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The Effects of Tidal Forcing on Nutrient Fluxes in the Tidal, Freshwater James River Estuary, VA

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by

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Abstract

A 12-month study (January to December 2015) focused on the effects of tidal forcing on nutrient fluxes in the tidal, freshwater segment of the James River Estuary (JRE). Discrete sampling of nutrient chemistry and continuous monitoring of tidal discharge were used to determine the volume and timing of the tides, and differences in nutrient concentrations between incoming and outgoing tides. The goal of this study was to improve understanding of tidal influence on nutrient fluxes and their role in nutrient transport to the lower estuary. Results suggested that differences in nutrient concentrations between incoming and outgoing tides were small throughout the year. This finding suggests that nutrient fluxes at the study site, near the tidal fresh-oligohaline boundary of the James, are largely determined by tidal volume owing to weak concentrations gradients. Changes in water quality during seaward and landward tidal excursions into deeper versus shallower segments were analyzed to infer biogeochemical processes. Differences in oxygen production and nitrate utilization suggest greater autotrophy during landward excursions, consistent with more favorable light conditions. This work was conducted as a collaborative effort between Virginia Commonwealth University, the USGS, Randolph-Macon College, and Washington and Lee University participating in the "Mountains to the Sea" project.

Introduction

Estuaries play a major role in biogeochemical cycling as they are the boundary between inland and coastal waters, and they receive inputs from large contributing areas (Damme et al. 2005). Excessive nutrient loading is problematic in estuaries worldwide. Nutrient sources to estuaries include riverine inputs as well as local point sources, such as wastewater treatment plants and other industry. Excess nutrient concentrations can lead to over- abundance of algae, including some species that may be toxic, increased water column turbidity, issues with drinking water supplies, low dissolved oxygen levels, decreased aesthetics of the water body, and various economic impacts including decreased recreational activity (Smith 2003). The two nutrients of primary concern are nitrogen and phosphorus as these are most often limiting to primary production (Boynton et al. 1995, Carstensen et al. 2011, Bala Krishna Prasad et al. 2010). Phosphorus is transported in association with particulates and therefore loading increases during storm events when discharge and sediment transport are higher (Howarth et al. 2006). Elevated discharge also increases nitrogen inputs to estuaries, which are delivered in both particulate and dissolved (e.g., nitrate, ammonia) forms. Estuarine responses to nutrient inputs are determined by an array of natural and anthropogenic factors particularly those related to water residence time such as riverine discharge and tidal exchange (Ramesh et al. 2009, Smith 2003, Carstensen et al. 2011).

Nutrient concentrations in estuaries are determined by both point and nonpoint source inputs (Figure 1). Point sources inputs are relatively constant year-round and therefore may be a more important source of nutrients to the estuary in summer when riverine inputs are low. In estuaries where point sources deliver the majority of dissolved nutrients, like the James River Estuary

(JRE), decreased riverine discharge in summer months leads to a shift in the ratio of particulate and dissolved nutrients where lower particulate concentrations result in a greater proportion of dissolved nutrients, which have greater bioavailability (Bukaveckas and Isenberg 2013). Estuaries often exhibit low nutrient concentrations in summer due to increased biotic uptake. Biotic uptake is higher during low discharge as increasing autotrophic and heterotrophic biomass drives higher rates of nutrient assimilation (Bukaveckas et al. 2011, Fichez et al. 1992). These processes may be particularly important in tidal, freshwater estuaries, which are known to exhibit high rates of biological production and biogeochemical cycling (Bukaveckas et al. 2011, Damme et al. 2005). Despite this, tidal freshwaters are comparatively understudied relative to the lower, saline segments of the estuary.

Biogeochemical processes that occur in estuaries allow them to mediate a portion of the anthropogenic nutrient load before it reaches coastal waters (Paerl et al. 1998). Biotic assimilation of dissolved inorganic nutrients converts them to particulate organic forms, which can lead to retention through sedimentation (Josefson and Rasmussen 2000). Phytoplankton assimilate nutrients and when these organisms die, remains may settle to the sediments. These nutrients may become sequestered (via sediment accretion), or remineralized and rereleased into the water column. Excess nutrient loading can inhibit an estuary's ability to reduce downstream nutrient transport because biotic uptake and other forms of retention mechanisms become saturated (Carstensen et al. 2011). Nutrient retention occurs year-round but rates are affected by seasonal fluctuations in riverine discharge, and prior work has shown that estuaries can retain up to 65% of total nitrogen and 55% of total phosphorus inputs (Nixon et al. 1996). High discharge decreases water residence time, which limits algal uptake of nutrients (Wood and Bukaveckas 2014), thereby resulting in lower nutrient retention within the estuary. Aside from nutrient export during high discharge, other loss mechanisms for nutrients include denitrification and tidal exchange (Boynton et al. 1995).

The ability of tides to increase and decrease water level and allow for the exchange of water and materials between the upper and lower segments of the estuary effects abiotic and biotic processes in estuaries (Davies and Ugwumba 2013). On a short time scale (hours), an outgoing tide creates advection of water, and its constituents, downstream. This is followed by an incoming tide causing the intrusion of water and constituents from the lower estuary. In this way, tidal exchange influences the nutrient concentration, salinity, and suspended particulate matter of an estuary (Montani et al. 1998). Intrusion of downstream water during incoming tides can alter nutrient concentrations in the upper estuary depending on the extent to which nutrient concentrations differ between the upper and lower estuary. Tides can alter suspended particulate matter, including nutrients in particulate form, through turbulent resuspension of sedimented particulate matter (Montani et al. 1997, Gilbert et al. 2013). Knowing the role the tides play in nutrient transport is an important aspect of the nutrient cycle in estuaries particularly to understanding nutrient availability to support primary production and effects on nutrient retention.

A nutrient mass balance approach can be used to determine nutrient inputs, outputs and retention within an estuary. Previous research on the JRE developed a monthly mass balance for N and P using data on riverine and point source inputs for the period 2007-2010 (Bukaveckas and Isenberg 2013). This study estimated tidal fluxes using a chloride mass balance approach (Bukaveckas and Isenberg 2013). The chloride mass balance approach assumes that chloride behaves conservatively within the estuary (i.e. inputs are equal to outputs because of low biological demand). Chloride concentrations were measured within the estuary to calculate the month-to-month change in mass of chloride. As Cl inputs were also known, the effect of tidal exchange (i.e., as a net gain or loss of Cl) could be inferred by difference. Net tidal exchange was correlated with the tidal prism (a product of tidal amplitude and surface area) and therefore continuous monitoring of water elevation could be used to derive estimates of tidal exchange. Nutrient fluxes were calculated based on these estimates of tidal exchange and incorporated in the mass balance to estimate nutrient retention. The results suggested that tidal exchange was responsible for a net loss of nutrients but that its role in the nutrient budget was minor because flux differences between inputs and outputs was less than 1% (Bukaveckas and Isenberg 2013).

The recent installation of a discharge and water quality monitoring station at Point Weyanoke provides an opportunity to directly measure tidal-driven water fluxes in the James River Estuary. In conjunction with discharge monitoring, nutrient concentrations were measured during incoming and outgoing tides to directly determine the chemical difference between tides. The findings from this study will contribute to a greater understanding of the influence of tides on nutrient availability in the tidal freshwater segment of the JRE and their role in nutrient transport to the lower (saline) estuary. The primary objective of this project is descriptive: examining how nutrient concentrations change during an incoming versus an outgoing tide (and how this varies seasonally). Additionally, there was a hypothesis testing component comparing changes in water chemistry during tidal excursions into deeper vs. shallower segments of the estuary. Specifically, I hypothesized that higher levels of productivity in shallower areas would allow for greater increases in dissolved oxygen and loss of nitrate by autotrophic assimilation relative to tidal excursions into deeper segments of the estuary. This work was conducted as part of a collaborative effort between VCU, the USGS, and other universities participating in the "Mountains to the Sea" project.

Methods

This was a 12-month study (January to December 2015) combining discrete sampling and continuous monitoring to determine the volume and timing of the tides, and differences in water quality and nutrient concentrations between incoming and outgoing tides. Water velocity data were used to determine the timing in ebb and flow, and, along with cross-sectional area, to determine the associated tidal discharge. Total nutrients, dissolved nutrients, total suspended solids, particulate organic carbon, dissolved organic and inorganic carbon, and chlorophyll a (March-October only) were measured each month during an incoming and outgoing tide. These data and continuous monitoring data were used to assess tidal effects on water quality.

Study area

The James River, VA is 340 miles long with a drainage area of 26,165 km^2 (Bukaveckas et al. 2011). From its headwater to the Fall Line at Richmond, the river is characterized by unidirectional flow. At the Fall Line, the river becomes tidal; this is where the JRE starts. The estuary is fresh water from Richmond to the confluence with the Chickahominy River. Point Weyanoke (USGS station 02042222), located near the downstream end of the tidal, freshwater segment, is the site where data were collected for this study (Figure 2). The relatively narrow channel at this location facilitates accurate measurement of discharge from continuous velocity measurements. Chemistry data collected at this location serve to characterize the exchange of materials across the oligohaline-tidal fresh boundary.

Continuous monitoring data were used to characterize changes in water quality during inland and seaward excursions from Point Weyanoke. The hypothesis is that water traveling inland will undergo chemical changes that differ in magnitude compared to water moving seaward; these effects were expected to differ between daytime and nighttime (Figure 3). During inland, daytime excursions it was expected that water would have greater increases in dissolved oxygen and loss of nitrate due to higher level of primary production, whereas on seaward, daytime excursions, water will have a smaller changes in dissolved oxygen and in nitrate. The expected results are due to the channel geomorphometry of the tidal, freshwater JRE.

Continuous monitoring

The continuous monitoring station (Point Weyanoke near Charles City, VA) is located within the tidal, freshwater JRE, 64 miles above the mouth of the James. The station is maintained by the USGS (#02042222) and records water velocity (m/s), surface elevation (m), and discharge (m^3/s) every six minutes. Water surface elevation is measured with an OTT Compact Bubbler Sensor (CBS) self-contained pressure sensor system, and velocity is measured with a Sontek SL-500 Acoustic Doppler Velocity Meter (ADVM). The ADVM uses horizontal and vertical beams to measure water velocity across a portion of the channel. Cross-sectional water velocity is estimated by relating ADVM measurements to periodic cross-channel velocity measurements made with a RiverRay Acoustic Doppler Current Profiler (ADCP). The channel cross-sectional area is multiplied by the continuous (6-min. interval) water velocity data to obtain continuous discharge data. Water temperature (^{o}C), specific conductance (μS/cm), turbidity (FNU), pH, and dissolved oxygen (mg/L) are measured every 15 minutes using a YSI-6920 multiparameter water quality sonde. Nitrate (mg/L) is measured every 15 minutes using a SATLANTIC Submersible Ultraviolet Nitrate Analyzer (SUNA) V2 nitrate monitor, which is a UV-nitrate sensor that determines nitrate concentrations based on in-situ ultraviolet spectroscopy. Data from this station are available from July 2, 2014 to present; data through December 31, 2015 were analyzed for this project.

Discrete sampling and laboratory analysis

Discrete sampling was conducted every four weeks using a Teledyne Isco 3700 autosampler programmed to take 15 hourly samples over a complete tidal cycle (inflow and outflow). The samples were kept on ice (in the ISCO and after sampling) and brought back to the lab for filtering and analysis. Samples were analyzed for total nutrients, dissolved nutrients, total suspended solids (TSS), particulate organic carbon, and dissolved organic and inorganic carbon and chlorophyll a. All parameters were measured monthly with the exception of chlorophyll, which was sampled during the warm-weather period (March to October).

For total nutrients, 40 mL of unfiltered sample was stored in a plastic centrifuge and frozen until analysis. For dissolved nutrients, a measured volume of sample was filtered through a 47 mm glass fiber filter and preserved with concentrated sulfuric for storage (at 4^{o}C for no more than 28 days) until analysis. A SKALAR CFAA System San++ Automated Wet Chemistry Analyzer (Continuous Flow Analyzer) was used for determination of total nitrogen, nitrate, ammonia, ortho-phosphate, total phosphorus, and chloride. Total nitrogen and total phosphorus were determined using an alkaline persulfate digestion (minimum detection limits 0.012 mg/L, 0.017 mg/L, respectively).

An oven-dried PALL 47 mm glass fiber filter was used for total suspended solids (TSS). 200-400 mL of sample was filtered through a pre-weighed filter using a GAST vacuum (DOA-P704-AA), and then dried at 70^{o}C for at least 72 hours. TSS is calculated by subtracting the initial filter weight from the sample weight and dividing by the volume of sample filtered. The same filter was used for particulate organic carbon and nitrogen analysis performed on a Perkin-Elmer CHN analyzer. Laboratory analysis completed by VCU Environmental Analysis Lab.

To determine chlorophyll-a concentrations, 50-200 mL of sample was filtered through a 47 mm glass fiber filter. The filter is frozen (up to 3 weeks) until analysis. For analysis, the filters are ground and extracted overnight in 10 mL of acetone. A sub- sample was analyzed using a TD-700 fluorometer. Reported chlorophyll a concentrations are total values (not corrected for pheophytin).

Data Analysis

Hydrodynamics

While many studies use stage to characterize tides, this study used water velocity because it more accurately describes the rate of water movement (Montani et al. 1998; Gilbert et al. 2013; Davies and Ugwumba 2013). Negative velocity values were used to characterize incoming tides (flow) and positive velocities were used to indicate outgoing tides (ebb) (Figure 4). Chemistry data were similarly analyzed in relation to the direction of water velocity to characterize differences in concentrations under ebb and flow conditions.

Data obtained from the ADVM were processed using JMP to derive average daily incoming and outgoing water velocity. The number of positive and negative velocity measurements was used to determine the total duration of incoming and outgoing tides for each day. Tidal durations were multiplied by the average discharge to derive daily incoming and outgoing discharge. Net tidal exchange was derived as the difference between outgoing and incoming daily discharge. Daily tidal amplitude was derived as the difference between daily maximum and minimum water surface elevation. Daily river discharge entering the tidal fresh segment was calculated by summing daily discharge measurements from three USGS river monitoring stations, Appomattox

River at Matoaca (#02041650), James River near Richmond (#02037500), and James River and Kanawha Canal near Richmond (#02037000).

Chemical difference between tides

Total nutrients, dissolved nutrients, total suspended solids, particulate organic carbon, dissolved organic and inorganic carbon, and chlorophyll a measurements obtained from the discrete hourly sampling were averaged for incoming and outgoing tides for the study period in each month. Two-way ANOVAs were performed using JMP with month, tide, and month*tide as explanatory factors to examine whether there were statistically significant differences in concentrations between tides and across months.

Excursion analysis

Changes in water quality during inland and seaward excursions were analyzed by comparing mean values during out-going and returning tides. Continuous temperature, dissolved oxygen, and nitrate data were obtained for tidal cycles that coincided with solar cycles throughout the study period. For daytime tides, these were tides starting between 06:15 and 08:06; for nighttime tides, it was tides starting between 21:15 and 23:00. Approximately 50-80 tides were used for each of the 4 scenarios (daytime and nighttime, and inland and seaward). Mean values for outgoing tides were subtracted from mean values for returning tides to estimate the change in water temperature, dissolved oxygen and nitrate during the tidal excursion. Results were compared for daytime vs. nighttime and inland vs. seaward excursions.

Results

Hydrodynamics

Daily discharge at Point Weyanoke was on average 118 million m^3/d for outgoing tides and 96 million m^3/d for incoming tides during 2015 (Figure. 5). Greater discharge for outgoing tides was associated with longer tidal duration relative to incoming tides (mean = 13 and 11 hours, respectively). By comparison, riverine discharge was generally less than 20 million m^3/d except during storm events (e.g., on 03/07/15 16,328 m^3/s, 04/22/15 42,399 m^3/s, 10/04/15 82,428 m^3/s, and 12/26/15 66,100 m^3/s). The influence of storm events produced a large range of variation in riverine discharge (up to 100 million m^3/d). Theoretically, the difference between incoming and outgoing tidal discharge (net daily discharge) should be equal to riverine discharge, since these are the main components of the estuary's water balance. The net daily discharge (outgoing minus incoming) averaged 22.5 million m^3/d while total riverine discharge averaged 16 million m^3/d. The discrepancy in the water budget (<10 million m^3/d) was small in relation to the magnitude of tidal and fluvial discharge (~100 million m^3/d). Overall, the main finding from the hydrodynamic data was that water fluxes in the tidal fresh segment of the James were largely driven by tides, with riverine discharge equivalent to ~10% of tidal fluxes. These results suggest a strong potential for tidal exchange to influence water quality conditions in the tidal fresh segment if chemical concentrations differ between incoming and outgoing tides.

Tidal influences on water chemistry

Daily average values derived from continuous monitoring data for July 2014 to December 2015 were used to assess patterns in seasonal variation in water quality (Figure 6). Temperature ranged from 0.5^{o} C in Winter 2015 to ~30^{o} C in summer. Specific conductance was elevated during fall months (>1100 μs/cm) likely due to low river discharge, which allows greater influence from the saline lower estuary. Specific conductance was low (<300 μs/cm) in other months reflecting dilute riverine inputs. Turbidity peaked during a storm event in September 2015 (547 FNU) while normally remaining below 50 FNU. Nitrate (NO_3) concentrations (from SUNA) peaked in Fall-Winter (~0.5 mg/L) followed by a decrease into late spring and summer (to ~0.1 mg/L). DO and pH showed an inverse relationship with DO increasing in cooler months (~11.8 mg/L) and dropping in warmer months (~7.5 mg/L) while pH increased to ~8.6 in warmer months and dropped to ~7.3 in cooler months. This evaluation of seasonal variation provides a context for examining finer-scale variation due to tidal exchange.

A comparison of the daily mean values of each water quality parameter for incoming and outgoing tides was used to assess the effects of tidal forcing on water quality conditions in the tidal fresh segment (Figure 7). Temperature differences were typically ~0.2 ^{o}C with no consistent difference between incoming and outgoing tides. Specific conductance showed little variation between tides except for the fall months when there were large differences between incoming and outgoing tides (up to 67 μs/cm) but little consistency as to which tides had higher values. This result was intriguing because it would be expected that specific conductance would be consistently higher on incoming tides. Dissolved oxygen was found to be higher on outgoing tides for the majority of the study period (with a mean difference of -0.2 mg/L ± 0.0). The mean difference in pH between incoming and outgoing tides was not significantly different from zero. Turbidity showed varying degrees of differences between tides, with differences ranging from 0 to 16 FNU (mean difference 1 FNU ± 0). A significant difference in nitrate concentrations was not observed (mean difference 0.01 ± 0.00). Overall, these data suggest that differences in water quality between incoming and outgoing tides were small (<10%) relative to the range of seasonal variation.

Discrete sampling data were analyzed using two-way ANOVAs to determine whether there were statistically significant differences in concentrations between tides (incoming vs. outgoing) and across months. Results from the ANOVAs suggested that differences in concentrations were significant across months but neither tide nor the combination of tide and month was found to be significant (Table 1, Figure 8). Total nitrogen, nitrate, and ammonia peaked during winter months while concentrations were lowest during summer months. Total nitrogen peaked at 0.98 mg/L in February and dropped to ~0.4 mg/L in the summer months. Total phosphorus peaked in the summer months (~0.05 mg/L) remaining below 0.03 mg/L in cooler months with the exception February (~0.04 mg/L). Particulate organic carbon and particulate organic nitrogen showed similar trends increasing throughout winter and spring, peaking in August, and then dropping off through fall and winter. When not observing by season, data suggest that incoming tides had greater nutrient concentrations more frequently than outgoing tides. This was true in December, March, July, and August. This result was not observed in other months, and as a result, tide was not found to be a significant predictor of variation in water chemistry.

Excursion analysis

Results from the daily averages of continuous monitoring and discrete sampling data suggest that chemical differences between incoming and outgoing tides were small. An excursion analysis was performed to determine whether differences between tides became apparent when correcting for the effects of solar cycles and taking into account inland vs. seaward water transport (Figure 9). Greater increases in temperature were seen during daytime inland excursions (0.51 ± 0.05 ^{o}C) compared to daytime seaward excursions (0.40 ±0.03 ^{o}C). Similarly, greater increases in dissolved oxygen were seen during daytime inland excursions (0.90 ± 0.10 mg/L) compared to daytime seaward excursions (0.23 ± 0.04 mg/L). Nitrate decreased during inland excursions (-0.005 ± 0.002 mg/L) while increases in nitrate occurred during seaward excursions (0.008 ± 0.001 mg/L). Nighttime excursions also showed consistent differences with greater temperature decreases occurring in inland excursions (-0.24 ± 0.03 ^{o}C) compared to seaward excursions (-0.15 ± 0.02 ^{o}C). Dissolved oxygen showed greater losses during nighttime seaward excursions compared to inland (-0.23 ± 0.02 mg/L, -0.13 ± 0.04 mg/L, respectively). Nitrate concentrations showed decreases during inland excursions (-0.006 ± 0.001 mg/L) and increases during seaward excursions (0.004 ± 0.002 mg/L). Hourly rates were calculated for each parameter to correct for potential effects of unequal tidal duration, but these demonstrated similar patterns and therefore are not presented here. Overall, this analysis showed that during inland excursions, changes in temperature, dissolved oxygen and nitrate were greater than those observed during seaward excursions.

Nitrate data comparison

Continuous data from the SUNA nitrate sensor were compared to monthly discrete sampling from Point Weyanoke and weekly discrete sampling at James River mile 56 and 69 to examine differences in nitrate concentrations and seasonal patterns resolved by the various methods of data collection. All three datasets showed similar seasonal trends increasing from summer to fall, peaking in late winter, and then dropping off summer months. Similar peak values were observed (~0.4 mg/L Winter 2015). However, there were differences among the methods during periods of low nitrate concentration (June – September 2015). SUNA values ranged from 0.09 – 0.27 mg/L while discrete data from Weyanoke and River mile 56 and 69 showed that nitrate concentrations fell to 0.00- 0.02 mg/L. There were discrepancies between the discrete sample at Weyanoke, and the discrete sampling at JMS 56 and 69, and SUNA values from September – December where Weyanoke discrete values were yielding lower values than the other methods. Weyanoke discrete values remained between 0.090 – 0.12 mg/L while the other data ranged from 0.19 – 0.54 mg/L. Results from linear regressions among the four datasets suggest that the SUNA data were most associated with the JMS 69 data (n = 52, r^2= 0.76), followed by JMS 56 (n = 50, r^2 = 0.67), and lastly the discrete samples collected at Weyanoke (n = 12, r^2 = 0.48). SUNA values tended to be higher than discrete sample values. The slopes of each regression were less than 1, falling between 0.70 – 0.92 with intercepts ranging from -0.04 - -0.07. All three time series for nitrate showed similar seasonal trends, but the data suggests that the SUNA values show more daily oscillation of nitrate and variation with more detail than weekly or monthly sampling can afford.

Discussion

Hydrodynamics

Continuous monitoring of water velocity at Point Weyanoke provided a basis to directly measure tidal exchange in the James River for the first time. The results show that tidal-driven water fluxes were large in comparison to riverine (watershed) inputs. Tidal water fluxes ranged from ~-65 million to 170 million m^3/d while riverine discharge was typically less than 20 million m^3/d. During storms, riverine discharge could approach and even exceed values for daily tidal inflow. Four such events were observed in 2015. Seasonal and event-driven variation in discharge is expected for a riverine-dominate estuary whereas little to no seasonal variation may be expected for a tidal-dominated estuary. Estuaries that undergo wet and dry seasons such as the Ord

Estuary in Western Australia experience drastic annual variation in discharge due to monsoons (Coleman and Wright 2016). Unlike the Ord where monsoons and evaporation largely drive riverine discharge, water uptake via evapotranspiration drives seasonal variation in riverine discharge in temperate regions. Results from this study show that riverine discharge to the James can occasionally exceed tidal inflow during rain events in winter months (November through March) when evapotranspiration is low.

Seasonal patterns in net tidal discharge were not observed as was for riverine discharge suggesting that other sources of water to the JRE may dampen seasonal variation. Other sources include point sources, groundwater inputs, small streams, and atmospheric deposition. It is unclear why the annual average of net daily discharge was 6.5 million m^3/d larger than total riverine discharge as these would be expected to equal (water input-output balance). Point sources, groundwater inputs, small streams, and atmospheric deposition were not included as inputs. Also, adjustments for tidal height variation were not included. These would not make up for such a large difference in discharge but could reduce this discrepancy. This result will need further investigation before it can be explained.

Chemical difference between tides

Seasonal variations in water quality conditions within the James were considered in the context of external factors (e.g., tidal and fluvial inputs) and internal processes such as primary production and decomposition. External factors likely played an important role in regulating water temperature, specific conductance, and turbidity. Their influences included seasonal effects on water temperature due to variable solar heating and ambient (air) temperature, and the occurrence of storm-driven variation in turbidity due to high discharge events. Nutrients, dissolved oxygen, and pH were influenced by these external factors and by internal processes, primarily by biotic activity. Nitrate concentrations were highest in late fall through the winter when there was low biotic uptake (autotrophic and heterotrophic assimilation; Bukaveckas and Isenberg 2013). Nitrate concentrations decreased in late spring and summer during peak biotic activity. Seasonal changes in DO reflect changes in water temperature as well as biological influences via photosynthesis and respiration (Spillman et al. 2007) Similarly, pH increases in summer because carbon dioxide, which acts as an acid, decreases with photosynthesis. In cooler months, when primary production decreases, DO concentrations return to atmospheric equilibrium, and pH decreases.

The availability of continuous monitoring data provided an opportunity to examine finer-scale variation to determine the effect of tidal exchange on water quality conditions. Temperature data did not reveal consistent differences between incoming and out-going tides, but excursion analysis that took into account the confounding effects of solar cycles showed differences in the rate of heat gain during tidal excursions above and below Point Weyanoke. The channel to surface area ratio played a role in that the inland reach had a greater surface area to volume ratio resulting in greater temperature gain. Changes in dissolved oxygen were also greater during inland excursions. Shallower depths on the landward side of Point Weyanoke not only favor greater heating, but also provide more favorable light conditions for phytoplankton (Wood and Bukaveckas 2014). Greater oxygen gain is attributed to higher productivity where highest chlorophyll-a levels are typically observed (Wood and Bukaveckas 2014). Nitrate concentrations were higher on incoming tides, suggesting that areas downstream of Point Weyanoke are a source of nitrate to the tidal fresh segment. This may be due to the high levels of productivity that occur above Point Weyanoke, which cause nitrate depletion.

Differences in concentration were observed between tides for many of the nutrient fractions, but the ANOVA results suggest that the direction of tides was not a significant predictor of variation in nutrient concentrations. A mass balance estimating the tidal exchange in the JRE had previously found that differences between nutrient input fluxes were small (Bukaveckas and Isenberg 2013). Despite large tidal volumes, the small differences in concentration between incoming and outgoing tides resulted in small differences in net nutrient fluxes. A short-term study on a tidal estuary in Japan found nutrient concentration and ratio changes due to tidal cycles and that the effect differed based on tidal amplitude where differences in concentration were greater when tidal amplitude was greater (Montani et al. 1998). A study based on an estuary in Nigeria found that tidal circulation played a significant role in nutrient availability for primary production due to periods of destabilization (Davies and Ugwumba 2013). For estuaries that exchange water directly with the marine environment, strong concentration gradients along the length of the estuary result in large tidal-driven mass fluxes. For long, narrow estuaries such as the James, weak concentration gradients in the upper estuary result in small differences in tidal fluxes, despite large tidal volumes.

Seasonal patterns in nutrient concentrations observed in the James are consistent with previous findings. The discrete (weekly, monthly) measurements of nitrate showed similar patterns to the continuous (SUNA) data, with nitrate peaking in the winter and decreasing in the summer. Total nitrogen and ammonia also peaked in the winter and decreased in summer months. Higher total nitrogen, nitrate, and ammonia in the winter months is likely due to greater riverine discharge, especially for particulate (TN) fractions, and lower biological demand within the estuary when water temperature is low.

Total phosphorus concentrations peaking in the summer may be evidence that sources of total phosphorus were not as upstream-dependent as total nitrogen. Previous work on the JRE found that approximately 80% of phosphorus loads came from riverine sources where phosphorus was carried in its particulate form during high discharge events (Bukaveckas and Isenberg 2013; Wood and Bukaveckas 2014). Tidal differences in TP and ortho-phosphate observed in this study were found to be insignificant.

Other studies have also found that many of the studied nutrient constituent concentrations were not significantly different between tides (Davies and Ugwumba 2013; Ribas-Ribas et al. 2012; Valiela et al. 1978). Researchers suggested differing causes for why the tides may not have lead to significant nutrient differences including biological influence (biotic uptake or sedimentation), light and dark variability (Ribas-Ribas et al. 2012), retention before the estuary (via assimilation), or denitrification (Gilbert et al. 2013). All of which would create a more complex nutrient cycle adding sources of nutrient import and export other than tidal exchange. In the JRE, high levels nutrient retention occur upstream of Point Weyanoke (Wood and Bukaveckas 2014; Bukaveckas and Isenberg 2013). However, variations in riverine discharge and nutrient concentrations suggest that nutrient concentrations were more determined by riverine and point sources than tidal exchange. Findings from the Bukaveckas and Isenberg study support this conclusion where it was observed that nutrient export from the study reaches followed riverine discharge patterns. Researchers from various studies linked the tides to remineralization due to turbulence (Davies and Ugwumba 2013; Gilbert et al. 2013; Morales-Zammorano et al. 1991), which may be the case with the JRE. Studies such as these suggest that though the tides may not always play a significant role in nutrient concentrations as a standalone factor, the tides may exacerbate already occurring processes in estuaries through resuspension or lengthened water residence time.

Excursion analysis

Although the tides may not play asignificant role in nutrient fluxes in the James, results from the excursion analysis suggested that continuous monitoring data may be used to better understand how channel geomorphometry influences ecosystem function. The results showed that daytime inland excursions were associated with larger increases in temperature and dissolved oxygen and decreases in nitrate. This suggests that autotrophs were assimilating nitrate and increasing dissolved oxygen as a result of photosynthesis. The nighttime results support this conclusion with losses in dissolved oxygen. These results differed from seaward excursions, which had smaller temperature and dissolved oxygen differences and increased rather than decreased nitrate concentrations. This difference in results between inland and seaward excursions may be explained by differences in channel morphometry above and below Point Weyanoke (Figure 11). Above Point Weyanoke (inland excursions), the channel is wide and shallow. This allows for greater light availability and water residence time, both supporting primary production. Downstream of Point Weyanoke, the channel is deeper and narrower decreasing light availability and water residence time. Both of which constrain primary productivity. Little to no biotic uptake may explain why excess nitrate remains in the water. On inland excursions, the surface area to volume ratio is higher than the ratio on seaward excursions. Therefore, inland excursions favor autotrophy while seaward excursions do not. Other research has supported this concept with results suggesting that light availability is one of the determining factors in primary production and that light availability can be inversely related to channel depth (Cloern 2001, Cloern 2007, Sellers and Bukaveckas 2003).

Nitrate data comparison

The SUNA and discrete sampling nitrate data generally showed good agreement throughout the study period. Discrepancies that occurred between SUNA data and discrete data when SUNA concentrations remained higher than discrete concentrations may have arisen from the minimum detection limit of the SUNA falling above the discrete sampling limit of detection. This would suggest that the SUNA over-estimates nitrate when the concentrations are low. Discrepancies that occurred when discrete Weyanoke values remained low while discrete samples from JMS 56 and JMS 69 and SUNA values increased may be due to an issue with inadequate sample cooling in the ISCO. If samples inside of the ISCO increased in temperature, biotic uptake may have occurred creating false low values for discrete Weyanoke samples. While each sampling method suggests similar seasonal trends, future research should be mindful of minimum detection limits of methods if being used in areas such as the JRE where concentrations are low in summer months and holding times must be taken into consideration if analysis is not in-situ. A study on the Mississippi River using the same technology found that SUNA-based nitrate measurements were highly correlated ($r^2 = 0.99$) with concentrations measured from discrete sampling (Pellerin et al. 2014). The discrete sampling may not be highly correlated with the SUNA data in the JRE due to a lower nitrate range, 0.00 – 0.48 mg/L, compared to 0.22 – 2.97 mg N/L in the Mississippi. In the JRE, the availability of high frequency nitrate data allowed for investigation of fine-scale nitrate changes that could be overlooked with even the hourly discrete monitoring as was seen with the excursion analysis.

Conclusions

Overall, results from this study suggest that the tides do not play a significant role in affecting the nutrient chemistry of the tidal fresh segment of the James River. These finding are supported by earlier estimates of tidal exchange that found that differences in nutrient input and output fluxes were < 1% (Bukaveckas and Isenberg 2013). With the use of continuous data, this study was able to examine the role of the tides in nutrient fluxes when tidal cycles coincide with solar cycles. These data suggested that in these cases the tides could lead to different effects based on direction of the tidal movement. In the case of the JRE, water travels through a channel with a high surface area to depth ratio upstream of Weyanoke and a channel with a smaller channel area to depth ratio downstream of Weyanoke. These differences in channel morphology lead to differences in rates of temperature gain, oxygen production and nitrate loss during tides that coincide with solar cycles. These results suggest that the tides alone do not cause significant differences in nutrient concentrations but differences may arise when factors are examined together. These findings illustrate the benefits of continuous monitoring for studying biogeochemical processes at fine-scale .

Table & Figures

Table 1. Two-way ANOVA comparing water chemistry parameters and inland or seaward tides and months using data from hourly discrete sampling one day each month during 2015 at Point Weyanoke, VA.

	Parameter p-Value									
Factor	Total Nitrogen	Total Phosphorus	Nitrate	Ammonia	Ortho-phosphate	Chloride	Total Suspended Solids	Chlorophyl-a	Particulate Organic Carbon	Particulate Organic Nitrogen
Month	<.001	0.358	<.001	<.001	<.001	0.003	0.015	0.022	0.302	0.024
Tide	0.846	0.674	0.794	0.560	0.160	0.554	0.187	0.597	0.925	0.588
Month*tide	0.248	0.639	0.132	0.057	0.309	0.417	0.239	0.655	0.536	0.354
Number of Observations	176	176	176	176	176	176	176	103	176	176

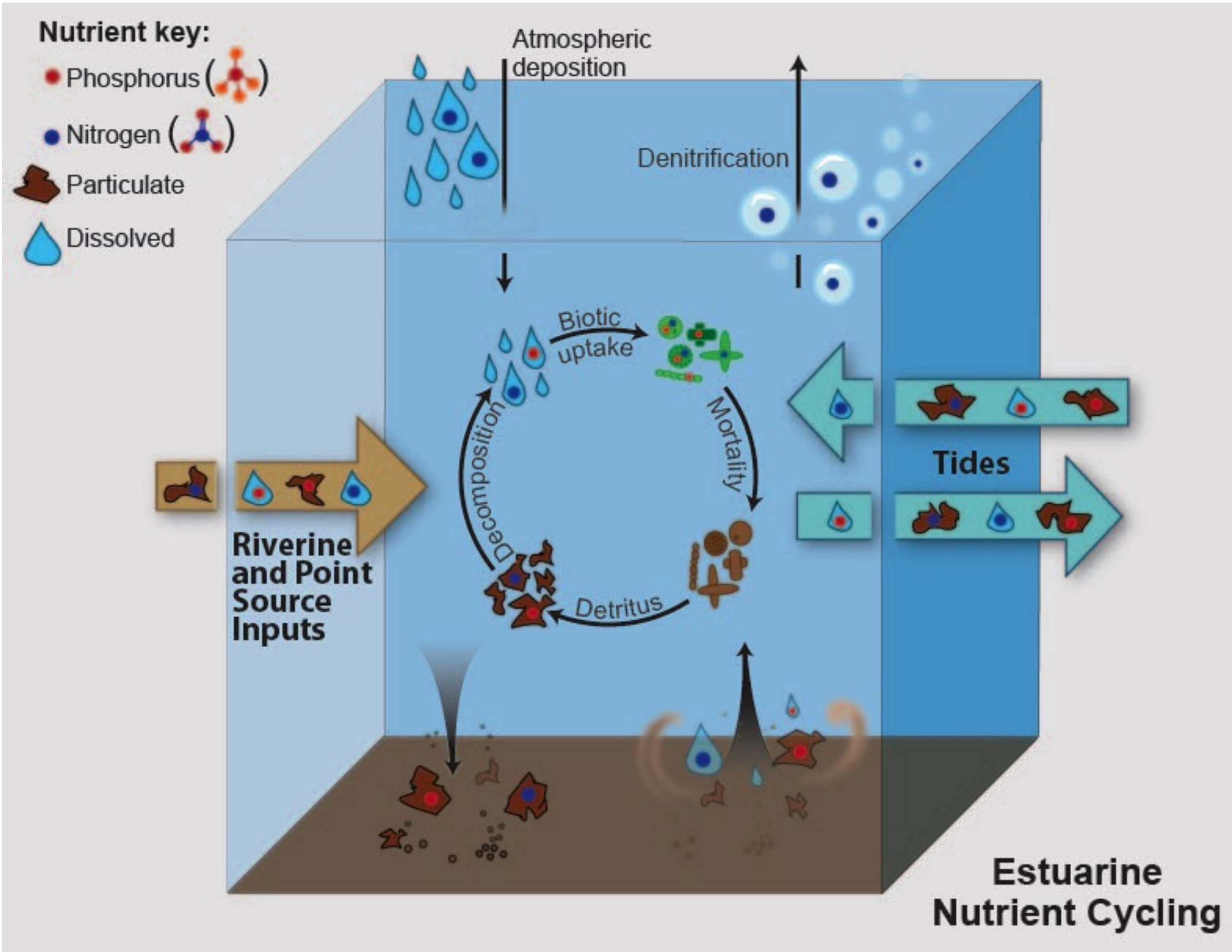

Figure 1. Nutrient cycling in the James River Estuary

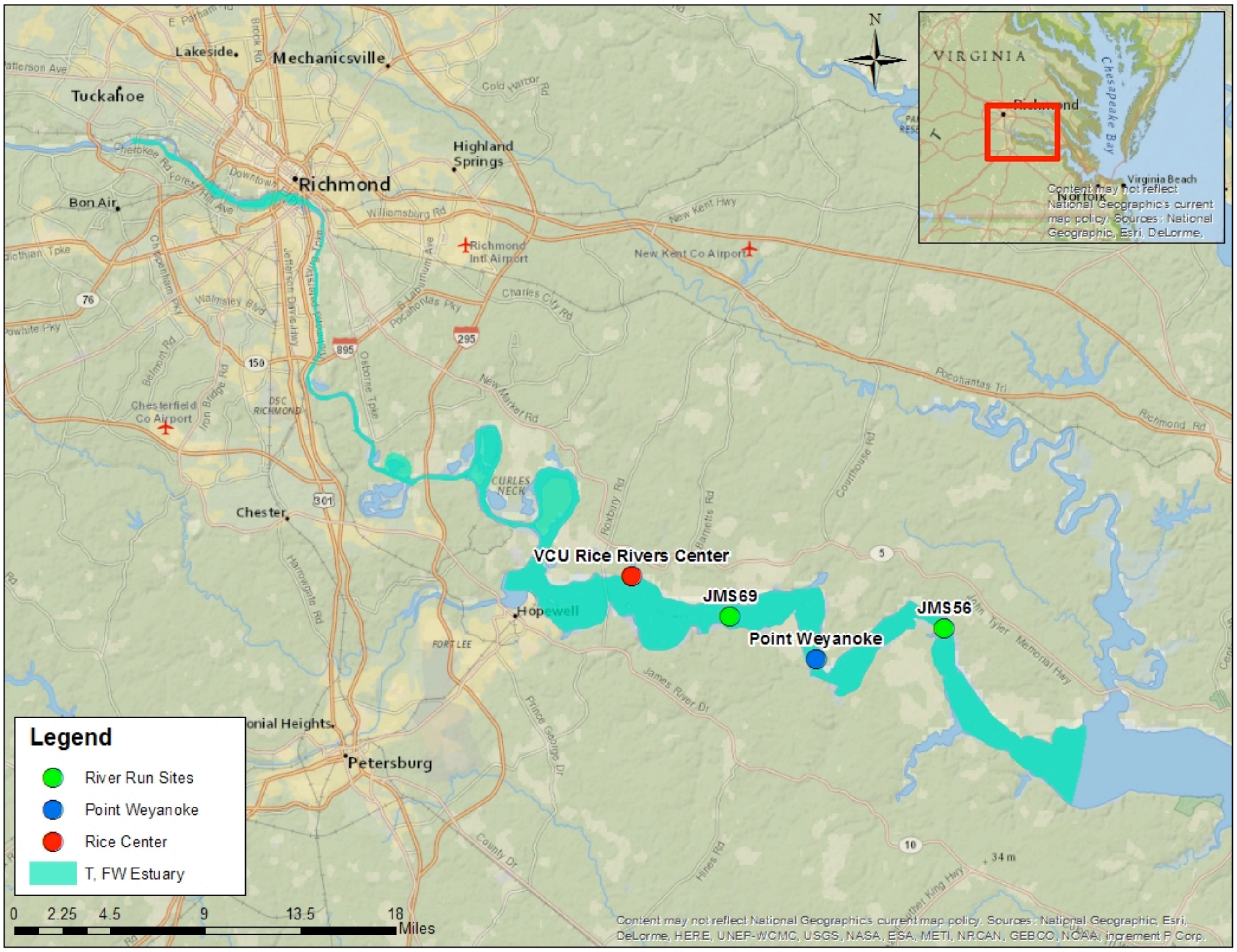

Figure 2. Map of the tidal, freshwater (T,FW) James River Estuary highlighting VCU's Rice research center and the study site, Point Weyanoke (USGS station 0204222), where all continuous monitoring and discrete sampling occurred.

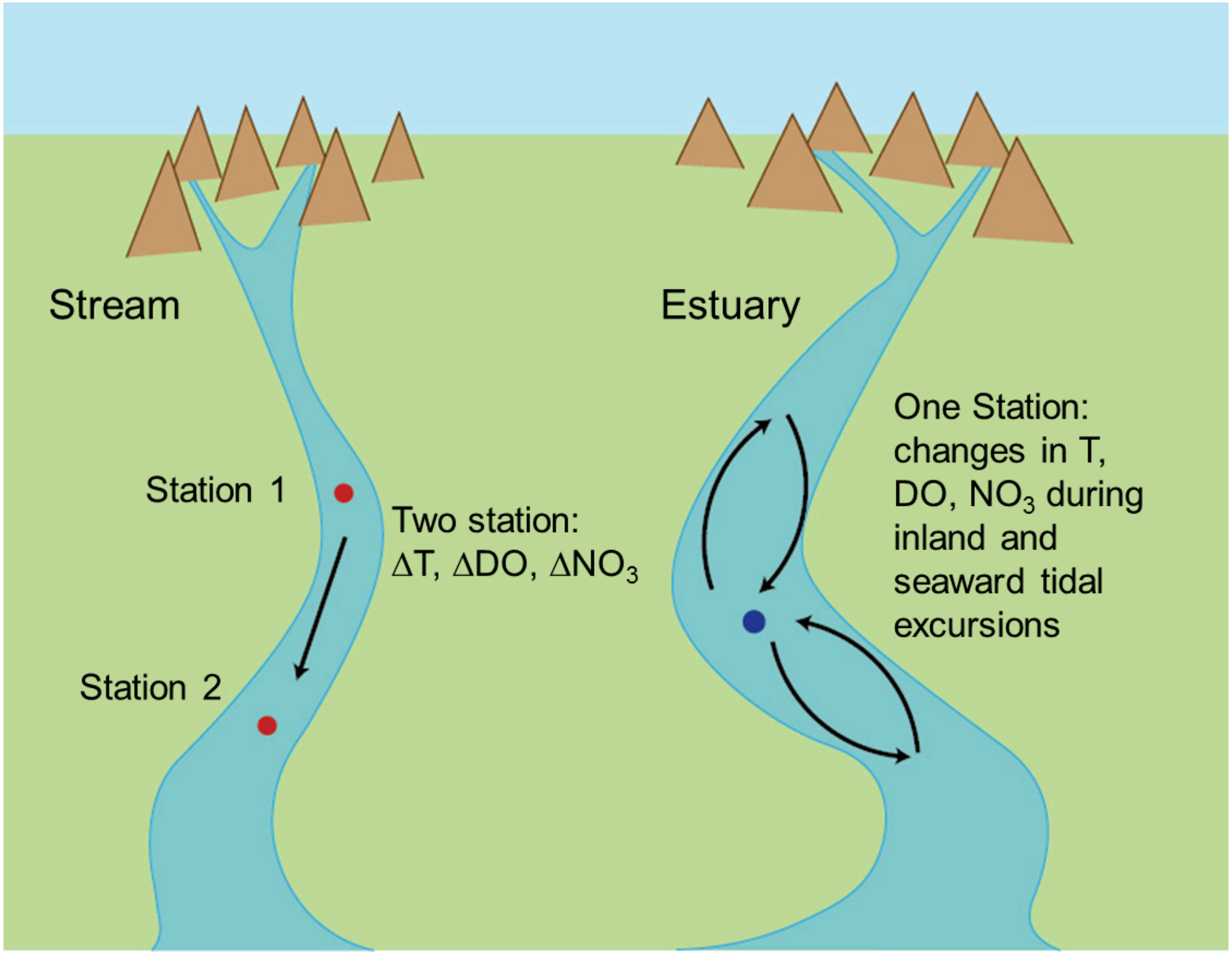

Figure 3. Comparison of how metabolism can be measured inflowing waters. Left: Uni-directional flow allows one to measure changes in temperature (T), dissolved oxygen (DO), and nitrate (NO_3) that occur between a station upstream and downstream. Right: Bi-directional due to the tides allows one to measure changes that occur between tides in both directions from one site (excursion analysis).

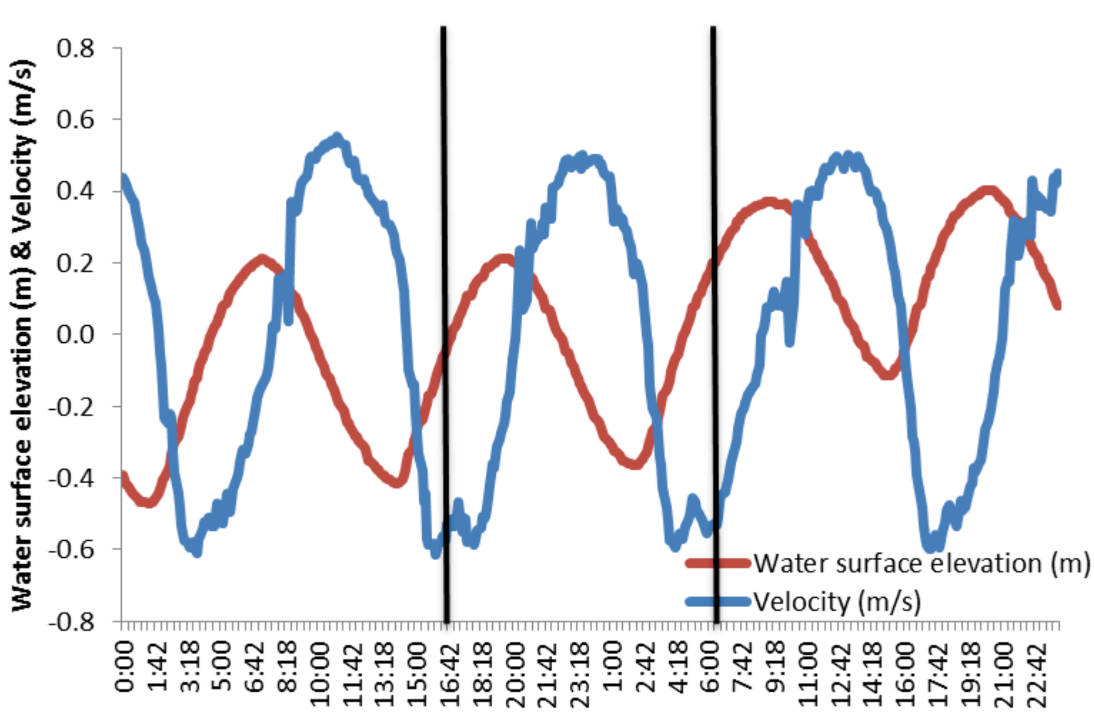

Figure 4. Water velocity (m/s) and surface elevation (m) of the James River at Point Weyanoke during February 25-26, 2015. Black lines denote the beginning and end of a tidal cycle during which an ISCO sampler was deployed to collect samples at 1-h intervals.

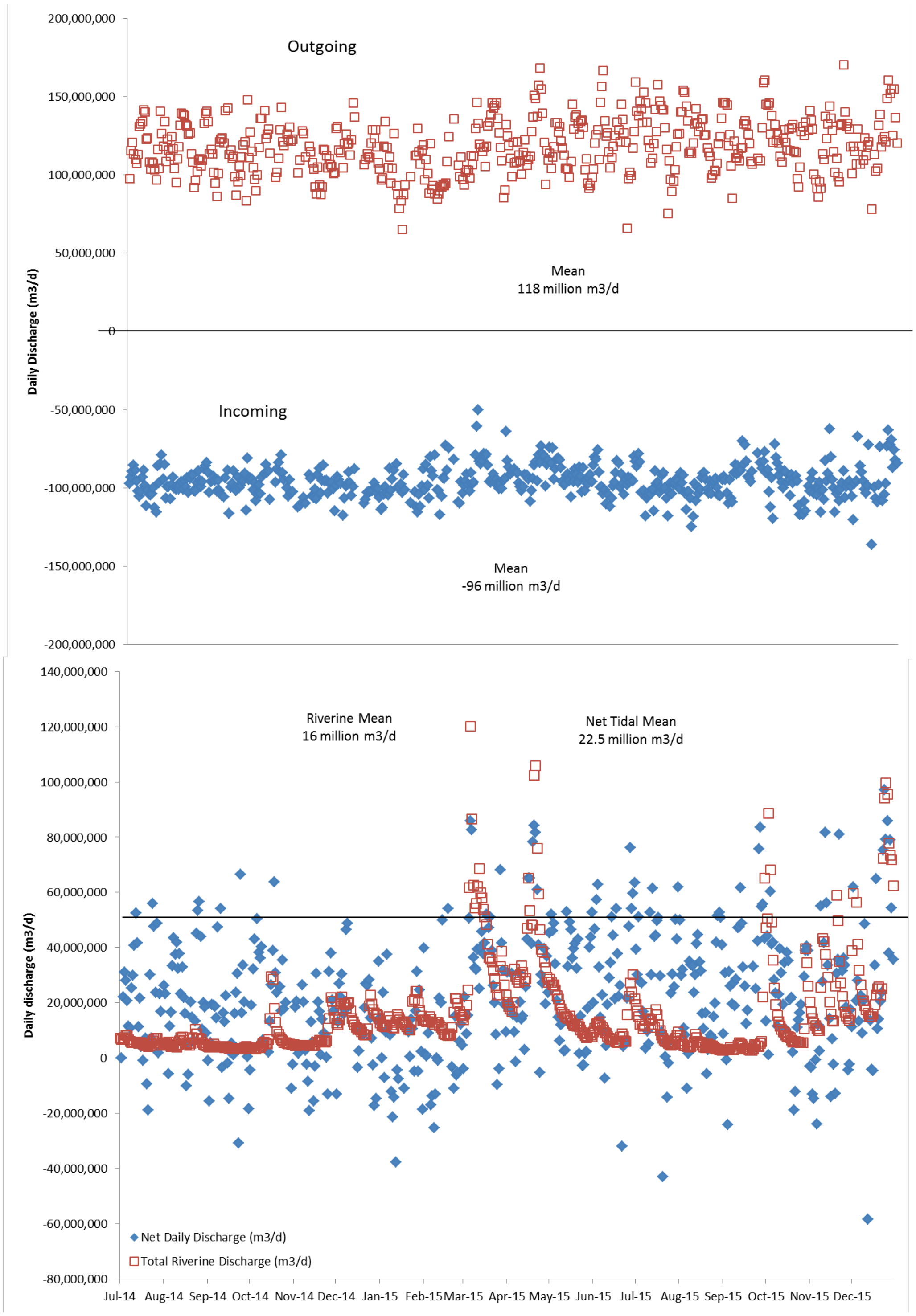

Figure 5. Upper panel: Daily total discharge (m^3/d) of incoming and outgoing tides at Point Weyanoke, VA. Lower panel: Net daily discharge from Point Weyanoke, VA compared to total daily riverine discharge. Riverine discharge calculated by summing daily discharge measurements from Appomattox River at Matoaca (#02041650), James River near Richmond (#02037500), and James River and Kanawha Canal near Richmond (#02037000).

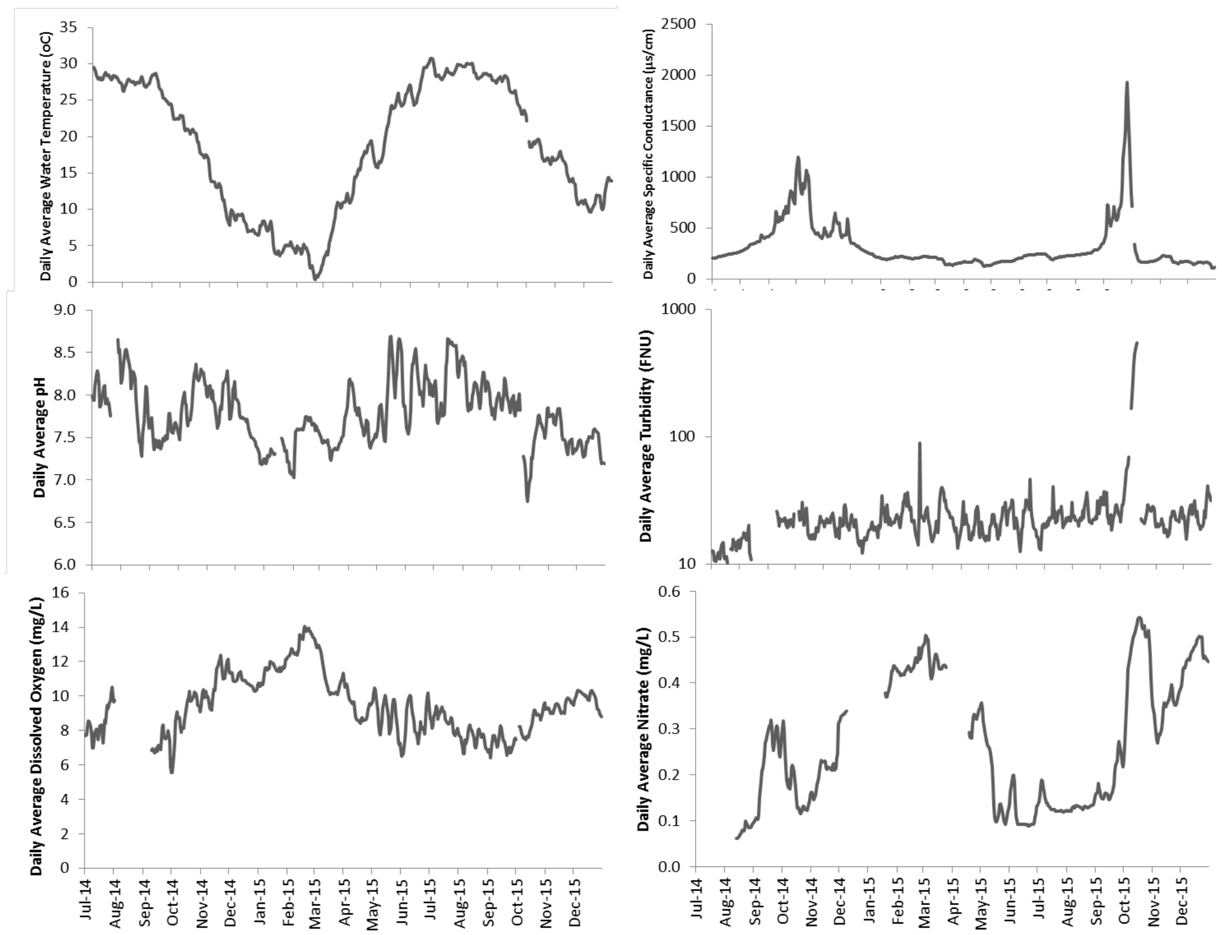

Figure 6. Daily average values for water temperature, specific conductance, pH, turbidity, dissolved oxygen, and nitrate from July 2014 to December 2015 at Point Weyanoke, VA (USGS station 0204222).

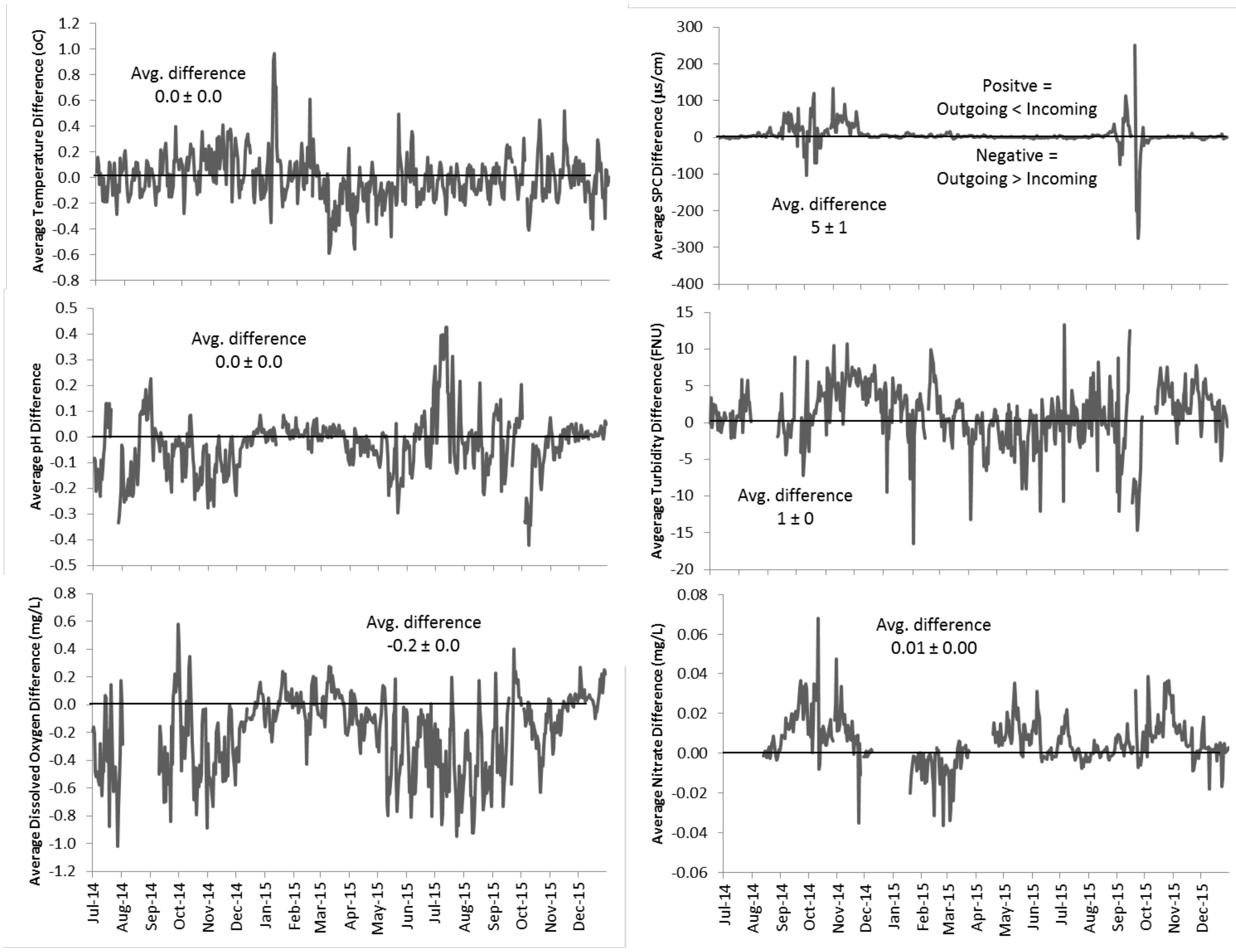

Figure 7. Daily average differences between incoming and outgoing tides for water temperature, specific conductance, pH, turbidity, dissolved oxygen, and nitrate from July 2014 to December 2015 at Point Weyanoke, VA.

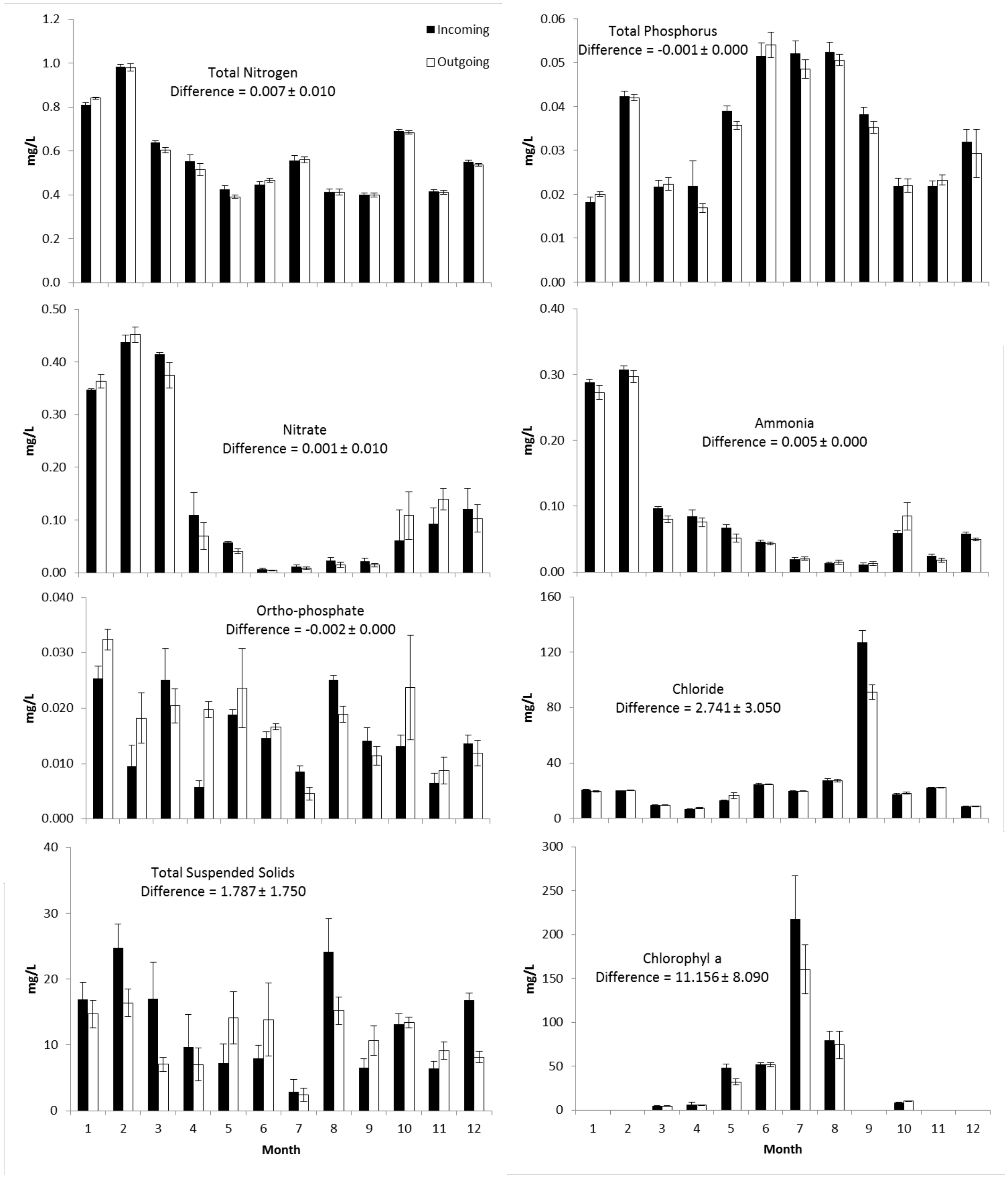

Figure 8. Average total nitrogen, total phosphorus, nitrate, ammonia, ortho-phosphate, chloride, total suspended solids, chlorophyll a, particulate organic carbon, and particulate organic nitrogen from monthly discrete samples for incoming and outgoing tides at Point Weyanoke, VA. Chlorophyll a only measured March – August and October 2015.

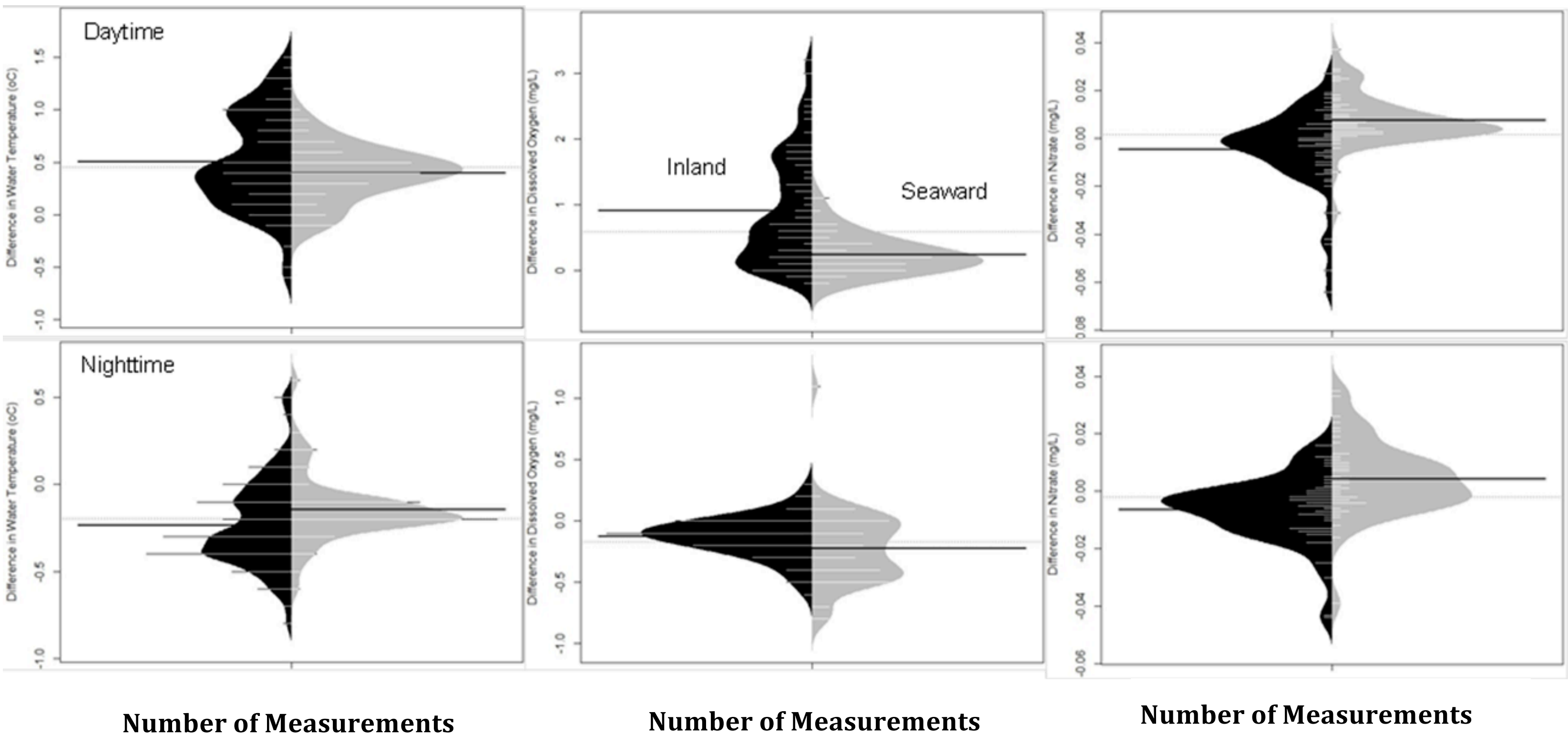

Figure 9. Tidal difference values (2nd tide subtracted from 1st tide) data from continuous monitoring at Point Weyanoke, VA for water temperature, dissolved oxygen, & nitrate for tides that coincided with solar cycles July 2014 – December 2015. Inland indicates water moving westward and back from Point Weyanoke while Seaward indicates water moving eastward and back to Point Weyanoke.

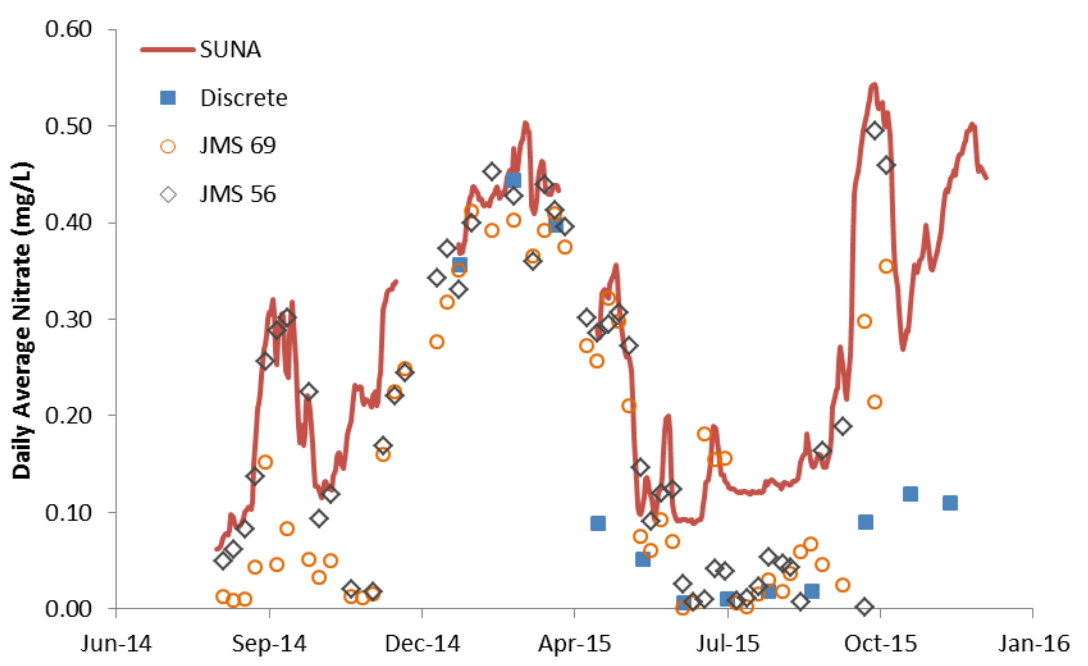

Figure 10. Comparison of nitrate concentrations between the continuous SUNA data (Point Weyanoke), monthly discrete samples (Point Weyanoke), and weekly sampling at James River mile 56, and 69.

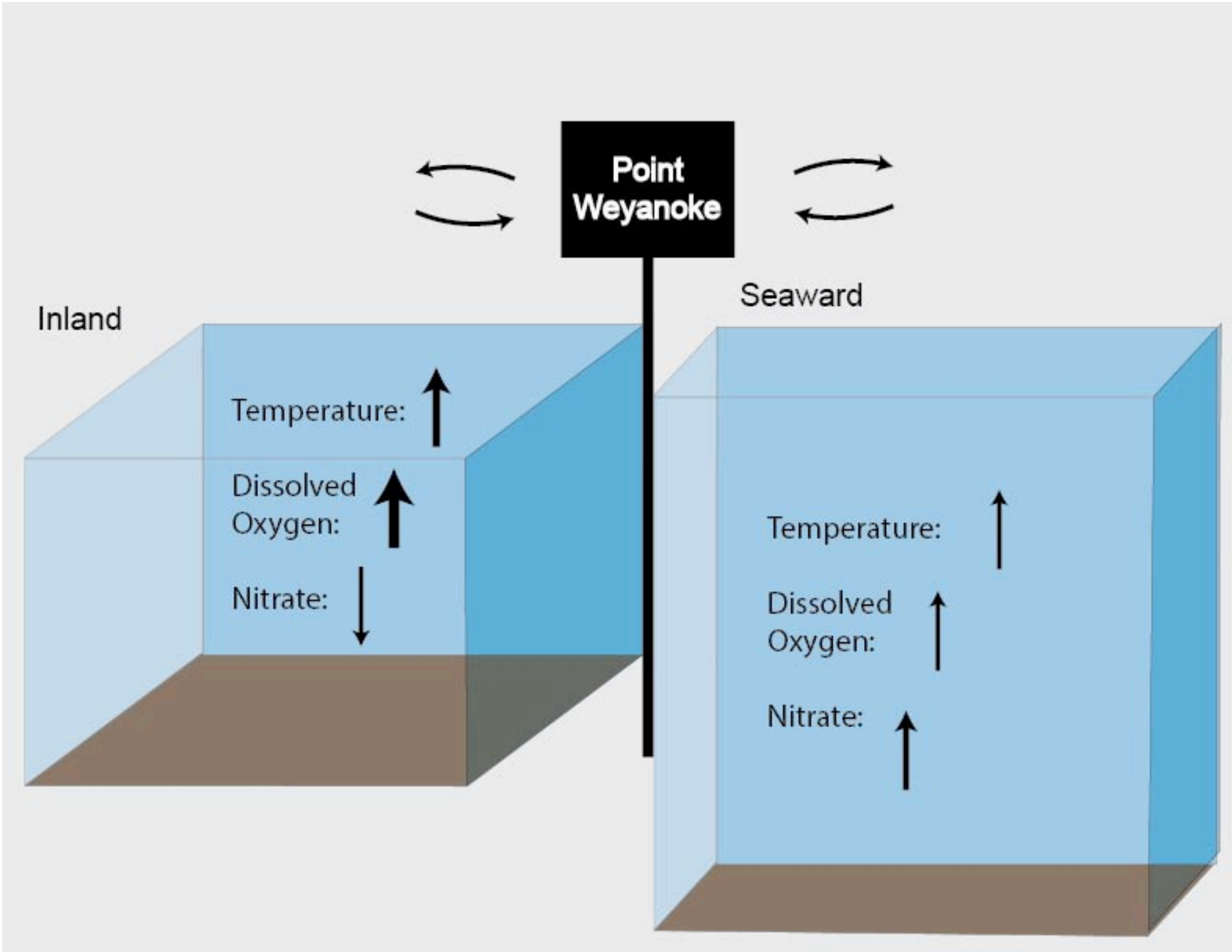

Figure 11. Difference in channel morphometry above and below Point Weyanoke. Size of the boxes signifies depth differences. This illustration is applicable during daytime excursions; nighttime excursions experience different changes in parameters.

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