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14. ABSTRACT

Terrestrial inputs largely govern nutrient delivery to the coastal ocean, and subsequent processes transform these nutrients in the land-ocean transition zone. Here, we describe spatial and temporal patterns in surface water chemistry from the Duplin, a salt marsh/tidal creek system located in coastal Georgia, USA. Key drivers of nutrient concentration patterns in the Duplin include discharge from the nearby Altamaha River, groundwater inputs, exchange with the marsh platform, and biological processes within the tidal creek. Altamaha River discharge is correlated with salinity in the Duplin, but the processes taking place within the Duplin watershed regulate the distribution of other dissolved and particulate materials. Long-term data sets advance our understanding of the relative importance of these processes in generating the observed patterns in surface water chemistry. This knowledge improves our ability to predict how coastal systems will respond to anthropogenic perturbations.

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Patterns and Controls of Nutrient Concentrations in a Southeastern United States Tidal Creek

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ABSTRACT. Terrestrial inputs largely govern nutrient delivery to the coastal ocean, and subsequent processes transform these nutrients in the land-ocean transition zone. Here, we describe spatial and temporal patterns in surface water chemistry from the Duplin, a salt marsh/tidal creek system located in coastal Georgia, USA. Key drivers of nutrient concentration patterns in the Duplin include discharge from the nearby Altamaha River, groundwater inputs, exchange with the marsh platform, and biological processes within the tidal creek. Altamaha River discharge is correlated with salinity in the Duplin, but the processes taking place within the Duplin watershed regulate the distribution of other dissolved and particulate materials. Long-term data sets advance our understanding of the relative importance of these processes in generating the observed patterns in surface water chemistry. This knowledge improves our ability to predict how coastal systems will respond to anthropogenic perturbations.

INTRODUCTION

More than a billion people live within 100 km of the ocean, and that number is constantly increasing (Small and Nicholls, 2003). Many of these individuals rely on coastal and marine resources for their livelihoods and/or sustenance. At the same time, human populations increase nitrogen and phosphorus inputs to the coastal ocean through sewage effluent, agricultural runoff, and industrial activities (Howarth, 2008). These activities culminate in over-fertilization of coastal waters, which harms coastal resources such as fisheries through species shifts, oxygen depletion, and harmful algal blooms (Nixon, 1995). Processing and removal of nutrients at the land-ocean interface (Nixon et al., 1996), including in salt marshes (Levin et al., 2001), has the potential to profoundly influence the health of marine ecosystems. When inundated by tides, marshes filter dissolved and particulate materials from the surface water (Stumpf, 1983). The chemical signature of tidal a creek is indicative of the processes taking place in the surrounding marsh, the creek bed sediment, and the water column (Nelson and Zavaleta, 2012).

One of the primary missions of the Georgia Coastal Ecosystems (GCE) Long Term Ecological Research project is to identify and explain patterns in nutrient concentrations in the coastal zone and how these patterns influence the ecology of the region. Here, we present a synthesis of nearly a decade of multidisciplinary GCE data from a large tidal creek draining some 10 km² of salt marsh located in coastal Georgia, USA. We describe the temporal and spatial patterns in creek water chemistry and aim to assess the relative importance of the various processes that drive these patterns. We first discuss the role of mixing between riverine freshwater and ocean water and then estimate the importance of within-watershed processes, including creek water microbial metabolism, groundwater discharge, and marsh inundation to establish a conceptual model of the tidal creek system.

THE DUPLIN WATERSHED

The Duplin is a large tidal creek, approximately 12.5 km long, located on the west side of Sapelo Island, Georgia, within the GCE domain and the Sapelo Island National Estuarine Research Reserve. It lies approximately 10 km north of where the main channel of the Altamaha River discharges into the Atlantic Ocean. The Duplin is typical of marsh-dominated, tidal creek watersheds in the southeastern United States (Wiegert and Freeman, 1990). Its 14 km² watershed is composed of tidal marsh complexes with upland influence and back barrier islands (Figure 1A; see also Di Iorio and Castelao, 2013, in this issue). Semidiurnal tides with an amplitude of 2 to 3 m largely drive circulation in the Duplin (Ragotzkie and Bryson, 1955; Boon, 1975), with some residual circulation due to precipitation and groundwater input. The lower 5 km of the Duplin exchange readily with Doboy Sound, while the middle and upper reaches of the Duplin are isolated by its sinuous channel, which dissipates tidal energy and mixing (Ragotzkie and Bryson, 1955; Imberger et al., 1983).

SPATIAL AND TEMPORAL PATTERNS IN DUPLIN CHEMISTRY

The data presented here are from GCE monitoring stations located in the upper Duplin (UD), Doboy Sound (DS), and the mouth of the Altamaha River (AR) (Figure 1A; AR is located south of the area shown). Nutrient samples were collected on consecutive high and low tides every three months from 2001 through 2006, and monthly from 2007 through 2010. This sampling design helped constrain the chemical composition of four distinct water parcels within the Duplin watershed. The upper reaches of the Duplin were characterized by measurements at low tide from UD, the middle Duplin was represented by high tide samples from UD and the lower Duplin by low tide samples from DS, and Doboy Sound was delineated by high tide samples from DS. Surface water samples were collected from all three sites to determine the concentrations of inorganic nutrients (e.g., ammonium [NH_4^+], nitrate [NO_3^-], phosphate [PO_4^{3-}], and silica [Si]); of organic materials (e.g., dissolved organic carbon [DOC], dissolved organic nitrogen [DON], and dissolved organic phosphorus [DOP]); and of particulate materials (including total suspended solids [TSS], particulate carbon [PC], particulate nitrogen [PN], and chlorophyll **a** [Chl-**a**]). Sample collection and analysis methods are available on the

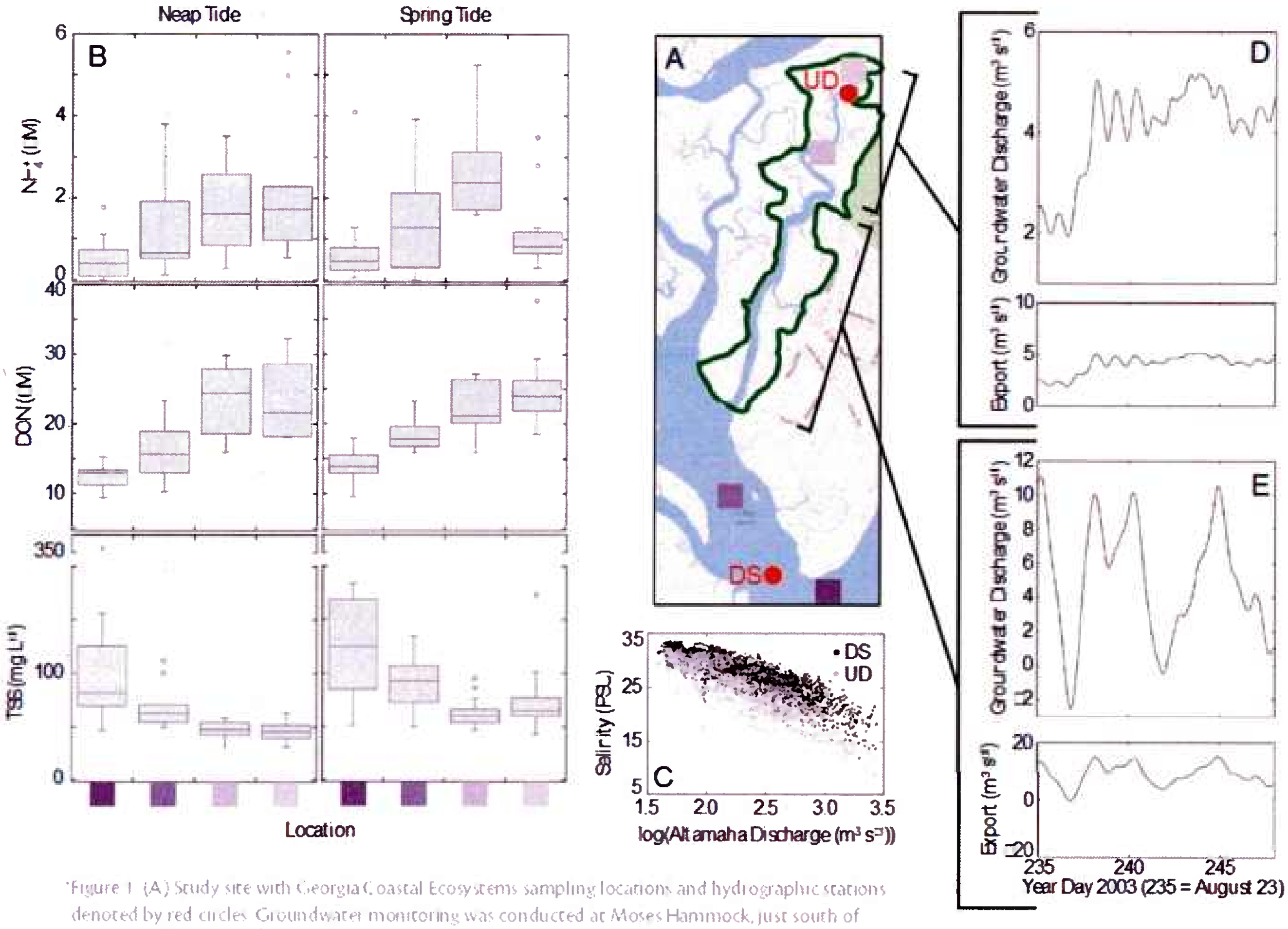

Figure 1. (A) Study site with Georgia Coastal Ecosystems sampling locations and hydrographic stations denoted by red circles. Groundwater monitoring was conducted at Moses Hammock, just south of upper Duplin. The green line represents the approximate boundary of the Duplin watershed. Map data ©2013 Google (B) Spatial and temporal patterns in Duplin surface water nutrient concentrations. The purple boxes represent approximate locations in (A) of water masses sampled at mean tidal elevation. (C) Relationships between the rate of Altamaha River discharge and salinity in the Duplin (gray dots) and Doboy Sound (black dots). Groundwater discharges into and surface water is exported from both the upper (D) and middle/lower (E) Duplin, respectively.

GCE website (Joye et al., 2009).

Concentrations of dissolved inorganic nutrients (represented by NH$_4^+$ in Figure 1B) increased from a minimum at the mouth of the Duplin to a maximum in the middle Duplin (UD high tide). Ammonium concentrations also exhibited a general increase from spring to fall (not shown), and maximum concentrations in the middle Duplin were higher on spring than on neap tides. Dissolved organic matter (DOM, represented here by DON in Figure 1B) concentrations increased from the mouth of the Duplin to the upper Duplin and from winter to summer (not shown). DOM concentrations in the upper Duplin (UD low tide) were higher on spring than on neap tides. The general spatial pattern observed for the dissolved materials was reversed for particulates (represented by TSS in Figure 1B), which had its minimum concentration in the upper Duplin. TSS concentrations in the upper Duplin were higher on spring than on neap tides.

ALTAMAHA RIVER DISCHARGE

The Altamaha River has a strong impact on the Duplin. Draining approximately one quarter of Georgia, the Altamaha is the most important source of freshwater, nutrients, and particulates to the Georgia coast (Weston et al., 2009). Our measurements showed that Duplin salinity varied with freshwater discharge from the river, ranging from 8 to 33 at UD and from 12 to 34 at DS (Figure 1C). Altamaha discharge was measured at the US Geological Survey gage station upstream of the study site in Doctortown, Georgia (United States Geological Survey, 2013). The absence of any relationship between local precipitation and Duplin salinity (not shown) suggests that Altamaha discharge was the dominant driver of salinity in the Duplin (see also Di Iorio and Castelao, 2013, in this issue). Although Altamaha discharge was also an important control on the concentrations of dissolved and particulate constituents of Duplin surface water, transformations that took place within the Duplin and its watershed modulated these concentrations.

DUPLIN WATERSHED PROCESSES

To evaluate the extent to which within-watershed processes impacted surface water chemistry, we developed a simple mixing model in which the Duplin's salinity was controlled solely by mixing between Altamaha River and Atlantic Ocean water. Marine end-member composition was represented by data from Doboy Sound with salinities greater than 32. Low tide measurements from the Altamaha River, characterized by minimum salinities, were used to estimate the chemical composition of the riverine end-member. The fraction that each end-member contributed to the composition of the Duplin was calculated based on the salinity of the Duplin at UD and the known salinities of the two end-members. This mixing ratio, combined with known nutrient concentrations of each end-member, was used to calculate a predicted concentration of each chemical constituent measured in the upper Duplin for each time point sampled in this 10-year data set. Measured concentrations above the predicted value indicate that the Duplin watershed was a source of the material, while lower measured concentrations indicate a sink.

The Duplin marsh/creek system acted as a sink for particulates throughout the year (as represented by TSS in Figure 2), reflecting that healthy marshes are efficient scavengers of sediment that is needed to maintain and build the marsh platform to keep pace with sea level rise (Cherry et al., 2009). The Duplin system was a sink of PO$_4^{3-}$ and NH$_4^+$ in the spring, but a source of these nutrients for the rest of the year (as represented by PO$_4^{3-}$ in Figure 2). NO$_3^-$ was an exception to the pattern displayed by the other inorganic nutrients; it was generally consumed within the Duplin. However, a brief period of net NO$_3^-$ production in August (data not shown) was observed, a pattern consistent with previously documented late summer blooms of nitrifying microorganisms (Caffrey et al., 2007; Hollibaugh et al., 2011). Finally, the Duplin watershed was a source of DOM throughout the year (as represented by DON, Figure 2). Salt marshes are highly productive ecosystems known to export DOM (Dame, 1989; Childers et al., 2000), whose sources are the vegetation and possibly also benthic diatoms that inhabit mudflats, the creek bank, or the

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creek bed (Porubsky, 2008). These results indicate that mixing between Altamaha and ocean water was insufficient to explain the observed concentrations of inorganic nutrients, organic matter, or particulates in the Duplin. Therefore, processes occurring within the watershed must have been responsible.

SEDIMENT AND WATER COLUMN MICROBIAL PROCESSES

There was a great deal of variability in nutrient concentrations measured in Duplin surface waters over the period of this study. However, while nutrient concentrations generally varied with mixing and exchange between various adjacent coastal water bodies, the ratio of dissolved inorganic nitrogen (DIN = NH_4^+ + NO_3^-) to dissolved inorganic phosphorus (DIP = PO_4^{3-}) was relatively stable (generally < 5) throughout the study period. The DIN to silica ratio was uniformly very low, generally less than 0.1.

The observed DIN:DIP ratio of 5:1 is well below the Redfield ratio of 16:1. Although primary production in coastal and marine waters is generally thought to be nitrogen limited (Howarth, 1988), DIN:DIP ratios alone are insufficient to prove that the Duplin is nitrogen limited. However, net consumption of DIN and production of PO_4^{3-} within the Duplin watershed throughout the year support the idea of nitrogen limitation. The presence of high DIP concentrations and low DIN:DIP ratios in marsh pore water (Weston et al., 2006) suggests that pore fluid exchange likely played an important role in maintaining year-round nitrogen limitation in the system. Mallin et al. (2004) used nutrient addition experiments to conclude that primary production in similar tidal creeks in North Carolina was nitrogen limited under most circumstances. Similar measurements are necessary to prove nitrogen limitation in the Duplin.

GROUNDWATER DISCHARGE

While groundwater discharge accounts for only a small fraction of the freshwater that enters estuaries, it contributes large quantities of nutrients and often rivals nutrient loading from rivers (Krest et al., 2000; Moore et al., 2006). To estimate groundwater discharge into the Duplin, an extensive survey of vertical and horizontal flow patterns was conducted in August 2003 (McKay and Di Iorio, 2008). In conjunction with measurements of cross-section area, these flow measurements allowed the quantification of changes in water storage within the upper, middle, and lower Duplin. These data revealed net export of water from the upper to the lower Duplin (Figure 1D) and from the lower Duplin to Doboy Sound (Figure 1E). This excess fluid was attributed to surface- and groundwater discharge from the adjacent marsh and upland. The largest input of groundwater was to the middle Duplin (Figure 1E), which is corroborated by observed point sources of fresh groundwater discharge (recent work of author Joye) and elevated radon concentrations along the Duplin's main axis (Richard Peterson, Coastal Carolina University, **pers. comm.**, April 8, 2013).

The NH_4^+ and PO_4^{3-} concentrations in submarsh groundwater immediately adjacent to the creek bank significantly exceeded those in the Duplin (Figure 3C), and groundwater became

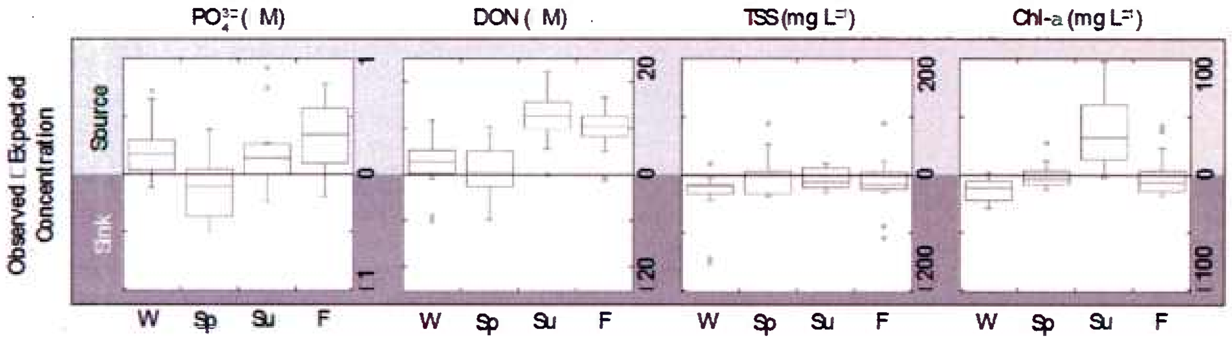

Figure 2. Source-sink behavior for the Duplin watershed. Seasons are represented on the x axes in these box and whisker diagrams (W = Winter, Sp = Spring, Su = Summer, F = Fall). Boxes above the middle line in each plot (light gray) represent the watershed acting as a source with respect to that material, while boxes below the line (dark gray) represent sink behavior. Phosphate (PO_4^{3-}) is representative of most of the inorganic nutrients, dissolved organic nitrogen (DON) is representative of the dissolved organic materials, and total suspended solids (TSS) is representative of particulates. Chl-a = Chlorophyll a

more reduced as it moved from the upland through the marsh on its way to discharging into the adjacent tidal creek (Figure 3B). Groundwater influence on surface water is higher on spring tide than on neap tide because a greater volume of groundwater discharges into the adjacent creek on spring compared to neap tides (Wilson and Morris, 2012). Therefore, groundwater discharge affected patterns of nutrient concentrations in Duplin surface water, generating the observed pattern of higher NH_4^+ and PO_4^{3-} concentrations on spring than on neap tides.

MARSH INUNDATION

The imprint of marshes on creek surface water chemistry depends on the extent of tidally driven interaction between surface waters and marsh platforms. From one- to two-thirds of the water entering the Duplin during floodtide is exchanged with the marsh (Ragotzkie and Bryson, 1955). The area of marsh flooded on any given tide was calculated by comparing a digital elevation model of the Duplin watershed (Viso et al., 2011; Hladik and Alber, 2012) with creek water elevations measured at UD. We estimate that more than twice the area of marsh was flooded on a median spring tide (13.8 km²) than on a median neap tide (5.1 km²). Therefore, marsh influence on Duplin chemistry should be much higher on spring than on neap tides. Marshes require deposition of particulates to keep pace with sea level rise (Stumpf, 1983), and marshes in the Duplin watershed indeed act as a sink of particulates (Chalmers et al., 1985), consistent with our model analysis.

Tidal marshes vary widely in their source/sink behavior with respect to DOM (Childers, 1994). DOM concentrations in the upper Duplin were higher on spring than on neap tides, particularly for DOC, and the watershed was a net producer of these materials. These patterns were not the result of marsh inundation, however, as Duplin marshes are not net exporters of DOC over tidal time scales (Chalmers et al., 1985). This suggests that benthic primary production supplies DOC to Duplin surface waters (Porubsky, 2008) as diatoms are scoured from the creek bed by higher amplitude, higher energy spring tides (Thorensen, 2004).

SYNTHESIS

Exploration of tidal creek-estuarine exchange in and around the Duplin watershed gave rise to the "Outwelling Hypothesis" (Odum, 1968), which states that the coastal ocean is supplied with nutrients and organic material through outwelling from marsh/estuarine systems. Since that time, extensive work has been done to determine how salt marsh systems process inorganic nutrients, organic matter, and particulate materials (Childers, 1994). Our model results demonstrate that within-watershed processes are important in structuring surface water chemistry and export to the adjacent estuary. These processes included groundwater discharge, exchange of creek water with the marsh platform, and benthic primary production (Figure 3). Each process influenced each group of materials in a different way, and their relative strengths varied over seasonal and tidal time scales.

Diatoms growing atop creek-bank sediment produced organic matter that they exported to the water column,

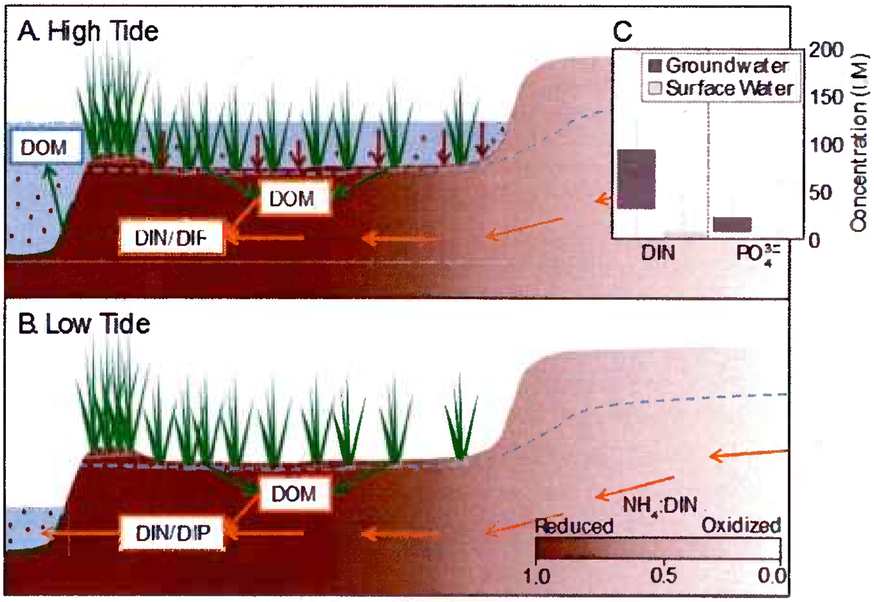

Figure 3. Internal processes within the Duplin watershed on high (A) and low (B) tide alter the chemical composition of creek water. Diatoms growing in the creek bed export dissolved organic matter (DOM) and are represented by green lines and arrows, respectively. Particulates in the water column (brown dots) are captured by the marsh on high tides (brown arrows). Groundwater flow and discharge are displayed as orange arrows. (C) Comparison of groundwater and surface water nutrient concentrations. DIN = Dissolved inorganic nitrogen. DIP = Dissolved inorganic phosphorus.

contributing to the observed net export of DOM from the Duplin (Porubsky, 2008). Maximum DOM concentrations occurred on spring tides when strong currents scoured the creek bed (Figure 3A). The Duplin watershed was a net sink for particulate materials because they were captured by the marsh, allowing it and the flora it hosted to grow (Figure 3A). When marsh plants died, they were broken down to DOM and further decomposed via microbial processes in the marsh sediment into inorganic nutrients (Figure 3). These microbial processes drove groundwater from a relatively oxidized to a reduced state as it flowed from the upland toward the tidal creek. Nutrient concentrations built up in marsh groundwater such that they exceeded concentrations in the adjacent creek water (Figure 3C). This nutrient-rich groundwater discharged into the creek on low tides (Figure 3B), with higher discharge occurring on spring than on neap tides. Thus, the Duplin watershed was a source of inorganic nutrients to the estuary.

Contrary to our observations, Vörösmarty and Loder (1994) documented lower nutrient concentrations on spring tides than on neap tides. They attributed these changes in concentration to uptake by the surrounding marsh as it was flooded by adjacent creek water on spring high tides. Assuming that marshes in the Duplin watershed followed this general trend, DIN and DIP inputs from groundwater must have more than offset marsh uptake.

> “ONE OF THE PRIMARY MISSIONS OF THE GEORGIA COASTAL ECOSYSTEMS LONG TERM ECOLOGICAL RESEARCH PROJECT IS TO IDENTIFY AND EXPLAIN PATTERNS IN NUTRIENT CONCENTRATIONS IN THE COASTAL ZONE AND HOW THESE PATTERNS INFLUENCE THE ECOLOGY OF THE REGION.”

The balance between the processes that control tidal creek chemical composition shifts over tidal and seasonal time scales. Quantifying such temporal variations is important for developing realistic estuarine nutrient budgets; this requires long-term data sets. Challenges remain as sampling strategies typically lack the tracers that can unambiguously distinguish between fluids exchanged with the marsh platform and those exchanged with groundwater, which is paramount in order to quantify nutrient dynamics. Similarly, our decadal data set cannot systematically capture events such as storms, which can have a strong influence on the environment and exchange fluxes (Drewry et al., 2009). This influence can only be quantified if these events are targeted for sampling or measurements are continuous, as recognized in the efforts to establish novel sensory networks such as the National Ecological Observatory Network.

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