4 Instream Nutrient Dynamics

A principal objective of this study was to gain a better understanding of the nutrient dynamics within these tidal creeks by focusing on changes in nutrients along the salinity gradient. This chapter describes results of assessments of nutrient dynamics using stoichiometric ratios of total and dissolved, inorganic and organic water quality constituents and assessing the observed mixing behavior of nutrients along the salinity gradient.

4.1 Stoichiometry

Stoichiometry is the study of elemental ratios; the most popular of which with respect to water quality is the Redfield Ratio (Redfield, A.C. 1934: 1958). The Redfield Ratio was used to characterize the elemental requirements of phytoplankton in oceanic waters and a 106:16:1 C:N:P ratio is often quoted as that which defines a breakpoint between nitrogen and phosphorus limitation. The original ratio was based on molar mass of nitrogen and phosphorus and based on inorganic forms of these elements assuming that nutrients were not limited; however, the ratio is sometimes used with total forms of nutrients and concentrations (e.g. mg/l). An example of the latter is the cutoff values for Florida's Trophic State Index calculations which is most often computed based on total forms of nutrients and their mass per unit volume. The C:N:P ratios based on median values of particulate C, N, and P (ug/l) converted to moles are provided for each creek in Table 4-1. Based on the particulate fractions of these constituents, the values are less than the Redfield ratios reported by Redfield (1934). When evaluating total forms of nutrients based on molar ratios, all creeks except Estero appear to be nitrogen limited with N:P ratios typically less than 16 (Figure 4-1). The exception was Estero which was principally phosphorus limited based on molar ratios. Estero would be considered a nutrient "balanced" system according to the Trophic State Index with a range in mass per unit volume N:P ratio between 10-30 (Figure 4-2). This outcome is likely due to the fact that there were NO23 inputs in the tidal portion of Estero in addition to the fact that the P concentrations in Estero were much lower than all other creeks in the study.

Table 4-1. Observed Redfield Ratios for creeks sampled in 2017 and 2018 using particulate carbon, nitrogen and phosphorus (ug/l) converted to molar weights.

Creek	Carbon	Nitrogen	Phosphorus
Estero	75	10	1
Frog	42	5	1
Mullet	57	8	1
South	37	5	1
Sweetwater	44	6	1
West Spring	60	8	1

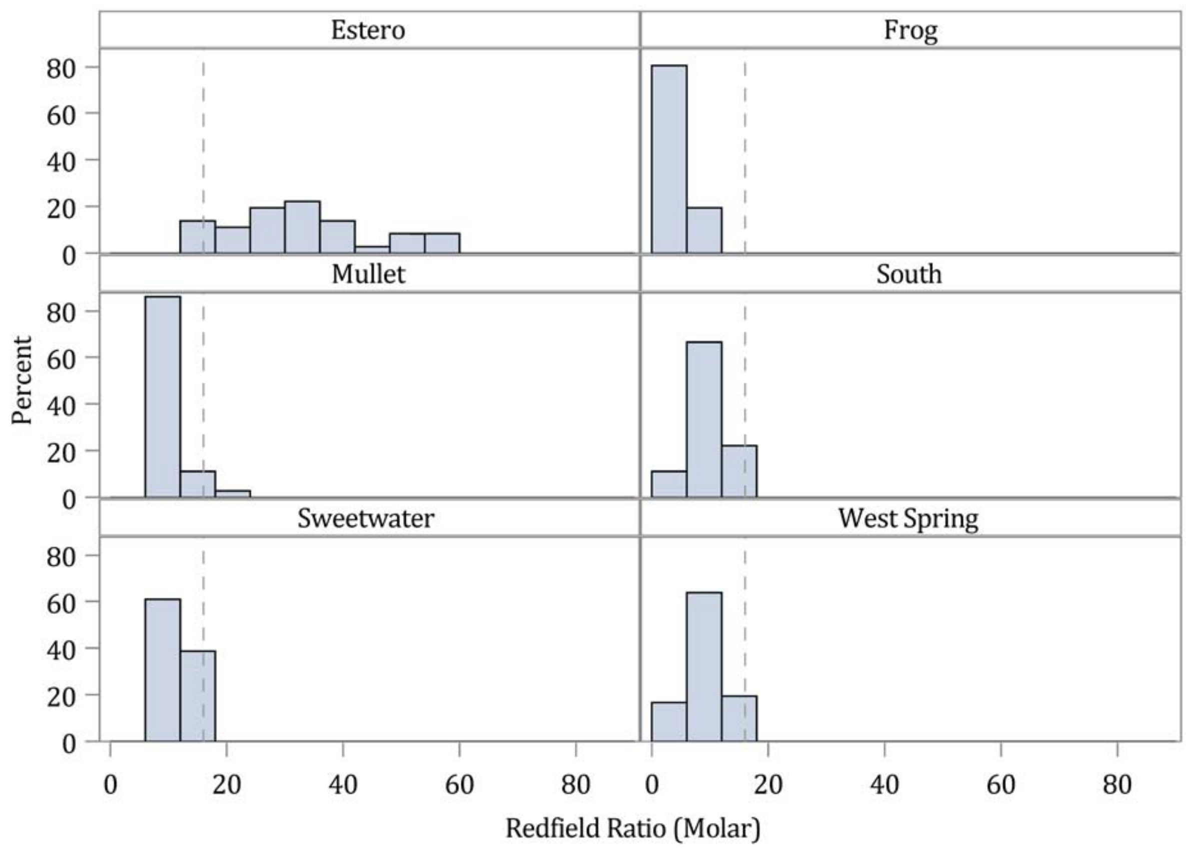

Figure 4-1. Distribution of nitrogen to phosphorus ratios based on molar weights.

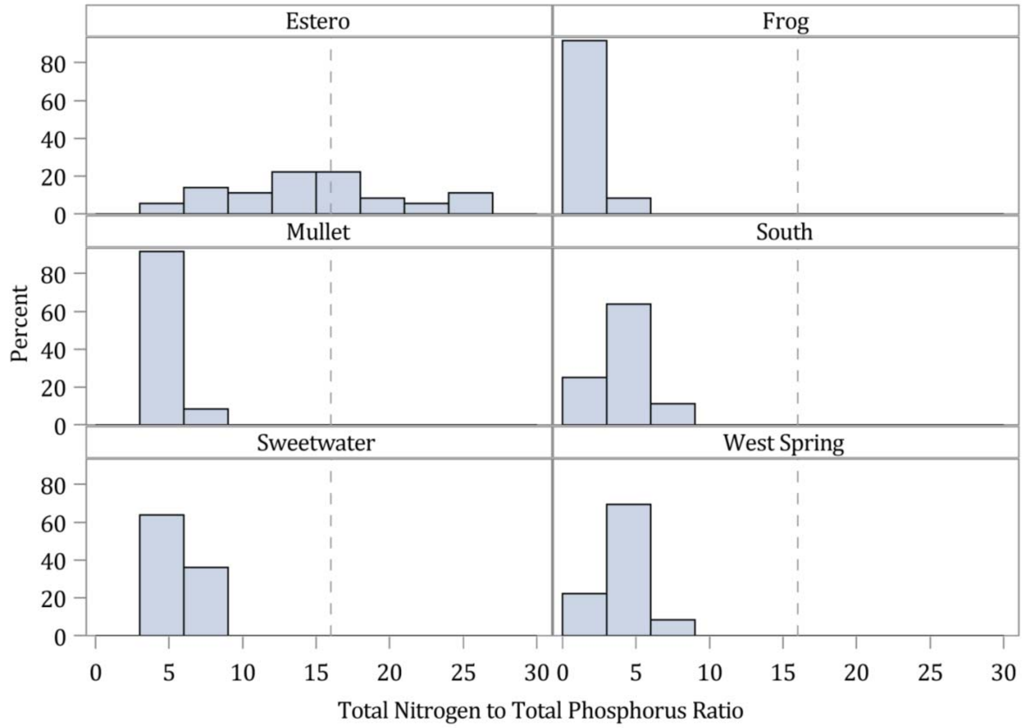

Figure 4-2. Distribution of nitrogen to phosphorus ratios based on mass per unit volume.

The ratio of dissolved nutrients based on molar weights is provided in Figure 4-3 and also suggests ratios indicative of nitrogen limitation with the exception of Estero in which half of the observations were above the Redfield Ratio of 16:1.

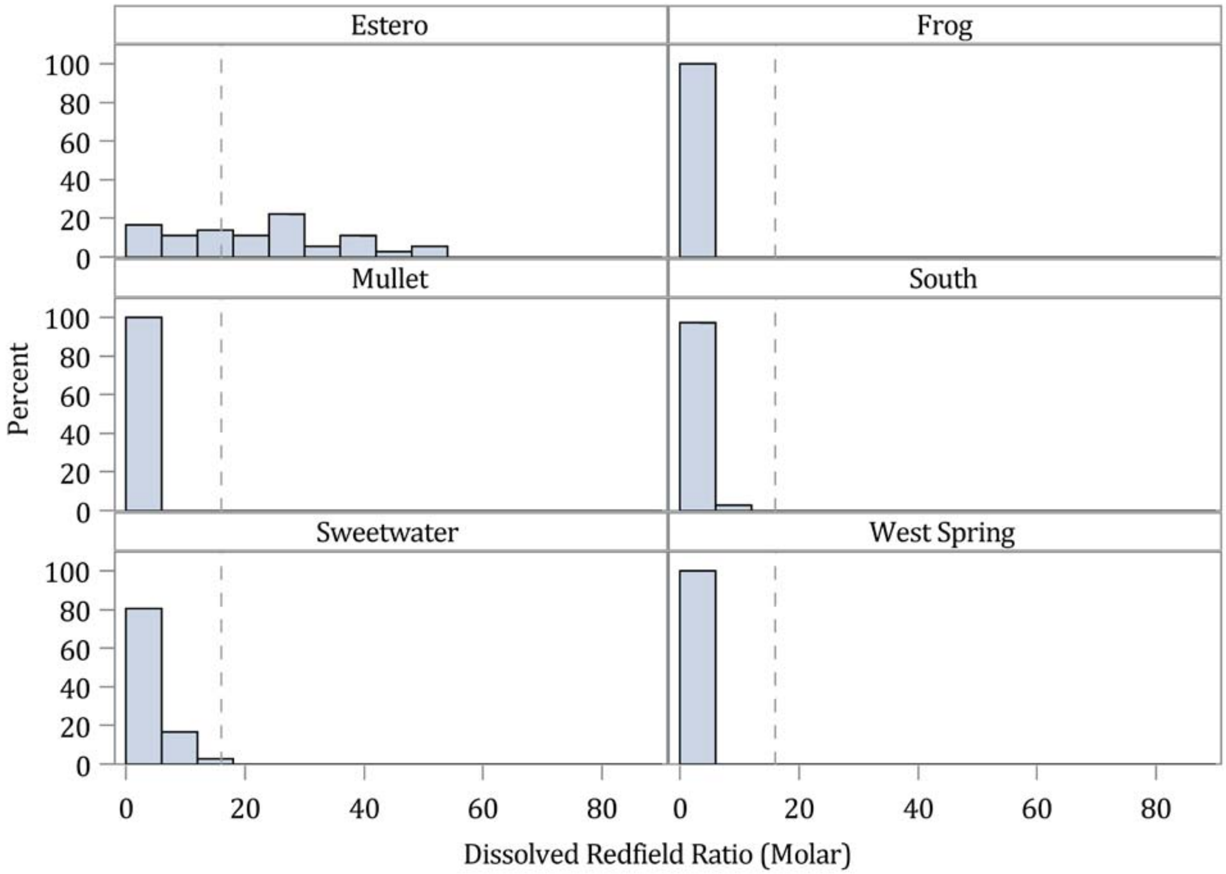

Figure 4-3. Distribution of nitrogen to phosphorus ratios based on molar weights and inorganic forms of nutrients.

Sediment nutrient ratios based on total kjeldahl nitrogen and total phosphorus also exhibited nitrogen limitation for all creeks other than Estero which was the only creek exhibiting ratio values above 16 (Figure 4-4). Together these findings suggest that most of the creeks are nitrogen limited; however, Estero may be the exception in that phosphorus values were low and addition of inorganic nitrogen inputs in the tidal portion of the system was observed resulting in ca. 50% of the samples above the Redfield Ratio threshold of 16.

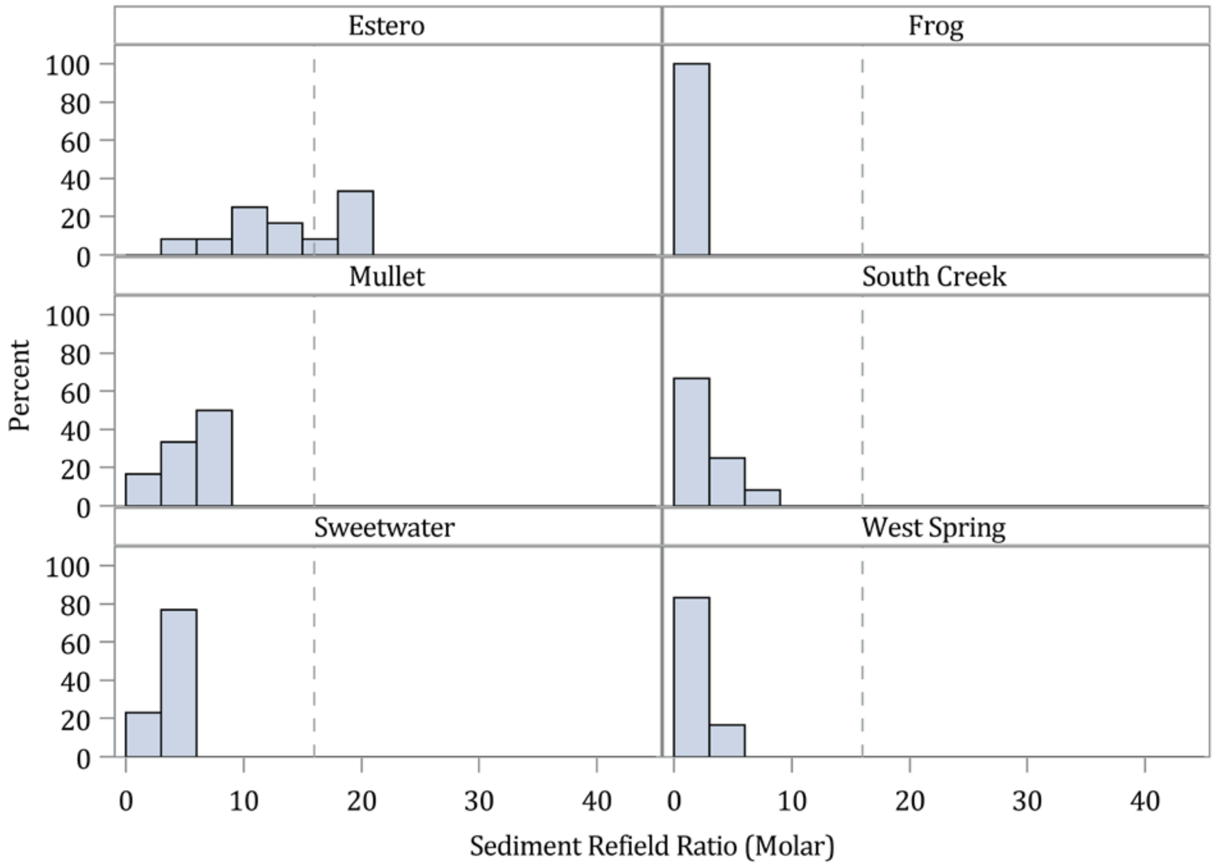

Figure 4-4. Sediment nutrient ratios based on molar weights of nutrients originally expressed as mg/kg.

4.2 Effects of Rainfall on Salinity and Nutrients

Rainfall and the resultant streamflow generated from surface water runoff is an important physical driver of instream nutrient dynamics. Direct estimates of flows were not available for all creeks in the study but the effects of rainfall as characterized in section 3.7 above were used to evaluate the effects of antecedent rainfall on salinity and nutrient delivery "events" to the tidal portion of the creeks. Salinity was highly statistically different among stations in all creeks which is an important consideration when evalauting changes in nutrient concentrations as a function of salinity. Only the lowermost stations in South Creek were not statistically different and this result may have been in part due to the low overall sample size of the study. Detailed results of the statistical analysis are provided in Appendix E.

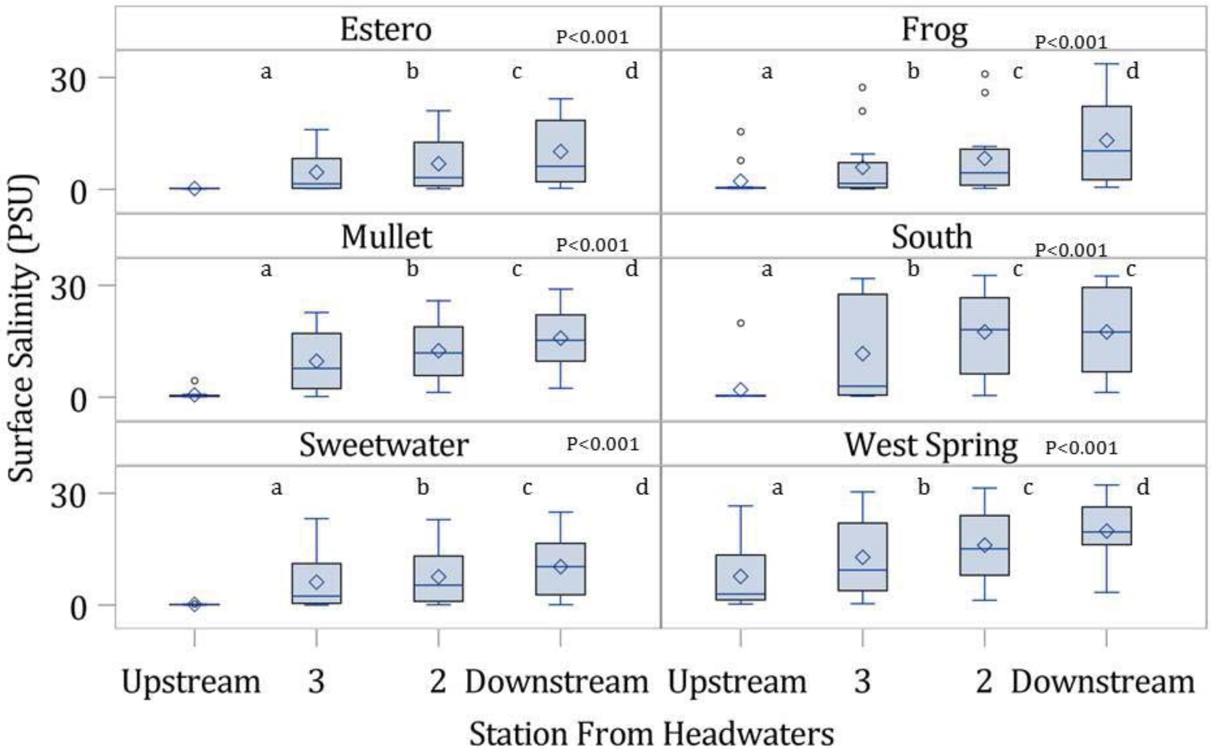

Figure 4-5. Results of analysis of variance for clustered data displaying significant differences between stations for each creek. Different letters represent significant differences.

An example of the differences in nutrient dynamics as a function of salinity is provided for Frog Creek in Figure 4-6. Each curve in each plot represents a sampling event with stations oriented from upstream to downstream and the 14 days total rainfall labeled. The June 2017 event for Frog Creek followed a total of 5.5 inches of rainfall in the 14 days prior to sampling. The entire creek was near freshwater during that June event as portrayed by the top left plot in Figure 4-6 (the green solid line). Dissolved inorganic nitrogen during the June event was 4 times the magnitude of the other two spring sampling events for that year (top right) and dissolved organic nitrogen (bottom left) was also substantially higher during the June event than during the other two events. This resulted in higher overall total nitrogen (bottom right) relative to the other events. These results point to the influence of rainfall and flows on resulting salinity and nutrient delivery in the tidal portion. Other "events" included an pulse delivery of particulate phosphorus to the tidal portion of Frog Creek during Spring 2018 which was an order of magnitude higher than any other event (Figure 4-7) and a spike in dissolved ammonia in Mullet Creek throughout the creek in May 2018 (Figure 4-8). Plots for all constituents are provided in Appendix E along with results of statistical evaluations comparing salinty, TN, TP and DNO23 among stations within each creek..

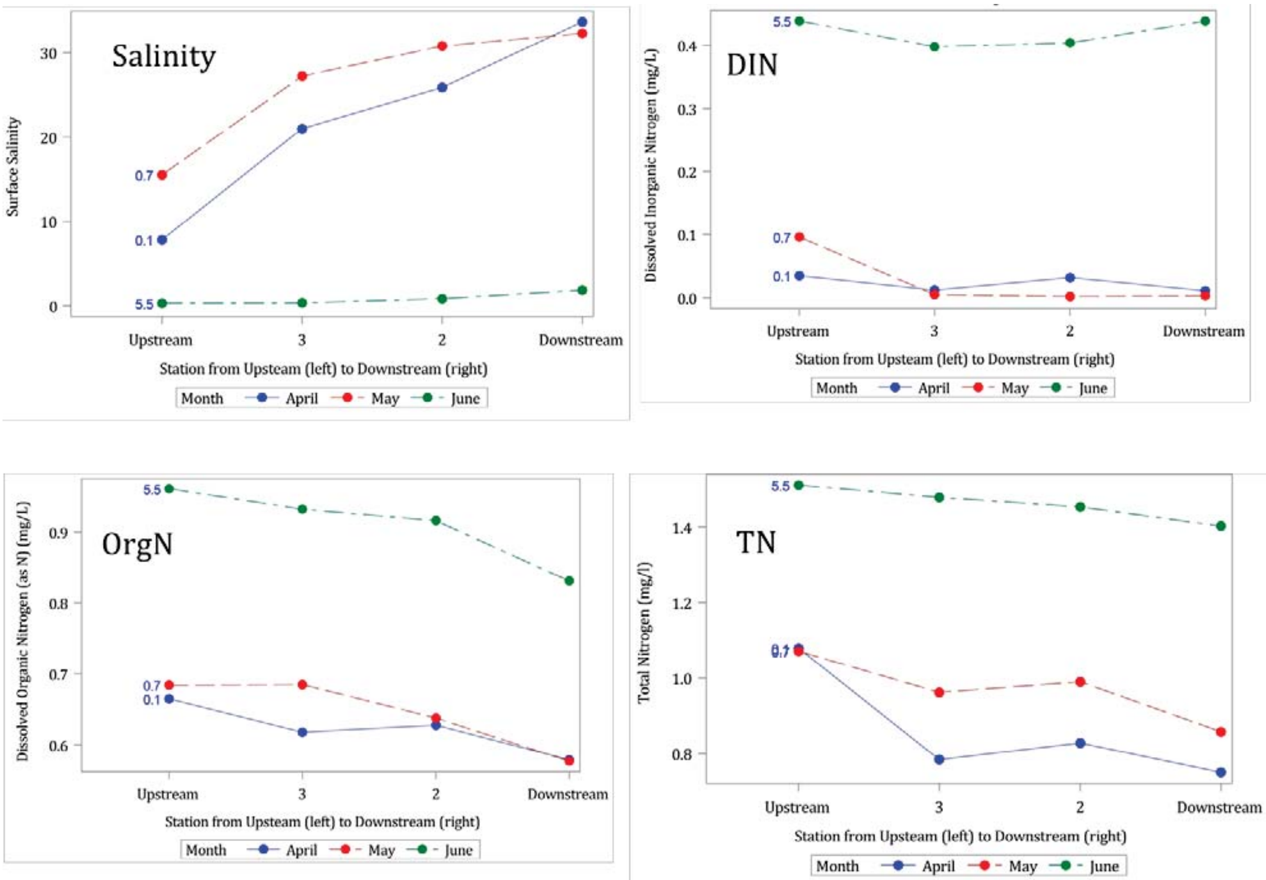

Figure 4-6. instream water quality dynamics in Frog Creek for Spring 2017 sampling events for salinity (top left), dissolved inorganic nitrogen (top right), organic nitrogen (bottom left) and total nitrogen (bottom right).

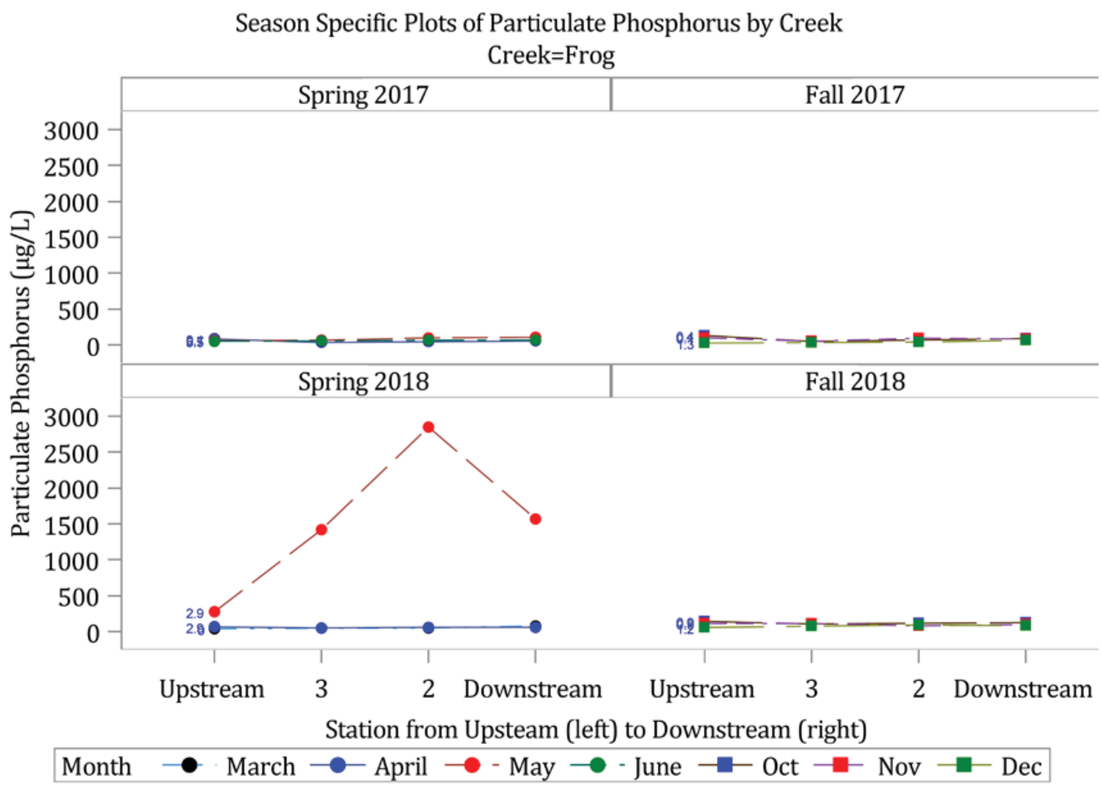

Figure 4-7. Particulate Phosphorus distribution for each sampling event in Frog Creek.

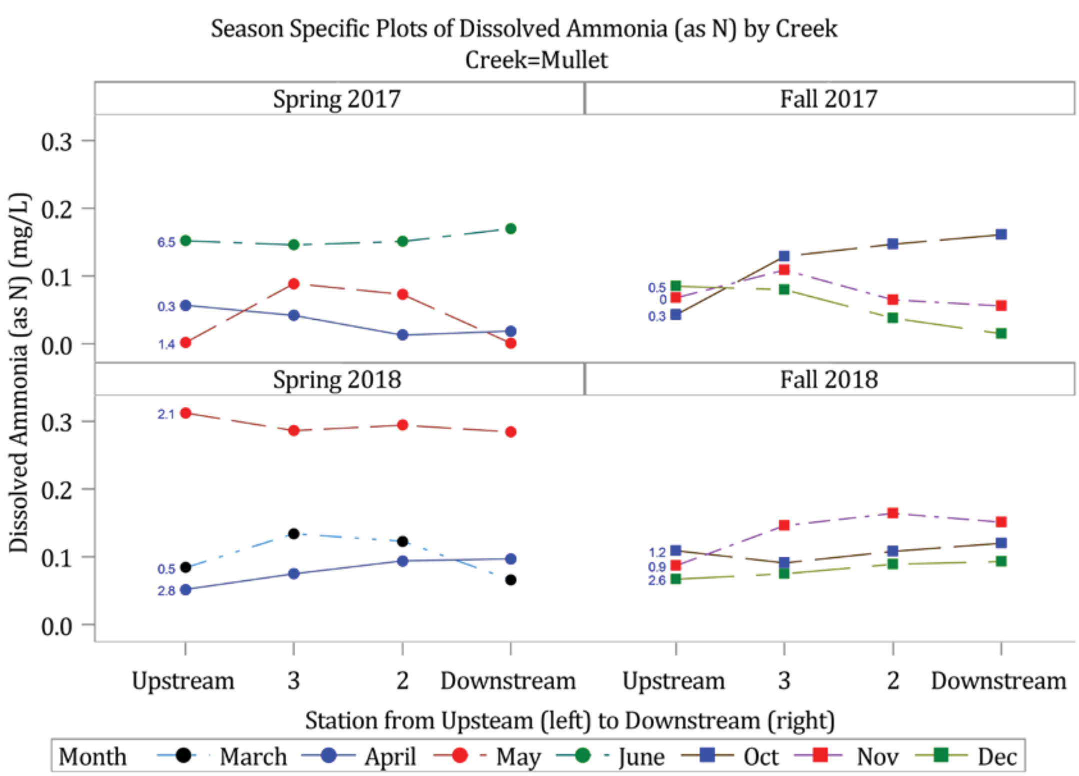

Figure 4-8. Distribution of dissolved ammonia for each sampling event in Mullet Creek.

4.3 Mixing Models and Nutrient Assimilation

The previous study found that nutrient concentrations, especially organic forms of nutrients, in the tidal portions of these creeks were generally in addition relative to the assumption of linear mixing within estuarine waters. Linear dilution lines provide a reference point from which to evaluate deviations from conservative assumptions about the dilution of nutrients along the salinity gradient. The sampling design used for this study was specifically constructed to evaluate whether nutrients acted as conservative substances within tidal creeks and to identify potential sources of nutrient addition in these creeks. By collecting water quality samples across the salinity gradient, generally within a four-hour window, the observed source water concentration was assumed to be representative of the expected inputs into the tidal creek. We used several methods based on conservative mixing principles of water quality constituents to describe the dilution of water quality in the tidal portion of the creek and evaluate different nutrient pools (e.g. organic versus inorganic nitrogen; total versus dissolved) to compare deviations from conservative mixing assumptions among these constituents. We understand that true instream dynamics are more complex than this and it is the deviations from the conservative mixing lines that is of interest in this analysis. For example, using a modification of the freshwater fraction equation (Sheldon and Alber, 2006), we calculated the expected concentration of nutrients in the tidal portion of the creek as a function of the source water concentration and the proportion of salinity relative to full strength seawater (i.e., 35‰). The expected nutrient concentration is:

$$En_c = n_f * (1 - (Sal_c / 35))$$

where:

En_c = Expected nutrient concentration at site c in tidal creek

n_f = Nutrient concentration at source water site

Sal_c = Salinity at site c in tidal creek

This equation allowed for the computation of an expected nutrient concentration at any sample location within the creek and a comparison of the expected concentration to the observed concentration at the sample location. When the salinity of the source water site was not zero, dilution was assumed to generate the expected value at zero salinity. This comparison was used to identify the behavior of nutrients in the tidal portions in the creek over various temporal and spatial scales. For example, the differences between the observed and expected nutrient concentrations (both total nitrogen and total phosphorus) from the previous study were mostly positive in all 16 creeks with the exception of TP in Doublebranch, Wildcat and Powell Creeks (Figure 4-9).

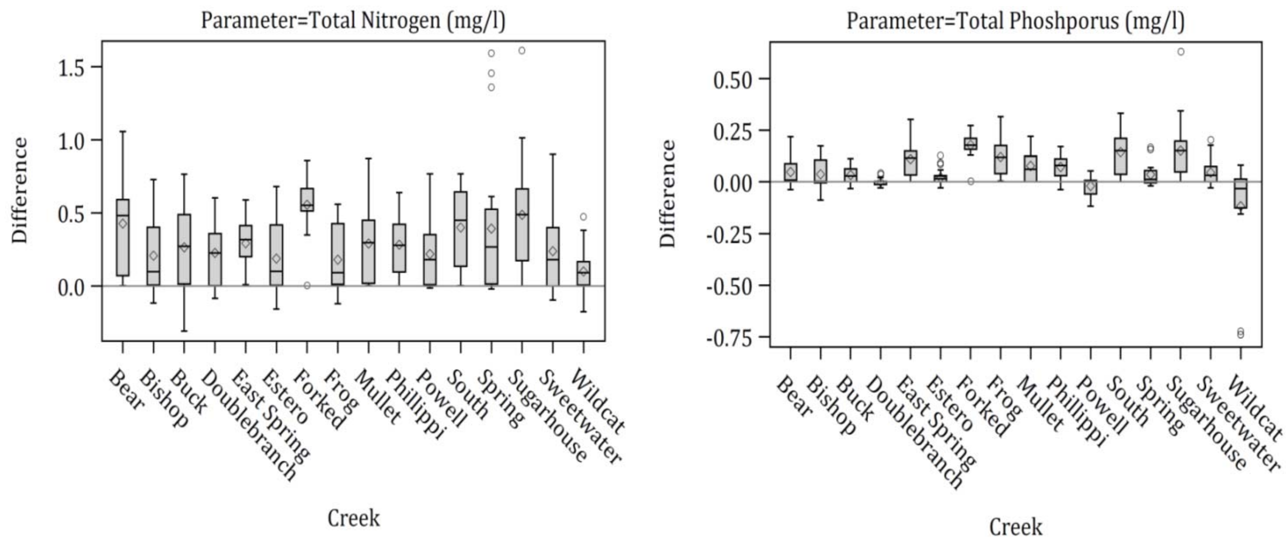

Figure 4-9. Distribution of differences between observed and expected concentrations of total nitrogen and total phosphorus for the 16 tidal creeks sampled in 2014.

The current study design included elements to help partition the sources of nutrients within the system to separate out effects of natural wetland function from anthropogenic sources based on observational data. These elements included:

- establishing the longitudinal transect to capture water quality information along the estuarine gradient within the creek;
- sampling during the typical dry season to minimize the influence of flushing and maximize the probability of capturing the organic wetland and internal cycling components of nutrient dynamics;
- evaluating the dissolved organic and inorganic pools of nutrients in the water column and sediment to provide information on nutrient cycling, and
- the collection and analysis of stable isotopes in an effort to identify nutrient sources and pathways within the tidal portion of the creeks.

To validate outcomes of the previous study, identical analysis was conducted on the samples taken from the 6 creeks surveyed for this study. This study targeted the typical dry season in southwest Florida to concentrate on instream nutrient dynamics when residence times tended to be greater and therefore biogeochemical activity more pronounced within the creek. For example, the distribution of differences for total nitrogen and total phosphorus are plotted in Figure 4-10. The nonparametric signed rank test (Zar 1984) was used to test if the differences were greater than zero and the results were highly statistically significant for most constituents (Table 4-2), with the exception being inorganic nitrogen, which was expected to be rapidly assimilated. However, Estero exhibited a different pattern than the other creeks in that inorganic forms of nutrients in Estero were in surplus in the tidal portion while CDOM, color and most organic forms of nitrogen appeared to follow the linear dilution curve. This was a peculiar finding and may indicate differential contributions from the south fork of Estero or possibly the presence of a spring vent in the upper tidal portion near Station 3.

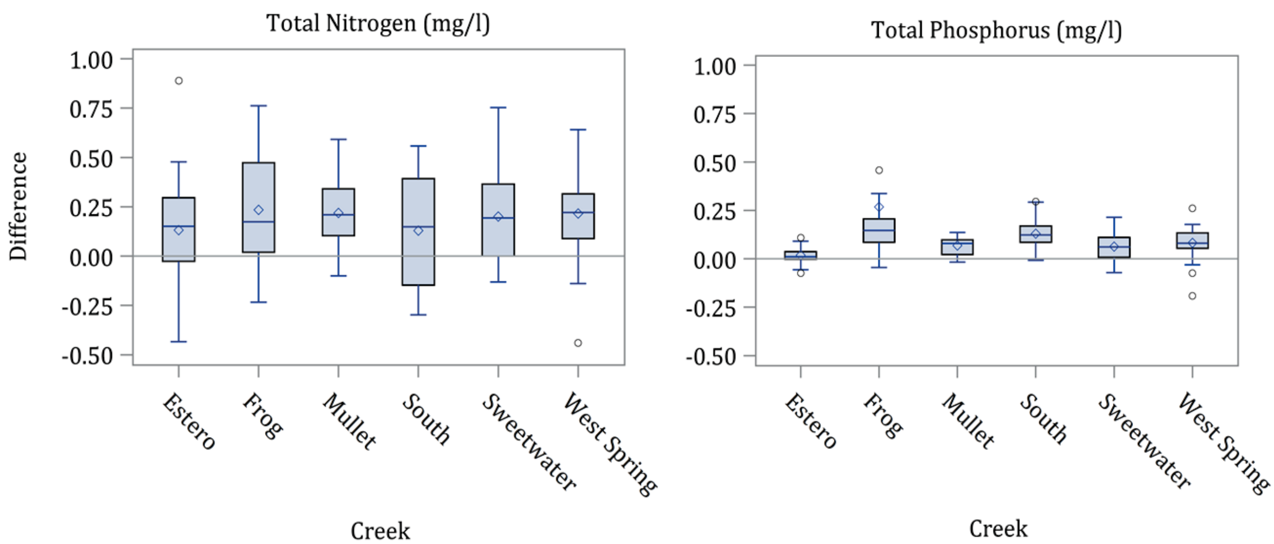

Figure 4-10. Distribution of differences between observed and expected concentrations of total nitrogen and total phosphorus for the 6 tidal creeks sampled in 2017-2018.

Table 4-2. Results of one sided signed rank test to evaluate if water quality constituent concentrations are greater than expected by dilution.

Constituent	Estero	Frog	Mullet	South	Sweetwater	West_Spring
CDOM_275	0.6441 #	<0.001	<0.001	0.0026	<0.001	<0.001
CDOM_465	0.0646 #	<0.001	<0.001	0.0049	0.0008	<0.001
Color_365	0.1976 #	<0.001	<0.001	0.0063	<0.001	<0.001
Nitrogen						
DNH3_mgl	0.0012	0.2246 #	<0.001	0.9841 #	<0.001	0.99 #
DNO23_mgl	<0.001	0.996 #	0.9099 #	0.7415 #	0.975 #	0.99 #
DIN_mgl	<0.001	0.9502 #	0.0008	0.9741 #	0.0732 #	0.99 #
DOrgN_mgl	0.8194 #	<0.001	<0.001	0.0036	<0.001	<0.001
DTKN_mgl	0.2246 #	<0.001	<0.001	0.0166	<0.001	<0.001
TKN_mgl	0.8541 #	<0.001	<0.001	0.0034	<0.001	<0.001
TDN_mgl	<0.001	0.0134	<0.001	0.0259	<0.001	<0.001
PN_ugl	0.9996 #	<0.001	0.0107	0.0023	0.0029	0.0188
TN_mgl	0.0012	<0.001	<0.001	0.0047	<0.001	<0.001
Phosphorus						
DOPO4_mgl	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
TDP_mgl	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
PP_ugl	0.9595 #	0.0034	<0.001	<0.001	0.2738 #	0.0498
TP_mgl	0.0038	<0.001	<0.001	<0.001	<0.001	<0.001

 # indicates non-significant result

The differences from those expected by dilution were then plotted as a percentage of the overall median value by station to evaluate the relative contributions spatially. For example, the differences for total nitrogen and total phosphorus were plotted for each station in Figure 4-11. The differences for the most upstream stations were zero, as expected, since these sites were located in fresh water. However, the downstream sites were all positive, with deviations from that expected by dilutions averaging ca. 40% of the median values for those stations. The same observation was made for two measures of dissolved organic matter (CDOM 465 and Color 365) as portrayed in Figure 4-12.

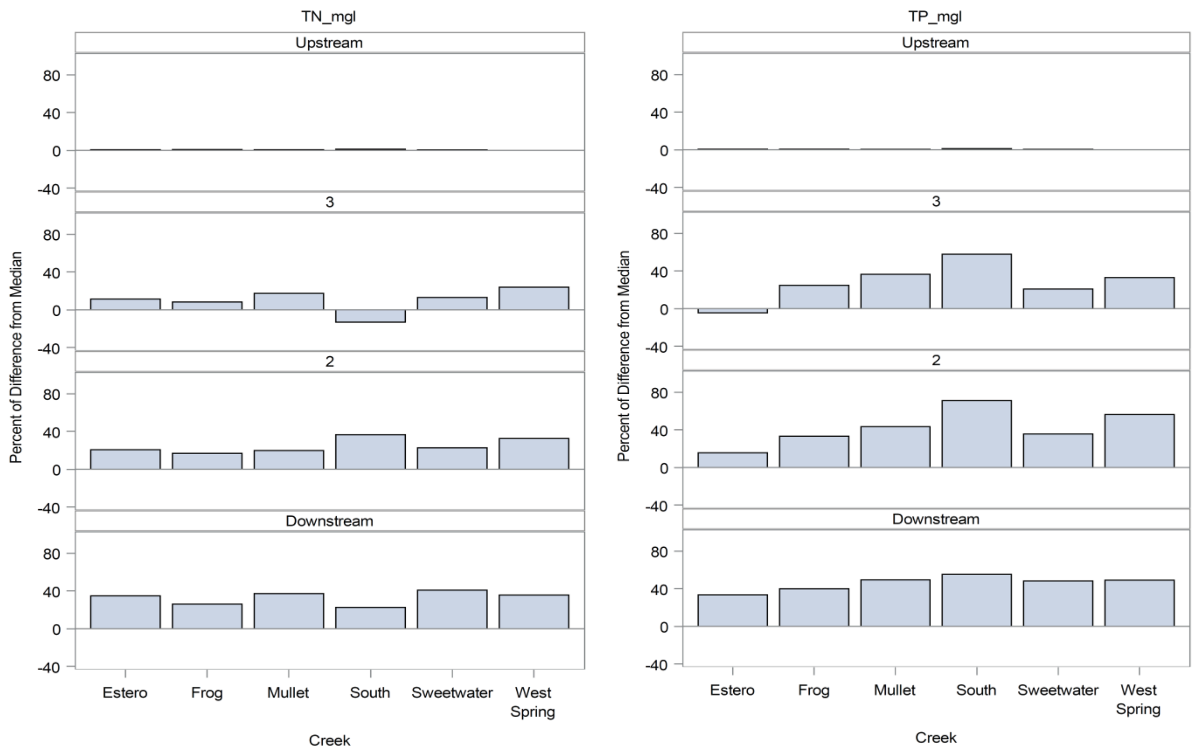

Figure 4-11. Differences from total nitrogen (left) and total phosphorus (right) concentrations expected by dilution expressed as a percentage of the overall median station value.

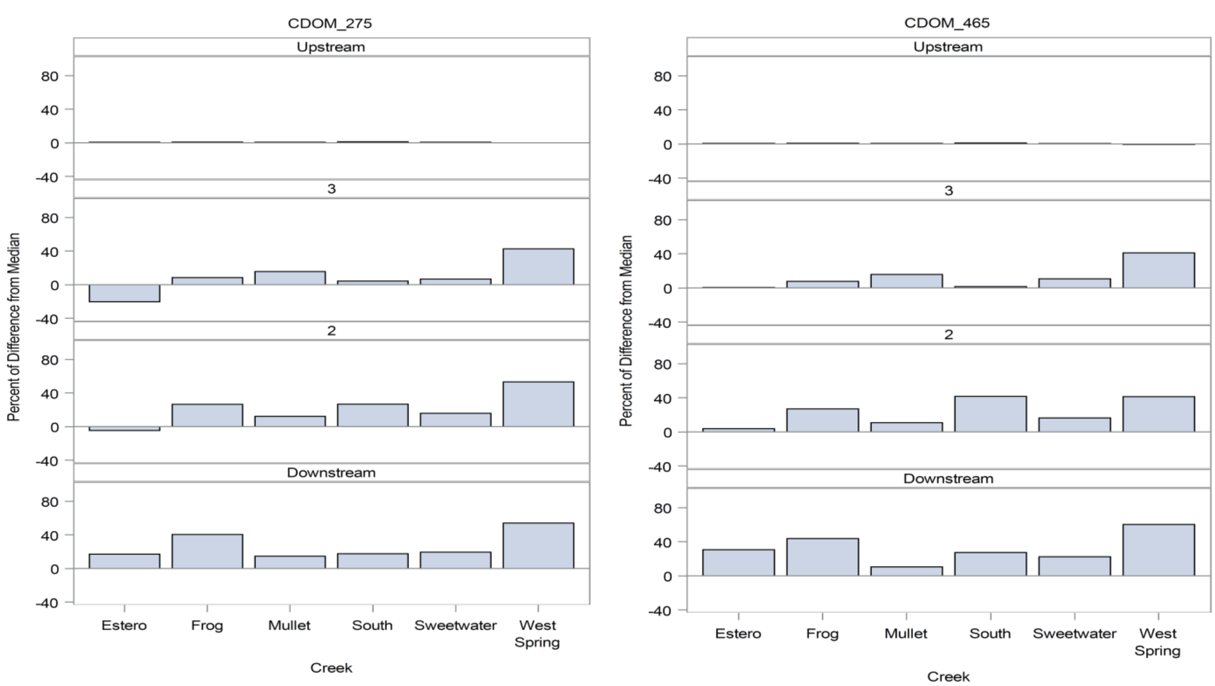

Figure 4-12. Differences in CDOM 275 (left) and CDOM 465 (right) from concentrations expected by dilution expressed as a percentage of the overall median station value.

A comparison of the principal constituents of organic and inorganic nitrogen can be seen in Figure 4-13 where organic nitrogen was in supply for most creeks while nitrite-nitrate was taken up within the system (with one notable exception) at rates higher than expected by dilution (assimilation). Nitrite-nitrate was in surplus at all three tidal stations in Estero while organic nitrogen was fairly conservative with marginal surplus at the most downstream site. This result indicates that the nitrogen delivery and assimilation in Estero is different than the other creeks. Further evidence that Estero has different nutrient dynamics than the other creeks is seen for particulate forms of nitrogen, phosphorus, and carbon. Again, it seems that organic nitrogen, phosphorus and carbon are either diluted in the upper estuarine stations in Estero while they are in surplus in the other creeks (Figure 4-14). The converse is also true; inorganic forms of nitrogen were depleted in most creeks while inorganic forms of nitrogen were in excess in Estero.

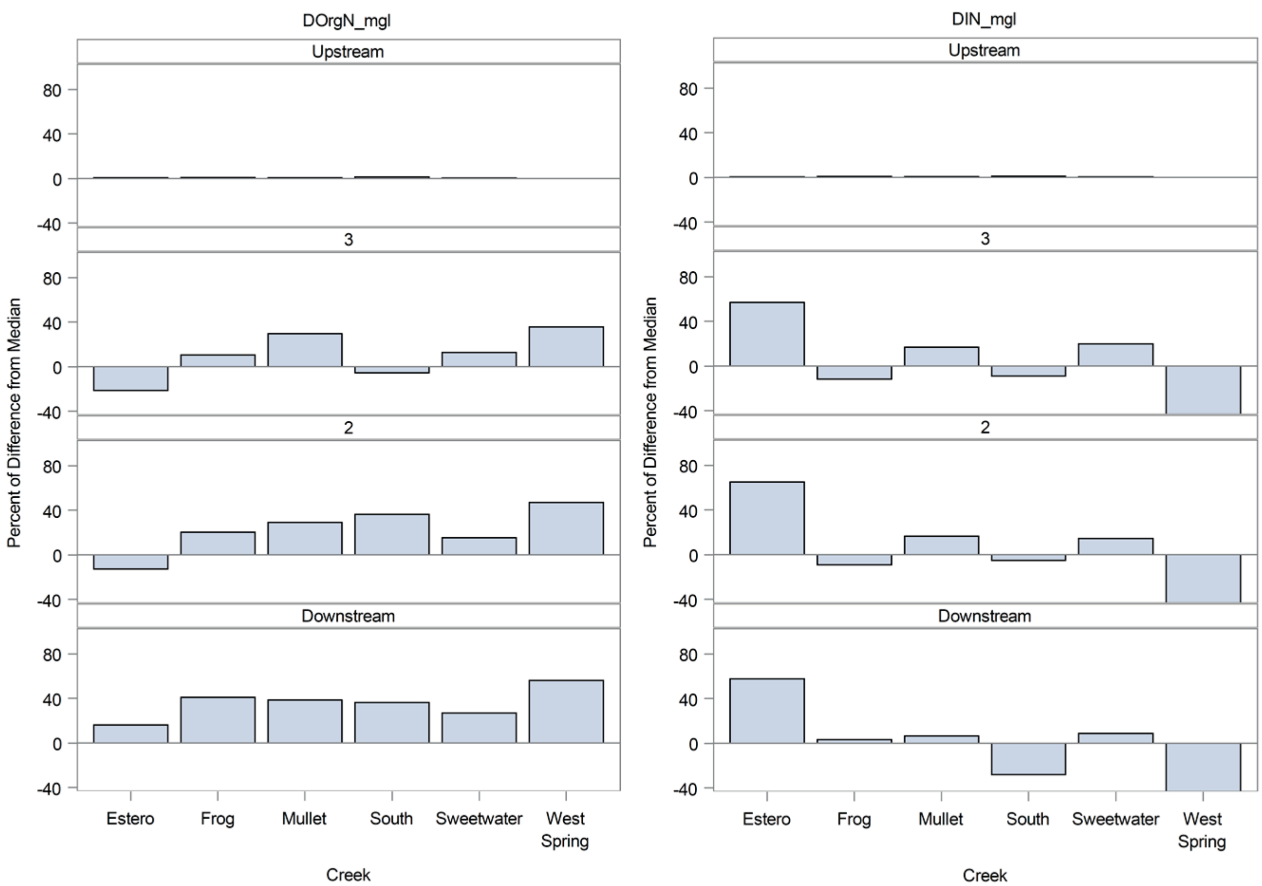

Figure 4-13. Differences in Dissolved Organic Nitrogen (left) and Dissolved Inorganic Nitrogen (right) from concentrations expected by dilution expressed as a percentage of the overall median station value.

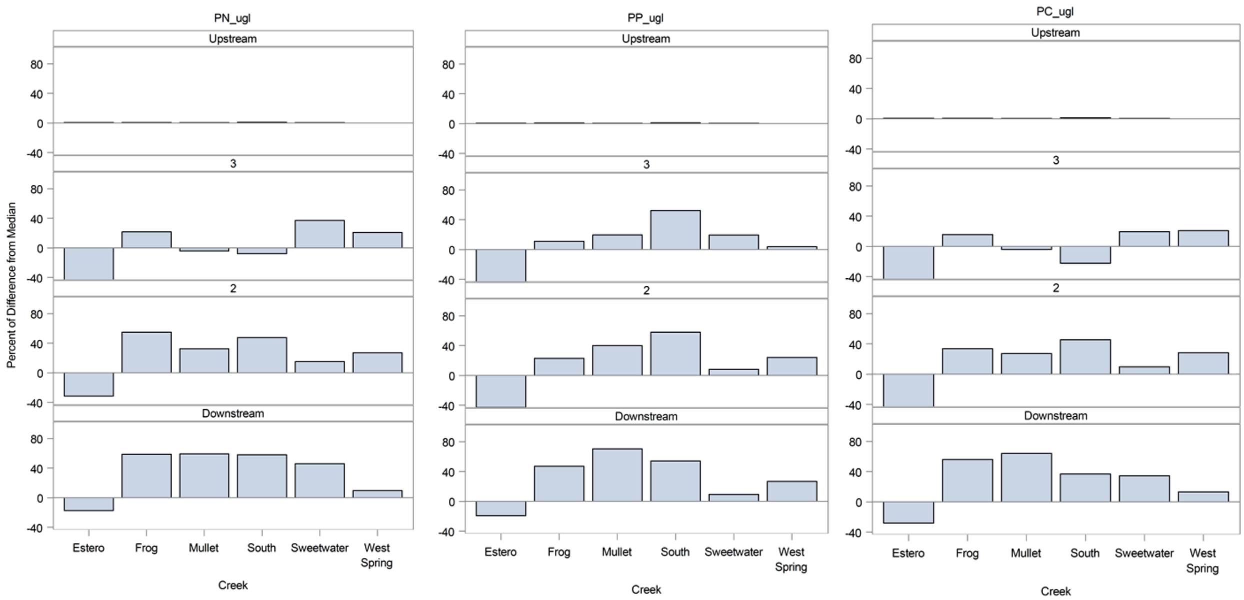

Figure 4-14. Differences from concentrations expected by dilution expressed as a percentage of the overall median station value for particulate nitrogen (left) particulate phosphorus (middle) and particulate carbon (right).

Alternative formulations of the dilution equation include: the Plew equation (Plew et al. 2018) which adds a concentration, such as the detection limit, to the downstream boundary; using the observed annual geometric average estuarine concentration of routine water quality monitoring data over the same time period (Figure 4-15); and using the EPA equation proposed to identify a downstream protective value by linear interpolation between the freshwater and estuarine numeric nutrient criteria (EPA 2012: Figure 4-16).

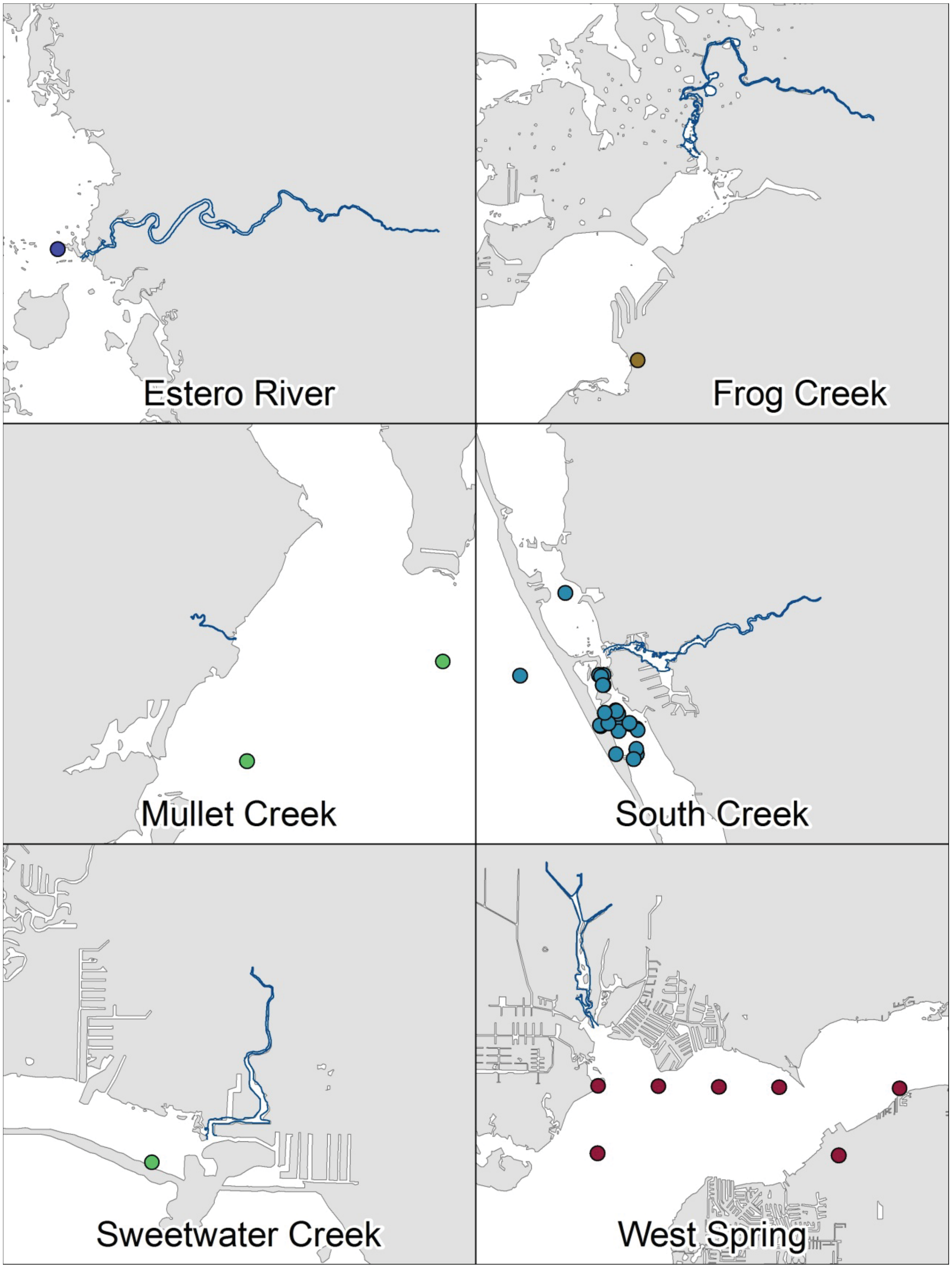

Figure 4-15. Estuarine sites used to calculate annual geometric average of estuarine nutrient concentration. Source = Impaired Waters Rule Run56 database).

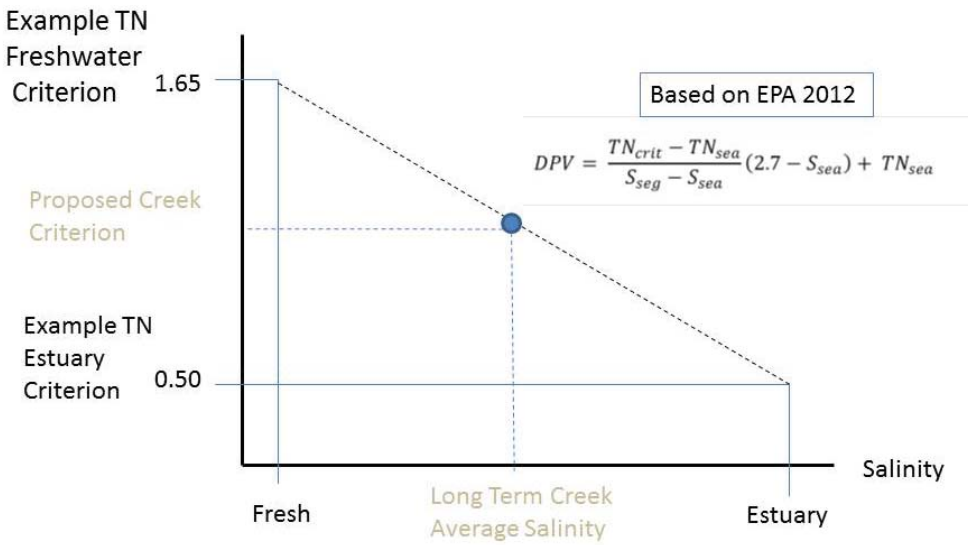

Figure 4-16. Method proposed to establish tidal creek criteria based on freshwater and estuarine criteria (EPA 2012).

While these methods produce plausible estimates of potential numeric nutrient criteria for tidal creeks, the linear dilution approach does not reflect observed or expected instream nutrient dynamics, making the reliability of this approach as protective criteria tenuous. We attempted to develop statistically based empirical nutrient-salinity relationships using nitrogen concentrations at the source water and most downstream sites as covariates to predict nutrient concentrations in the middle reaches of the tidal segment. The results suggested that salinity was not a useful predictor of nutrient concentrations in the middle reaches of the creek if the source water and downstream nutrient concentrations were known. That is, if the nitrogen concentration being delivered from the source water and at the most downstream station are both known, salinity was not a useful predictor of the nitrogen concentration for the two intermediate stations. An example prediction for each creek is provided in Figure 4-17 where salinity increases (green line) did not result in a decreased observed TN concentration in the middle sections of the creek and therefore the predicted nutrient concentrations (red line) were not a function of salinity. This confirms that, while higher salinity creeks may have lower nutrients on average, linear dilution curves do not necessarily represent within-creek nutrient dynamics and, therefore, applying linear dilution type models to establish criteria for tidal creeks would not result in site-specific protective standards. The linear mixed effects model output used for this analysis is provided in Appendix F along with resultant plots for all dates and all creeks.

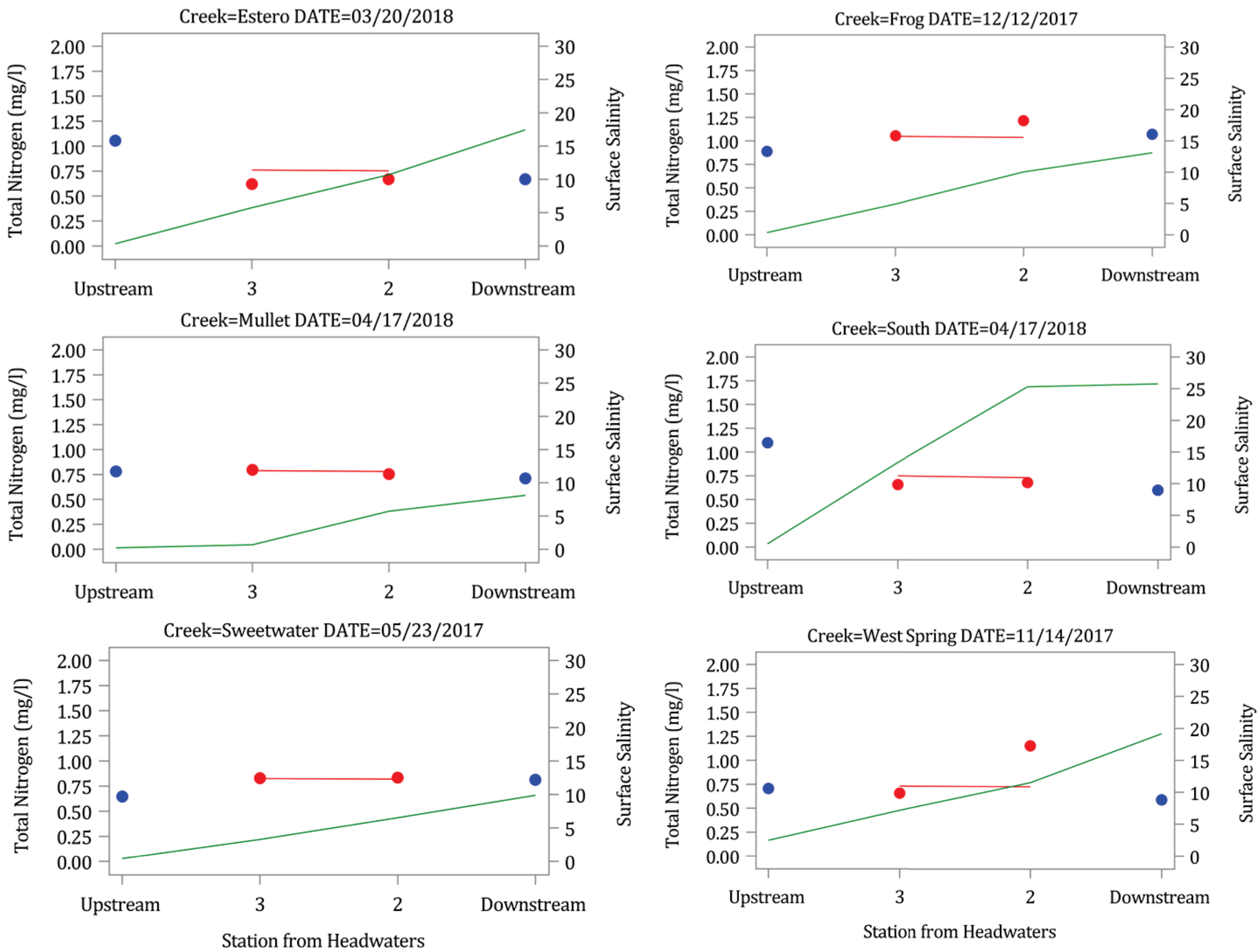

Figure 4-17. Results of linear mixed model TN predictions (red horizontal line) for middle stations based on knowing source water TN and TN at the most downstream station. Green line is surface salinity associated with each sample and dots are observed total nitrogen.

To gain a better understanding of the observed relationships between total nitrogen and salinity in creeks with long term data collection programs, we used the Impaired Water Rule database (Run 56) to identify creeks with water quality (i.e. nutrients and salinity) data collected at multiple locations within the creek on the same date to examine the date-specific nitrogen–salinity relationship in these creeks. For example, the date-specific nutrient-salinity relationships in Bullfrog Creek (Hillsborough County) are provided in Figure 4-18. The majority of curves are flat indicating little change in nitrogen as a function of changes in salinity. When TN concentrations in the freshwater portion of the creek are above 1, there is a higher probability that the curve will have a negative slope and the nutrient concentrations downstream will tend to be less than upstream concentrations.

Using all data in the IWR dataset culled for this analysis, a significant relationship between higher source water TN concentrations and the proportion of slopes that declined as a function of salinity was observed (Figure 4-19). That is, the higher the source water concentration, the more likely that those concentrations were diluted within the estuary. While this seems intuitive, it has important ramifications when drawing inferences based on dilution curves. In addition, the proportion of samples with declining slopes was indicative of the nutrient dynamics in the system as further described below.

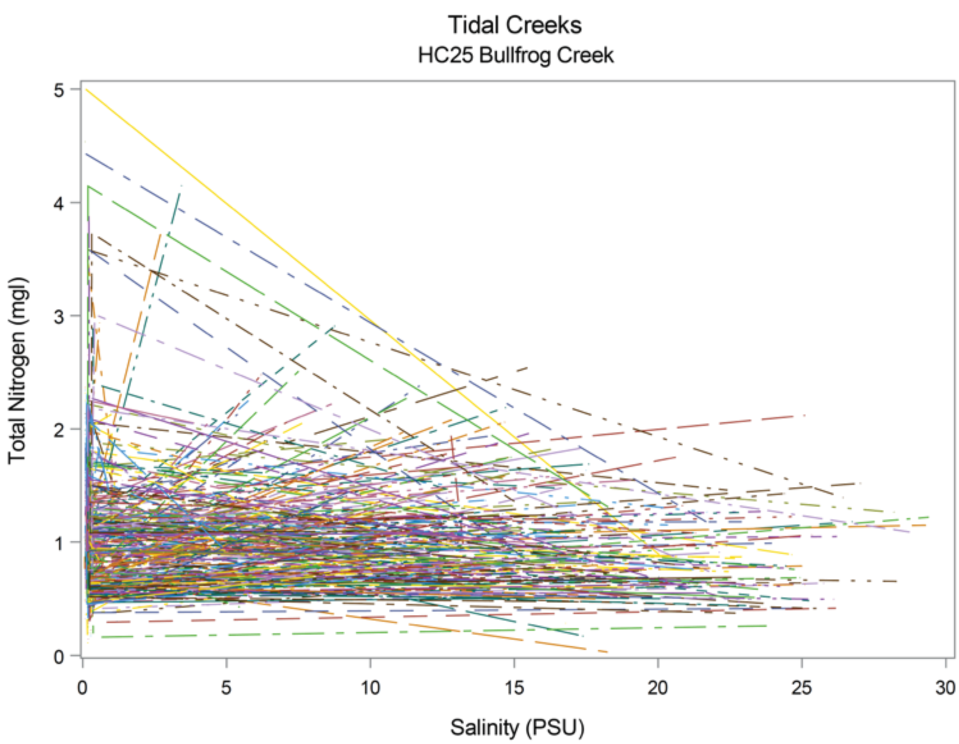

Figure 4-18. Date specific nutrient salinity curves for available data for Bullfrog Creek from IWR Run 56.

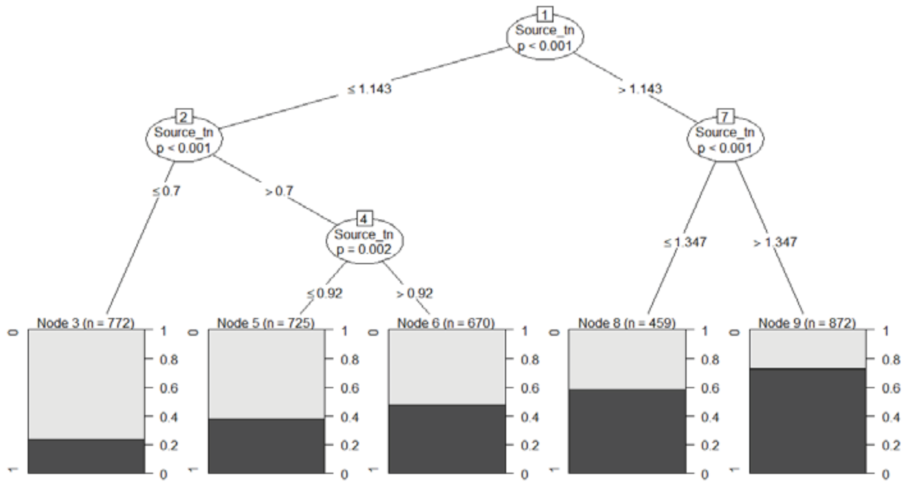

Figure 4-19. Proportion of negative date specific TN Salinity slopes as a function the source water Total nitrogen concentration showing statistically significant breakpoints separating the groups.

The proportion of curves with a declining slope for all creeks in the IWR dataset with sufficient data is listed in Table 4-3. The median percentage of negative slopes was ca. 52%. Plots of the distribution end members (i.e. Delaney and Philippi Creeks) are presented in Figure 4-20.

Table 4-3. Proportion of negative slopes between nitrogen and salinity in tidal creeks with multiple sites sampled on the same date.

Creek	Percent Declining Slopes
Delaney Creek	13.6
Mullock Creek	23.7
Spring Creek	26.8
Saint Joes Creek	38.6
Chantry Canal	47.9
Bullfrog Creek	47.9
Whisky Creek	49.1
Allen Creek	50.0
Estero River	53.8
Cross Bayou	61.2
Sweetwater Creek	63.0
Billy Creek	67.1
Rocky Creek/Channel G	68.4
Catfish/North Creek	68.8
Gottfried Creek	70.0
Hancock Creek	73.4
Phillippi Creek	87.5

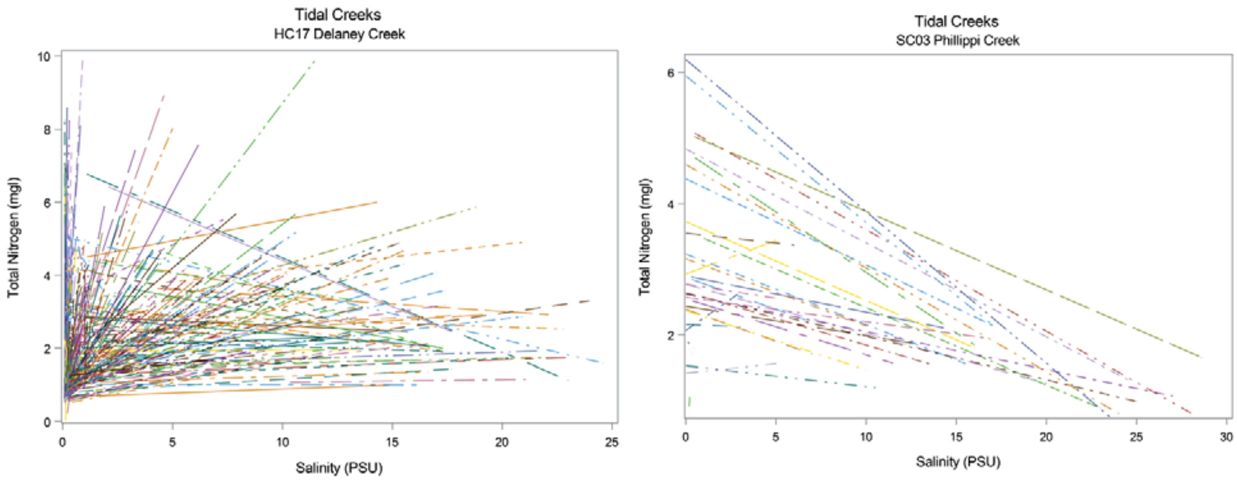

Figure 4-20. Date specific TN – salinity relationships in Delaney Creek (left) and Phillippi Creek (right).

Delaney Creek has a historical point source discharge just above the tidal portion of the creek resulting in increased TN concentrations in the tidal portion relative to its source water. The dataset for Phillippi Creek in the IWR database only has data that met the criteria for evaluation from the 1980's but demonstrates that Phillippi has historically been susceptible to high source water nitrogen concentrations. Creeks with few declining slopes may indicate either low source water concentrations or a potential source in the tidal portion of the creek. Creeks with an extremely high proportion of negative slopes indicate either high source water concentrations or rapid dilution or assimilation. In our study, South Creek had 100% of the dates sampled exhibited a declining slope and also had the highest source water TN concentrations of any creek. Isotope results did not reveal a distinct wastewater signature in South Creek though more work would need to be completed to confirm whether the source of high nitrogen inputs from the source water is natural or anthropogenic. Evaluating nutrient dynamics in this manner provides an indicator that can be further investigated to understand the spatio-temporal dynamics in nutrient delivery to these creeks. While these responses were clearly creek-specific, they can be used to generalize a conceptual expectation for the response of nitrogen in southwest Florida tidal creeks. In general, the nutrient dynamics in Southwest Florida tidal creek consist of three expected phases as described below and depicted in (Figure 4-21):

- **Dry Phase**: In this phase a low volume of freshwater is delivered to the tidal portion of the creek under "base flow" conditions. Source water nutrient concentrations tend to be lower than average and nutrient concentrations in the tidal portion of the creeks are similar to source water concentrations. The tidal concentrations represent an integration of source water inputs, assimilation, organic decomposition of both allochthonous and autochthonous material, outwelling from adjacent mangroves, and potentially sediment flux.

- **Pulse Wet Phase**: Characterized by conditions that generate storm water runoff and direct storm water infrastructure inputs. Freshwater pulses containing higher nutrient concentrations are delivered to the tidal portion of the creek and attenuated by the differential between source and tidal water concentrations. Salinity is a reasonable surrogate for estimation of the dilution of nutrients within the tidal portion of the creek under this phase.

- **Saturated Wet Phase**: Under these conditions the entire creek is essentially freshwater. Nutrient concentrations tend to be (but are not necessarily) higher and there is little to no gradient in nutrient concentrations along the length of the creek.

An observation that the slope in the nitrogen-salinity relationship is consistently positive, as was the case for Delaney Creek, should lead to the investigation for a potential source of high nutrient input in the tidal portion of the creek. Other deviations from this expectation, such as consistently negative slopes, may lead to an investigation of the source water for indications of excessive nutrients contributing to the tidal segment. This simple calculation requires proper sampling design, but can be a powerful tool to identify and eliminate potential sources of nitrogen and would serve as a useful indicator of creek condition. Further examples of this type of outcome are described in Chapter 5.

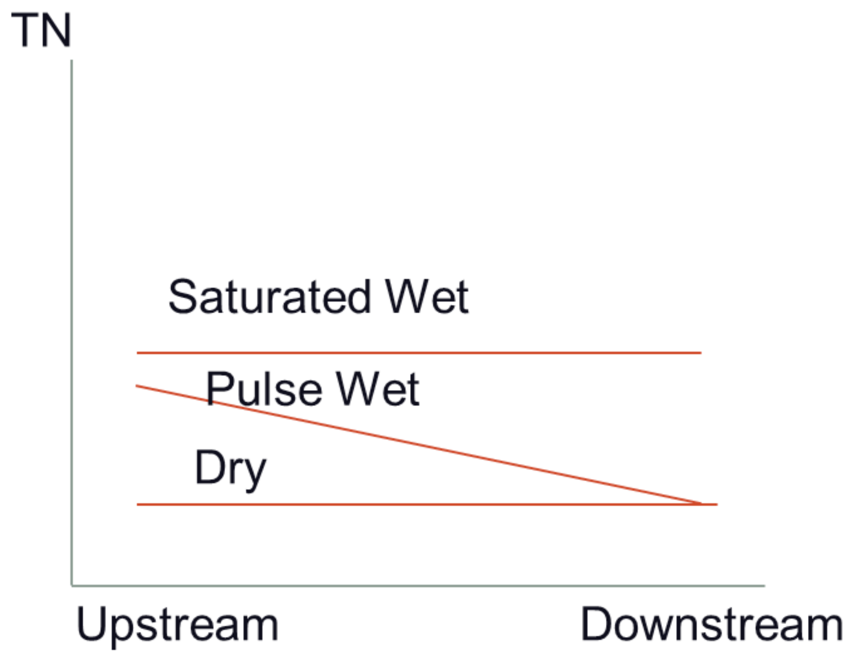

Figure 4-21. Conceptual expectation of nutrient dynamic responses to seasonal or antecedent rainfall conditions in tidal creeks.