ABSTRACT

Title of Dissertation: EFFECTS OF SEA LEVEL RISE ON TIDAL FRESHWATER, OLIGOHALINE, AND BRACKISH MARSHES: ACCRETION, NUTRIENT BURIAL, AND BIOGEOCHEMICAL PROCESSES

Jenny Rose Allen, Doctor of Philosophy, 2019

Dissertation directed by: Andrew Baldwin, Department of Environmental Science and Technology

Tidal wetlands provide critically important ecosystem services such as storm surge and flood attenuation, pollution retention and transformation, and carbon sequestration. The ability of tidal wetlands to maintain surface elevation under accelerated sea level rise is critical for their persistence. Saltwater intrusion can further threaten tidal freshwater marshes by decreasing primary production and organic matter accumulation as well as cause shifts in microbial pathways, leading to increases in organic matter decomposition and an overall decrease in marsh elevation. The objectives of this research were to examine accretion dynamics across the estuarine gradient of the Nanticoke River, a major tributary of the Chesapeake Bay, and determine the relative contribution of organic and inorganic matter to accretion in the marshes; determine the accumulation rates of C, N, and P across the estuarine gradient; and examine the effects of sulfate intrusion on biogeochemical transformations and marsh surface elevation in tidal freshwater marsh soil. Results of the collective studies suggest that the mechanisms controlling accretion dynamics and nutrient accumulation are complex and are likely driven by site-specific factors rather than estuary-wide factors. Accretion rates and nutrient accumulation rates were highly variable across the estuarine gradient, but were largely dependent on both organic matter accumulation and inorganic sedimentation. Only 8 out of the 15 subsites had accretion rates higher than relative sea level rise for the area, with the lowest rates of accretion found in the oligohaline marshes. Organic matter accumulation is especially important in marshes with low mineral sediment supply, particularly mid-estuarine oligohaline marshes, but may not be enough to help keep these marshes above relative sea level. The tidal marshes along the Nanticoke River removed approximately 15% and 9% of the total N and P load entering the system, but their ability to continue to remove nutrients may be compromised due to rising sea levels. Shifts in microbial pathways and increases in organic matter decomposition due to saltwater intrusion further threaten the ability of these marshes to keep pace with sea level rise, potentially resulting in the loss of an extremely valuable ecosystem.

EFFECTS OF SEA LEVEL RISE ON TIDAL FRESHWATER, OLIGOHALINE, AND BRACKISH MARSHES: ACCRETION, NUTRIENT BURIAL, AND BIOGEOCHEMICAL PROCESSES

by

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Chapter 1: Introduction

Tidal wetlands are among the most productive ecosystems in the world. They provide critically important habitat for fish and wildlife, pollutant retention and transformation, storm surge and flood attenuation, organic carbon production, and sediment entrapment (Mitsch and Gosselink 2007, Barbier et al. 2011). Due to increasing sea level, these wetlands are being threatened worldwide. Global sea levels have risen an average of 1.2 mm yr^{-1} between 1901 and 1990 and 3.1 mm yr^{-1} between 1993 to 2017 (IPCC 2014, Hay et al. 2015, Nerem et al. 2018, WCRP Global Sea Level Budget Group 2018).

The ability of tidal wetlands to maintain surface elevation under accelerated sea level rise is critical for their persistence and is largely driven by the accumulation of both organic matter and mineral sediments (Reed 1995, Morris et al. 2002, Cahoon et al. 2006, Neubauer 2008). Increased rates of sea level may exceed the ability of some marshes to accrete vertically, resulting in marsh submergence and loss of marsh area (Moorehead and Brinson 1995, Reed 1995, Kearney et al. 2002, Morris et al. 2002). Model simulations based on the IPCC predictions have shown that salt marshes could decline in area by 20-45% and tidal freshwater marshes may decline by 2-39% by 2100 (Craft et al. 2009). In coastal Louisiana, for example, an estimated wetland loss of 66 km^2 yr^{-1} has resulted from a relative sea level rise of 3-12 mm yr^{-1} (Britsch and Dunbar 1993, Blum and Roberts 2009, Jankowski et al. 2017). Rates of relative sea level rise in the Chesapeake Bay have been 3.24-5.11 mm yr^{-1} between 1969 and 2014 and have been accelerating by 0.08-0.22 mm yr^{-1} (Boon and Mitchell 2015), resulting in extensive marsh loss, such as those at Blackwater National Wildlife Refuge on Maryland's eastern shore (Stevenson et al. 1985). Many studies have documented the potential effects of sea level rise on salt and brackish marshes (Reed 1995, Morris et al. 2002, Mudd et al. 2009, Kirwan et al. 2010), but less is known about how tidal freshwater marshes will respond to increases in water level and salinity.

Tidal freshwater marshes (TFM, salinity <0.5 ppt) and oligohaline marshes (salinity 0.5-5 ppt; Cowardin et al. 1979, Tiner and Burke 1995) are extensive, biologically diverse, and highly productive ecosystems with tremendous ecological and socioeconomic importance. There are an estimated 164,000 ha of these marshes along the Atlantic Coast and 210,000 ha in the delta plain of the Mississippi River in Louisiana (Gosselink 1984, Odum et al. 1984). Tidal freshwater marshes occupy about 30% of the coastal marshes of the Mississippi Delta (Gosselink 1984) and in Maryland, tidal freshwater and oligohaline marshes span about 25% (16,000 ha) of the area of salt and brackish marshes (Cowardin et al. 1979, Tiner and Burke 1995).

The low salinity levels in tidal freshwater and oligohaline marshes allow for a more diverse plant community than salt and brackish marshes (Odum 1988) and tidal flooding supplies abundant nutrients, creating high primary production (Mitsch and Gosselink 2007). High productivity and high plant diversity create an environment that supports diverse fish and wildlife populations. Almost 300 species of birds have been reported in tidal freshwater marshes and many commercially important fish rely on tidal freshwater marshes for some phase of their life cycle (Odum et al. 1984, Odum 1988). These wetlands are also used heavily for hunting, fishing, and nature observation by humans, and act to protect shoreline properties from coastal erosion and storm surges

(Mitsch and Gosselink 2007). Despite the extent and ecological importance of tidal freshwater marshes, much less scientific research has been conducted on these wetlands in comparison to salt marshes.

The proximity of tidal freshwater and oligohaline marshes to developed areas may result in elevated nutrient inputs to them due to the presence of industry, wastewater treatment plants, agriculture, and other non-point sources. Tidal wetlands sequester carbon, nitrogen, and phosphorus (Craft et al. 1988, Morse et al. 2004, Craft 2007, Loomis and Craft 2010), likely mitigating anthropogenic stresses further down the estuary. As sediment accretes vertically, organic and mineral matter is incorporated, trapping nutrients within this matrix (Merrill and Cornwell 2000). The ability of these wetlands to serve as sinks for C, N, and P may be compromised due to rising sea levels (Craft et al. 2009), causing detrimental impacts on water quality further downstream.

The tidal marsh plant community plays a key role in marsh accretion by supplying organic matter, trapping allochthonous sediments from tidal waters, and influencing particle settlement rates (Reed 1995, Pasternack and Brush 2001, Fagherazzi et al. 2012). Rising sea levels can lead to an upstream migration of the freshwater-saltwater mixing zone, leading to saltwater intrusion in tidal freshwater marshes. Salinity-induced stress and sulfide toxicity can adversely impact plant productivity, leading to declines in primary production and organic matter accumulation in tidal freshwater marshes (Koch and Mendelssohn 1989, McKee and Mendelssohn 1989, Lamers et al. 1998, Willis and Hester 2004, Spalding and Hester 2007). Organic matter accumulation is responsible for 62% of vertical marsh accretion in tidal freshwater marshes across the Northeast, Southeast, and Gulf coast of the U.S. (Neubauer 2008), so changes in rates of organic matter production can significantly affect the ability of tidal freshwater marshes to keep pace with rising sea levels.

Saltwater intrusion can also lead to shifts in the rates and pathways of microbial organic matter mineralization (Weston et al. 2006, 2011). Microbial methanogenesis (Capone and Kiene 1988) and iron reduction (Roden and Wetzel 1996) are the dominant anaerobic organic matter mineralization processes in freshwater sediments. In marine sediments, however, the greater availability of sulfate (SO_4^{2-}) causes sulfate reduction, an energetically superior pathway to methanogenesis, to become the dominant anaerobic pathway (Jorgensen 1982, Capone and Kiene 1988). An increase of salinity in tidal freshwater systems may lead to a shift from methanogenesis to sulfate reduction and a subsequent increase in organic matter decomposition (Weston et al. 2006, 2011, Neubauer et al. 2013), making these systems extremely vulnerable to sea level rise.

Objectives and Hypotheses

The overall goal of my dissertation research was to understand the effects of sea level rise on the tidal freshwater, oligohaline, and brackish marshes and evaluate how these ecosystems are adapting to both changes in water levels and salinity. The specific research objectives and hypotheses were:

- Objective 1: Examine accretion dynamics between marshes across the estuarine gradient of the Nanticoke River and determine the relative contribution of organic and inorganic matter to accretion in these marshes.
    - *Hypothesis 1*: Rates of accretion will be highest in the tidal freshwater marshes and decrease down the estuary due to less fluvial sediment input.

    - *<u>Hypothesis 2</u>*: Inorganic sedimentation will have a larger influence on accretion in the upper reaches of the estuary and as fluvial inputs decrease downstream, organic matter accumulation will have a larger influence on accretion in marshes downstream.

- <u>Objective 2</u>: Determine the accumulation rates of C, N, and P in the tidal freshwater, oligohaline, and brackish marshes of the Nanticoke River.
    - *<u>Hypothesis 1</u>:* C and N accumulation will be positively related to organic matter deposition due to high levels of organic C and N in organic matter.
    - *<u>Hypothesis 2</u>:* P accumulation will be positively related to organic matter accumulation as well as inorganic sedimentation due to the sorption of P to iron in mineral sediment.
- <u>Objective 3</u>: Examine the effects of sulfate intrusion on biogeochemical transformations and marsh surface elevation in tidal freshwater marsh soil.
    - *<u>Hypothesis 1</u>:* Increased concentrations of sulfate in tidal freshwater marsh soil will lead to increased organic matter decomposition, causing a decrease in surface elevation.
    - *<u>Hypothesis 2</u>:* Increased concentrations of sulfate in tidal freshwater marsh soil will reduce plant biomass due to sulfide toxicity.

Chapter 2: Soil accretion in tidal wetlands across a Chesapeake Bay subestuary as determined using lead-210 core dating

Introduction

Tidal wetlands are under an increasing threat from rising sea levels. On average, global sea level rose approximately 1.2 mm yr^{-1} between 1901 and 1990 and 3.1 mm yr^{-1} between 1993 to 2017 (IPCC 2014, Hay et al. 2015, Nerem et al. 2018, WCRP Global Sea Level Budget Group 2018). Along the east coast of the US, a 1,000-km stretch of coastline north of Cape Hatteras has been identified as a “hotspot” for accelerated sea level rise (Sallenger et al. 2012). This includes the Chesapeake Bay region, where relative sea level rise rates ranged from 3.24-5.11 mm yr^{-1} between 1969 and 2014 and have been accelerating by 0.08-0.22 mm yr^{-1} (Boon and Mitchell 2015). Regional land subsidence plays a major role, with approximately 53% of relative sea level rise due to local subsidence within the Chesapeake Bay (Boon et al. 2010).

The ability of tidal wetlands to maintain surface elevation under accelerated sea level rise is critical for their persistence and depends on many factors including accretion of mineral and organic matter, rates of decomposition, plant community structure, and productivity (Reed 1995, Morris et al. 2002, Cahoon et al. 2006, Neubauer 2008). Marsh accretion is a balance between deposition and erosion on the marsh surface and belowground plant production and decomposition of both mineral and organic materials (Bricker-Urso S. et al. 1989, Reed 1995, Morris et al. 2016). These processes may vary across the range of tidal wetlands types and within individual wetlands as the sediment load changes and as wetland plant communities shape these dynamics (Neubauer et al. 2002, Callaway et al. 2012, Butzeck et al. 2014).

The overall response of tidal wetlands to relative sea level rise is dependent on the deposition of inorganic and organic matter (Bricker-Urso S. et al. 1989, Turner et al. 2000, Neubauer 2008), and the supply of fluvial or estuarine mineral sediment dictates the balance of organic and inorganic contributions to accretion. For example, in regions where sediment supply is low, such as in Louisiana and the Northeast U.S., organic matter accumulation drives vertical accretion. In the Southeast U.S., where sediment supplies are greater, the marshes are more mineral-rich (McCaffrey and Thomson 1980, Nyman et al. 2006, Weston 2014). However, the maximum rate of organic matter accretion is limited by plant productivity, so although organic matter accumulation drives accretion in some marshes (Turner et al. 2000, Nyman et al. 2006, Callaway et al. 2012), organic matter accumulation alone may not be enough to keep pace with sea level in many tidal wetland systems (Weston 2014, Boyd et al. 2017).

Accretion dynamics vary depending on the position of tidal marshes along the estuary. Previous studies have found that accretion rates often decrease with increasing salinity in estuarine systems along the Atlantic coast of the U.S. (Kearney and Ward 1986, Orson et al. 1990, Craft 2007), indicating that rivers are a major source of suspended sediment supplied to these systems. However, mid-Atlantic U.S. estuaries are microtidal (mean tidal range less than 2 m) and characterized by weak tidal current velocities with little capacity to transport suspended sediment (Kearney and Turner 2016). Within smaller tributary estuaries, river dynamics may overwhelm the weaker tidal forces and develop a pronounced tidal asymmetry that creates a dominant ebb tide and net sediment export (Stevenson et al. 1988). As a result, accretion rates are typically highest in the upper reaches of the estuary and decrease downstream as sediment inputs decrease.

The overall goal of this study was to evaluate accretion rates in tidal wetlands across a Chesapeake Bay subestuary using ^{210}Pb dating of soil cores, a method that determines accretion over an approximately 100-yr timeframe. Specifically, the objectives of this study were to examine accretion dynamics between marshes across the estuarine gradient and to determine the relative contribution of organic and inorganic matter to accretion in these marshes. I hypothesized that rates of accretion will be highest in the tidal freshwater marshes and decrease down the estuary due to less fluvial sediment input. Further, I hypothesized that inorganic sedimentation will have a larger influence on accretion in the upper reaches of the estuary and as fluvial inputs decrease downstream, organic matter accumulation will have a larger influence on accretion in marshes downstream.

Methods

Site Description

The Nanticoke River, a major tributary estuary of the Chesapeake Bay, drains over 200,000 hectares of Maryland and Delaware's coastal plain in the central Delmarva Peninsula (Chesapeake Bay Foundation 1996). The main stem of the river flows from Delaware and west into Maryland. The river widens proceeding downstream, and is bordered by expansive tidal wetlands, including tidal forested wetlands and estuarine-meander marshes in the upper estuary and submerged-upland marshes in the lower estuary (Kearney et al. 1988). The estuary is ebb-dominated and microtidal, with a mean tidal range of 0.7 m (NOAA water level station 8571773, Vienna, MD). Salinity ranges from approximately 15 ppt at the mouth to less than 0.5 ppt in the tidal freshwater zone (Beckett et al. 2016). The watershed is dominated by agriculture (39.2%) and forested areas (40.9%) (Chesapeake Bay Foundation 1996, Jacobs and Bleil 2008). The Nature Conservancy designated the Nanticoke River watershed as a bioreserve and a "Last Great Place" in 1991. Within the watershed, there are approximately 200 plant species and 70 animal species listed as rare, threatened or endangered, and 20 plant and 5 animal species that are globally rare (The Nature Conservancy 1998).

The study sites were chosen based on proximity to previously established Surface Elevation Tables (SETs) that were part of a larger study looking at accretion rates and elevation changes (Beckett et al. 2016). Five sites were selected along the salinity gradient of the Nanticoke River, and three subsites were established within interior marsh sections of each site (Fig. 2.1). Sites 1 and 2 were located downstream in mesohaline marshes, sites 3 and 4 were located within oligohaline marshes, and site 5 was located upstream in tidal freshwater marshes. Additionally, sites 1-3 were located in large marshes with extensive tidal creeks, while sites 4 and 5 were located in smaller marshes closer to the main river channel. The average salinity levels and dominant vegetation for each site is detailed in Table 2.1.

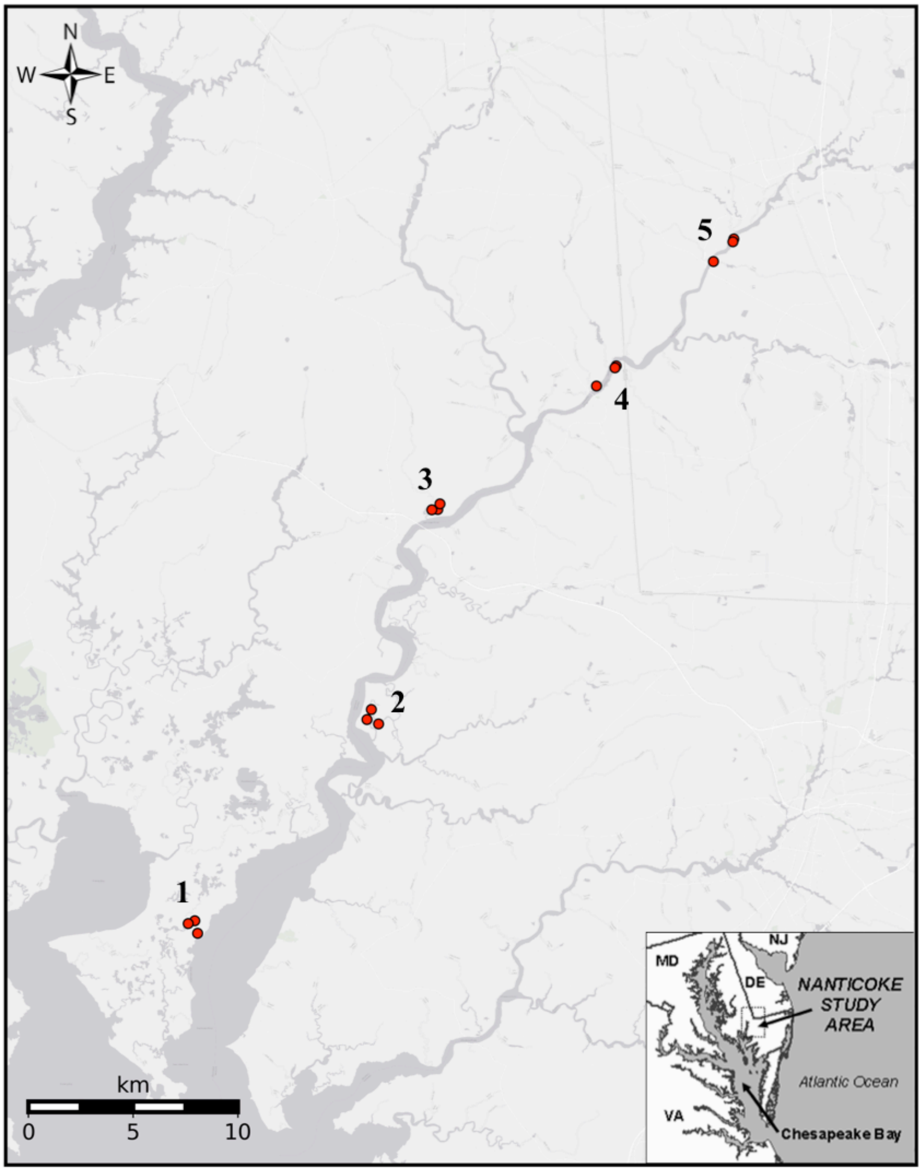

Figure 2.1: Location of study sites along the Nanticoke River. Each site contains three subsites.

Table 2.1: Salinity regime, average salinity, distance from the mouth along the river channel, and the dominant vegetation for each site along the Nanticoke River (average salinity levels were obtained from Becket et al. 2016; plant nomenclature is according to the USDA PLANTS database, https://plants.sc.egov.usda.gov, accessed [May 28, 2019]).

Site	Salinity Regime	Average Salinity (ppt)	Distance from Mouth (km)	Dominant Vegetation
1	Mesohaline	10	12	*Juncus roemerianus, Spartina alterniflora, Distichlis spicata, Spartina patens, Bolboschoenus robustus*
2	Mesohaline	5	25	*Spartina alterniflora, Spartina patens, Spartina cynosuroides, Distichlis spicata, Bolboschoenus robustus*
3	Oligohaline	2	40	*Peltandra virginica, Mikania scandens Bidens laevis, Typha* sp., *Polygonum punctatum*
4	Oligohaline	1	50	*Polygonum arifolium, Impatiens capensis, Bolboschoenus fluviatilis, Peltandra virginica, Pilea pumila*
5	Tidal Freshwater	0.1	60	*Peltandra virginica, Polygonum arifolium, Zizania aquatica, Impatiens capensis, Nuphar lutea*

Field and Laboratory Measurements

Sediment cores were collected from each of the 15 subsites in August 2008. Cores were taken from a random location approximately 10 meters from the SETs using a McAuley corer, which collects a 100-cm by 7.5-cm diameter half-cylinder core while minimizing vertical compaction. Each core was divided into 2.5-cm sections within the top 10 cm, 5-cm sections from 10 to 50 cm, and 10-cm sections from 50 to 100 cm. Samples were brought back to the laboratory, dried at 70ºC for 48 hours and analyzed for water content and bulk density. The dried soil was then placed in a muffle furnace at 400ºC for 16 hours to determine organic matter content by loss on ignition (LOI; Sparks et al. 1996).

Average bulk density and organic matter for the entire 100-cm core was calculated using the following steps: (1) averaging the upper four 2.5-cm sections to get an average for the top 10 cm; (2) averaging the two 5-cm sections together for each of the four 10-cm interments from 10 to 50 cm; and (3) averaging these five 10-cm increments with the five 10-cm increments from the 50 to 100 cm depth.

Lead-210 Dating

Sediment cores were dated using the radioisotope lead-210 (^{210}Pb), a naturally occurring isotope deposited from the atmosphere. ^{210}Pb originates from uranium-238, which through five intermediates, decays to radium-226 (^{226}Ra) in the earth's crust. ^{226}Ra decays to gaseous radon-222 (^{222}Rn, half life 3.8 days), which diffuses to the atmosphere and subsequently decays through a series of short-lived daughters to ^{210}Pb. There is also some decay of ^{222}Rn that occurs in the ground and contributes a relatively constant background supply of ^{210}Pb, termed "supported" ^{210}Pb. Atmospherically derived ^{210}Pb binds to particulate matter in the atmosphere and falls back to earth where it is deposited and incorporated into sediment, producing a concentration of "unsupported" or excess ^{210}Pb. The activity of unsupported ^{210}Pb decreases as a function of time, controlled by its half-life of 22.3 years, making it extremely useful for dating sediments within the last 100 years (Faure 1977).

Lead-210 was counted using polonium-210 (^{210}Po), a daughter nuclide of ^{210}Pb that is assumed to be in equilibrium with ^{210}Pb. Due to its shorter half-life (138 days), emission of alpha particles, and strong sorption to silver plating, ^{210}Po is easier to measure than its long-lived, beta-emitting parent, ^{210}Pb. Sediment core sections were analyzed according to the methods described by Flynn (1968). Samples were weighed to 1.0 g and spiked with 1 ml of Polonium tracer (^{209}Po). Nitric acid (HNO_3) and hydrochloric acid (HCL) were added (10 ml each) to digest all organic matter and strip the ^{210}Po from the sediments. After an overnight digestion, samples were centrifuged to remove residual sediment, and the supernatant was dried overnight at 60-80°C. The dried supernatant was re-dissolved with 2 ml of concentrated HCL and evaporated to dryness twice in order to remove any residual HNO_3, which can interfere with the plating procedure. Samples were then dissolved in 0.1N HCL and ascorbic acid was added to prevent iron precipitation. Silver plates (17 mm x 17 mm) coated with acrylic paint on one side were added to each Po solution (painted side down) and allowed to sit overnight at 70°C to sorb Po from the solution. Plates were subsequently removed from solution and rinsed with deionized water. Activity of plated $^{209, 210}$Po was counted on a four channel Alpha Spectrometer (Tennelec TC-256).

Accretion Rates

Accretion rates were calculated using the Constant Initial Concentration (CIC) model (Robbins et al. 1978). This model assumes there is a constant input of ^{210}Pb through time as well as a constant sedimentation rate through time. Based on these assumptions, the excess (unsupported) ^{210}Pb activity will decrease exponentially with depth in the sediment (Bricker-Urso et al. 1989). Using the CIC model, unsupported ^{210}Pb was calculated by subtracting the supported ^{210}Pb activity (background activity representing ^{222}Rn found in the sediment) from the total ^{210}Pb activity. Supported ^{210}Pb was determined from the average ^{210}Pb activity taken at depths in the core where ^{210}Pb decreased to a constant value. A linear regression of the natural log of unsupported ^{210}Pb versus cumulative mass (g cm^{-2}) was used to calculate sedimentation rates in terms of annual mass burial (g cm^{-2} yr^{-1}). Marsh accretion rates were determined by dividing the sedimentation rate by the average bulk density (g cm^{-3}), generating depth-based rates (cm y^{-1}).

Mass Accumulation Rates

Mass accumulation rates were calculated using the sedimentation rates (g cm^{-2} yr^{-1}) determined from the ^{210}Pb profiles. Organic accumulation (g cm^{-2} yr^{-1}) for each site was determined by multiplying the sedimentation rate by the organic content (LOI, averaged over depth of 100 cm). Similarly, inorganic accumulation (g cm^{-2} yr^{-1}) was calculated by multiplying the sedimentation rate by the inorganic content (1-LOI, averaged over depth of 100 cm).

In order to determine how much of the total marsh accretion was attributable to organic and inorganic matter, the equation described by Bricker-Urso S. et al. (1989) was used:

$$S_i = ((S_t)(LOI))/D_i$$

where S_t = total average sediment accumulation (g cm^{-2} yr^{-1}), LOI= ratio of loss on ignition (%LOI/100 for organic, 1-%LOI/100 for inorganic), D_i = sediment density (1.1 g cm^{-3} for organic and 2.6 g cm^{-3} for inorganic, DeLaune et al. 1983), and S_i = organic or inorganic sediment accretion (cm yr^{-1}). The amount of accretion due to water/porespace was also determined by subtracting both the organic and inorganic accretion from the total accretion.

Data Analysis

Analysis of variance (ANOVA) was used to test for differences between sites in bulk density, organic matter, organic and inorganic accumulation, and accretion rates. Tukey's Honestly Significant Difference test was used to make post-ANOVA comparisons. (SAS 9.2, SAS Institute Inc., Cary, NC). Simple linear regressions were used to understand the relationship between accretion vs. bulk density, accretion vs. organic matter, and accretion vs. distance from the mouth of the river. Additionally, the relationships between accretion vs. organic accumulation, accretion vs. inorganic accumulation, organic vs. inorganic accumulation, and percent water vs. the log of percent organic matter were tested. A curvilinear relationship was tested for organic matter vs. bulk density (R stats package, version 3.5.1, R Core Team 2018). Unless otherwise noted, $P \leq 0.05$ was used as the critical value for all tests of significance.

Results

Soil Characteristics

Bulk density and organic matter content did not differ between the sites ($F_{4, 10} = 1.99$, $p = 0.172$; $F_{4, 10} = 0.61$, $p = 0.666$, respectively). Additionally, there was no relationship between accretion rates and bulk density or organic matter content ($p = 0.557$, $p = 0.955$, respectively). The soil profiles follow a general pattern of increasing bulk density and decreasing organic matter with depth, but there was a large amount of variability between the subsites (Fig. 2.2). Across the individual subsites, bulk density values ranged from 0.1170-0.3753 g cm^{-3} and organic matter content ranged from 21-

57% (Table 2.2). Overall, there was an inverse relationship between bulk density and organic matter values ($R^2 = 0.52$, Fig. 2.3a).

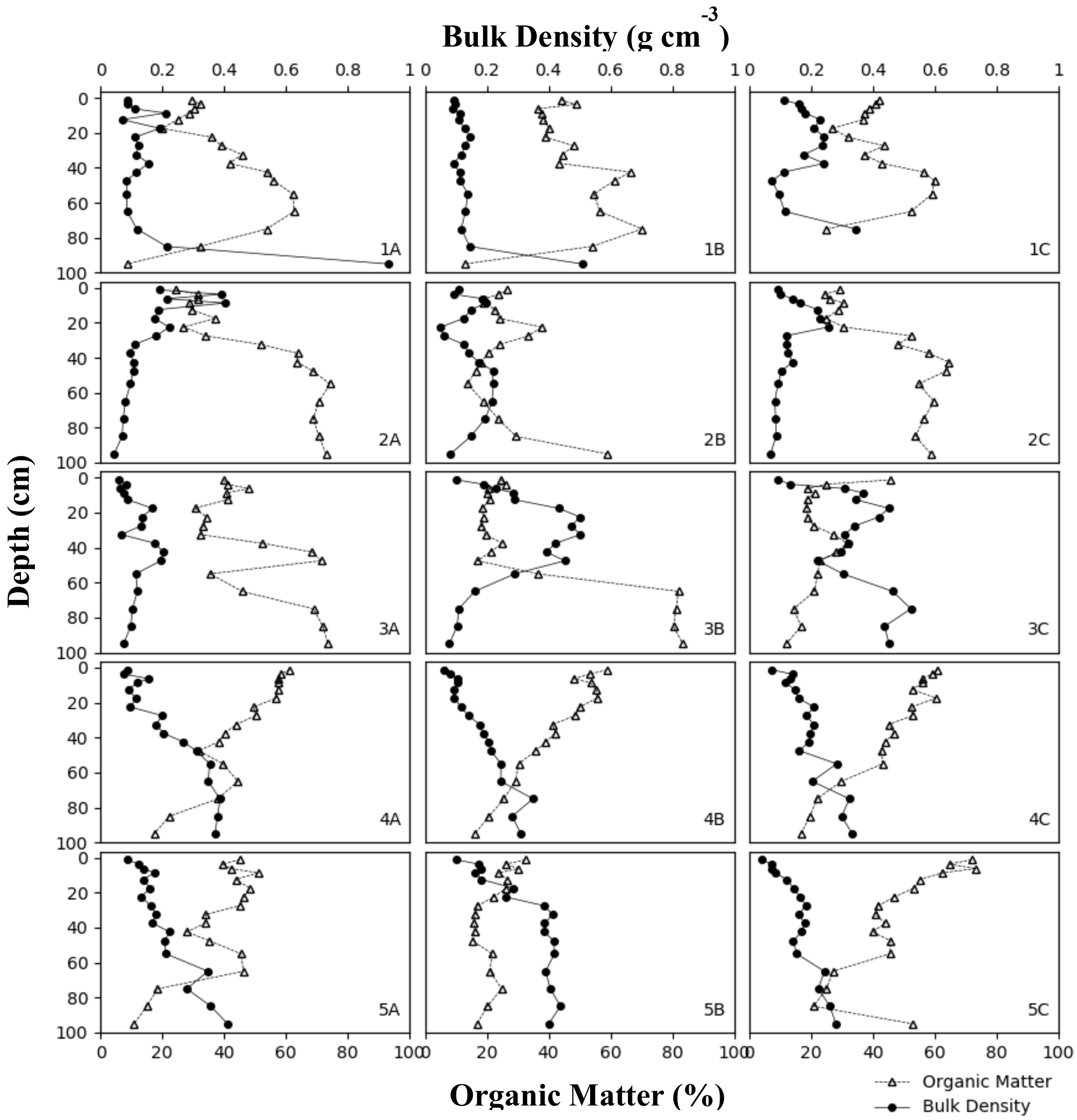

Figure 2.2: Bulk density (g cm^{-3}) and organic matter (%) values vs. depth across 100-cm cores for each subsite along the Nanticoke River.

Table 2.2: Vertical accretion, bulk density and organic matter (averaged over 100-cm core (n=10)), accumulation rates, and the percent of accretion that is contributed by organic (Org) and inorganic matter (Inorg) and water/porespace (W/P) for each subsite along the Nanticoke River.

Sub site	**Accretion (cm/yr)**	**Bulk Density (g cm^{-3})**	**Organic Matter (%)**	**Accumulation Rates (g cm^{-2} y^{-1})**		**Percent of Accretion**		
				Org	**Inorg**	**Org**	**Inorg**	**W/P**
1A	0.3772	0.1242	44.49	0.0210	0.0262	5.07	2.68	92.26
1B	1.0611	0.1618	48.11	0.0745	0.0803	6.38	2.91	90.71
1C	0.3045	0.1835	42.95	0.0221	0.0293	6.59	3.70	89.71
2A	0.5674	0.1265	57.49	0.0686	0.0507	11.00	3.44	85.57
2B	0.6537	0.1539	26.59	0.0253	0.0699	3.52	4.12	92.36
2C	0.2397	0.1195	49.62	0.0172	0.0175	6.53	2.81	90.66
3A	0.2833	0.1170	52.07	0.0134	0.0124	4.31	1.68	94.01
3B	0.2133	0.2683	46.67	0.0289	0.0330	12.32	5.96	81.72
3C	0.2240	0.3753	20.68	0.0134	0.0512	5.42	8.80	85.78
4A	0.2259	0.2687	40.51	0.0135	0.0198	5.44	3.38	91.18
4B	0.2781	0.2142	35.99	0.0121	0.0215	3.95	2.97	93.08
4C	0.4415	0.2285	38.73	0.0279	0.0441	5.74	3.84	90.43
5A	1.0252	0.2431	33.86	0.0521	0.1019	4.62	3.82	91.56
5B	0.4445	0.3571	21.10	0.0228	0.0852	4.66	7.37	87.97
5C	0.4081	0.1857	42.26	0.0193	0.0264	4.31	2.49	93.20

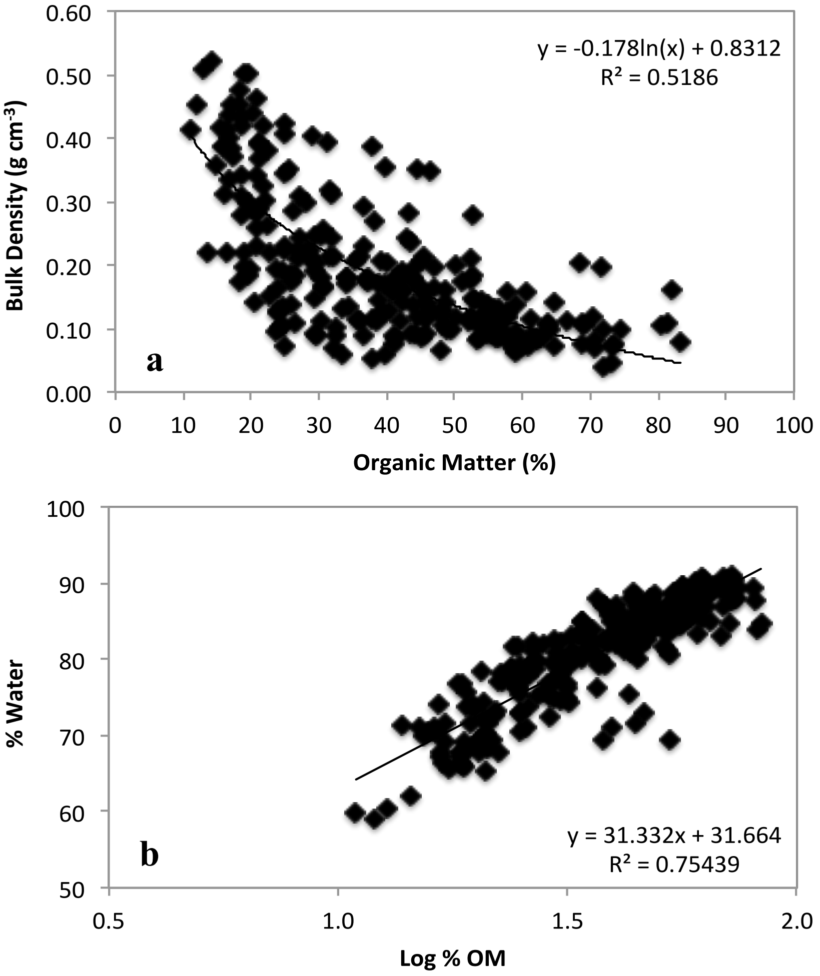

Figure 2.3: Relationships between (a) organic matter (%) and bulk density (g cm^{-3}) and (b) the log of percent organic matter versus percent water for soil cores taken at each subsite along the Nanticoke River.

Accretion Rates

All 15 soil cores exhibited interpretable ^{210}Pb profiles (Fig. 2.4). The linear regressions of the ln excess ^{210}Pb vs. cumulative mass yielded goodness of fit (R^2) values ranging from 0.381 to 0.965. All of the regressions were significant ($p < 0.05$) except for cores 3C and 5A (Appendix I).

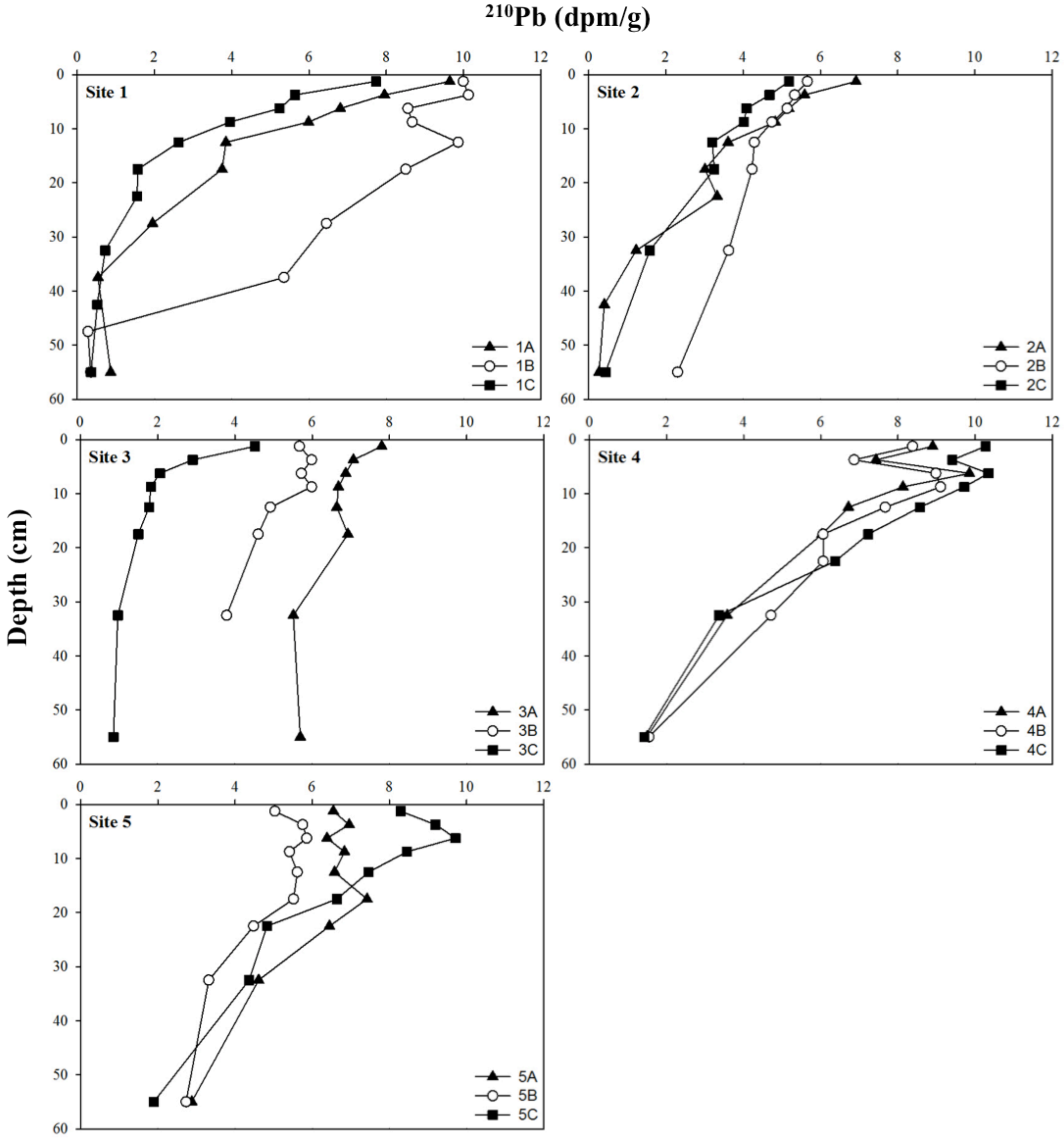

Figure 2.4: Lead-210 profiles for each site along the estuarine gradient of the Nanticoke River.

Mean accretion rates for the sites ranged from 0.240 to 0.626 cm yr^{-1} (Fig. 2.5) and there was no significant difference in accretion rates between sites ($F_{4,\,10} = 1.74$, $p = 0.217$). The accretion rates for the individual subsites were highly variable. At sites 1 and 2 (mesohaline marshes), two out of the three subsites had rates of accretion higher than mean sea level rise (0.377 cm yr^{-1} for Cambridge, MD, NOAA water level station

8571892), while at site 5 (tidal freshwater marshes), all of the subsites had accretion rates higher than mean sea level. In contrast, all of the subsites at site 3 (oligohaline marshes) had accretion rates lower than mean sea level, and at site 4 (oligohaline marshes), two out of the three sites were below mean sea level. Despite differences in the rates of accretion across the different estuarine positions, there was no significant relationship between accretion and distance from the mouth of the river (p = 0.756). There was also no significant relationship between accretion and bulk density or organic matter (p = 0.557, 0.955, respectively).

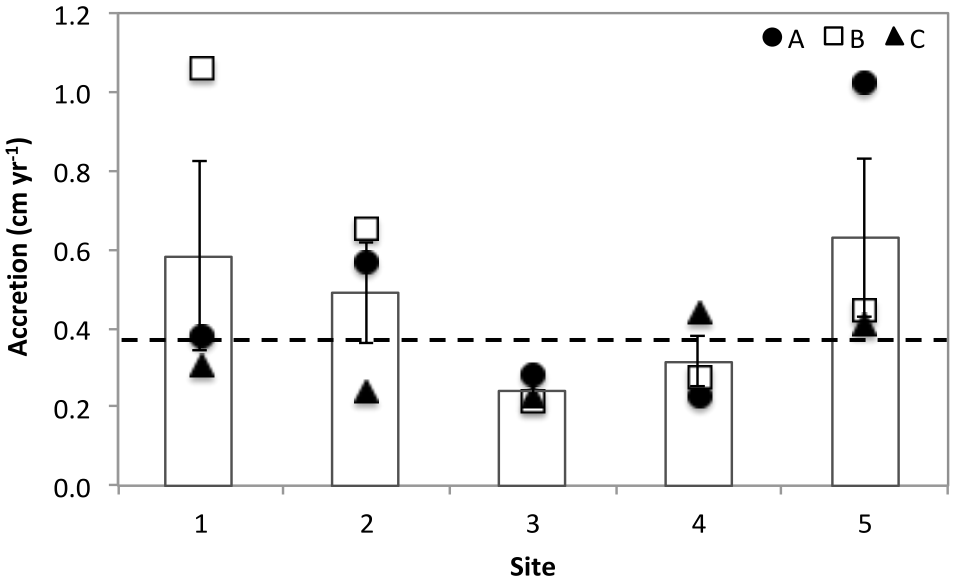

Figure 2.5: Accretion rates (cm yr^{-1}) for each site along the Nanticoke River (mean +/- SE). Symbols indicate accretion rates for each subsite. Dotted line indicates mean sea level rise for Cambridge, Maryland (0.377 cm yr^{-1}) from 1943 to 2018 (http://www.tidesandcurrents.noaa.gov/).

Mass Accumulation Rates

Rates of organic and inorganic accumulation did not significantly differ between sites ($F_{4,\,10} = 0.703$, $p = 0.607$; $F_{4,\,10} = 1.12$, $p = 0.4$ respectively), but were positively related to each other ($p < 0.05$, $R^2 = 0.37$, Fig. 2.6a). Overall, most subsites received similar contributions of organic and inorganic accumulation (Table 2.2). Subsites 2B, 3C, 4B, 5A, and 5B had 2-3 times more inorganic accumulation than organic; however, when looking at the percent each component contributes to vertical accretion, only three of these sites (2B, 3C, and 5B) had a higher percentage of inorganic than organic contribution. At the remaining 12 sites, organic matter contributed approximately 1.5-3 times more towards accretion than did the inorganic component. Water/porespace contributed the largest percentage towards accretion, accounting for 82-94% of the total accretion (Table 2.2).

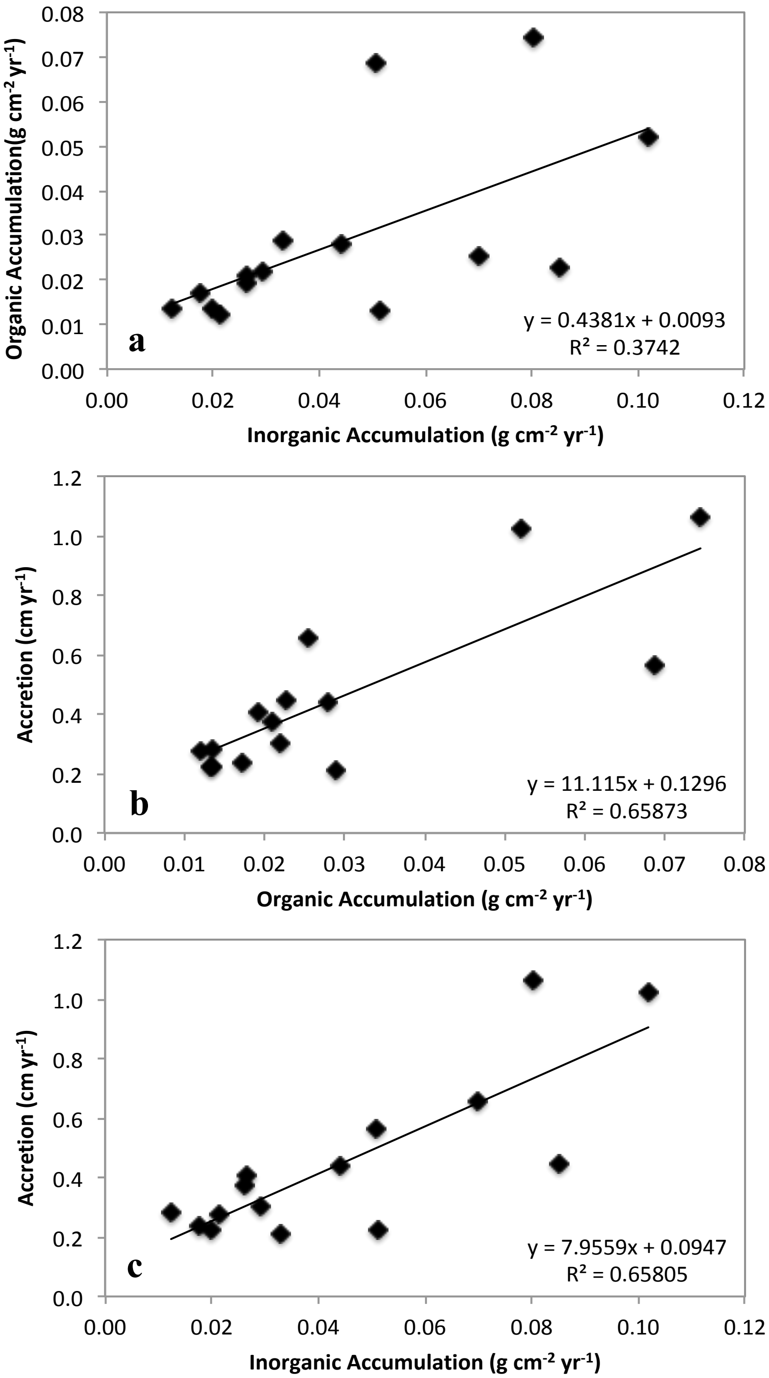

Figure 2.6: Relationships between (a) organic accumulation (g cm^{-2} yr^{-1}) and inorganic accumulation (g cm^{-2} yr^{-1}), (b) accretion (cm yr^{-1}) and organic accumulation (g cm^{-2} yr^{-1}), and (c) accretion (cm yr^{-1}) and inorganic accumulation (g cm^{-2} yr^{-1}) for subsites along the Nanticoke River.

There was a significant positive relationship between both organic and inorganic accumulation rates and accretion rates ($p < 0.001$, Fig. 2.6b-c). Organic and inorganic accumulation each explained about 66% of the variability in vertical accretion rates. The slope coefficient for accretion vs. organic accumulation was higher than the slope coefficient for accretion vs. inorganic accumulation, suggesting that the input of organic matter resulted in a greater increase in volume than the same input of mineral matter per unit mass.

Discussion

Marsh Accretion Dynamics

Accretion rates were expected to be highest in the tidal freshwater marshes and decrease downstream as salinity levels increased; however, accretion rates were highly variable across the Nanticoke River subestuary. Only 8 out of the 15 subsites had accretion rates higher than relative sea level rise for the area (0.377 cm yr^{-1} for Cambridge, Maryland). The highest rates of accretion were found in the tidal freshwater and mesohaline sites (sites 1, 2, and 5). The oligohaline marshes found in the mid-estuary sites (sites 3, 4) had the lowest rates of accretion (Fig. 2.4), with only one of the subsites (4C) accreting at a rate faster than relative sea level rise for the area. A previous study done on the Nanticoke River using surface elevation tables (SET) to measure elevation changes also found that the mid-estuarine sites are losing elevation despite high rates of accretion (Beckett et al. 2016). Noe et al. (2016) also found that long-term sediment accumulation rates declined downstream from the tidal freshwater forested wetlands to the oligohaline marshes, however this study only examined sites in the upper estuary. The high accretion rates found in the tidal freshwater marshes at site 5 are likely due to riverine sediment input and are consistent with high accretion rates found by Kearney and Ward (1986). They found that accretion rates in the tidal freshwater marshes had the highest rates of accretion in the estuary and have more than doubled since European settlement of the watershed.

The accretion dynamics along the Nanticoke River differ from other studies that found decreasing rates of accretion with increasing salinity in estuaries of varying tidal amplitude along the Atlantic coast of the U.S. (Kearney and Ward 1986, Orson et al. 1990, Craft 2007). As sediment gets trapped in the in the upper reaches of the estuary, accretion rates generally decline down estuary (Kearney and Ward 1986). As a result, the oligohaline marshes located mid-estuary receive little allochthonous sediment input (Kearney et al. 1988). The low accretion rates found at both sites 3 and 4 on the Nanticoke River suggest that these marshes are receiving little sediment input. Further, the marshes at site 3 are located in tidal creeks off of the main channel of the river, so these marshes are likely accreting more slowly due to less frequent tidal flooding (Temmerman et al. 2005, Kearney and Turner 2016).

The Nanticoke River is ebb dominated and microtidal, and river dynamics may overwhelm weak tidal currents and increase net sediment transport (Stevenson et al. 1988, Kearney and Turner 2016), so the marshes in the lower estuary are more likely dependent on autochthonous organic matter production or sediment brought in from major storm events. Therefore, it is surprising that in the lower reaches of the estuary, the brackish marshes had accretion rates similar to the tidal freshwater marshes. The lack of a clear trend across the estuary and the variability of accretion rates across the subsites indicates that the mechanisms controlling accretion dynamics are complex and likely driven by site-specific factors rather than estuary-wide factors.

Contribution of Organic and Inorganic Matter to Accretion

The contribution of organic and inorganic matter to accretion can vary depending on the location of the tidal marsh within the estuary. Vertical accretion in salt marshes is largely driven by organic matter accumulation (Turner et al. 2000, Nyman et al. 2006), while in tidal freshwater marshes, both mineral and organic matter accumulation influence accretion (Neubauer 2008). It was expected that inorganic accumulation would have a larger influence on accretion in the tidal freshwater marshes while organic accumulation would play a larger role downstream in the brackish marshes. Instead, most sites had similar rates of organic and inorganic accumulation, with both explaining 66% of the variability in marsh accretion rates (Fig. 2.6b-c). However, when looking at the percent each component contributes to vertical accretion, the organic contribution was higher at 12 out of the 15 sites (Table 2.2). Further, the water/porespace accounted for 82-94% of the total accretion (Table 2.2), and the relationship between loss-on-ignition and water content in the marsh cores suggests that the water retained by the marsh sediment is associated with the organic component (Fig 2.3b). When associated waters were considered, organic matter accounted for 91-98% of vertical accretion across the estuary (Fig. 2.7; Bricker-Urso et al. 1989). Additionally, the slope coefficient for accretion vs. organic accumulation was higher than the slope coefficient for accretion vs. inorganic accumulation, resulting in a greater increase in volume than the same input of mineral matter (Fig. 2.6b-c; Neubauer 2008). These findings suggest that organic matter accumulation has a large influence on accretion across the estuary regardless of location of the marsh.

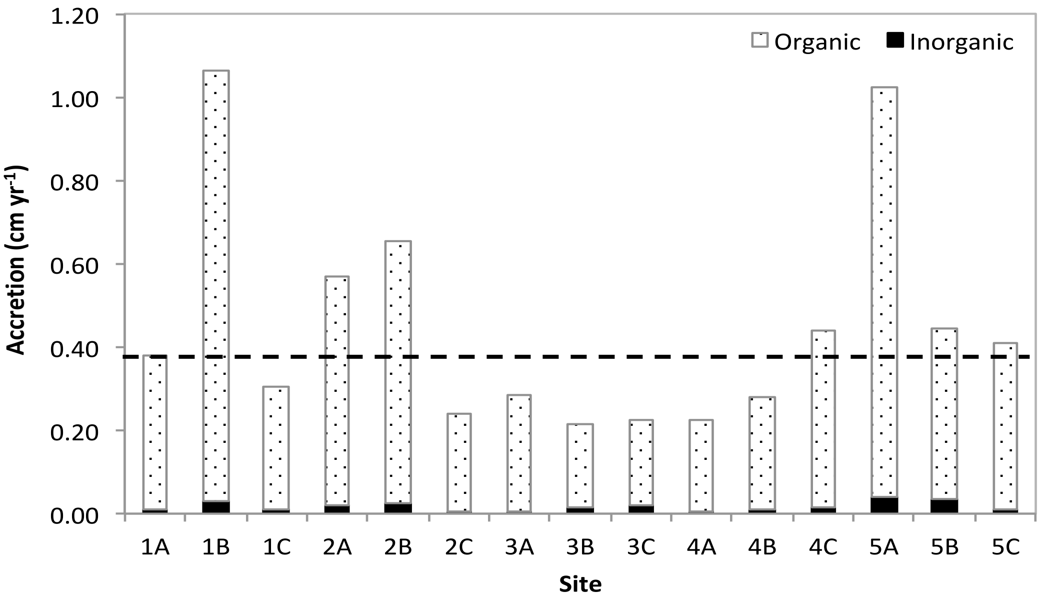

Figure 2.7: Vertical accretion rates (cm yr^{-1}) along the Nanticoke River with contributions from organic (including water/porespace) and inorganic inputs. Dotted line indicates mean sea level rise for Cambridge, Maryland (0.377 cm yr^{-1}) from 1943 to 2018 (http://www.tidesandcurrents.noaa.gov/).

Although organic matter accumulation plays a large role in vertical accretion, inorganic sediment also plays an important role (Morris et al. 2016). The biogeomorphic feedbacks between inorganic sediment and the plant biomass strongly influence the ability of a marsh to keep pace with sea level rise (Fagherazzi et al. 2012). The presence of plants on the marsh surface enhances inorganic sedimentation (Gleason et al. 1979), and increased nutrient-rich sediment enhances plant growth (DeLaune et al. 1981, Morris et al. 2002). However, the elevation of the marsh also plays a role, and plants have an optimum elevation at which they are most productive (Morris et al. 2002). If the marsh elevation is lower than the optimum elevation for plant growth, an increase in the depth of tidal flooding will lead to a decrease in plant productivity, and thus a decrease in sedimentation (Fagherazzi et al. 2012). The positive relationship between organic and inorganic accumulation across the sites supports the idea that both inputs are important for maintaining marsh surface elevation (Fig. 2.6a).

Boyd et al. (2017) concluded that in order to avert marsh submergence, accretion deficits that cannot be offset by increased organic accumulation must be accompanied by increased sediment accumulation. Along the Nanticoke River, inorganic inputs may be too low and organic matter accumulation may not be enough to keep these marshes above relative sea level.

Conclusion

Accretion rates were highly variable across the estuarine gradient with the lowest rates of accretion found in the oligohaline marshes. Only 8 out of the 15 subsites across the Nanticoke River subestuary had accretion rates higher than relative sea level rise for the area. Organic matter accumulation had a large influence on accretion rates across the estuary, regardless of the location. Interestingly, inorganic sedimentation was also important across the estuary, suggesting that both inputs play a key role in marsh surface elevation in these marshes. Organic matter contribution is especially important in microtidal marshes with low mineral sediment supply, particularly mid-estuarine oligohaline marshes. If organic matter accumulation is not sufficient, these marshes are at risk to being lost to rising sea levels.

Chapter 3: Mechanisms driving accumulation rates of carbon, nitrogen, and phosphorus in tidal freshwater, oligohaline, and brackish marshes

Introduction

The proximity of tidal freshwater and oligohaline marshes to developed areas may result in elevated nutrient inputs to them due to the presence of industry, wastewater treatment plants, agriculture, and other non-point sources. Tidal wetlands sequester carbon, nitrogen, and phosphorus (Craft et al. 1988, Loomis and Craft 2010); therefore, these marshes are likely to be important in mitigating anthropogenic stresses further down the estuary. Organic matter retention and deposition of particulates in sediment is a sink for nutrients from surrounding ecosystems. As sediment accretes vertically, organic and mineral matter is incorporated, trapping nutrients within this matrix (Merrill and Cornwell 2000). Several studies have demonstrated the role tidal marshes play in burying C, N, and P, including in the Chesapeake Bay (Morse et al. 2004, Craft 2007, Boynton et al. 2008, Loomis and Craft 2010, Palinkas and Cornwell 2012).

Tidal marshes sequester C, N, and P through nutrient retention and transformation. Soluble inorganic N is transformed into organic N, which is buried over time (Bowden et al. 1991), while inorganic P bound to iron or aluminum is buried through sedimentation (Wolaver and Spurrier 1988a, Craft 1997, Coelho et al. 2004). P can also be incorporated into organic matter and sequestered as organic P (Paludan and Morris 1999). High rates of plant productivity and low rates of decomposition due to anaerobic conditions in wetland soils (Odum et al. 1984) allows nutrients to accumulate in high rates in marsh soils (Bowden 1987, Hussein et al. 2004). Tidal marshes have been shown to be a net sink for C, N, and P from the adjacent estuary, with a largest proportion in particulate form (Wolaver et al. 1983, Wolaver and Spurrier 1988b).

Studies of tidal freshwater, brackish, and salt marshes have shown that C, N, and P concentrations vary along the estuarine gradient (Paludan and Morris 1999, Sundareshwar and Morris 1999, Craft 2007, Loomis and Craft 2010). In a survey of 61 published studies, Craft (2007) found that tidal freshwater and brackish marsh soils had significantly higher C, N, and P concentrations than salt marsh soils, regardless of geographic location. Accumulation rates of C, N, and P can also vary along the salinity gradient, with the higher rates found in tidal freshwater and brackish marshes than salt marshes (Craft 2007, Loomis and Craft 2010).

Organic matter accumulation and inorganic sedimentation in tidal marshes also play an important role with the accumulation of C, N, and P. In the oligohaline and tidal freshwater marshes of the Patuxent River, Merrill and Cornwell (2000) found higher P accumulation in low elevation sites with high rates of mineral sedimentation, while interior marshes, which had low mineral sediment inputs, were driven by organic matter retention and had higher rates of N accumulation. In riverine floodplains, patterns of N and C accumulation were found to be associated with organic matter accumulation rates, while P was associated with mineral sediment deposition (Noe and Hupp 2005).

The overall objective of this study was to determine the accumulation rates of C, N, and P in the tidal freshwater, oligohaline, and brackish marshes of the Nanticoke River. Accretion rates along the Nanticoke River were not linked to position along the estuary and instead were strongly influenced by organic matter accumulation and inorganic sedimentation (see Chapter 2). Thus it was expected that nutrient accumulation rates across the estuary would also be linked to rates of organic and inorganic accumulation. Specifically, I hypothesized that: (1) C and N accumulation would be positively related to organic matter accumulation due to the high levels of organic C and N in organic matter; and (2) P accumulation would be positively related to organic matter accumulation as well as inorganic sedimentation due to the sorption of P to iron in mineral sediment.

Methods

Site Description

The Nanticoke River is a major tributary estuary of the Chesapeake Bay, flowing from Delaware and west into Maryland. The river contains tidal marshes of differing geomorphic types, including tidal forested wetlands and estuarine-meander marshes in the upper estuary and submerged-upland marshes in the lower estuary (Kearney et al. 1988) The estuary is ebb-dominated and microtidal, with a mean tidal range of 0.7 m (NOAA water level station 8571773, Vienna, MD). Salinity ranges from approximately 15 ppt at the mouth to less than 0.5 ppt in the tidal freshwater zone (Beckett et al. 2016). The watershed is dominated by agriculture (39.2%) and forested areas (40.9%) (Chesapeake Bay Foundation 1996, Jacobs and Bleil 2008).

Five sites were selected along the salinity gradient of the Nanticoke River, and three subsites were established within interior marsh sections of each site (Fig. 3.1). The study sites were part of a larger study looking at accretion rates and elevation changes along the Nanticoke River (Beckett et al. 2016). Sites 1 and 2 were located downstream in mesohaline marshes, sites 3 and 4 were located within oligohaline marshes, and site 5 was located upstream in tidal freshwater marshes (Fig. 3.1). Additionally, sites 1-3 were located in large marshes with extensive tidal creeks, while sites 4 and 5 were located in smaller marshes closer to the main river channel. More detailed information on the sites, including their salinity and plant communities, can be found in Chapter 2.

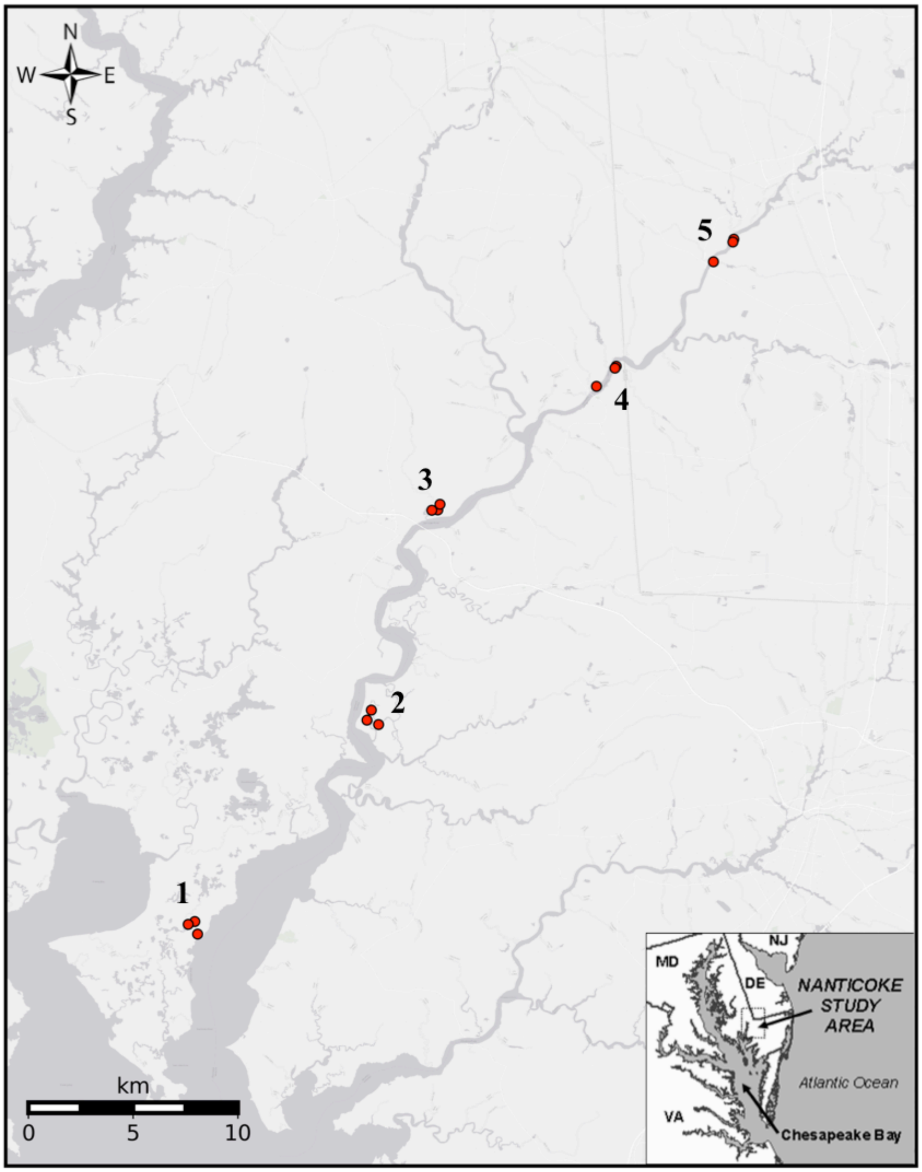

Figure 3.1: Location of study sites along the Nanticoke River. Each site contains three subsites.

Field and Laboratory Measurements

Sediment cores were collected from each of the 15 interior marsh subsites in August 2008. Cores were taken with a McAuley corer, which collects a 100-cm by 7.5-cm diameter half cylinder core while minimizing vertical compaction. Each core was divided into 2.5-cm sections within the top 10 cm, 5-cm sections from 10 to 50 cm, and 10-cm sections from 50 to 100 cm. Samples were brought back to the laboratory, dried at 70ºC for 48 hours, then placed in a muffle furnace at 400ºC for 16 hours to determine organic matter content by loss on ignition (Sparks et al. 1996).

Accumulation Rate Measurements

Particulate carbon and nitrogen content was measured using CHN analysis (Exeter Analytical, Inc. Model CE-440 Elemental Analyzer) and phosphorus (total and inorganic) was analyzed using the molybdenum blue technique (Parsons et al. 1984) for samples collected at the 10 cm, 20 cm, and 30 cm depth of each sediment core. Using the carbon measurements, a linear regression of carbon versus organic matter content was used to calculate carbon concentrations based on loss on ignition (LOI) for the entire depth of each core. This process was repeated using the nitrogen measurements. A weak relationship was found between phosphorus and organic matter content, so average phosphorus concentrations for each subsite were only based on the three measured depths (10, 20, and 30 cm; Appendix II).

Accumulation rates were determined by multiplying the average C, N, and P concentrations by the sedimentation rates (g m^{-2} yr^{-1}) determined by the linear regression of the ^{210}Pb data on the cumulative mass (g cm^{-2}) for each subsite. This calculation corrects for sediment compaction to the depth of the limit of ^{210}Pb (Merrill and Cornwell 2000) (see Chapter 2 for details on the calculation of sedimentation rates).

Data Analysis

Analysis of variance (ANOVA) was used to test for differences between sites for C, N, and P concentrations, C:N, C:P, and N:P ratios, and accumulation rates. Tukey's Honestly Significant Difference test was used to make post-ANOVA comparisons (R stats package, version 3.5.1, R Core Team 2018). Simple linear regressions were used to understand the relationship between C, N, and P accumulation rates vs. accretion, C, N, and P accumulation rates vs. organic accumulation, and C, N, and P accumulation rates vs. inorganic accumulation. Unless otherwise noted, $P \leq 0.05$ was used as the critical value for all tests of significance.

Results

Sediment C, N, and P concentrations

Mean total C and N concentrations were generally higher in the brackish marshes and decreased moving upstream to the tidal freshwater marshes (Fig. 3.2); however, the differences were not significantly different between the sites ($F_{4, 10} = 0.609$, $p = 0.665$; $F_{4, 10} = 0.604$, $p = 0.669$, respectively. Mean total P concentrations did differ significantly across sites ($p < 0.05$, Fig. 3.2) with the highest concentrations at the upper portion of the estuary. Site 4, located within oligohaline marshes, had average P concentrations 1.5 times greater than sites 1, 2, and 3, which were located downstream in brackish (sites 1 and 2) and oligohaline marshes (site 3). Concentrations across the subsites ranged from 9 to 27% for C, 0.7 to 1.8% for N, and 0.4 to 0.8 mg g^{-1} for P (Table 3.1). Across the estuary, C:N ratios ranged from 14 to 21, C:P ratios ranged from 693 to 1108, and N:P ratios ranged from 41 to 61 (Table 3.1).

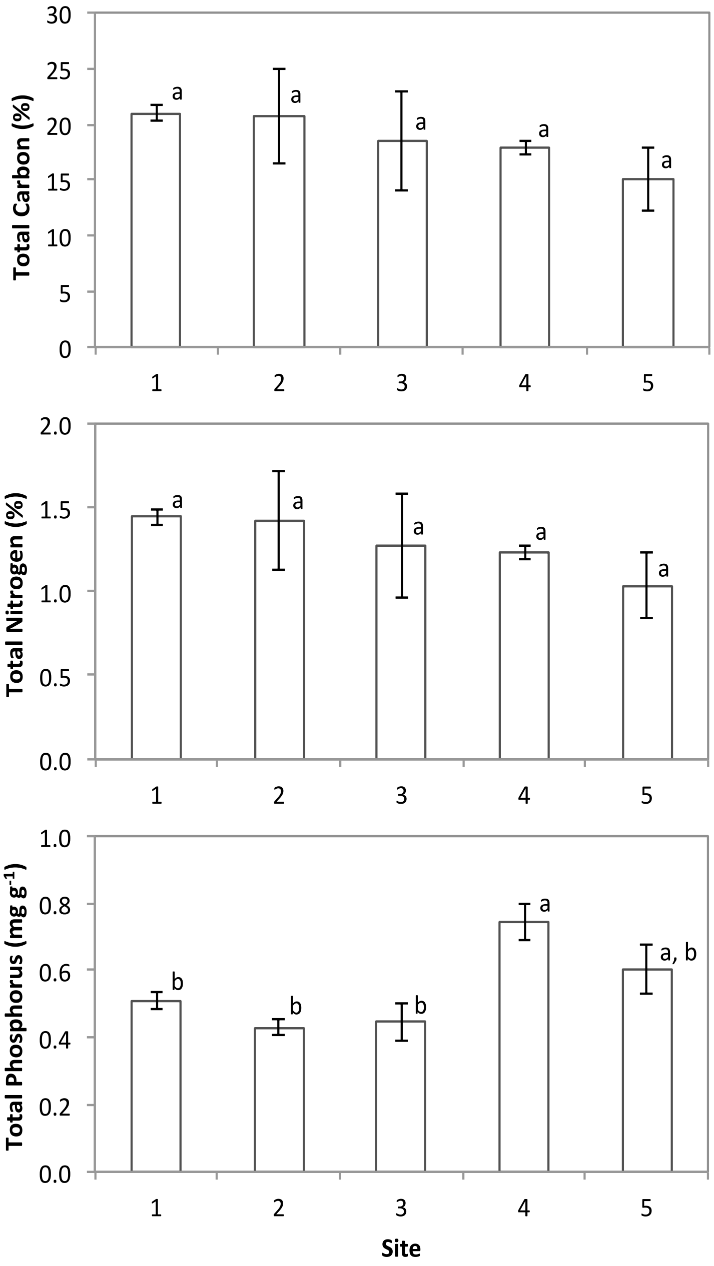

Figure 3.2: Total carbon, nitrogen, and phosphorus concentrations (mean +/- SE) for each site along the Nanticoke River. Letters denote statistical differences ($p < 0.05$) from Tukey's Honestly Significant Difference post-ANOVA comparisons.

Table 3.1: Accumulation rates of organic and inorganic matter; concentrations (averaged over 100-cm core (n=10)) of total carbon, nitrogen, and phosphorus; and C:N, C:P, and N:P ratios (averaged over 0-30 cm depth) for each subsite along the Nanticoke River.

	Accumulation Rates ($g\ m^{-2}\ y^{-1}$)								
Sub site	**Organic**	**Inorganic**	**I:O**	**Total C (%)**	**Total N (%)**	**Total P (mg g^{-1})**	**C:N**	**C:P (molar)**	**N:P**
1A	210	262	1.2	20.7	1.4	0.557	21	858	41
1B	745	803	1.1	22.4	1.5	0.488	17	877	52
1C	221	293	1.3	20.0	1.4	0.482	18	906	50
2A	686	507	0.7	26.7	1.8	0.479	21	1076	50
2B	253	699	2.8	12.4	0.9	0.402	21	898	43
2C	172	175	1.0	23.1	1.6	0.409	21	1108	52
3A	134	124	0.9	24.2	1.7	0.553	16	801	50
3B	289	330	1.1	21.7	1.5	0.380	15	725	47
3C	134	512	3.8	9.6	0.7	0.403	17	717	43
4A	135	198	1.5	18.8	1.3	0.668	16	974	61
4B	121	215	1.8	16.7	1.2	0.844	18	842	46
4C	279	441	1.6	18.0	1.2	0.716	15	738	50
5A	521	1019	2.0	15.7	1.1	0.662	15	693	45
5B	228	852	3.7	9.8	0.7	0.459	14	748	53
5C	193	264	1.4	19.6	1.4	0.691	16	924	57

Accumulation Rates

Accumulation rates for C, N, and P did not differ significantly across the sites ($F_{4,10} = 0.884$, $p = 0.507$; $F_{4,10} = 0.884$, $p = 0.507$; $F_{4,10} = 1.085$, $p = 0.415$ respectively). There was a large amount of variability across the subsites, with values ranging from 46 to 315 g C m^{-2} yr^{-1}, 3 to 21 g N m^{-2} yr^{-1}, and 0.14 to 1.02 g P m^{-2} yr^{-1} (Fig. 3.3). Rates of C and N accumulation followed the same general pattern, with the highest rates of accumulation in the lower and upper ends of the estuary (sites 1 and 5, respectively) and the lowest rates in the mid-estuarine, oligohaline marshes (site 3). P accumulation rates were highest in the tidal freshwater marshes (site 5) and lowest in the oligohaline marshes of site 3. Accumulation rates of C, N, and P were strongly related to accretion ($R^2 = 0.85$, 0.85, and 0.83, respectively), and as accretion rates increased, accumulation of C, N, and P increased (P < 0.001, Fig. 3.4).

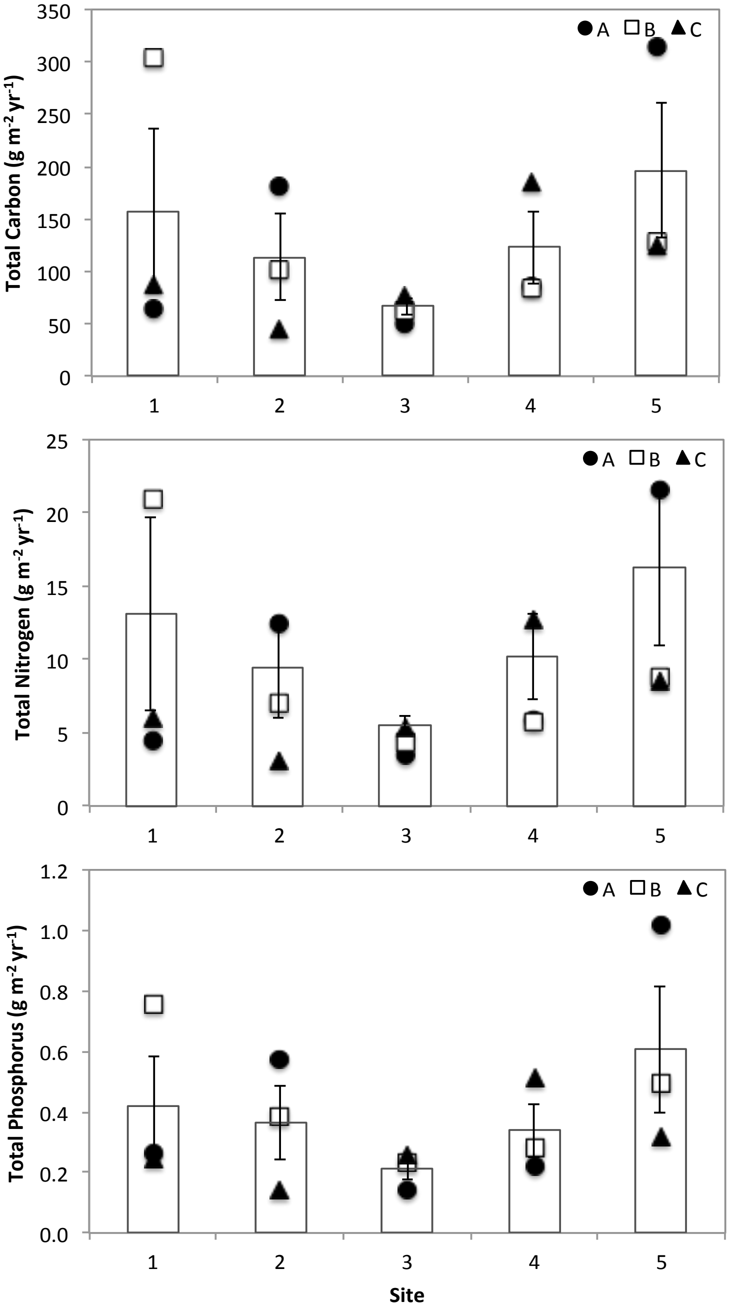

Figure 3.3: Accumulation rates (g m^{-2} yr^{-1}) of carbon, nitrogen, and phosphorus (mean +/- SE) for each site along the Nanticoke River. Symbols indicate accumulation rates for each subsite.

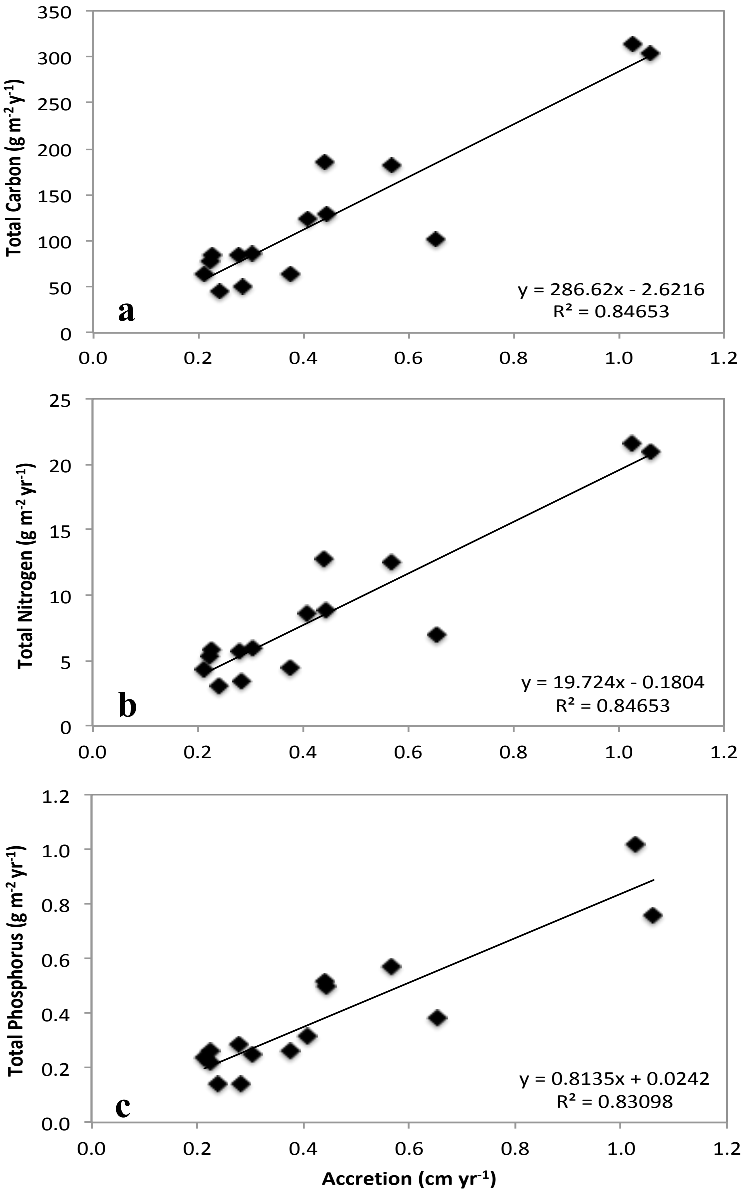

Figure 3.4: Relationships between accretion (cm yr^{-1}) and (a) total carbon, (b) total nitrogen and (c) total phosphorus accumulation rates (g m^{-2} yr^{-1}) for subsites along the Nanticoke River.

Relationship Between C, N, and P Accumulation and Organic and Inorganic Accumulation

There was a significant positive relationship between C, N, and P accumulation rates and both organic and inorganic accumulation ($p < 0.001$, Fig. 3.5, Fig. 3.6). C and N were both strongly related to organic accumulation ($R^2 = 0.68$), while P had a stronger relationship with inorganic accumulation ($R^2 = 0.74$, Fig. 3.6). In general, inorganic accumulation was highest at sites 4 and 5, which are located at the upper end of the estuary (Table 3.1). P accumulation (though highly variable across the subsites) was also generally higher at the upper end of the estuary (Fig. 3.3).

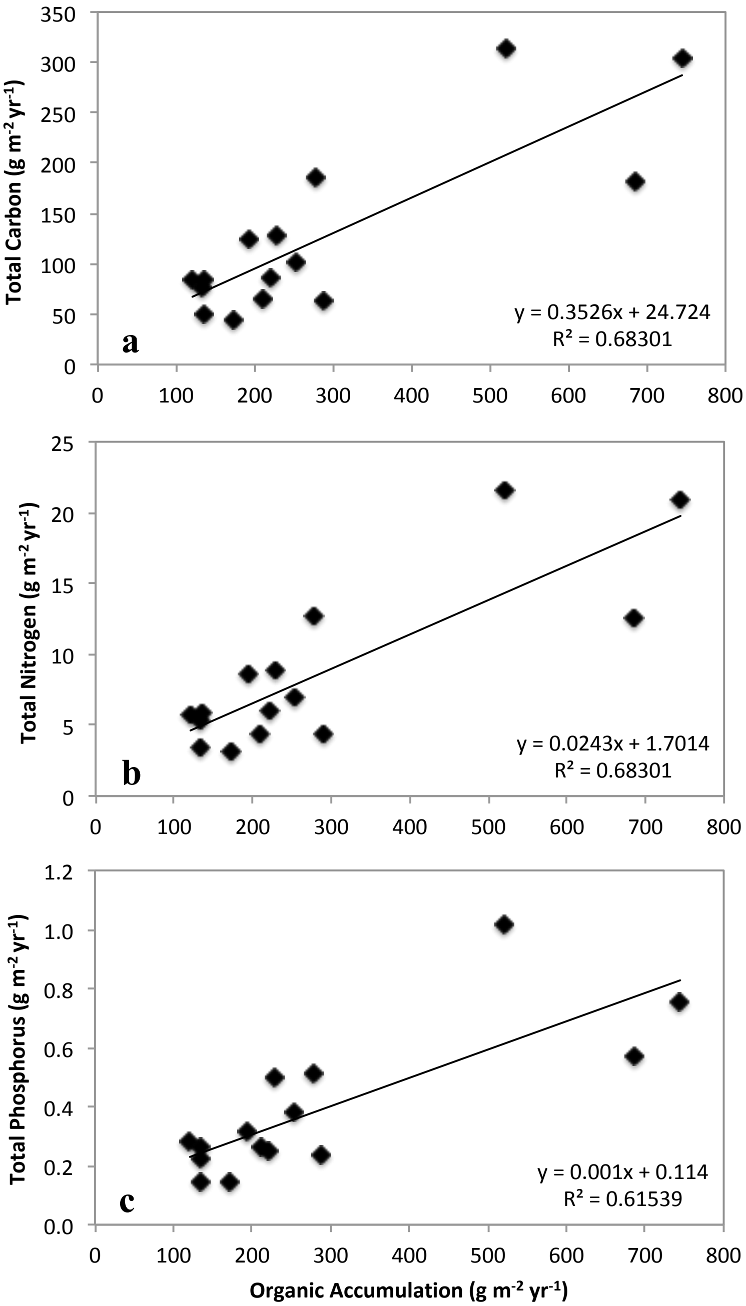

Figure 3.5: Relationships between organic matter accumulation (g m^{-2} yr^{-1}) and (a) total carbon, (b) total nitrogen and (c) total phosphorus accumulation (g m^{-2} yr^{-1}) for subsites along the Nanticoke River.

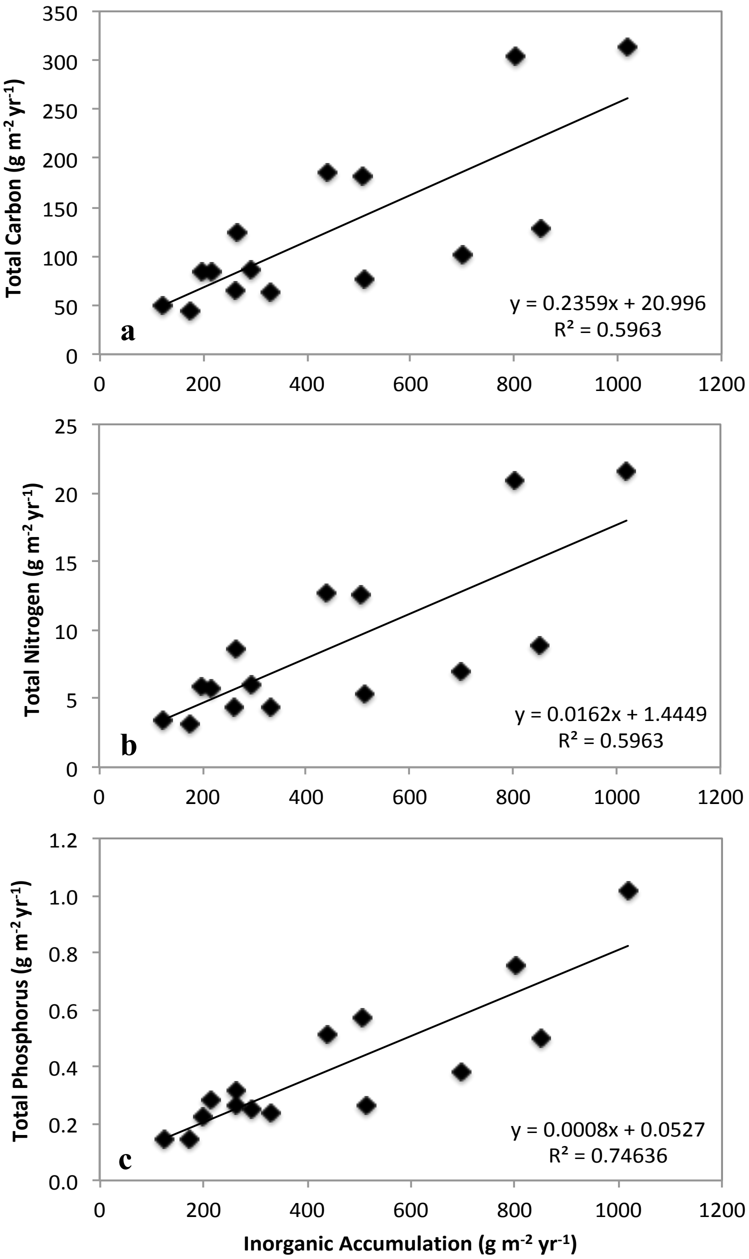

Figure 3.6: Relationships between inorganic matter accumulation (g m^{-2} yr^{-1}) and (a) total carbon, (b) total nitrogen and (c) total phosphorus burial (g m^{-2} yr^{-1}) for subsites along the Nanticoke River.

Discussion

Accumulation of C, N, and P

Tidal wetlands are an important sink for C, N, and P. Accumulation of C, N, and P in the tidal marshes of the Nanticoke River ranged from 46 to 315 g C m^{-2} yr^{-1}, 3 to 21 g N m^{-2} yr^{-1}, and 0.14 to 1.02 g P m^{-2} yr^{-1} (Fig. 3.3). These findings are consistent with accumulation rates measured in other tidal marshes in the Chesapeake Bay. Estimates of nutrient accumulation in the Patuxent River ranged from 3 to 12 g N m^{-2} yr^{-1} and 0.7 to 3.5 g P m^{-2} yr^{-1} (Boynton et al. 2008). Along the Southeast coast, Craft (2007) reported ranges of accumulation from 20 to 150 g C m^{-2} yr^{-1}, 1.5 to 8 g N m^{-2} yr^{-1}, and 0.8 to 1.3 g P m^{-2} yr^{-1}. Similarly, Loomis and Craft (2010) reported ranges from 27 to 142 g C m^{-2} yr^{-1}, 1.6 to 9.3 g N m^{-2} yr^{-1}, and 0.2 to 1.2 g P m^{-2} yr^{-1}. Although the marshes along the Southeast coast have differing geomorphic characteristics, they exhibit similar rates of nutrient accumulation.

Previous studies have found that accumulation rates of C, N, and P vary along the salinity gradient, with the highest rates found in the tidal freshwater marshes and brackish marshes (Craft 2007, Loomis and Craft 2010). Accumulation rates of C, N, and P did not significantly differ among the sites along the salinity gradient of the Nanticoke River, but accumulation rates were generally higher at the lower and upper ends of the estuary, where the brackish and tidal freshwater marshes are located (Fig. 3.3). Accumulation rates were positively related to accretion (Fig 3.4) and followed the same general pattern as accretion rates, which were not linked to estuarine position (see Chapter 2). This suggests that the accumulation of C, N, and P was also not influenced by the location of the marsh along the Nanticoke River.

Role of Organic and Inorganic Accumulation

It was expected that accumulation rates would be strongly influenced by organic and inorganic accumulation (based on findings from chapter 2), with rates of C and N accumulation controlled by organic matter deposition, and rates of P accumulation controlled by inorganic sedimentation. In general, C and N accumulation had a stronger relationship with organic accumulation than with inorganic accumulation ($R^2 = 0.68$ vs. 0.59, respectively), while P had a stronger relationship with inorganic accumulation ($R^2 = 0.74$) compared to organic accumulation ($R^2 = 0.62$, Fig. 3.5 and 3.6). However, the relationship between organic accumulation and P accumulation was similar to both C and N accumulation (explaining about 62% of the variability in P accumulation vs. 68% variability in C and N accumulation), indicating that organic accumulation also plays a role in P accumulation (Fig. 3.5).

Inorganic accumulation was generally higher at sites 4 and 5, which are in located in oligohaline and tidal freshwater marshes in the upper end of the estuary (Table 3.1) where riverine sediment input is highest (Kearney and Ward 1986). P accumulation was generally highest at the upper end of the estuary in the tidal freshwater marshes (site 5), but C and N accumulation rates were also higher at site 5 (Table 3.1, Fig. 3.3). Therefore, despite a strong relationship between organic accumulation and C and N accumulation and between inorganic accumulation and P accumulation, it is not clear that organic and inorganic accumulation differentially control the accumulation of C, N, and P. This is in contrast to other studies that have found rates of C and N accumulation were controlled by organic matter accumulation and P accumulation was controlled by inorganic sedimentation (Merrill and Cornwell 2000, Noe and Hupp 2005).

Landscape Storage of N and P

Across the Nanticoke River, the tidal wetlands play an important role in removing nutrients coming into the system. Based on the accumulation rates measured for this study, the tidal marshes removed approximately 15% of the total N load and 9% of the total P load entering the system (Table 3.2). Brackish marshes sequestered 10% of N and 6% of P, oligohaline marshes sequestered 4 % N and 3% P, and tidal freshwater marshes sequestered 0.9% N and 0.6% P. Although the accumulation rates were only determined for marshes, if the tidal freshwater forested wetlands are assumed to bury nutrients at the same rate as marshes, the percentage of N and P removed by the tidal wetlands increased to 26% and 16%, respectively (Table 3.2). In other systems within the Chesapeake Bay, tidal marshes were responsible for removing 30% of N and 31% of P inputs in the Patuxent River (Boynton et al. 2008) and approximately 5% of N inputs in the Corsica River (Palinkas and Cornwell 2012). Tidal marshes in Georgia have been estimated to remove 2 to 20% (13 to 32% when accounting for denitrification and N_2 fixation) of N inputs into river-dominated estuaries (Loomis and Craft 2010).

Table 3.2: Estimation of nitrogen and phosphorus removal (from burial only) from the marshes and tidal fresh forested wetlands of the Nanticoke River. Wetland area values were obtained from Tiner 2005 and total loading rates of N and P for the Nanticoke River were obtained from the Chesapeake Bay TMDL report (U.S. Environmental Protection Agency 2010).

Wetland Area (ha)		**Total Burial (kg yr^{-1})**		**Total Load (kg yr^{-1})**		**Percent of Removal**	
		Total N	**Total P**	**Total N**	**Total P**	**Total N**	**Total P**
Brackish Marsh	4137	371,523	16,292	3,860,054	294,534	9.6	5.5
Oligohaline Marsh	2712	169,466	7,499			4.4	2.5
Tidal Fresh Marsh	273	35,526	1,667			0.9	0.6
Tidal Fresh Forest	3308	430,147	20,188			11.1	6.9
Total TF Wetlands	3581	465,672	21,855			12.1	7.4
Total Marsh Only						14.9	8.6
Total Including Tidal Fresh Forest						26.1	15.5

Conclusion

Tidal wetlands play a critical role in mitigating anthropogenic stresses further down the estuary. The ability of tidal freshwater, oligohaline, and brackish marshes to remove nutrients is important for improving water quality and decreasing the impacts of eutrophication further downstream. However, the marshes along the Nanticoke River are at risk of being lost to rising sea levels, compromising their ability to remove nutrients from the system. Thus, it is vital that these wetlands be conserved, managed, and restored in order for them to continue providing this valuable ecosystem service.

Chapter 4: Isolating the biogeochemical effects of sulfate intrusion on surface elevation in tidal freshwater marsh soils: a mesocosm study

Introduction

As sea level rises, the potential for seawater intrusion into tidal freshwater increases. Salinity-induced stress on freshwater plant communities can decrease primary production and organic matter accumulation (McKee and Mendelssohn 1989, Willis and Hester 2004, Spalding and Hester 2007). Rates and pathways of microbial organic matter mineralization can also shift in response to changes in salinity. Microbial competition for substrates is dependent on the energetic efficiency of individual pathways, creating shifts of microbial activity associated with changes in the abundance of electron acceptors and donors (Megonigal et al. 2004). This competition for electrons can be seen in river-estuarine systems. Microbial methanogenesis (Capone and Kiene 1988) and iron (Fe(III)) reduction (Roden and Wetzel 1996) are the dominant anaerobic organic matter mineralization processes in freshwater sediments. In marine sediments, however, the greater availability of sulfate (SO_4^{2-}) causes sulfate reduction, an energetically superior pathway to methanogenesis, to become the dominant anaerobic pathway (Jorgensen 1982, Capone and Kiene 1988). An increase of salinity in tidal freshwater systems may lead to a shift from methanogenesis to sulfate reduction and a subsequent increase in organic matter mineralization (Weston et al. 2006, 2011). Additionally, a shift to sulfate reduction in freshwater marsh soils can lead to sulfide toxicity and a reduction in plant biomass (Koch and Mendelssohn 1989, Lamers et al. 1998).

Many tidal freshwater marshes have organic-rich soils. Studies of tidal freshwater marshes on both the Atlantic and Gulf of Mexico report ranges from 6 to 68% organic matter (Mitsch and Gosselink 2007). Soils in the Nanticoke River (Maryland and Delaware) range from 40% to 80% organic matter (Kearney et al. 1988). Tidal freshwater marsh soils are also highly porous (e.g. 63-76%; (Van der Nat and Middelburg 2000), so losses of small quantities of organic matter may result in disproportionately large decreases in soil volume. Thus, the potential increase in organic matter decomposition due to saltwater intrusion combined with the high porosity of the soil may result in rapid subsidence. In a 21-month greenhouse experiment, Portnoy and Giblin (1997) found that freshwater soil subsided 6-8 cm when exposed to saline water. Weston et al. (2006) found that rates of organic matter mineralization doubled following saltwater intrusion. These studies suggest that saltwater intrusion into tidal freshwater marshes may increase the decomposition rate of organic matter, leading to a decrease in elevation of the marshes.

Studies have also found that microbial iron reduction can suppress both sulfate reduction (Kostka et al. 2002) and methanogenesis (Roden and Wetzel 1996, Frenzel et al. 1999), suggesting that iron reduction may be the dominant anaerobic pathway at both ends of the river-estuarine salinity gradient. Neubauer et al. (2005) found that changes in rates of iron reduction and methanogenesis in tidal freshwater marshes were directly affected by plant activity, whereas the biogeochemical processes in brackish marshes were influenced more by factors such as water table depth and iron-sulfur interactions, suggesting that in freshwater marshes iron reduction was influenced by high rates of radial oxygen loss and Fe(II) oxidation. Neubauer et al. (2005) also found that during the early part of the growing season, continuous regeneration of Fe(III) oxides in the rhizosphere supported high rates of iron reduction. Later in the growing season, plant senescence and lower rates of radial oxygen loss caused a decline in available Fe(III) oxides, causing Fe(III)-reducing bacteria to become Fe(III)-limited. As a result, methanogenesis became the dominant microbial pathway. Roden and Wetzel (1996) found that iron reduction accounted for 65% of total carbon metabolism in vegetated sediment, whereas methanogenesis dominated carbon metabolism (72%) in unvegetated sediment cores. Collectively, these findings suggest that the presence of vegetation is an important control on the biogeochemical response of tidal freshwater marshes to saltwater intrusion.

Although studies have documented the impact saltwater intrusion may have on plant communities (Koch and Mendelssohn 1989, McKee and Mendelssohn 1989, Willis and Hester 2004, Spalding and Hester 2007) and pathways of microbial organic matter mineralization (Weston et al. 2006, 2011, Chambers et al. 2013, Neubauer 2013, Neubauer et al. 2013), the ecosystem responses to increased salinity are conflicting. For example, Weston et al (2011) found that saltwater intrusion in freshwater marsh soils resulted in greater rates of organic matter decomposition, but higher rates of CH_4 production, while Neubauer et al (2013) found that saltwater intrusion led to a decline in ecosystem productivity, but organic matter decomposition did not increase and CH_4 fluxes declined. The response to saltwater intrusion and long-term impacts on tidal freshwater marsh soils are still not well understood.

The objective of this study was to examine the effects of sulfate intrusion on biogeochemical transformations and marsh surface elevation in tidal freshwater marsh soil. I hypothesized that increased concentrations of sulfate in tidal freshwater marsh soil would lead to (1) increased organic matter decomposition, causing a decrease in surface elevation; and (2) reduced plant biomass due to sulfide toxicity.

Methods

Experimental Design and Set Up

Twenty-five soil cores were collected from marshes at Jug Bay on the Patuxent River, Maryland in April 2011. The cores were collected in PVC cylinders (15 cm wide x 50 cm long) that were fitted with a bottom cap with a valve to collect effluent. Additionally, portholes were placed at depths of 25 and 40 cm on the side of the core to allow for porewater sampling. The cylinders were driven into the substrate and then excavated to remove a soil core of 45 cm length (to maintain 5 cm of freeboard above the soil surface) and efforts were taken to collect the cores in areas with similar vegetation to ensure the vegetation communities within the mesocosms were consistent. The dominant vegetation in the mesocosms included *Leersia oryzoides*, *Eleocharis sp*., *Murdannia keisak*, *Bolboschoenus fluviatilis*, and *Polygonum arifolium*.

The cores were mounted on benches in the greenhouse and placed in a randomized block design to account for any spatial variation within the room (i.e., each replicate block contained all treatment combinations in a random arrangement) and treatments were randomly assigned within each block. Once the cores were in the greenhouse, they were flushed with water collected from the Patuxent River (PRW) and allowed to equilibrate for two weeks before beginning sulfate treatments.

Sodium sulfate was added to deionized water to make concentrations of sulfate equivalent to amounts found in 0, 2, 5, 10, and 20 ppt salt water (e.g., 20 ppt = 2.43 g/L

Na_2SO_4), hereafter referred to as treatments 0, 2, 5, 10, and 20. Flow through the mesocosms was maintained daily by draining 500 ml of effluent from the bottom of each mesocosm and replenished with 500 ml of Patuxent River water. Twice a week, the sodium sulfate solution was added to each mesocosm. If necessary, each mesocosm received extra PRW to maintain water levels 2-3 cm above the soil surface in order to maintain anaerobic conditions. Under the assumption that soil porosity is 0.7 (Van der Nat and Middelburg 2000), the addition of approximately 500 ml/day PRW resulted in about a 10-day residence time in the cores. Treatments began on June 15, 2011 and the last treatment was applied on August 30, 2011.

Porewater Measurements

Porewater samples were drawn from sampling ports at depths of 25 cm and 40 cm using Rhizon soil moisture samplers (Elijkelkamp Soil & Water, Netherlands). The Rhizon soil moisture samplers were placed into each sampling port and sealed with caulk to prevent oxygen exchange from outside of the mesocosm. A syringe was attached to the connector of the Rhizon soil moisture sampler and approximately 5 ml of water was extracted. The water was filtered through a 0.45 μm filter and 500 μl was aliquoted into vials for analysis of ammonium (NH_4^+), reduced iron (Fe^{2+}), and soluble reactive phosphorus (SRP). Samples for Fe^{2+} were preserved by adding 100 μl of 5N HCL and refrigerated until analyzed. Samples for NH_4^+ and SRP were frozen until analyzed. Samples were taken prior to the start of the experiment, and then once weekly after sulfate treatments began throughout the duration of the experiment (77 days). Attempts to collect CH_4 and CO_2 from the porewater were discontinued due to experimental errors made in the removal and preservation of samples.

Concentrations of NH_4^+ were measured using colorimetric analysis (Parsons et al. 1984), Fe^{2+} concentrations were measured using ferrozine colorimetry (Gibbs 1979), and SRP concentrations were measured using phosphomolybdate colorimetry (Parsons et al. 1984).

Elevation Measurements

Surface elevations in the mesocosms were measured over time using a miniature surface elevation table (SET; Cahoon et al. 2000, Langley et al. 2009). The mini-SET consisted of a metal bracket fitted across the mesocosm with 5 holes spaced at regular intervals for 5 fiberglass pins, allowing for consistent measurements in all of the mesocosms. Pins were lowered to the soil surface and the length of each pin above the bracket was measured. Elevation measurements were taken three times during the experiment: prior to the introduction of sodium sulfate treatments, day 42, and on day 77 prior to the breakdown of the experiment. Incremental elevation change (cm) was determined by averaging the change in individual pin heights ($n = 5$) from the initial measurements (day 0) to day 42 and from day 42 to day 77 for each mesocosm. Cumulative elevation change (cm) was determined by averaging the change in individual pin heights from day 0 to day 42 and from day 0 to day 77 for each mesocosm.

Redox Measurements

Soil redox potential measurements were conducted on day 77 (August 31, 2011) of the experiment, prior to the breakdown of the experiment. In each mesocosm, 5 replicate Pt electrodes were placed at depths of 25 cm and 40 cm, along with a calomel reference electrode. Voltage measurements (mV) were taken using a multimeter modified for high resistance (Rabenhorst 2009, Rabenhorst et al. 2009) and the internal offset error of the device was recorded to account for deviations due to the resistance modifications (Rabenhorst 2009). Temperature (°C) and pH and were also measured for each depth in each mesocosm.

The raw mV reading for each Pt electrode was corrected using the internal offset value and the Eh was calculated by adding 244 (calomel reference electrode correction) to the offset-corrected mV measurement. The Eh values for each Pt electrode were averaged together (n = 5) for each depth and each mesocosm. In order to determine if the soil conditions were reducing, the Eh measurements were plotted on an Eh-pH stability diagram (Patrick et al. 1996).

IRIS tubes (Indicator of Reduction in Soil) were also used to assess reducing conditions (Castenson and Rabenhorst 2006, Rabenhorst 2008). Due to the limited availability of IRIS tubes, tubes were only used in mesocosms with the sulfate treatments equivalent to 20 ppt to check for the presence of sulfides. Three tubes were inserted into each mesocosm (n = 5 for a total of 15 IRIS tubes) and left for one hour. They were then extracted, rinsed immediately in a bucket of water, and visually examined to identify any black spots, which indicates the presence of sulfides (Rabenhorst et al. 2010).

Biomass Harvest/Experiment Breakdown

At the end of the experiment, all aboveground biomass was clipped at the surface of the soil and placed in paper bags for drying and weighing. The mesocosms were then broken down into 10 cm sections (upper 10 cm was divided into two 5 cm sections). Subsamples of soil were collected from each depth using a 4.8 cm diameter x 10 cm long cylindrical corer, dried at 70ºC for 48 hours, and analyzed for water content and bulk density. Belowground biomass was collected by washing each section over a 1 x 2 mm mesh screen and then placed in paper bags to be dried in order to ensure that all of the soil material was removed from the biomass (Megonigal and Day 1992). All biomass (above and below) was dried to a constant weight in an environmental chamber at 35.2ºC with 12% humidity for at least 12 days.

Data Analysis

Replicated mesocosms were averaged together for each treatment (0, 2, 5, 10, and 20; n = 5) for all parameters measured. Analysis of variance (ANOVA) as a randomized block design was used to test for the effect of the sulfate treatments 0, 2, 5, 10, and 20 on aboveground biomass, belowground biomass, and root:shoot ratios. Repeated measures ANOVA was used to examine the effects of the treatments 0, 2, 5, 10, and 20 on NH_4^+, Fe^{2+}, and SRP and time for each depth (25 cm and 40 cm). Tukey's Honestly Significant Difference test was used to make post-ANOVA comparisons of treatment means (SAS 9.2, SAS Institute Inc., Cary, NC). Assumptions of normality and variance homogeneity were checked and data were log10(x) transformed for NH_4^+ to meet assumptions. Data are presented as arithmetic means ±SE. A Pearson parametric correlation analysis was used to investigate relationships between aboveground biomass, belowground biomass, NH_4^+, Fe^{2+}, SRP, bulk density (at depths of 5 cm, 15 cm, 25 cm, and 35 cm), and Eh for depths of 25 cm and 40 cm (R corrplot package, version 3.5.1, R Core Team 2018). Unless otherwise noted, $P \leq 0.05$ was used as the critical value for all tests of significance.

Results

Porewater Analysis

Concentrations of NH_4^+ were significantly different between treatments and between different days at both the 25 cm and 40 cm depths (Table 4.1, Fig. 4.1). The effect of sulfate treatment was independent of time, as reflected in non-significant sulfate x day interactions (Table 4.1) When comparing the treatment means (averaged over the entire length of the experiment), there were significant differences in NH_4^+ concentration between sulfate treatments but not a linear relationship between NH_4^+ and sulfate addition level (Table 4.2). At the 25 cm depth, NH_4^+ concentrations peaked at 20 and were significantly greater than at treatment 10; other treatments had concentrations that fell between the 10 and 20 treatments (Table 4.2). At the 40 cm depth, treatments 0 and 2 were significantly lower than treatment 5, and other treatments were intermediate (Table 4.2). There was a spike in NH_4^+ concentrations between days 7 and 21 for all treatments at both depths of 25 cm and 40 cm (Fig. 4.1). There was an additional spike in concentrations between days 42 and 56 for all treatments and depths except for treatment 10, which only experienced a spike for the depth of 40 cm. In general, the concentrations of NH_4^+ fluctuated throughout the experiment; however, the concentrations at the start and the end of the experiment were about the same, with slightly lower concentrations on day 77 at the 25 cm depth for treatments 5 and 10, and at the 40 cm depth for treatment 20, and slightly higher concentrations found at the 25 cm depth for treatment 0 and the 40 cm depth for treatment 5 (Fig. 4.1).

Table 4.1: ANOVA table results for NH_4^+, Fe^{2+}, and SRP at depths 25 cm and 40 cm. Statistical significance is noted using the following symbols: *p <0.05, **p <0.01, ***p <0.001.

		Type 3 Test of Fixed Effects		
Variable	**Sulfate**	**Day**	**Sulfate * Day**	**Block**
NH4 depth_25	$F_{4,192} = 3.74$*	$F_{10,192} = 7.46$***	$F_{40,192} = 0.73$	$F_{4,192} = 3.83$*
NH4 depth_40	$F_{4,180} = 8.9$***	$F_{10,180} = 4.46$***	$F_{40,180} = 0.88$	$F_{4,180} = 6.81$***
Fe depth_25	$F_{4,189} = 0.6$	$F_{10,189} = 2.44$*	$F_{40,189} = 0.78$	$F_{4,189} = 1.83$
Fe depth_40	$F_{4,180} = 2.18$	$F_{10,180} = 3.34$**	$F_{40,180} = 0.95$	$F_{4,180} = 2.45$*
SRP depth_25	$F_{4,185} = 2.88$*	$F_{10,185} = 3.30$**	$F_{40,185} = 1.21$	$F_{4,185} = 5.66$**
SRP depth_40	$F_{4,175} = 1.34$	$F_{10,175} = 0.61$	$F_{40,175} = 1.05$	$F_{4,185} = 3.61$*

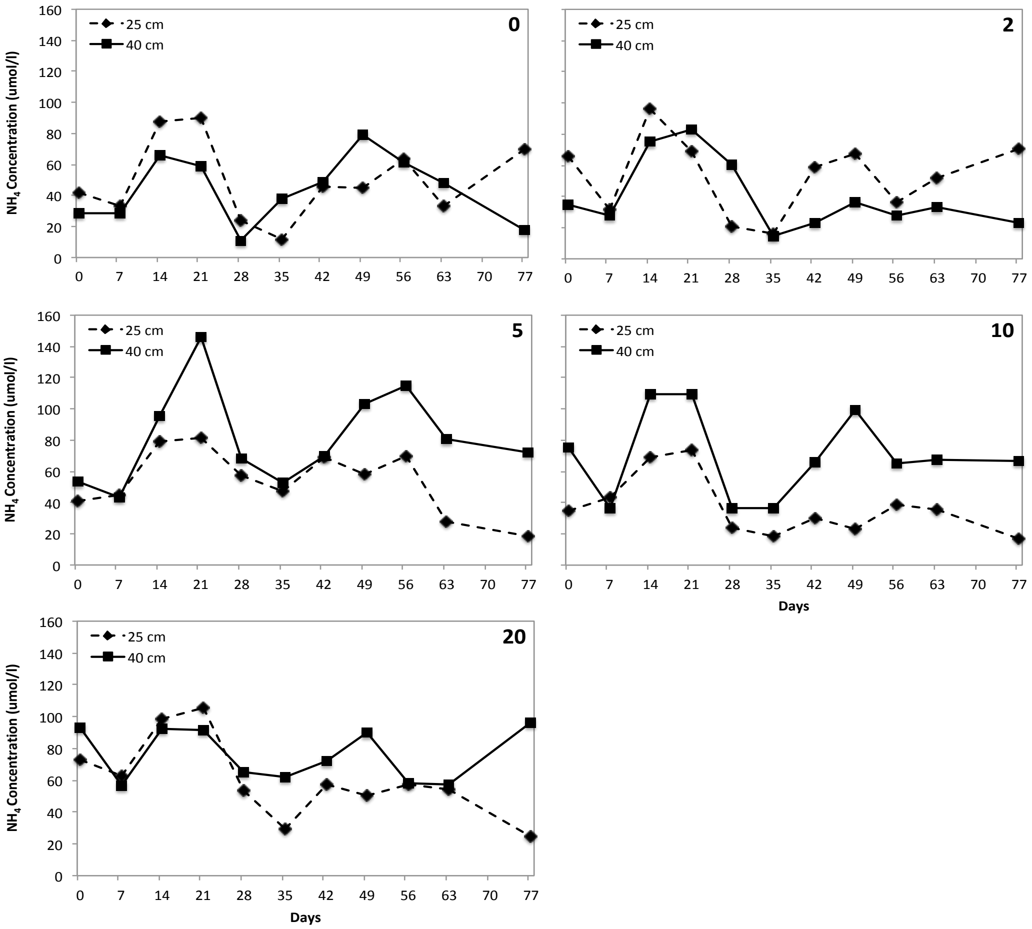

Figure 4.1: Porewater concentrations for ammonium (NH_4^+, umol/l) measured over 77 days at depths of 25 cm and 40 cm. Replicated mesocosms for treatments 0, 2, 5, 10, and 20 were averaged together for each treatment on each day (n = 5).

Table 4.2: Mean porewater concentrations (+/- SE) for NH_4^+, Fe^{2+}, and SRP averaged over the entire length over the experiment for depths of 25 cm and 40 cm. Letters denote statistical differences ($p < 0.05$) from Tukey's Honestly Significant Difference post-ANOVA comparisons.

	NH4		**Fe**		**SRP**	
Treatment	**25 cm Depth**	**40 cm Depth**	**25 cm Depth**	**40 cm Depth**	**25 cm Depth**	**40 cm Depth**
0	48.88 +/- 6.04 AB	44.95 +/- 5.71 BC	31.70 +/- 1.66 A	30.85 +/- 1.34 A	8.50 +/- 2.90 AB	14.57 +/- 3.86 A
2	51.65 +/- 7.65 AB	41.92 +/- 5.10 C	34.20 +/- 1.73 A	32.62 +/- 1.77 A	8.35 +/- 2.63 AB	9.83 +/- 2.69 A
5	54.61 +/- 5.89 AB	82.14 +/- 8.09 A	31.94 +/- 1.95 A	33.22 +/- 1.71 A	11.10 +/- 3.76 A	10.17 +/- 4.22 A
10	37.02 +/- 3.98 B	70.66 +/- 7.58 AB	34.05 +/- 2.11 A	31.77 +/- 1.56 A	2.78 +/- 1.23 B	12.10 +/- 3.07 A
20	60.53 +/- 6.57 A	76.20 +/- 7.61 AB	31.42 +/- 1.75 A	36.29 +/- 2.20 A	12.97 +/- 3.53 A	25.29 +/- 7.04A

Concentrations of Fe^{2+} were not significantly different between treatments, but did significantly differ between different days at both depths of 25 cm and 40 cm over time (Table 4.1, Fig. 4.2). There was no significant difference between the treatment means averaged over the length of the experiment (Table 4.2). The dip observed at day 21 seen for treatments 2, 5, 10, and 20 is possibly due to an analytic error (perhaps due to lack of preservation of some samples). Despite some fluctuations, the overall concentration of Fe^{2+} did not change much from the start to the finish of the experiment. Slight increases of Fe^{2+} concentrations occurred at the depth of 25 cm of treatment 0, 2, and 10 (Fig. 4.2).

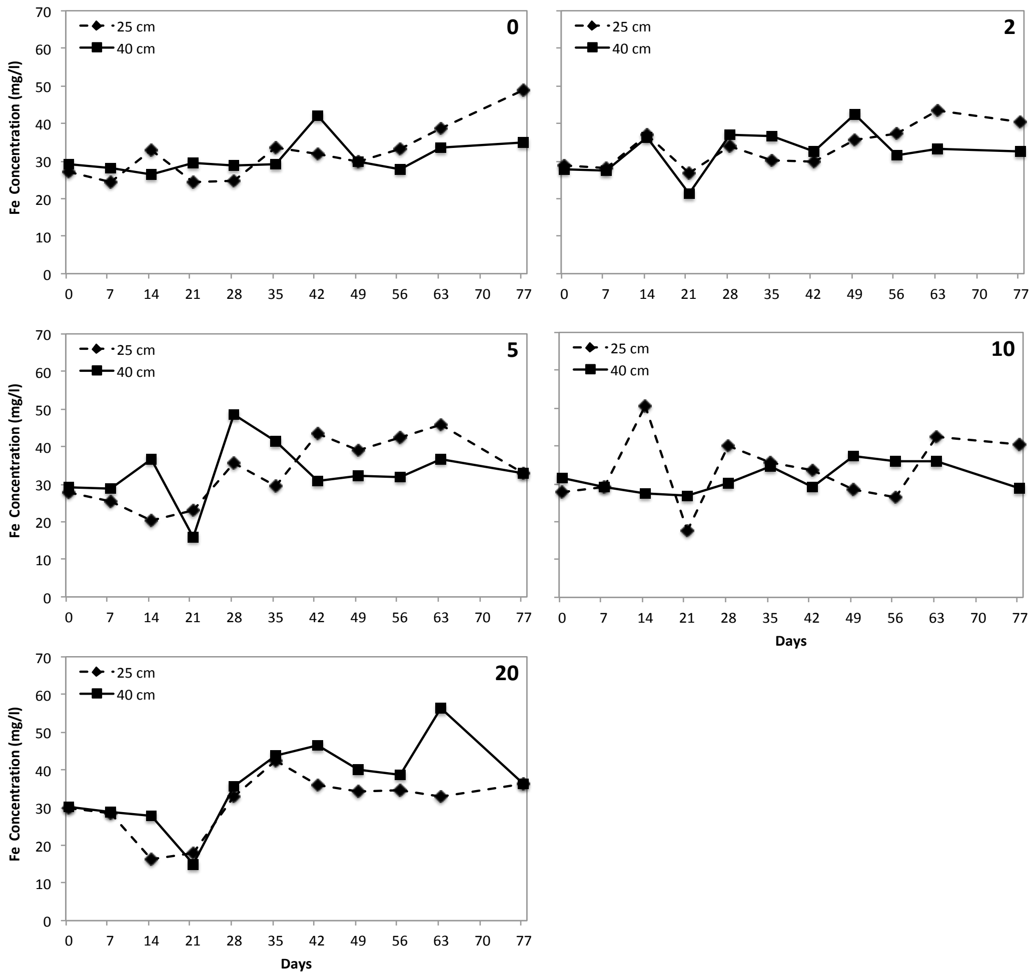

Figure 4.2: Porewater concentrations for reduced iron (Fe^{2+}, mg/l) measured over 77 days at depths of 25 cm and 40 cm. Replicated mesocosms for treatments 0, 2, 5, 10, and 20 were averaged together for each treatment (n = 5). Note: there was a possible analytical error that resulted in only zero values on day 21 for all treatments.

Concentrations of SRP were highly variable over time and across the treatments, and did not show a linear relationship with sulfate addition, but there was a significant treatment effect at the depth of 25 cm (Table 4.1, Fig. 4.3). When looking at the treatment means averaged over the length of the experiment, SRP in treatment 10 was significantly lower than in treatments 5 and 20 at the depth of 25 cm, and there was no significant difference between the treatments at the depth of 40 cm (Table 4.2). Similar to NH_4^+ and

Fe^{2+} concentrations, the overall concentrations did not change much from the start to the finish of the experiment except in treatment 20, which had higher concentrations on day 77 for both depths.

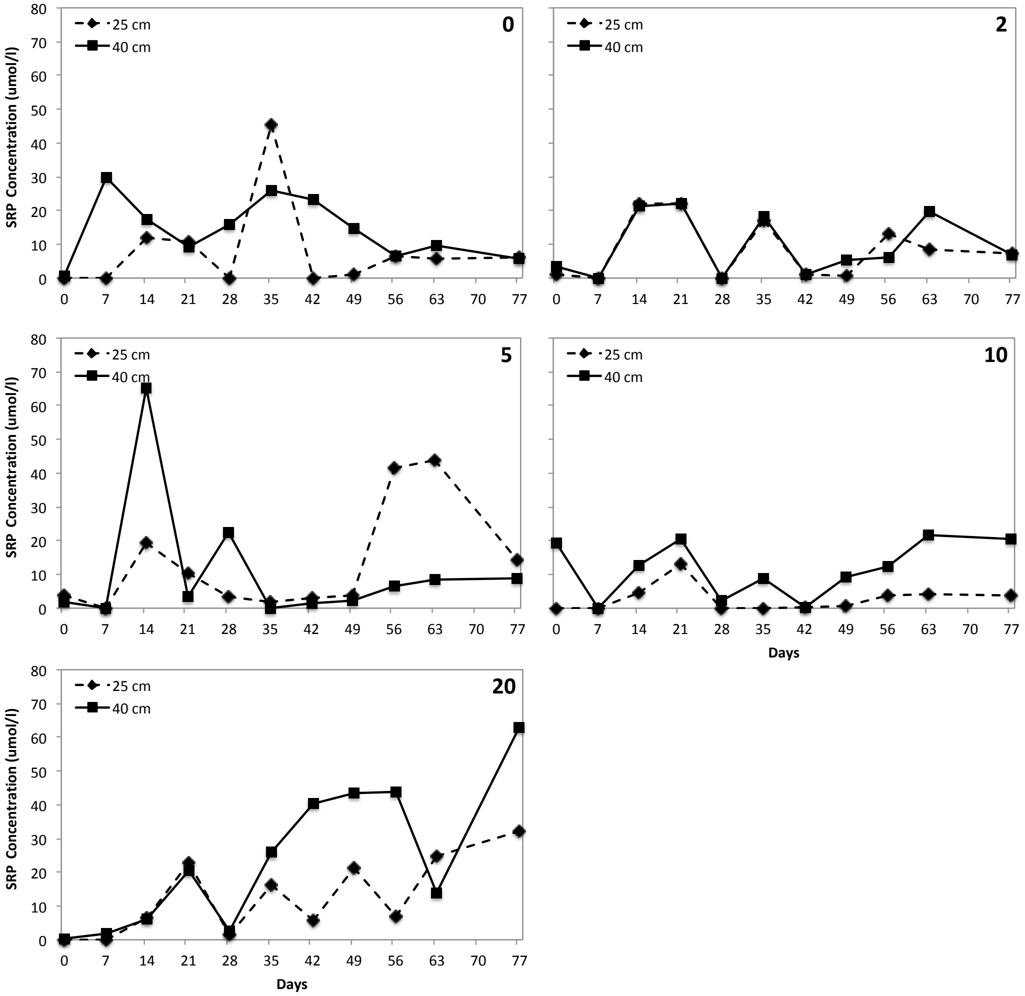

Figure 4.3: Porewater concentrations for soluble reactive phosphorus (SRP, umol/l) measured over 77 days at depths of 25 cm and 40 cm. Replicated mesocosms for treatments 0, 2, 5, 10, and 20 were averaged together for each treatment (n = 5).

Elevation Change

Elevation increased for all treatments from day 0 to day 42, with values ranging from 0.7 cm to 1.8 cm (Table 4.3). The greatest increase in elevation from day 0 to day

42 was observed in treatments 5 and 20. Elevation decreased from day 42 to day 77, with values ranging from -0.42 cm to -1.2 cm. Overall, elevation increased from day 0 to day 77 (0.11 cm to 0.6 cm) but was lower than the elevation change during the first half of the experiment. The greatest cumulative elevation increase was observed in treatments 5 and 20 (Table 4.3). None of the mesocosms experienced a cumulative decrease in elevation.

Table 4.3: Elevation change (cm) for treatments 0, 2, 5, 10, and 20 for days 42 and 77 (mean +/- SE, n = 5). The incremental elevation change is the change from day 0 to day 42 and from day 42 to day 77. The cumulative elevation change is the change from day 0 to day 42 and the change from day 0 to day 77.

Incremental Elevation Change (cm)					
Day	**0**	**2**	**5**	**10**	**20**
42	0.70 +/- 0.17	0.82 +/- 0.18	1.80 +/- 0.34	0.71 +/- 0.25	1.16 +/- 0.18
77	-0.42 +/- 0.14	-0.43 +/- 0.13	-1.20 +/- 0.29	-0.60 +/- 0.24	-0.56 +/- 0.15

Cumulative Elevation Change (cm)					
Day	**0**	**2**	**5**	**10**	**20**
42	0.70 +/- 0.17	0.82 +/- 0.18	1.80 +/- 0.34	0.71 +/- 0.25	1.16 +/- 0.18
77	0.29 +/- 0.15	0.38 +/- 0.27	0.60 +/- 0.18	0.11 +/- 0.27	0.60 +/- 0.23

Redox Conditions

Eh measurements were plotted on the Eh-pH stability diagram to determine if the conditions were oxidizing or reducing. All but one of the Eh measurements fell below the Ferrihydrite line at the 25 cm depth and all of the measurements fell below the line at the 40 cm depth, indicating that the conditions were reducing with respect to Fe (Fig. 4.4). IRIS tubes placed in mesocosms for treatment 20 had visible but small spots of black on the tubes (Fig. 4.5), indicating that sulfides were present in the soil.

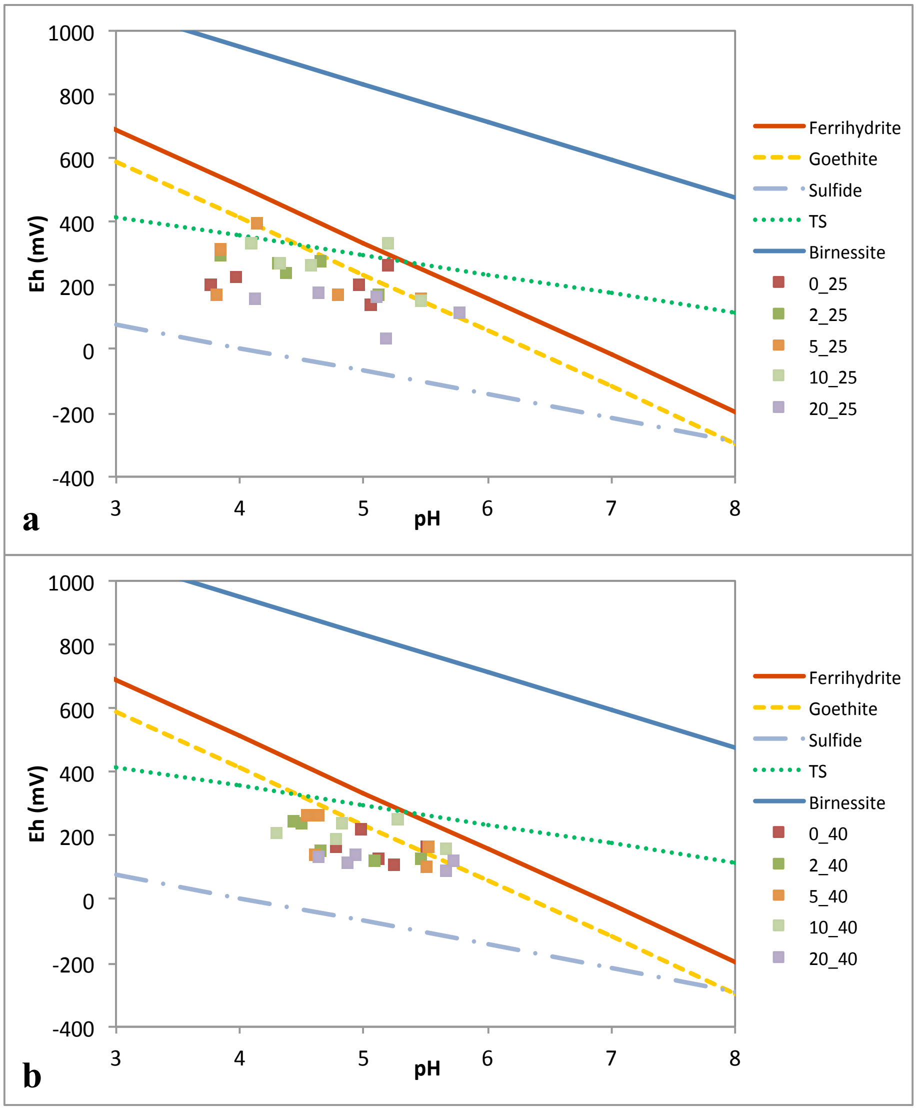

Figure 4.4: Eh-pH stability diagram for Eh measurements for each mesocosm at depths (a) 25 cm and (b) 40 cm.

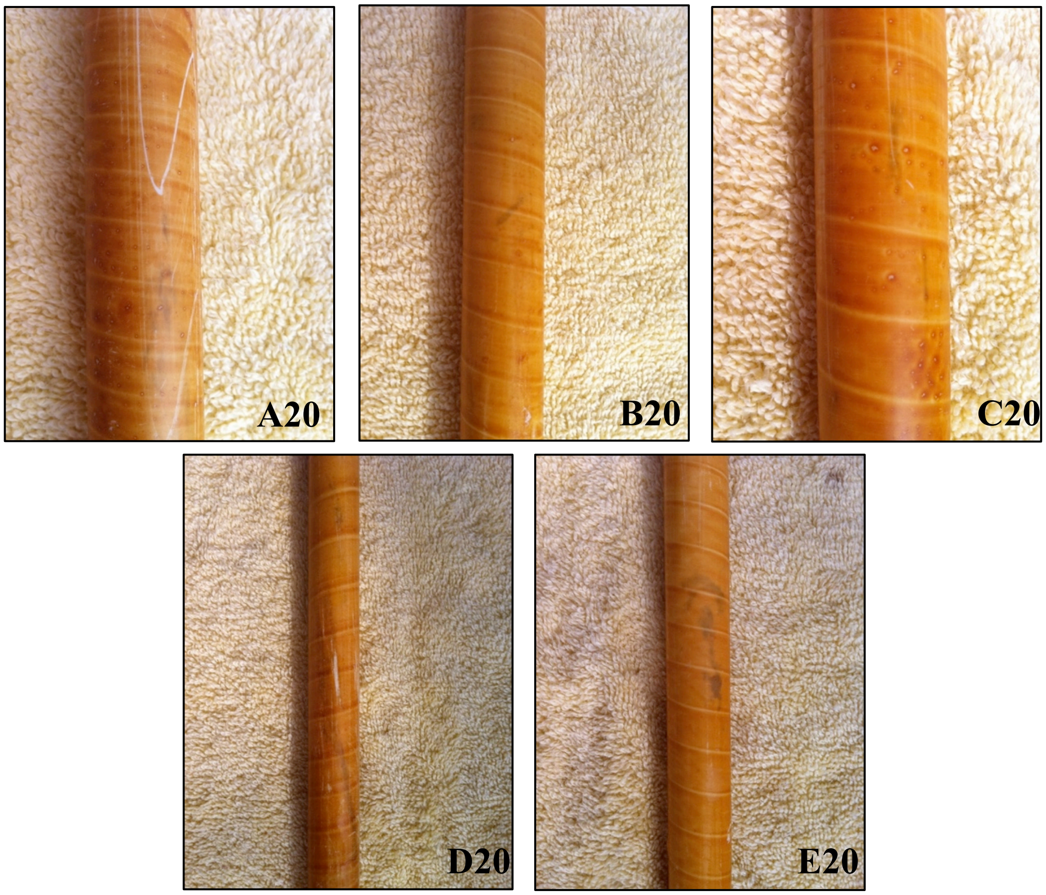

Figure 4.5: Images of IRIS tubes after being placed in mesocosms for treatment 20 for one hour. Black spots on IRIS tube indicate presence of sulfides (Rabenhorst et al. 2010).

Biomass Estimates

Mean aboveground biomass was highest for treatments 0 and 2, and decreased as the sulfate treatments increased (Fig. 4.6) and differed significantly between treatments ($F_{4, 16} = 3.4$, $p < 0.05$). Aboveground biomass in individual mesocosms ranged from 25.2 g (treatment 20) to 51 g (treatment 2) (Table 4.4). Belowground biomass did not differ significantly between treatments ($F_{4, 16} = 1.45$, $p = 0.262$); however, the belowground biomass was generally higher in treatments 0, 2, and 5, and decreased in treatments 10 and 20 (Fig. 4.6). Values of belowground biomass were variable and ranged from 124.6 g (treatment 5) to 276.4 (treatment 5) (Table 4.4). Root:shoot ratios also did not differ significantly between treatments ($F_{4, 16} = 0.36$, $p = 0.831$).

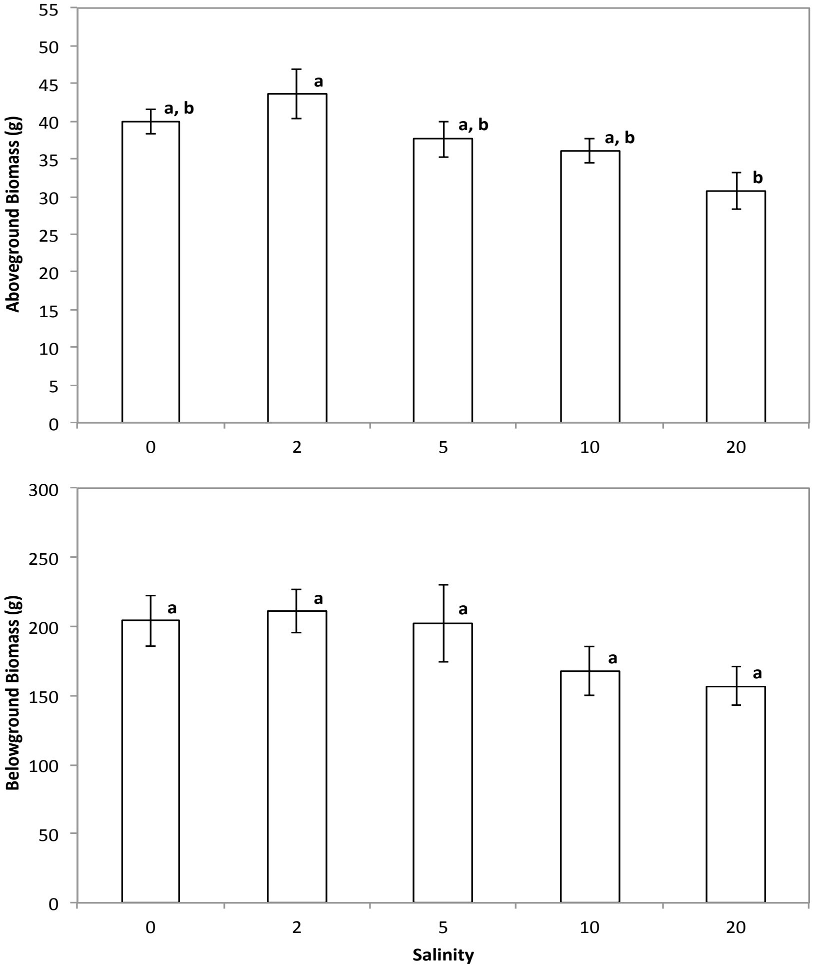

Figure 4.6: Aboveground and belowground biomass for each treatment (mean +/- SE). Letters denote statistical differences ($p < 0.05$) from Tukey's Honestly Significant Difference post-ANOVA comparisons.

Table 4.4: Bulk density (g cm^{-3}), aboveground biomass (g), belowground biomass (g), and the root:shoot ratio for each mesocosm.

Mesocosm	**Treatment**	**Bulk Density (g cm^{-3})**	**Aboveground Biomass (g)**	**Belowground Biomass (g)**	**Root: Shoot**
A0	0	0.2500	46.1	209.9	4.6
B0	0	0.2463	36.7	159.7	4.4
C0	0	0.3439	38.5	221.3	5.7
D0	0	0.2842	40.6	260.3	6.4
E0	0	0.3301	38.0	168.8	4.4
A2	2	0.3614	48.4	234.6	4.8
B2	2	0.2851	32.4	163.5	5.0
C2	2	0.2654	51.0	187.3	3.7
D2	2	0.3621	41.1	246.4	6.0
E2	2	0.2959	44.9	222.6	5.0
A5	5	0.2891	32.9	193.8	5.9
B5	5	0.2904	44.5	276.4	6.2
C5	5	0.3066	33.3	124.6	3.7
D5	5	0.2499	34.9	165.0	4.7
E5	5	0.2882	42.3	250.1	5.9
A10	10	0.2535	31.2	166.3	5.3
B10	10	0.2775	34.6	158.8	4.6
C10	10	0.2704	36.9	150.8	4.1
D10	10	0.3319	40.9	234.4	5.7
E10	10	0.3381	36.7	129.1	3.5
A20	20	0.2669	25.2	136.1	5.4
B20	20	0.2959	38.1	145.1	3.8
C20	20	0.2924	32.5	206.4	6.3
D20	20	0.2849	25.5	170.1	6.7
E20	20	0.3051	32.5	126.5	3.9

Correlation Analysis

Aboveground biomass was positively related to belowground biomass ($p < 0.05$), NH_4^+ ($p < 0.05$) and bulk density ($p < 0.1$), and was negatively correlated with SRP at both depths (25 and 40 cm) ($p < 0.1$ and $p < 0.05$, respectively; Table 4.5). Belowground biomass was positively related to bulk density and NH_4^+ at the depth of 25 cm ($p < 0.05$) (Table 4.5).

Table 4.5: Comparisons from a Pearson's correlation matrix. Only variables that were significant were listed. + indicates significance at 0.1 level, all other p values are less than 0.05.

Variables	**r**	**p**
Aboveground biomass vs. belowground biomass	0.6072	0.0013
Aboveground biomass vs. Eh_depth 25cm	0.3862	0.0565+
Aboveground biomass vs. bulk density_depth 25 cm	0.3687	0.0698+
Aboveground biomass vs. NH_4_depth 25 cm	0.4593	0.0416
Aboveground biomass vs. SRP_depth 25 cm	-0.4021	0.0636+
Aboveground biomass vs. SRP_depth 40 cm	-0.5740	0.0052
Belowground biomass vs. Bulk density_depth 25 cm	0.4657	0.0190
Belowground biomass vs. NH_4_depth 25 cm	0.4729	0.0352
Bulk density_depth 5 cm vs. Bulk density_depth 25 cm	0.4127	0.0403
Bulk density_depth 15 cm vs. Bulk density_depth 35 cm	0.3511	0.0852+
Fe_depth 25 cm vs. Fe_depth 40 cm	0.4958	0.0508+
Eh_depth 25 cm vs. Eh_depth 40 cm	0.8410	0.0000
Eh_depth 40 cm vs. Bulk denisty_depth 35 cm	0.3559	0.0808+
Eh_depth 25 cm vs. SRP_depth 25 cm	-0.4653	0.0291
Eh_depth 25 cm vs. SRP_depth 40 cm	-0.6651	0.0007
Eh_depth 40 cm vs. SRP_depth 40 cm	-0.4493	0.0359

Discussion

Saltwater intrusion into tidal freshwater marsh soils has been shown to cause shifts in microbial pathways and increase overall rates of organic matter decomposition (Weston et al. 2006, 2011). Based on previous studies, it was expected that the introduction of sulfate into tidal freshwater marsh soils would result in a shift to sulfate reduction over time, leading to an increase in organic matter decomposition and a decrease in surface elevation. However, due to complications with the experimental design and sampling procedures (see Experimental Design Considerations section below), rates of sulfate reduction and methanogenesis could not be quantified. Despite the complications, some interesting relationships were observed in the porewater concentrations of NH_4^+, Fe^{2+}, and SRP.

Results from the experiment show that there were significant differences in NH_4^+ concentrations across days and different treatments, however; overall the concentrations did not change appreciably during the experiment (Fig. 4.1). A spike in NH_4^+ concentrations occurred between day 7 and 21, suggesting an initial response to the sulfate additions, similar to observations from Weston et al. (2006); however, the spike was also seen in the control mesocosms. Differences in mean NH_4^+ concentrations were observed in treatments 10 and 20, but overall it is not clear if the sulfate treatments were the cause of changes in NH_4^+ concentrations. Previous studies have shown that increased salinity levels detrimentally affect the uptake of NH_4^+ (McKee and Mendelssohn 1989, Spalding and Hester 2007), causing increases in interstitial NH_4^+ levels and reductions in plant production. However, results from the Pearson's correlation analysis do not support this idea, showing a positive rather than negative relationship with aboveground biomass and NH_4^+ at the depth of 25 cm ($r = 0.4593$, $p = 0.0416$, Table 4.5). The impact of sulfate intrusion on NH_4^+ mineralization rates cannot be determined solely from porewater concentrations, making it difficult to interpret the impact of sulfate addition on the balance on N supply and N demand.

Sulfate treatments did not have a significant effect on Fe^{2+} concentrations, and the concentrations were generally the same between all treatments (Fig. 4.2). Fe^{2+} concentrations remained fairly consistent throughout the length of the experiment for all treatments, indicating that conditions were reduced, but only with respect to Fe. Eh measurements confirmed that conditions were reduced with respect to Fe (Fig. 4.4). There was a small amount of sulfides detected in treatment 20 using IRIS tubes (Fig. 4.5), but without analytic measurements of sulfides, sulfate reduction cannot be quantified.

The lack of change in Fe^{2+} concentrations is likely due to the abundance of iron the in the soil (Keller et al. 2013) and the length of the experiment, which was likely not long enough to deplete the iron and see a shift to sulfate reduction. It is possible that the presence of vegetation played a role in inhibiting a shift from iron reduction to sulfate reduction in the treatments with higher amounts of sulfate by regenerating Fe(III) in the rhizosphere (Neubauer et al. 2005); however Keller et al (2013) found that the presence of plants did not necessarily facilitate iron reduction. Without non-vegetated controls, the effect of vegetation on iron reduction cannot be verified.

The lack of change in Fe^{2+} concentrations over the length of the experiment may also explain the why the concentrations of SRP did not change much from the start to the end of the experiment (Fig. 4.3). Despite some fluctuations over the course of the experiment, it is evident that P remained bound to Fe in all but treatment 20, which did have higher concentrations of SRP by the end of the experiment. The higher amount of sulfate added to treatment 20 likely caused a release of P bonded to Fe (Caraco et al. 1989), increasing the amount of available SRP. Deposition of FeS on the IRIS tubes (Fig. 4.5) was small, suggesting that rates of sulfate reduction in treatment 20 were relatively low.

Biomass and Elevation Changes

In general, aboveground biomass declined with increased sulfate, with a significant difference between treatments 2 and 20 (Fig. 4.6). The decline in biomass with increased sulfate concentrations suggests that higher amounts of sulfate may be causing sulfide toxicity to the plants. This is consistent with previous studies that have found a decrease in biomass due to sulfide toxicity (Koch and Mendelssohn 1989, Lamers et al. 2013).

Previous studies have documented increases in organic matter decomposition (Weston et al. 2006, 2011) and subsequent subsidence (Portnoy and Giblin 1997) due to saltwater intrusion. Therefore, surface elevations were expected to decrease with increased sulfate exposure. Surface elevations increased in all mesocosms during the first 42 days of the experiment, which is likely due to initial root growth during the early part of the growing season (Langley et al. 2009). Later in the growing season, root growth likely slowed, so during the second half of the experiment (day 42 to day 77), surface elevations decreased (Table 4.3). The overall elevation (from day 0 to day 77) increased, with the highest elevation change in treatments 5 and 20 and the lowest elevation change in treatment 10. These results are consistent with the porewater results, which suggest that iron reduction is the dominant pathway in the mesocosms and the addition of sulfate is not enough to cause a shift to sulfate reduction. Thus, organic matter decomposition was not likely high enough to cause negative changes in overall elevation.

Experimental Design Considerations

Issues with sampling, analysis, and experimental design caused a large amount of uncertainty in the results. For example, having vegetated and non-vegetated cores would have been helpful in understanding how plants impact microbial pathways in the soil and influence carbon cycling. Also, taking redox measurements throughout the experiment rather than just at the end would have been useful to help understanding the reducing conditions in the mesocosms. Issues with sampling and analysis led to missing important parameters (i.e., sulfate, sulfides, methane) that would have been helpful in understanding the dominant pathways in tidal freshwater marsh soils and potential shifts caused by the addition of sulfate. Further, during the experiment, many of the mesocosms became root bound, making it difficult (and mostly impossible) to properly drain the mesocosms. It also became difficult to extract porewater, causing missing samples on many of the sampling dates. Redesigning the experiment and thinking through what will work and not work in a greenhouse setting would help to make a new version of this experiment very interesting and become an important resource in the literature.

Conclusion

Despite the flaws in this experiment, several interesting findings emerged. The introduction of sulfate into tidal freshwater marsh soils did not appear to cause a shift to sulfate reduction and instead, iron reduction remained the dominant pathway in the soils. The lack of shifts in microbial pathways likely prevented a decrease in surface elevation as decomposition rates likely stayed steady throughout the length of the experiment. The presence of black spots on the IRIS tubes in addition to the increase of SRP in treatment 20 indicates that some sulfate reduction was taking place, which may have contributed to a decline in aboveground plant biomass due to sulfide toxicity resulting from increased sulfate addition. Overall, the results of this experiment show that iron reduction plays a key role in organic matter mineralization.

Chapter 5: Conclusions

The overall goal of my dissertation research was to understand the effects of sea level rise on the tidal freshwater, oligohaline, and brackish marshes by (1) examining accretion dynamics across the estuarine gradient of the Nanticoke River and determining the relative contribution of organic and inorganic matter to accretion in these marshes; (2) determining the accumulation rates of C, N, and P across the estuarine gradient of the Nanticoke River; and (3) examining the effects of sulfate intrusion on biogeochemical transformations and marsh surface elevation in tidal freshwater marsh soil.

I hypothesized that rates of accretion would be highest in the tidal freshwater marshes and decrease downstream as salinity levels increased; however, accretion rates were highly variable across the estuarine gradient. Only 8 out the 15 subsites had accretion rates higher than relative sea level rise for the area, with the lowest rates of accretion found in the oligohaline marshes. Further, I hypothesized that inorganic sedimentation would have a larger influence on accretion in the upper reaches of the estuary while organic matter accumulation would have a larger influence on accretion in the marshes in the lower reaches of the estuary. Instead, I found organic matter accumulation had a large influence on accretion rates across the estuary, regardless of the location. Inorganic accumulation across the estuarine gradient also appeared to be important, suggesting that both inputs are important for maintaining marsh surface elevation. Overall, these findings suggest that along the Nanticoke River, where almost half of the marshes sampled had accretion rates lower than relative sea-level rise, inorganic inputs may be too low and organic matter accumulation may not be enough to keep these marshes above sea level.

It was expected that accumulation rates of C, N, and P would be strongly influenced by organic and inorganic accumulation based on the findings from the accretion study. Therefore, I hypothesized that rates of C and N accumulation would be controlled by organic matter deposition, and rates of P accumulation would be controlled by both inorganic sedimentation and organic matter accumulation. In general, C and N had a strong relationship with organic matter accumulation, and P had a strong relationship with both inorganic and organic accumulation. However, the tidal freshwater marshes, which generally had higher rates of inorganic accumulation, also had high rates of C and N accumulation, indicating that there is a not a clear dominance of either organic or inorganic accumulation on the burial of C, N, and P in these marshes.

These tidal marshes play an important role in removing nutrients coming into the system. Based on the accumulation rates measured for this study, the marshes removed approximately 15% of the total N load and 9% of the total P load entering the system. If tidal freshwater forested wetlands are factored in (with the assumption that they bury nutrients at the same rate as the marshes), the percentage of N and P removed by the tidal wetlands on the Nanticoke River increased to 26% and 16% respectively.

Lastly, I hypothesized that increased concentrations of sulfate in tidal freshwater marsh soil would lead to increased organic matter decomposition, causing a decrease in surface elevation and reduced plant biomass due to sulfide toxicity. The experimental implementation was flawed causing inconclusive results; however, some interesting findings did emerge. The introduction of sulfate did not appear to cause a shift to sulfate reduction and instead, iron reduction remained the dominant pathway in the soils. There was some evidence that a small amount of sulfate reduction was taking place at the highest treatment level, which may have contributed to a decline in aboveground biomass due to sulfide toxicity. The lack of major shifts in microbial pathways likely prevented a decrease in surface elevation, as decomposition rates remained relatively steady throughout the experiment. Overall, the results show that iron reduction plays a key role in organic matter mineralization.

Collectively, the results of my research suggest that the mechanisms controlling accretion dynamics and nutrient burial along an estuarine gradient are complex and likely driven by site-specific factors rather than estuary-wide factors. Rising sea levels threaten the health of tidal freshwater, oligohaline, and brackish marshes, and organic mater accumulation may not be enough to help keep these marshes above relative sea level, especially in areas where inorganic inputs may be too low. These marshes provide a valuable ecosystem service by removing nutrients from the system and losing them could have detrimental impacts on water quality further down the estuary. Saltwater intrusion can further threaten these marshes by decreasing primary production and organic matter accumulation as well as potentially cause shifts in microbial pathways, leading to increase organic matter decomposition and an overall decrease in marsh elevation. If marshes are already accreting at rates lower then relative sea level rise, complete submergence of the marsh is possible, resulting in the loss of an extremely valuable ecosystem.

Appendix I

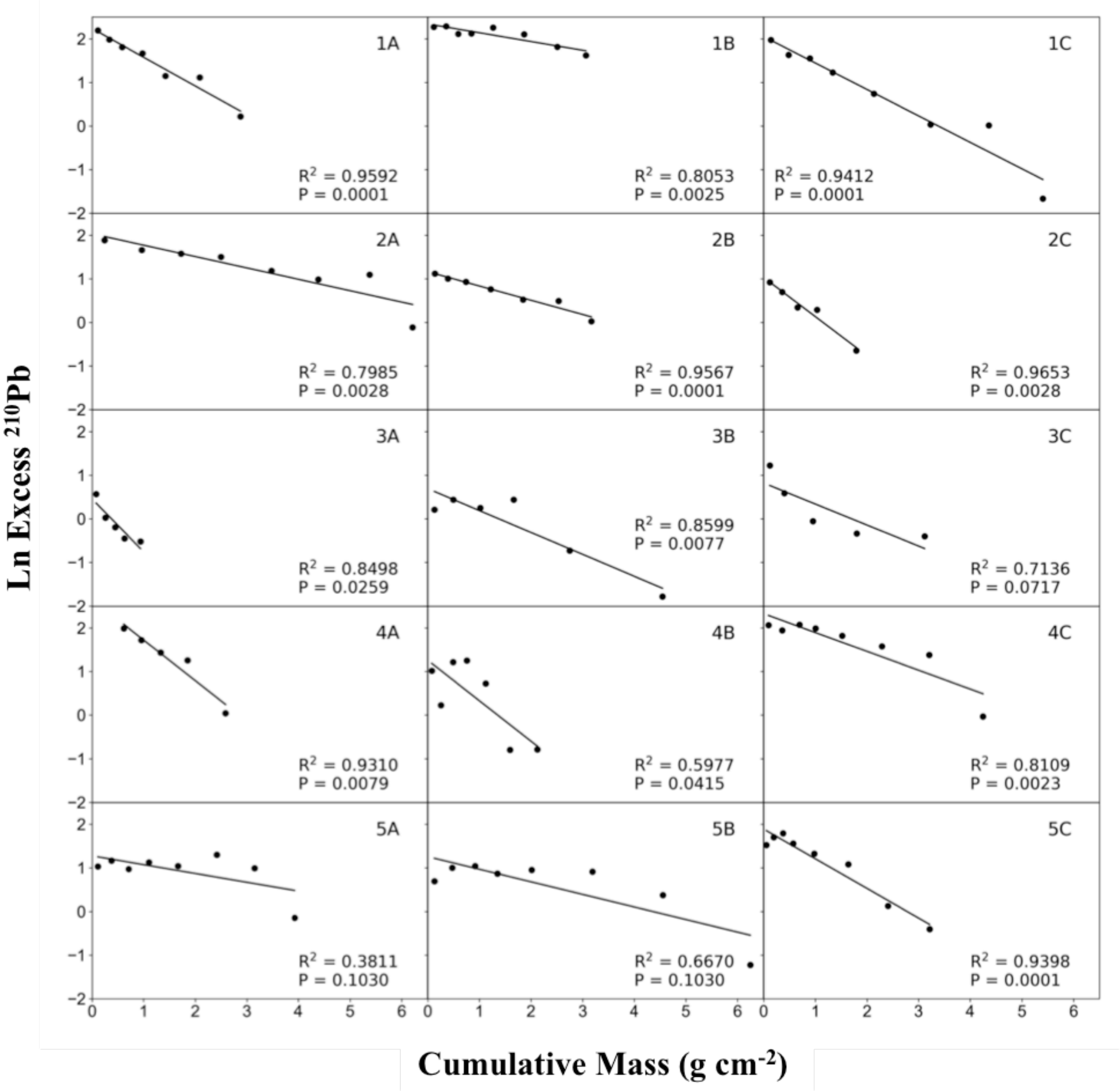

Figure AI.1: Linear regression of the natural log of unsupported ^{210}Pb versus cumulative mass (g cm^{-2}) for each subsite along the Nanticoke River.

Appendix II

Table AII.1: Results of the linear regressions used to calculate concentrations based on LOI for the entire depth of each sediment core (100-cm). Based on the weak relationship between phosphorus and organic matter, phosphorus concentrations were not calculated using LOI.

Regression	**Slope**	**R^2**	**p value**
% Carbon vs. % Organic Matter	0.465	0.79	$p < 0.001$
% Nitrogen vs. % Organic Matter	0.032	0.77	$p < 0.001$
% Phosphorus vs. % Organic Matter	0.001	0.58	$p < 0.001$

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