, creating the observed negative flux. Wade Creek in SP18 and Shell Point in F18 exhibited the next greatest negative air–sea CO₂ flux values of -10 mmol m⁻² d⁻¹ and -7.57 mmol m⁻² d⁻¹, respectively (Fig. 11). CO₂ under-saturation at these sites was comparable to that of Williston Creek (Fig. 8), suggesting that similar processes—such as excessive photosynthesis due to a small-scale phytoplankton bloom—were likely active in SP18 Wade Creek and F18 Shell Point, and contributed to the local sequestration of small amounts of atmospheric CO₂ by these estuarine waters. Of the few remaining samples with negative fluxes, the greatest negative flux was -3.77 mmol m⁻² d⁻¹, with the majority of values >-2 mmol m⁻² d⁻¹ (Fig. 11). Because these values are so close to zero, they are assumed to be negligible CO₂ fluxes.

The positive air–sea CO₂ fluxes <5 mmol m⁻² d⁻¹ are similarly considered to be negligible. Excluding the five samples falling into this category, the remaining 37 samples exhibited significant positive fluxes (ranging from 5.44–1087 mmol m⁻² d⁻¹), leading to the conclusion that the waters of this estuary are overall a source of CO₂ to the atmosphere (Fig. 11). The upstream section of Smyrna Creek showed the highest air–sea CO₂ flux of all sites during every season, likely due to the aforementioned narrow, shallow nature of this marsh-creek allowing for significant accumulation of dissolved CO₂ in the waters (Fig. 8). This abundance of CO₂ promoted abnormally high degassing rates as the super-saturated creek waters sought to achieve equilibrium with the atmosphere. The most extreme air–sea CO₂ flux value in the estuary (1087 mmol m⁻² d⁻¹) was observed in Smyrna Creek in the Summer, revealing that CO₂-producing processes were most active during this season.
Spatially, air–sea CO$_2$ flux exhibits a generally decreasing trend progressing away from the marsh-creeks and bay toward the marine endmember of the estuary (Fig. 11). This trend agrees with that identified by Cai (2011), in which estuaries yield a positive overall air–sea CO$_2$ flux, and continental shelves exhibit a negative flux (Fig. 1a). The shift in flux away from high positive values up-estuary in the Cape Lookout region toward a flux of zero or less outside of the estuarine mouth demonstrates this transition toward CO$_2$ sequestration on the shelf which contrasts the degassing nature of estuarine waters. Figure 15 depicts this trend as a schematic of the Summer flux values of all sampled areas, with red markers representing the greatest fluxes and flux values decreasing progressively through the color spectrum. Visually, the decreasing down-estuary air–sea CO$_2$ flux trend is clear, although two sites stand out as unusual—Williston Creek (violet marker near top of estuary) and Westmouth Bay (orange marker directly north of Harkers Island). The flux at Williston Creek was abnormally low for an up-estuary marsh-creek; however, this occurrence has been previously attributed to a local phytoplankton bloom. The flux at Westmouth Bay, represented by an orange marker, stands out as atypically high for its mid-estuary location. POC concentration was also previously observed to be unusually high at this site (Fig. 5), and a phytoplankton bloom was eliminated as a likely source of this anomaly. Therefore, it is possible that the same factors responsible for the abnormal accumulation of POC in this area are also responsible for the high flux of CO$_2$ from this site. One such factor was identified as semi-isolation of this site from the rest of the estuary due to its positioning between two islands, potentially causing partial cut-off of these waters from free mixing with the rest of the estuary. Such a circumstance could increase CO$_2$ degassing rates from this site as CO$_2$ accumulates in these waters and is not able to be transported in full out of this area because of limited mixing.

### 3.2 Total system flux

This estuary exhibited a positive overall daily air–sea CO$_2$ flux of 13.4 mmol m$^{-2}$ d$^{-1}$ over all seasons (Table 1). This value was calculated with weighted averages based on estuarine surface area as to
mitigate any potential skewing of data by the remarkably high flux values observed in Smyrna Creek. The area of this creek accounted for a mere 0.12% of the total estuarine area, but the average air–sea CO$_2$ flux for Smyrna creek over all sampled seasons was 303.5 mmol m$^{-2}$ d$^{-1}$ (Table 1). This flux was significantly higher than the average CO$_2$ flux from any of the other three estuarine regions, despite their much greater relative areas—the bay and other marsh-creeks make up 6.4% of the system and yielded a flux of 22.9 mmol m$^{-2}$ d$^{-1}$; Core Sound makes up 75.9% of the system, with a flux of 12.5 mmol m$^{-2}$ d$^{-1}$; and the small section of the ocean sampled near the mouth of the estuary accounted for 17.6% of the system and had a flux of 11.5 mmol m$^{-2}$ d$^{-1}$ (Table 1) (Fig. 16). The positive nature of these four flux values—as well as that of the weighted and averaged value of 13.4 mmol m$^{-2}$ d$^{-1}$ for the full system—supports the notion that the waters of this estuary are consistently a source of CO$_2$ to the atmosphere.

A similar study by Jiang et al. (2008) evaluated the carbon dynamics of three different estuaries along the Georgia coast: Sapelo Sound, Doboy Sound, and Altamaha Sound. Due to the similarities in location, environment, and climate between these three estuaries and the Cape Lookout estuary, the air–sea CO$_2$ flux values reported by Jiang et al. (2008) are considered to be comparable to those values obtained from this study. Since flux is generally higher in river-dominated estuaries, comparisons were made between the two marine-dominated estuaries (Sapelo Sound and Doboy Sound) and the marine-dominated Cape Lookout estuary. Jiang et al. (2008) reported air–sea CO$_2$ flux values of 28.7 mmol m$^{-2}$ d$^{-1}$ and 29.4 mmol m$^{-2}$ d$^{-1}$

<table>
<thead>
<tr>
<th>Site</th>
<th>Air–sea CO$_2$ flux (mmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smyrna Creek</td>
<td>303.5</td>
</tr>
<tr>
<td>Jarrett Bay and other marsh-creeks</td>
<td>22.9</td>
</tr>
<tr>
<td>Core Sound</td>
<td>12.5</td>
</tr>
<tr>
<td>Marine section</td>
<td>11.5</td>
</tr>
<tr>
<td>Total system</td>
<td>13.4</td>
</tr>
<tr>
<td>Sapelo Sound (Jiang et al., 2008)</td>
<td>28.7</td>
</tr>
<tr>
<td>Doboy Sound (Jiang et al., 2008)</td>
<td>29.4</td>
</tr>
<tr>
<td>Altamaha Sound (Jiang et al., 2008)</td>
<td>69.3</td>
</tr>
</tbody>
</table>
for Sapelo and Doboy sounds, respectively (Table 1). These values are slightly higher than the flux of 13.4 mmol m$^{-2}$ d$^{-1}$ obtained for this estuary, but all three of these values are relatively small positive numbers on the same order of magnitude, indicating that the data from this study promotes the existing perspective of marine-dominated estuaries as important sources of CO$_2$ to the atmosphere. The CO$_2$ fluxes from Sapelo and Doboy sounds were likely slightly greater than that from the Cape Lookout estuary because of their relatively larger size. Altamaha River was the largest estuary sampled by Jiang et al. (2008); due to its size and designation as a river-dominated estuary, the comparatively high total CO$_2$ flux value of 69.3 mmol m$^{-2}$ d$^{-1}$ for this system was not surprising (Table 1). These variations in flux values dictated by differing estuarine types and sizes illustrates the importance of studying a broad range of systems when attempting to quantify a parameter such as global estuarine air–sea CO$_2$ flux.

In addition to the daily flux values, average annual air–sea CO$_2$ flux was also calculated for the four estuarine regions within the Cape Lookout estuary, as well as one total value for the entire system (Fig. 16). These values were calculated by factoring in the full surface area of each region, thus yielding results in Gg of CO$_2$ emitted per year, a unit that is independent of area. This eliminates any potential skewing of the total system flux value by the very high flux observed in the small region of Smyrna Creek. The annual air–sea CO$_2$ flux was 0.59 Gg yr$^{-1}$ for Smyrna Creek, 2.34 Gg yr$^{-1}$ for Jarrett Bay and other marsh creeks, 15.01 Gg yr$^{-1}$ for Core Sound, and 3.2 Gg yr$^{-1}$ for the small ocean section (Fig. 16). In total, this estuary emitted an annual CO$_2$ flux of 21.14 Gg yr$^{-1}$ into the atmosphere, a value comparable to the amount of CO$_2$ emitted by more than 4500 cars in a single year (based data reported by the EPA stating that a typical passenger car emits ~4.6 metric tonnes of CO$_2$ per year). This substantial emission of CO$_2$ is given off by an estuary only 98 km$^2$ in size, which is a relatively small area when compared to the abundance and magnitude of other estuaries around the globe. Additionally, it is crucial to note that
carbon involved in estuarine cycling may be primarily modern carbon that has recently been taken from the atmosphere, whereas the carbon emitted from cars is ancient carbon sourced from fossil fuels. As such, these findings promote the importance of estuaries in the global carbon cycle and urge that these systems be considered when attempting to model total oceanic carbon flux.

CONCLUSIONS

Estuaries are critical constituents of the marine coastal system, promoting extensive cycling of both organic and inorganic carbon, despite accounting for less than 1% of the total global marine surface area. Marine-dominated estuaries exhibit slightly different carbon dynamics than river-dominated estuaries; therefore, differentiating between these two types of estuaries and thoroughly studying both is crucial for attempting to determine an accurate estimate of global oceanic carbon fluxes. Due to a bias of available data toward river-dominated estuaries, this study focuses on a marine-dominated estuary in the Cape Lookout region of North Carolina’s Outer Banks. This system is influenced by both surrounding agricultural land as well as adjacent salt marshes, with isotopes of estuarine organic carbon indicating a substantial contribution of organic carbon from upland plant and agricultural inputs, and a significantly smaller contribution by the native salt marsh cordgrass *Spartina alterniflora*. Covarying DIC and TA concentrations in the estuarine water column across the salinity gradient indicate that several different processes are responsible for contributing inorganic carbon to the system, including CO₂ invasion, denitrification, sulfate reduction, and aerobic respiration. Throughout the estuary, these processes perform to varying extents, with the latter three dominating in the up-estuary regions, and CO₂ invasion dominating toward the marine endmember. Conservative mixing of the estuarine waters occurred during the high-flow seasons of Spring and Summer, while low flow and high up-estuary decomposition rates inhibited full system mixing in the Fall. Accumulation of CO₂ in the estuarine waters during all seasons led to the observed over-saturated nature of the waters compared to the atmosphere. This over-saturation of CO₂ fostered significant positive air–sea CO₂ fluxes throughout the estuary, revealing this system to be a source of CO₂ to the atmosphere, with an average total flux of 13.4 mmol m⁻² d⁻¹. This small positive air–sea CO₂ flux is similar to those reported for other marine-dominated estuaries, demonstrating the importance of considering estuarine systems when attempting to calculate total marine carbon flux.

Further research concerning the Cape Lookout estuary may include measurement of calcium ion concentrations throughout the waters of the estuary in order to determine if the process of calcium carbonate dissolution is active and influencing the DIC and TA concentrations. Additionally, analysis of the ¹⁴C of the estuarine DIC could indicate the age of the carbon fluxing throughout the system, thus
providing further insight into the type of carbon dynamics active in the estuary and the related consequences, as modern ages would reveal that the carbon was recently removed from the atmosphere, and old ages would indicate that this carbon is similar to that preserved in fossil fuels. On a global scale, continued research into the carbon dynamics and fluxes of marine-dominated estuaries would benefit the scientific community by balancing out the existing data bias toward river-dominated estuaries and by emphasizing the significance of estuaries in the global carbon cycle.
REFERENCES


Borges, A.V., 2005. Do we have enough pieces of the jigsaw to integrate CO2 fluxes in the coastal ocean?. Estuaries, 28(1), pp.3-27.


Dickson, A.G., 1990. Standard potential of the reaction AgCl(s) + .5H2 (g) = Ag(s) + HCl(aq) and the standard acidity constant of the ion HSO4− in synthetic sea water from 273.15 to 318.15 K. The Journal of Chemical Thermodynamics, 22(2), pp.113-127.


