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Sources and Fates of Nutrients in the Tidal, Freshwater James River

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SOURCES AND FATES OF NUTRIENTS IN THE TIDAL, FRESHWATER JAMES RIVER

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

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Table of Contents

Page

Acknowledgements ii

List of Tables iv

List of Figures v

List of Appendix Figures vi

Abstract………. vii

Chapter 1. 1

Introduction 1

Materials and Methods 5

Results 13

Discussion 18

Literature Cited 25

Tables and Figures 28

Appendix 41

Vita 48

List of Tables

Page

Table 1: Physical dimensions and distribution of sampling locations within the five zones comprising the study reach..28

Table 2: Data sources used to construct a nutrient mass balance for the tidal freshwater James River 29

Table 3: Average daily fluxes (±SE) to and from the tidal freshwater James River during 2007-2010 30

Table 4: Mean nutrient concentrations of riverine (James, Appomattox) and point source inputs to the tidal freshwater James River during 2007-2010 (±SE).................31

Table 5: Areal loading rates for different coastal systems and the tidal freshwater James River during 2007-2010 32

List of Figures

Page

Figure 1: Distribution of estuarine sampling stations and the 5 study reach zones within the tidal freshwater James River 33

Figure 2: Riverine and point source inputs of water and nutrients to the study reach. 34

Figure 3 Longitudinal variation in CHLa, nutrient concentrations, and point source inputs to the tidal freshwater James River during 2007-2010 (±SE) 35

Figure 4: Water and nutrient budgets depicted as daily average values by month for 2007-2010 36

Figure 5: Interannual variation in nutrient inputs, outputs, and retention in the tidal freshwater James River during 2007-2010 37

Figure 6: Seasonal variation in proportional retention, absolute retention, CHLa, and residence time in the tidal freshwater James River 38

Figure 7: Variation in annual mean retention estimates arising from uncertainty in individual budget components 39

Figure 8: Relationship between water residence time and TN-TP export based on data from this study and values reported in Nixon et al. (1996) 40

Appendix

Page

Table 1: Nutrient concentrations in strormwater runoff during four events monitored by the City of Richmond Department of Public Utilities during 2009 41

Figure 1: Flow chart illustrating sources of data used to derive budget components 42

Figure 2: Observed and predicted volume weighted chloride concentrations for the study area from July 2010 to June 2011 43

Figure 3: Monthly TN and TP fluxes associated with CSO events during 2007-2010..... 44

Figure 4: Four year (2007-2010) time series of average daily discharge for the James and Appomattox Rivers 45

Figure 5: Relationships between discharge, chlorophyll-a, and water temperature for the tidal freshwater James River during 2007-2010 46

Figure 6: Longitudinal profiles of TSS, TP, and average water velocity in the tidal freshwater James River during three high discharge events 47

Abstract

SOURCES AND FATES OF NUTRIENTS IN THE TIDAL, FRESHWATER JAMES RIVER

By William N. Isenberg, B.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Studies at Virginia Commonwealth University.

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Tidal freshwater reaches of estuaries may play an important role in mitigating nutrient fluxes from watersheds to the coastal zone due to their location at the interface between riverine and estuarine systems. We developed annual N and P budgets for the tidal, freshwater James River over 4 calendar years (2007-2010) taking into account riverine inputs at the Fall Line, local points sources (including CSO events), ungagued inputs, riverine outputs, and tidal exchange. The tidal freshwater James River experiences high areal loading rates of TN (383 mg/m^2/d) and TP (70 mg/m^2/d) due to the combined effects of large watershed area and local point source discharges. On an annual basis, riverine sources dominated TN and TP inputs (59% and 84%, respectively), whereas during low discharge summer months (May-Oct) point sources were more important. Proportional retention of TP inputs (59±7%) was greater than TN retention (27±4%) with annual absolute retention being 1,800±350 kg TP/d, and 5,900±2,700 kg TN/d. Proportional retention of TN and dissolved inorganic fractions of N and P was highest during the low discharge summer months due to reduced loading rates and increased residence times and biotic activity. TP retention was greatest during high discharge winter months (Nov-Apr) when loading rates were highest. High retention during this period of low biotic activity suggests that trapping of riverine derived particulate-bound P via sedimentation was an important mechanism of P retention. Understanding this seasonal variation in nutrient inputs and retention can help to inform management decisions regarding reducing nutrient inputs to the Chesapeake Bay and improving local water quality.

INTRODUCTION

In response to the growing human population, the increase in human nutritional requirements has lead to greater demand for nitrogen (N) and phosphorus (P) fertilizers (Nixon, 1995). Uneven distribution of fertilizer application, transportation of food across watershed boundaries, and the growth of urban centers have lead to a general increase in N and P transport to coastal environments (Nixon, 1995; NRC, 2000). Increases in N and P transport can lead to eutrophic conditions, which are associated with a range of detrimental effects including decreases in biodiversity, harmful algal blooms, and a reduction in submerged aquatic vegetation (Howarth et al., 2000). Accordingly, this increase in N and P transport is currently considered the greatest pollution problem for coastal environments of the United States (NRC, 2000).

Nutrient loads are delivered by point sources that discharge directly into the river or estuary (i.e., industrial waste water, municipal waste water treatment plants; WWTPs), and by non-point sources distributed throughout the watershed (i.e., farm and pasture fields, atmospheric deposition across the watershed). In temperate climates, the magnitude and timing of nutrient loads are affected by seasonal variation in watershed runoff. During winter, low rates of evapotranspiration result in greater runoff and large associated non-point source nutrient loads (Ensign et al., 2006; Murrell et al., 2007). During summer, low river discharge and elevated rates of terrestrial biogeochemical processes result in smaller non-point source loads, thereby increasing the relative importance of point sources, which are relatively constant year-round (Correll et al., 1992; Lampman et al., 1999). Jarvie et al. (2006) argued that annualized nutrient loads to UK estuaries were dominated by high discharge events occurring during winter months, but because of cold temperatures, biological responses to nutrient inputs were reduced. Thus point sources may be of greater importance in causing eutrophication despite accounting for a smaller proportion of annualized inputs. Therefore, an understanding of nutrient sources requires consideration of seasonal variation in inputs and sensitivity of receiving waters.

Aquatic ecosystems act to both transform and retain nutrient inputs from their watersheds. Both biotic and abiotic processes change the total mass, physical form, and bioavailability of N and P exported from estuaries (Froelich, 1988; Seitzinger, 1988; Nedwell et al., 1999). Such biotic processes include denitrification and algal assimilation of N and P. In the case of denitrification, bacteria reduce nitrate (NO_3) under anaerobic conditions to oxidize organic matter in the sediments producing non-bioavailable N_2 gas, which ultimately outgases into the atmosphere (Seitzinger, 1988; Nedwell et al., 1999). Rates of denitrification increase with increases in temperature, benthic organic matter content, and water column NO_3 concentrations (Seitzinger, 1988; Nedwell et al., 1999). Algal assimilation of inorganic N and P into cellular tissues transforms the nutrients into a less bioavailable particulate organic state and is positively related to light availability, temperature, and nutrient availability (Cole et al., 1992; Nedwell et al., 1999). Abiotic factors that affect the bioavailability and retention of N and P in estuaries include phosphate (PO_4) adsorption to sediments and the sedimentation and subsequent burial of particulate forms of N and P in the sediments. PO_4 adsorption is a process that transforms bioavailable PO_4 into a non-bioavailable particulate inorganic state via the attachment of PO_4 to sorption sites on terrestrially derived sediments (Froelich, 1988; Nedwell et al., 1999). This process is influenced by the number of sorption sites on the sediments, which is a function of watershed geology, and the phosphate buffering mechanism that is controlled by the balance between the concentration of PO_4 in the water and PO_4 adsorbed to the sediments (Froelich, 1988; Nedwell et al., 1999). Particulate forms of N and P are subject to gravity and thus undergo sedimentation and become buried in the sediments (Nedwell et al., 1999). Although the long term retention of particulate N and P in the sediments is not certain, biogeochemical processes within the sediments can act to retain and/or alter nutrient forms (Nedwell et al., 1999).

The efficiency of the different biotic and abiotic processes to transform and retain nutrients in estuaries is affected by the complex interplay of different environmental variables. Because water residence time affects the amount of time different biotic and abiotic processes can alter nutrient loads, greater water residence times have been shown to retain a larger proportion of N and P inputs (Nixon et al., 1996). However, because this retention-residence time relationship was developed using annualized values Arndt et al. (2009) argued that the complex interplay of residence time and factors that affect the rates of biogeochemical processes influences retention on seasonal and shorter time scales. The percentage of N and P retained in estuaries varies seasonally (Lampman et al., 1999; Jarvie et al., 2006; Boynton et al., 2008; Arndt et al., 2009) due to temperature effects on rates of estuarine biotic and abiotic processes (Lampman et al., 1999; Nedwell et al., 1999; Arndt et al., 2009) and the effect of seasonal variation in discharge on both nutrient loads and water residence times (Ensign et al., 2006; Murrell et al., 2007; Arndt et al., 2009). Accordingly, the efficiency with which estuaries retain nutrients is influenced by the magnitude and timing of inputs (Nedwell et al., 1999; Howarth et al., 2006; Jarvie et al., 2006). During warm months, high rates of primary production and long water residence time favor greater processing of N and P (Nixon, 1995; Nixon et al., 1996; Nedwell et al., 1999; Arndt et al., 2009). Tidal freshwater zones may play a particularly important role in mitigating nutrient fluxes from watersheds to the coastal zone, due to their location at the interface between riverine and estuarine systems (Schuchardt et al., 1993;

Lampman et al. 1999; Bukaveckas et al., 2011). Large nutrient loading rates coupled with high biological production may allow for high rates of nutrient retention in tidal freshwaters.

The tidal freshwater portion of the James River experiences persistent algal blooms during summer months (Bukaveckas et al., 2011) and is considered impaired due to persistently high chlorophyll a (CHLa) concentrations. This has led to efforts to reduce nutrient loads to improve local water quality as part of the 2010 Chesapeake Bay TMDL. Because N and P limit algal production, a study characterizing seasonal variation in point and non-point source inputs would provide a timely contribution to understanding the sources of nutrients supporting persistent algal blooms. In addition, comparisons of input and output fluxes provide a basis for quantifying retention and its role in mitigating nutrient export to Chesapeake Bay. Accordingly, the objectives of this study were to characterize seasonal and interannual variation in nutrient inputs, outputs, and retention over four calendar years (2007-2010) using a mass balance approach.

MATERIALS AND METHODS

Study Area

The James River is formed by the confluence of the Jackson and Cowpasture Rivers and flows 368 km eastward to the Fall Line at Richmond, VA. Below this point is the James River Estuary, which extends 177 km to its confluence with Chesapeake Bay (Smock et al., 2005). The James River is the third largest tributary of the Chesapeake Bay by discharge and nutrient loads (Belval & Sprague, 1999). Its watershed (26,164 km^2) is predominantly forested (71%) with the remaining land use being agricultural (23%) and urban (6%; Smock et al., 2005). Major urban centers are located at the Fall Line (Richmond Metro area; population = 1,258,000) and near the confluence with Chesapeake Bay (Virginia Beach-Norfolk-Newport News Metro area; population = 1,649,000).

A nutrient mass balance was constructed for the 58 km segment extending from the Fall Line (ca. river mile 110) to river mile 74 (near Hopewell, VA; Figure 1). The study reach comprises two-thirds of the tidal freshwater segment (which extends to river mile 55) and includes the site of the CHLa maximum located at river mile 75 (Bukaveckas et al. 2011). The study reach receives nutrient inputs from the majority of the James River watershed (22,753 km^2) and point source discharges from the Richmond Metro Area. Annual average discharge of the James River is 213 m^3/s (at the Fall Line). The Appomattox River is the largest tributary of the James contributing on average 38 m^3/s (~15% of annual combined discharge). In terms of freshwater replacement time, the average water residence time for the study reach is 4 days. The major point sources of N and P include 4 industrial facilities and 6 municipal WWTPs with a total combined discharge averaging 13 m^3/s. Point sources include Richmond combined sewer overflow (CSO) events in which untreated sewage and stormwater are discharged to the James during periods when rainfall exceeds treatment and storage capacity.

The study reach was sub-divided into 5 zones based on historical sampling locations with 1-3 sampling stations occurring in each zone (Figure 1; Table 1). Zones 1-3 (upper segment) are characterized by a narrow, deep riverine channel whereas Zone 4 (near Hopewell, VA) includes extensive shallow areas lateral to the main channel. Zone 5 is the tidal portion of the Appomattox River. Data from a station located 8 km beyond the study reach (at river mile 69) were used to infer the chemistry of incoming tidal waters. The study reach experiences semi-diurnal tides of 0.78 m in amplitude resulting in a large tidal prism (32,991,000 m^3/tide) relative to the storage volume (80,793,000 m^3; Table 1).

Nutrient Budgets – Overview

Budgets were constructed for total nitrogen (TN), total phosphorus (TP), ammonia (NH_3), nitrate/nitrite (NO_x), and phosphate (PO_4). Greater retention of dissolved inorganic nutrients (NH_3, NO_x, & PO_4) was expected as these forms are the most biologically available (Nedwell et al. 1999; Middelburg & Nieuwenhuize, 2000). Budgets were constructed by quantifying major inputs and outputs to and from the study reach. Nutrient inputs included riverine sources (upper James and Appomattox River watersheds), local point sources (municipal WWTPs, industry, and CSO), ungauged inputs, and tidal exchange. Direct atmospheric inputs of N were small (<1% of total N inputs based on local deposition values; Jaworki et al., 1997) and therefore were not included in the budget. Outputs from the study reach included downstream export (to the lower estuary) due to displacement by riverine inputs and tidal exchange. Nutrient retention was estimated by difference from inputs and outputs taking into account changes in storage:

(1) $$\text{Retention} = IN_{riv} + IN_{point} - OUT_{riv} \pm TE \pm \Delta\text{Storage}$$

where IN_{riv} represents riverine and ungauged inputs, IN_{point} represents the local point source inputs, OUT_{riv} represents the riverine outputs, TE represents net tidal exchange, and ΔStorage represents the change in storage (Appendix Figure 1). Storage effects take into account changes in nutrient concentrations within each of the 5 zones over the monthly budget period. Changes in water level were not considered as these were assumed to be small given the large ratio of water inputs to storage volume within the study reach. Due to the constraints of data availability, retention estimates were derived at monthly time steps. Results are reported as annual, monthly, and average daily rates.

Riverine Inputs

Nutrient inputs from the James and Appomattox watersheds were calculated as the product of average daily discharge and measured nutrient concentrations (N = 17-23 per year) obtained from the USGS River Input Monitoring Program (USGS; Table 2; Appendix Figure 1; http://nwis.waterdata.usgs.gov/va/nwis/qwdata). James River discharge and nutrient concentrations were measured at Cartersville, VA. Regressions relating concentration to discharge showed significant relationships for TN and TP (R^2= 0.61 and 0.83, respectively; $p < 0.0001$), but weak relationships for inorganic nutrient fractions ($R^2 < 0.3$). Concentration-discharge relationships developed from the Cartersville site were used in conjunction with discharge measurements at Richmond to derive riverine fluxes because the Richmond site is proximal to the study reach and exhibits higher discharge (~8%). For inorganic fractions, concentrations on dates in-between measurements were set equal to the closest sampling date. Appomattox River inputs were derived using nutrient concentrations and discharge measured at

Matoaca, VA. No significant concentration-discharge relationships were found for the Appomattox and therefore concentrations were set equal to those of the proximal sampling date for all nutrient fractions. Ungauged inputs from the watershed area that drains directly to the study reach represent 8% of the total watershed area. As a result, we increased riverine input fluxes by 8% to incorporate this contribution (Boynton et al., 1995; Robson et al., 2008).

Point Source Inputs

Municipal WWTPs and industrial dischargers report monthly effluent discharge and nutrient concentrations to the EPA National Pollutant Discharge Elimination System (NPDES; Table 2; Appendix Figure 1) database. Monthly nutrient fluxes for each point source were derived as the product of mean effluent discharge and mean nutrient concentrations. Individual point source fluxes were summed to derive the total monthly input. Nutrient inputs from Richmond CSO events were included with other point sources. Due to the unpredictable, event-based nature of CSO events, monitoring of effluent discharge and concentration is lacking. However, model-derived estimates of CSO discharges were available from the City of Richmond Department of Public Utilities. Data for the three largest outfalls (representing 92% of total CSO discharge) were available for all four years. Nutrient concentrations were measured by the City of Richmond at the largest CSO outfall (Shockoe) during four events in 2009. Concentrations of NO_x (mean = 0.6 mg/L) and PO_4 (mean = 0.4 mg/L) were similar among the 4 events (CV = 9% and 26%), whereas concentrations of NH_3 (mean = 3.7 mg/L; range = 0.9 - 7.4 mg/L), TN (mean = 7.9 mg/L; range = 4.4 - 13.4 mg/L) and TP (mean = 1.0 mg/L; range = 0.4 - 1.6 mg/l) were more variable (Appendix Table 1). These average values were used in conjunction with the monthly outfall estimates to determine nutrient loads associated with CSO inputs throughout the period of study.

Riverine Outputs

Output fluxes due to displacement by riverine inputs were estimated as the product of river discharge (including ungauged inputs) and measured nutrient concentrations at JMS75. Data from JMS75 were used to estimate nutrient export to the lower estuary because it is the most downstream sampling station within the study reach. Nutrient concentrations at this station were measured monthly throughout the study period by the Virginia Department of Environmental Quality (VaDEQ; Table 2; Appendix Figure 1) as part of the EPA Chesapeake Bay Monitoring Program (CBMP). Supplemental data were available for 2007 (weekly, April-November; Bukaveckas et al. 2011), 2009 (bi-weekly, August-October; Bukaveckas unpubl.), and 2010 (weekly, July-December; Bukaveckas unpubl.). No data were available for August 2008 and therefore the average of July and September was used. On January 12, 2009, a barge carrying ammonium sulfate sank near river mile 73 (Hopewell, VA) and released an estimated 1.1 million kg of ammonium sulfate (http://www.deq.state.va.us/info/esound/February2009.html#article2). This event affected NH_3 and TN concentrations and fluxes during January and February. To facilitate comparisons with other years, we substituted average values from January and February of other years when calculating total annual retention for 2009.

Tidal Exchange

Tidal exchange was not measured directly as part of this study as this would require high frequency measurements of water level and velocity over each tidal cycle to determine the volume entering and leaving the study reach. Moreover, much of the water leaving the study reach on an out-going tide is likely to return during the subsequent incoming tide. For a mass balance analysis, the property of interest is the difference between the input and output fluxes (i.e., net tidal exchange). This property may be estimated using a chloride (Cl) budget approach (Robson et al., 2008). As Cl behaves conservatively, retention is assumed to be negligible and the terms of the mass balance equation can be re-arranged to solve for net tidal exchange based on measured changes in the mass of Cl in the estuary and measured Cl concentrations in incoming and outgoing tidal waters. Weekly Cl data were available for a 12-month period (July 2010-June 2011) during which concentrations were measured for incoming river water (at Richmond), 7 stations within the study reach and one station located below the study reach (JMS69; Table 2; Appendix Figure 1). By solving for differences between observed and predicted volume-weighted, Cl concentrations within the study reach, we determined that net tidal exchange was on average 2.5% of the tidal prism (Appendix Figure 2). This value was used to infer tidal exchange throughout the budget period based on measured tidal amplitudes (NOAA; Table 2; Appendix Figure 1). Residual error between observed and predicted volume-weighted Cl concentrations averaged 6% for the 12-month calibration period, corresponding to a mean difference in Cl of 5.4 mg/L over an observed range of 6.5 to 136.4 mg/L. Given this margin of error in the Cl budgets, we assumed that nutrient retention estimates exceeding 6% were indicative of source or sink effects within the study reach. In addition, we performed a sensitivity analysis whereby net tidal exchange was increased from 2.5% to 5%, 10%, and 20% of the tidal prism to assess the effects on retention estimates.

Storage Effects

Nutrient inputs and outputs affect concentrations within the waterbody such that changes in the stored mass must be accounted for in monthly balances. The mass of nutrients stored within the study reach was calculated by summing the products of concentration and water volume for each of the 5 zones (Table 2; Appendix Figure 1). For Zone 3, concentration measurements were available from three sources though one of these (JMS87; VaDEQ Ambient Water Quality Monitoring program) was limited to TN and TP measurements only, whereas the others (JMS79 & JMS87; Bukaveckas et al., 2011, Bukaveckas unpubl.) had limited temporal coverage (~20 of 48 months). A regression model relating inorganic nutrient concentrations at this site to the average of concentrations from two proximal sampling locations (Zone 2 and 4) showed good predictive power for NO_x and PO_4 (R^2 = 0.86 and 0.78, respectively) though the relationships for NH_3 was weaker (R^2 = 0.39). The regression models were used to infer missing values for the inorganic fractions in Zone 3.

<u>Budget Uncertainty</u>

Hypothesis testing statistics are not typically used in ecosystem nutrient budgets. However, the propagation of error that occurs as budget terms are derived requires an estimation of uncertainty in retention estimates. As fluxes were the product of nutrient concentrations (c) and discharge (d), error was calculated using the equation from Eyre et al. (2011):

(2) $$\text{Flux Error} = ((\text{mean}_c * \text{error}_d)^2 + (\text{mean}_d * \text{error}_c)^2 + (\text{error}_c * \text{error}_d))^{0.5}$$

where mean_c is the mean nutrient concentration, mean_d is the mean discharge, error_c is the standard error for nutrient concentrations, and error_d is the standard error of discharge. In order to directly measure the propagation of error in retention estimates, flux errors were added in quadrature:

(3) $$\text{Retention Error} = ((\text{error}_{RI})^2+(\text{error}_{PS})^2+(\text{error}_{RO})^2+(\text{error}_{TE})^2)^{0.5}$$

where $error_{RI}$ is the riverine input standard error, $error_{PS}$ is the point source standard error, $error_{RO}$ is the riverine output standard error, and $error_{TE}$ is the tidal exchange standard error. In addition, the influence of cumulative error on retention estimates was simulated by adjusting each flux up and down by its associated standard error to generate a simulated range of retention estimates.

RESULTS

Riverine & Point Source Inputs

Riverine inputs averaged 13,000±1,500 kg/d of TN and 2,500±290 kg/d of TP over the 4-year study (Table 3). During this period, discharge averaged 198 m^3/s and was below the 40-year mean of 250 m^3/s. Annual average discharge was lowest in 2008 (140 m^3/s) and highest in 2009 (240 m^3/s). Interannual variation in nutrient loads ranged from 7,800 to 16,400 kg TN/d and from 1,050 to 3,600 kg TP/d. TN and TP combined inputs (IN_{riv} + IN_{point}) were dominated by riverine sources which represented 59% and 84% of inputs, respectively. Seasonal variation in river inputs followed trends in discharge which was highest in winter months (Figure 2). TN and TP concentrations were positively correlated with discharge (See *Methods: Riverine Inputs*) and therefore high discharge periods accounted for a disproportionately greater fraction of annual loads. For example, TN inputs were 4-fold higher (21,100 kg/d vs. 5,400 kg/d) during high discharge months (Nov-April; mean = 296 m^3/s) compared to low discharge months (May-Oct; mean = 102 m^3/s). Seasonal differences were even larger for TP with average daily loads 6-fold higher in November-April (4,300 kg/d) compared to May-October (700 kg/d).

Point source inputs averaged 9,100±200 kg TN/d and 470±15 kg TP/d (Table 3) with little intra- or inter-annual variation. The proportion of annual combined inputs contributed by point sources ranged from 36% to 53% for TN (mean = 41%) and from 10% to 31% for TP (mean = 16%) over the 4 years. Point source inputs were relatively constant on a seasonal basis, and therefore accounted for a greater fraction of total inputs during summer months when riverine inputs were low (Figure 2). Point sources accounted for 62% of TN and 42% of TP inputs during May-October. Point sources were particularly important for dissolved inorganic fractions (NH_3, NO_x, & PO_4) as concentrations in effluent were an order of magnitude higher than riverine concentrations (Table 4). Annual combined inputs of TN were comprised of 13% NH_3 and 42% NO_x, with 19% of TP combined inputs accounted for by PO_4. Point sources contributed 89% of NH_3, 53% of NO_x, and 64% of PO_4 combined annual inputs. During May-October, these proportions increased to 93% for NH_3 and 75% for both NO_x and PO_4 inputs. Over the 4-year study, annual point source inputs of PO_4 decreased by one third due to reductions in effluent concentrations at the Richmond WWTP. CSO inputs were a relatively minor contribution accounting for less than 7% of point source inputs for all nutrient fractions. CSO events occurred in every month, though their discharge varied widely (896-135,687m^3/mo), at times accounting for up to 12% of TN (Sep. 2010) and 30% of TP (Nov. 2009) in monthly point source inputs. There was no consistent seasonal pattern in CSO nutrient loads (Appendix Figure 3).

Because point sources discharge at discrete locations along the estuary they affected longitudinal patterns of nutrient concentrations within the study reach (Figure 3). For example, NO_x and PO_4 concentrations increased 3-fold below the Richmond WWTP/CSO (at river mile 109), which accounted for 46% and 39% of NO_x and PO_4 point source inputs, respectively. Similarly, NH_3 concentrations were highest at river mile 75, which was near two point sources (at river mile 76.5) that accounted for 76% of point source NH_3 loads. Although TN and TP increased below the Richmond WWTP/CSO, their concentrations generally showed stronger correspondence with trends in CHLa than the location of point sources. In summary, riverine sources accounted for the majority of total annual TN and TP inputs, whereas point sources dominated inputs of dissolved inorganic fractions, particularly during summer, low-discharge conditions.

Riverine Outputs, Tidal Exchange, & Storage Effects

Riverine outputs averaged 16,200±2,200 kg TN/d and 1,200±200 kg TP/d over the 4-year study period (Table 3), with annual averages ranging from 14,000 kg/d to 18,400 kg/d for TN and 970 kg/d to 1,400 kg/d for TP. Variation in riverine outputs was predominantly driven by discharge and secondarily by seasonal variation in nutrient concentrations in the estuary (Figure 4). During May-October, riverine outputs averaged 8,200 kg TN/d and 720 kg TP/d whereas during November-April outputs averaged 24,400 kg TN/d and 1,700 kg TP/d. For inorganic N fractions, riverine outputs were 4-fold greater during the winter months (2,600 kg NH_3/d and 11,700 kg NO_x/d) than during summer months (680 kg NH_3/d and 2,600 kg NO_x/d). Similarly, riverine outputs of PO_4 were 3-fold greater during winter months than during summer months (340 kg/d vs. 120 kg/d). For TN, NH_3, TP, and PO_4, monthly combined inputs exceeded riverine outputs during most months (>90%). However for NO_x, outputs were equal to or greater than inputs during half of the winter months. Tidal exchange and storage effects were minor components of the nutrient budgets (Figure 4). On an annual basis, tidal exchange resulted in a net loss of nutrient from the study reach though the difference in fluxes was small (≤1% of outputs) due to small differences in concentration between in-coming (JMS69) and out-going (JMS75) tidal waters (Figure 3; Table 3). Similarly, monthly changes in storage were 1% or less of inputs for all nutrient fractions.

Retention

Annual retention averaged 5,900±2,700 kg TN/d and 1,800±350 kg TP/d, with inter-annual variation ranging from 2,500 kg/d to 9,200 kg/d for TN and 550 kg/d to 2,700 kg/d for TP (Figure 5). The amount of TN and TP retained was positively related to the magnitude of inputs with highest retention occurring in 2010. Regressions relating monthly retention to nutrient inputs exhibited strong and significant relationships for TN (R^2=0.50; p <0.0001) and TP

(R^2=0.99; p <0.0001). Relationships between loads and retention for inorganic nutrients were weak (R^2<0.2) and not significant. Retention of TN averaged 27±4% of inputs whereas proportional retention of TP averaged 59±7% of inputs. Proportional retention of NH_3, NO_x, and PO_4 were 42±6%, 23±2%, and 59±5%, respectively. Annual variation in proportional retention ranged from 16% to 36% for TN and 36% to 68% for TP. A greater proportion of TP inputs were retained relative to TN inputs in all years.

The proportion and mass of nutrients retained varied seasonally (Figure 6). Seasonal variation of proportional and absolute retention for inorganic nutrients was similar, with the highest retention rates (1,660 kg NH_3/d, 3,800 kg NO_x/d, and 430 kg PO_4/d) during the summer months (May-Oct) when CHLa and water residence time were greatest. Proportional retention for inorganic nutrients approached 100% during this period. During winter months, retention of NH_3 and NO_x were 2- and 8-fold smaller (790 and 450 kg/d, respectively), with negative retention of NO_x occurring in late winter. Similarly, absolute retention of PO_4 was 2-fold lower (260 kg/d) during winter, although unlike inorganic N fractions, proportional retention typically exceeded 50% during most months. Seasonal patterns of proportional and absolute retention for TN and TP differed. Although proportional retention of TN peaked during summer months, there was little seasonal variation in absolute TN retention as average winter retention (6,970 kg/d) was only slightly greater than average summer retention (5,670 kg/d). For TP, absolute retention was 6-fold greater during winter months (3,000 kg/d) than in summer months (480 kg/d) and proportional retention was relatively constant year round.

Sensitivity Analysis & Uncertainty

Retention estimates were derived by difference and therefore are subject to uncertainty that is influenced by underlying errors in each of the budget terms. Of these, tidal exchange estimates were of particular concern since these were not measured directly. To assess the influence of underestimating tidal exchange, the effective net tidal exchange (2.5% of tidal prism) was doubled to 5%, 10%, and 20%. The simulated changes in tidal exchange were found to have little influence on annual retention estimates. At tidal exchange values 8 times greater than was used for nutrient budgets, the mean annual retention of NH_3 decreased by 4%, TN and NO_x by <3%, and TP and PO_4 by <1%. Budget uncertainty was also assessed by evaluating the relative magnitude of flux errors, and by incorporating flux errors into retention estimates. With the exception of tidal exchange, flux errors for each of the budget terms were less than 25% of flux means (Table 3). Because tidal exchange represents a minor component of the nutrient budgets (Figure 4), the proportionally larger errors associated with tidal exchange means were not a significant source of uncertainty. When each of the flux terms was adjusted by its corresponding error to assess the cumulative influence on retention estimates (Figure 7), the simulated ranges of retention values showed that the variation about actual retention estimates was not that big, although ranges for N fractions were greater than those for P fractions. Accordingly, there was greater uncertainty in N retention estimates relative to P. However, all results were much greater than zero suggesting that retention estimates were robust given the small water residence time of the study reach and uncertainties in estimating tidal exchange and other flux terms in the budget.

DISCUSSION

Compared to other estuaries, areal loading rates of N and P to the tidal freshwater James River are exceptionally high (Table 5). It is important to note that all but two of the systems in Table 5 are entire estuaries. Both the upper Patuxent Estuary (Boynton et al., 2008) and the tidal freshwater James River are freshwater portions of entire estuaries. While the smaller estuarine surface area inflates the areal inputs of N and P for both of these systems, it emphasizes the magnitude of nutrient loads that are intercepted by these tidal freshwater reaches. These segments of estuaries receive the entirety of riverine nutrient loads in addition to local point sources. Using the proportion of the James River watershed down river of the study reach (13%), and NPDES point source allocation totals, we estimated that about 70% of the total N and P inputs for the entire James River watershed enter our study reach. Accordingly, tidal freshwater reaches play an important role in retaining nutrient inputs relative to other areas in the watershed (Lampman et al., 1999).

The magnitude and composition of nutrient inputs affects the efficiency of retention, and for the study reach this was largely affected by seasonal changes in river discharge. During the winter months, low rates of evapotranspiration drove high river discharge for the James and Appomattox Rivers (Smock et al., 2005; Appendix Figure 4). These periods of high discharge delivered large riverine nutrient loads in addition to the steady point source loads. The riverine inputs for the James were comprised of predominantly particulate and/or organic nutrients (annually, DIN = NH_3 + NO_x = 36% of TN & PO_4 = 8% of TP), which is similar to other tributaries of the Chesapeake Bay (Boynton et al., 1995). Thus during these high discharge winter months, the dominance of riverine inputs diluted the inorganic rich point source inputs, resulting in inorganic loads that were only 51% of the TN and 12% of the TP loads. Jarvie et al.

(2006) observed a similar dilution effect in 54 different rivers in the UK. Although large loads were delivered to the study reach during these high discharge winter months, residence times, algal biomass, and water temperature were low, which likely resulted in the low proportional retention of TN and inorganic nutrients. Conversely, during summer months, elevated rates of evapotranspiration resulted in low river discharge, and thus relatively smaller riverine inputs. Because the magnitude of riverine inputs decreased during low discharge summer months, total nutrient loads to the study reach decreased and point sources tended to dominate. During these periods, loads were reduced by 50% for TN and by 75% for TP relative to winter months, while the proportion of loads accounted for by inorganic nutrients increased to 63% of TN and 45% of TP loads. Furthermore, the reduction in river discharge resulted in greater water residence times, greater algal biomass, and greater proportional retention of TN and inorganic nutrients.

Given the apparent relationship between retention and residence time, we compared our results and residence time estimates with those of Nixon et al. (1996; Figure 8). Although our TP export did not fit well to the regression line derived by Nixon et al. (1996), our TN estimates did. Annual proportional TN export estimates for 2007-2010 in the tidal freshwater James River were high (65-85%) and related to low estimated average annual residence times (0.12-0.20 months). These high TN export values are likely due to short residence times in conjunction with large areal loading rates of tidal freshwaters. Furthermore, because 55% of the annual TN inputs are dissolved inorganic nutrients, the relatively short residence time does not allow much time for biogeochemical processes to alter and ultimately retain the N inputs. However, during the low discharge summer months when water residence time, algal biomass, and temperature are at a maximum, the majority of DIN retention occurs. Due to the high retention of DIN during these summer months, the majority of proportional TN retention also occurs. Although

DIN retention approaches 100% of inputs during the summer months, TN retention only approaches 60% of inputs, suggesting that the ecosystem functions as a transformer of nutrients converting DIN into organic nitrogen. While the processes that work to retain N were not directly measured, it can be assumed that during these summer months some of this retention was due to denitrification and some was due to burial of algal assimilated N in the sediments. For the Delaware and Potomac River Estuaries, denitrification within the tidal freshwater reaches accounted for 20% and 35% of inputs (Seitzinger, 1988). However these two studies were only conducted during the summer and fall, which for our study reach represented the periods of greatest DIN retention. Therefore, it is conceivable that a large proportion of the DIN retention is due to algal assimilation at the CHLa maximum at JMS75. The lower proportional retention of TN relative to DIN may be due to the advection of algal assimilated N from the study reach. Over 75% of CHLa and particulate organic nitrogen within the tidal freshwater James River have been shown to remain suspended in the water column after one day (Schlegel, 2011). This may explain the lower proportional retention of TN relative to DIN, however as residence times increase in the low discharge summer months (up to 30 days at times), this fraction of suspended algal nitrogen will ultimately fall out of the water column and become buried in the sediments. When regressions relating river discharge, CHLa concentration, and estuarine water temperature to monthly retention estimates were run, it was found that all three environmental variables were significant and strong predictors of retention, although all three variables were also significantly strongly related to each other (Appendix Figure 5). Because discharge (inversely related to residence time) was negatively related to retention while CHLa concentration and water temperature were positively related to retention, it appears that as Arndt et al. (2009) suggested, it is the complex interplay of residence time and factors affecting biogeochemical reaction rates that influences TN retention on monthly time scales in our study reach.

The tidal freshwater James River has exceptionally high TP retention estimates for such low residence times relative to the other estuaries plotted in Figure 8. This high proportional retention is likely due to the sedimentation of riverine derived particulate phosphorus (PP), given that the majority of annual TP inputs were riverine (84%) and that these were predominantly particulate in nature. Of the systems plotted in Figure 8, all but our study reach are entire estuaries, and 4 out of the 6 other estuaries received the majority of their P loads from rivers. Given this tendency for the majority of P inputs to be from riverine sources, it is possible that if the residence times were calculated for the entire James River Estuary, our data points may fit the line in Figure 8 because the increases in inputs from downstream sources would be small compared to increases in residence time. Given that an estimated 70% of the total James River P load enters our study reach and that residence time at the mouth of the estuary is about 95 days (Shen & Lin, 2006), the suggestion that increases in residence time are much greater than increases in inputs is likely to be true. Moreover, this result suggests that residence time is not necessarily a good predictor of TP retention. In fact, unlike TN, when regressions relating discharge, CHLa concentration, and estuarine water temperature to our TP retention estimates were compiled, the only significant and strong predictor of TP retention was discharge. Furthermore, unlike TN, the relationship between discharge and TP retention was positive (i.e., residence time was negative). This explains the strong positive relationship between inputs and TP retention since TP inputs were dominated by riverine inputs that increased with discharge. However, although absolute retention increased with inputs, proportional retention remained relatively constant year round, suggesting that during the low discharge summer months, retention of TP is governed by a mechanism different than the sedimentation of riverine derived PP. Thus, there are two mechanisms for TP retention that vary with discharge and season.

The most important mechanism of retention for the tidal freshwater James River is the abiotic process of PP sedimentation during high discharge periods. Because of the strong positive relationship between discharge and TP concentration, as river discharge increases there is a disproportionate increase in TP inputs as well. However, although discharge increases, concentrations of TP at JMS75 tend to remain relatively constant, resulting in riverine outputs that increase only due to discharge. Accordingly, riverine inputs are much greater than riverine outputs during these periods and retention is high. During three high discharge events (640 – 1359 m^3/s), longitudinal concentrations of TSS and TP decreased in the downstream direction by up to 13- and 6-fold, respectively (Appendix Figure 6). Because the cross sectional area of the estuary increases in the downstream direction, velocity therefore decreases, allowing the PP to settle out of the water column and bury in the sediments, which is a phenomenon observed in many tidal freshwater reaches (Schuchardt et al., 1993; Boynton et al., 1995). This abiotic mechanism of retention is perhaps the most important for P retention because during these high discharge winter months 86% of the annual absolute retention occurs.

The low discharge mechanism of TP retention is likely controlled by autochthonous PP sedimentation when longer residence times and more inorganic rich inputs allow for greater algal assimilation and sediment adsorption with subsequent burial in the sediments. During summer months when river discharge decreases, TP inputs are 4-fold smaller and thus absolute retention was lower than the high discharge periods, although proportional retention remained relatively constant. Because the relative contribution of point sources increases during these low discharge periods, the proportion of inputs that are PO_4 increased from 12% during high discharge periods to 45%. Here, residence time and algal production became major drivers of retention, similar to the summertime retention of TN. However, in the case of TP, it is also possible that a proportion of inorganic P inputs adsorbed to the tidally suspended sediments and ultimately became buried in the sediments. Because neither process was measured directly, the presence of the CHLa maximum at JMS75 suggests that algal uptake may be more important, although more research is necessary in order to know the relative importance of both processes. Regardless, it is therefore possible that the high proportion of annual TP retention relative to TN is predominantly due to burial of TP in the sediments, which is driven by a high discharge and a low discharge mechanism.

Given that the end fate of TP is in the sediments, it is likely that the maintenance of the navigational channel through dredging and subsequent removal of sediments to an upland storage basin (USACE, pers. comm.) is a possible permanent removal of TP from the study reach. Using an average ratio of water column TP:TSS (0.006 mg/mg; CV=76%) and assuming conservation of this ratio from the water column to the sediments, an average of about 20% of TP inputs would be removed through dredging based on an average of 74,000 m^3 of sediments removed each year (1,550,106 m^3 removed between 1990 and 2011; USACE, pers.comm.; Schlegel, 2011). However, because this conservative assumption is potentially unrealistic, we used a sediment TP:TSS ratio (0.001 mg/mg) that was measured at JMS75 in 1994 (Meyers, 1994). Using this ratio, less than 10% of TP inputs were removed through dredging suggesting that the majority of TP inputs are retained in the sediments. This 6-fold discrepancy between water column TP:TSS and sediment TP:TSS suggests that TP retained in the sediments does not necessarily remain within the sediments. Because sediment PO_4 release rates for the upper Potomac, Patuxent, and Choptank Rivers represented substantial losses of P from sediments to the water column (740-5816 mg P/m^2/d; Boynton et al., 1995), it is therefore possible that long term storage of P in the sediments may not be as high as our estimates suggest. However, because there were no direct measurements of sediment-water exchange of P, more research focused on these sediment-water nutrient exchanges must be conducted to understand the long term fate of N & P retained in the sediments of the tidal freshwater James River.

Conclusions

Our study reach received large areal loading rates of nutrients relative to other estuaries. While this is an artifact of the smaller estuarine surface area of tidal freshwater reaches relative to entire estuaries, it emphasizes the role that these segments of estuaries play in intercepting nutrient loads from the watershed. Seasonal variation in river discharge drives differences in the magnitude and composition of nutrient loads with high discharge winter months having large loads that are predominantly composed of particulate and/or organic nutrients and low discharge summer months having relatively smaller and more inorganic loads. These seasonal variations in river discharge also directly affect residence time and thus the retention of nutrients. Annually, TN retention was a function of residence time, although at monthly intervals, the retention of TN may be driven by the complex interaction of residence time, water temperature, and algal biomass. Alternatively, annual retention of TP was not a function of residence time, but instead it was driven by two different mechanisms. Both mechanisms involved the ultimate burial of TP in the sediments with the high discharge retention mechanism being the sedimentation of riverine derived PP, and the low discharge mechanism being the sedimentation of autochthonous PP that increases in efficiency with long residence times. Finally, because the end fate of P is in the sediments, more research must be done on sediment P fluxes in order to determine if the sediments function as a permanent sink for a large proportion of retained P.

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Table 1. Physical dimensions and distribution of sampling locations within the five zones comprising the study reach.

	Stations	Area m2	Mean Depth m	Volume m3	Area %	Volume %	Data Source
Zone 1	JMS110, 107, & 104	2,066,000	*3.000*	6,197,000	5%	8%	USACoE Navigational Charts
Zone 2	JMS99 & 94	6,348,000	2.480	15,744,000	15%	19%	NOAA Estuarine Bathymetric Data Set
Zone 3	JMS87, 79	11,884,000	3.029	35,998,000	28 %	45%	NOAA Estuarine Bathymetric Data Set
Zone 4	JMS75	14,046,000	1.616	22,703,000	33%	28%	NOAA Estuarine Bathymetric Data Set
Zone 5	APP1.5	8,012,000	0.019	151,000	19%	<1%	CBP 2004 Segmentation Scheme Report
Total		42,356,000	1.907	80,793,000			

Table 2. Data sources used to construct a nutrient mass balance for the tidal freshwater James River.

	Estuary Water Chemistry				Riverine Inputs (USGS)		Point Sources (NPDES)			Tides (NOAA)
	VCU			VaDEQ						
	2007	**2009**	**2010-2011**	**CBMP & AWQM**	**Discharge**	**Chemistry**	**Municipal WWTPs & Industry**	**Richmond CSO**		**Hopewell & Sewells Tidal Amplitude**
Sample Frequency	Bi-monthly	Bi-weekly	Weekly	Monthly	Daily	Monthly & Storm Events	Monthly	Monthly	Event Based	3-4 Times Daily
Sampling Dates	12	29	20	48	4383	161	442	48	4	6336
Time Period	Apr-Nov 2007	Aug-Oct 2009	Jul 2010 - Jun 2011	Dec 2006 - Nov 2010	Jan 2007 - Dec 2010	Jan 2007 - Dec 2010	Jan 2007 - Jun 2011	Jan 2007 - Jun 2011	Sep - Nov 2009	Jan 2007 - Jun 2011
Sampling Locations, Gauging Sites, Permits	JMS99 JMS94 JMS87 JMS79 JMS75 JMS69	JMS110 JMS107 JMS104 JMS99 JMS94 JMS87 JMS75	JMS110 JMS107 JMS104 JMS99 JMS94 JMS87 JMS75 JMS69	JMS110 JMS104 JMS99 JMS87 JMS75 JMS69 APP1.5	USGS 02035000 02037500 02041650	USGS 02035000 02041650	VA0063177 VA0024996 VA0060194 VA0066630 VA0063690 VA0025437 VA0002780 VA0026557 VA0004669 VA0005291	VA0063177	VA0063177	NOAA Tidal Gauge 8638610 8638481
Parameters Measured	TN, NH_3, NO_x, TP, PO_4, & CHLa	TN, NH_3, NO_x, TP, PO_4, CHLa, TSS, & Cl	TN, NH_3, NO_x, TP, PO_4, CHLa, TSS, & Cl	TN, NH_3, NO_x, TP, PO_4, CHLa, & TSS	Discharge	TN, NH_3, NO_x, TP, & PO_4	TN, NH_3, NO_x, TP, PO_4, & Flow	Discharge	TN, NH_3, NO_x, TP, & PO_4	Surface Water Elevation

Table 3. Average daily fluxes (±SE) to and from the tidal freshwater James River during 2007-2010. Output fluxes are shown as negative values to indicate their value in equation 1. Quadrature adition was used to derive standard error of retention estimates based on standard errors of component fluxes.

Budget Term	TN	NH_3	NO_x	TP	PO_4
			(kg/d)		
Riverine Inputs	13,090 ± 1,488	319 ± 41	4,343 ± 524	2,498 ± 287	203 ± 35
Point Source Inputs	9,137 ± 210	2,599 ± 139	4,973 ± 115	470 ± 15	357 ± 15
Riverine Outputs	-16,227 ± 2,229	-1,661 ± 405	-7,130 ± 811	-1,214 ± 195	-230 ± 33
Tidal Exchange	-67 ± 19	-18 ± 5	-38 ± 8	-1 ± 1	0 ± 0
Retention	5,932 ± 2,689	1,239 ± 430	2,148 ± 973	1,753 ± 348	331 ± 50

Table 4. Mean nutrient concentrations (mg/L) of riverine (James, Appomattox) and point source inputs to the tidal freshwater James River during 2007-2010 (±SE). Point source concentrations are a volume-weighted average for the ten major outfalls that discharge to the study reach.

	James River	Appomattox River	Point Sources
TN	0.524±0.004	0.649±0.005	8.02±0.21
NH_3	0.010±0.001	0.023±0.001	2.28±0.23
NO_x	0.173±0.003	0.230±0.004	4.36±0.10
TP	0.061±0.002	0.053±0.001	0.412±0.036
PO_4	0.012±0.001	0.013±0.001	0.313±0.031

Table 5. Areal loading rates for different coastal systems and the tidal freshwater James River during 2007-2010. Areal rates are derived by dividing the flux by the estuarine surface area.

System	Estuarine Surface Area	TN	TP
	m^2	$mg/m^2/d$	
Pawcatuck: Little Narragansett Bay[a]	9,600,000	128	12
Chincoteague Bay[a]	328,500,000[b]	8	1
Greenwhich Bay, RI[a]	12,000,000[c]	24	6
Thames[d]	248,000,000	411	
Medway[d]	57,000,000	1	
Moreton Bay[e]	1,775,000,000	<1	
Swan River (dry)[f]	31,000,000	45	3
Swan River (wet)[f]	31,000,000	116	8
Baltic Sea[g]	374,600,000,000	8	<1
Chesapeake Bay[g]	11,542,000,000	36	3
Delaware Bay - Delaware-New Jersey[g]	1,989,000,000	73	13
Narragansett Bay, Rhode Island[g]	328,000,000	71	10
Guadalupe Estuary, Texas 1984[g]	551,000,000	21	6
Guadalupe Estuary, Texas 1987[g]	551,000,000	79	15
Potomac Estuary[g]	1,210,000,000	80	4
Ochlockonee Bay, Florida[g]	24,000,000	230	
Boston Harbor, Massachusetts[g]	108,000,000	349	56
Scheldt Estuary[g]	277,000,000	514	88
Upper Patuxent Estuary (Pre-BNR; 1986-1990)[h]	26,000,000	205	13
Upper Patuxent Estuary (Post-BNR; 1993-1999[h]	26,000,000	209	18
Tidal Freshwater James River (2007)	42,400,000	371	68
Tidal Freshwater James River (2008)	42,400,000	330	36
Tidal Freshwater James River (2009)	42,400,000	435	83
Tidal Freshwater James River (2010)	42,400,000	396	93
Tidal Freshwater James River (Mean 2007-2010)	42,400,000	383	70

[a]Fulweiler & Nixon, 2005
[b]Pritchard, 1960
[c]Granger et al., 2000
[d]Devlin et al., 2011
[e]Ferguson & Eyre, 2010
[f]Robson et al., 2008
[g]Nixon et al., 1996
[h]Boynton et al., 2008

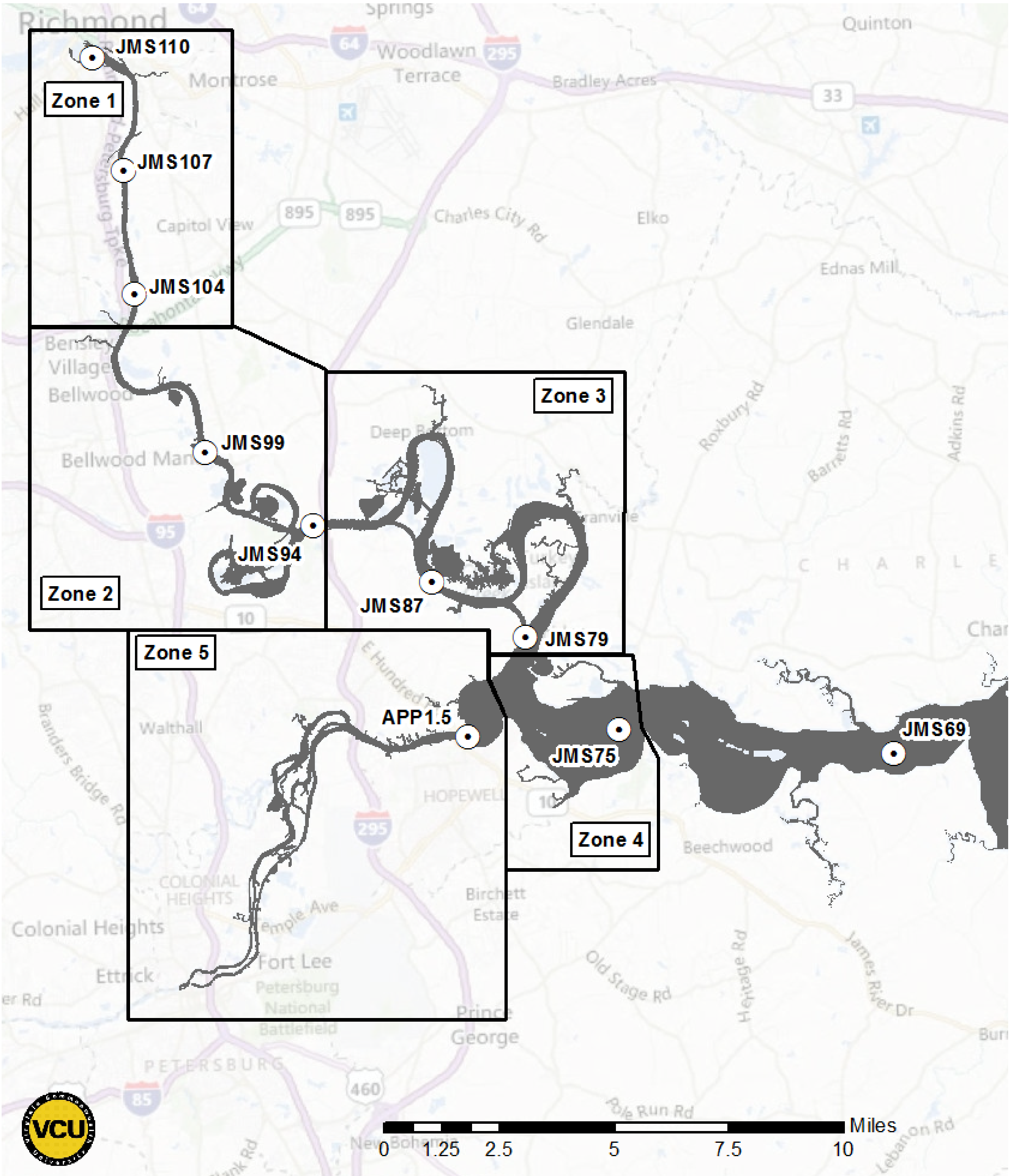

Figure 1. Distribution of estuarine sampling stations and the 5 study reach zones within the tidal freshwater James River.

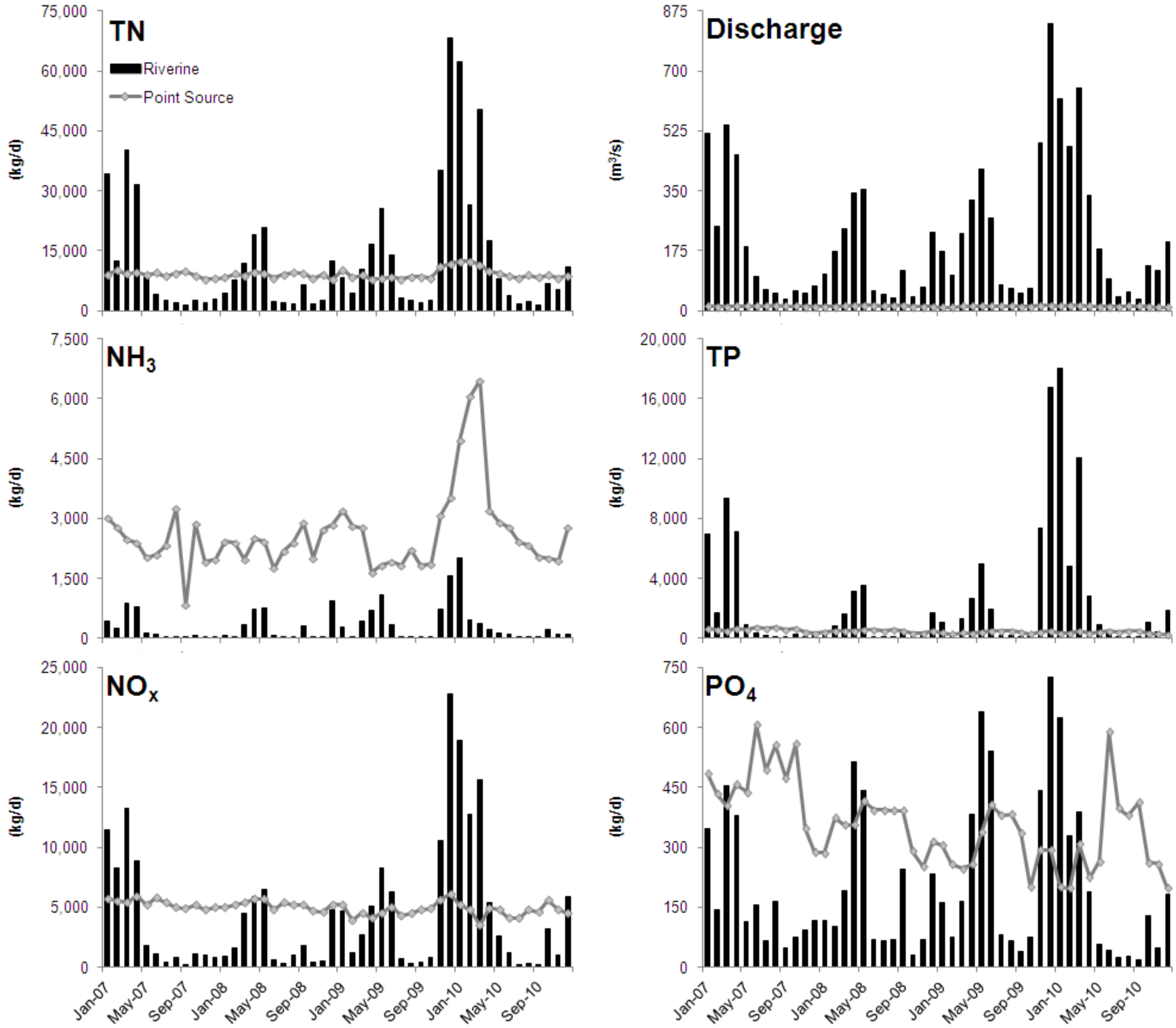

Figure 2. Riverine and Point Source inputs of water and nutrients to the study reach.

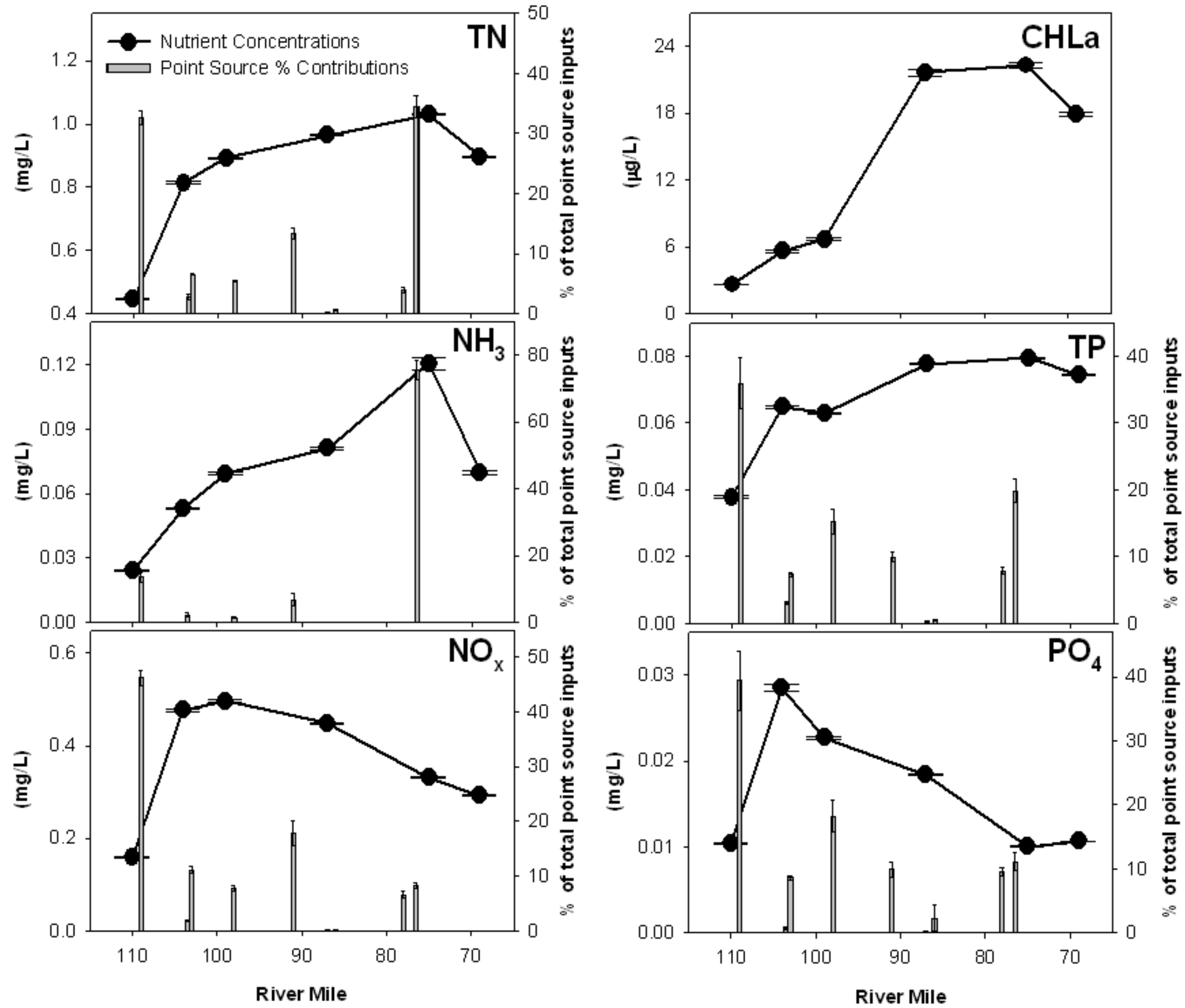

Figure 3. Longitudinal variation in CHLa, nutrient concentrations, and point source inputs to the tidal freshwater James River for 2007-2010 (±SE). Data are four year means. Bars denote proportional contributions by individual point sources, with the exception of the Hopewell WWTP and Honeywell Inc., which are both located at river mile 76.5.

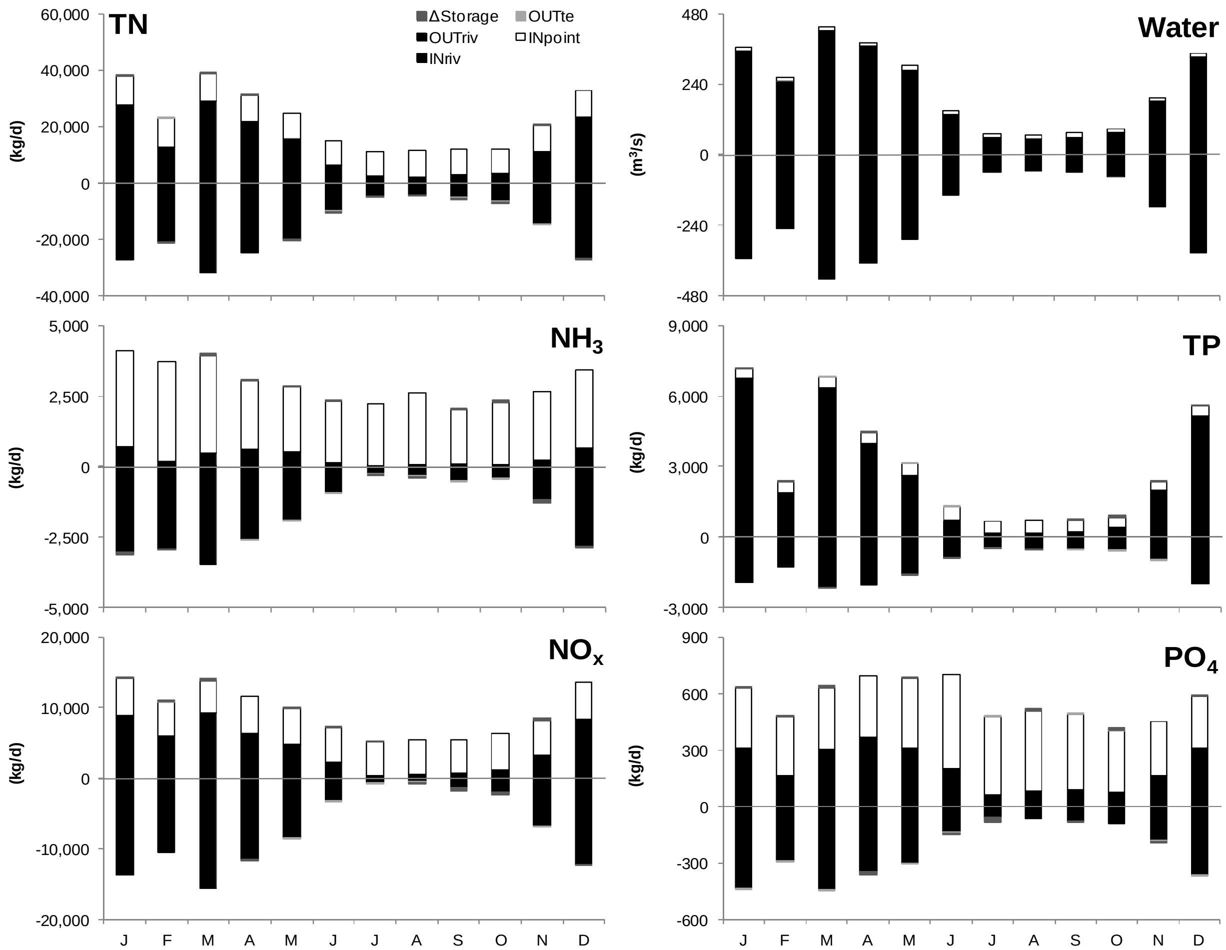

Figure 4. Water and nutrient budgets depicted as daily average values by month for 2007-2010. Storage and tidal exchange values are too small to be apparent in some cases.

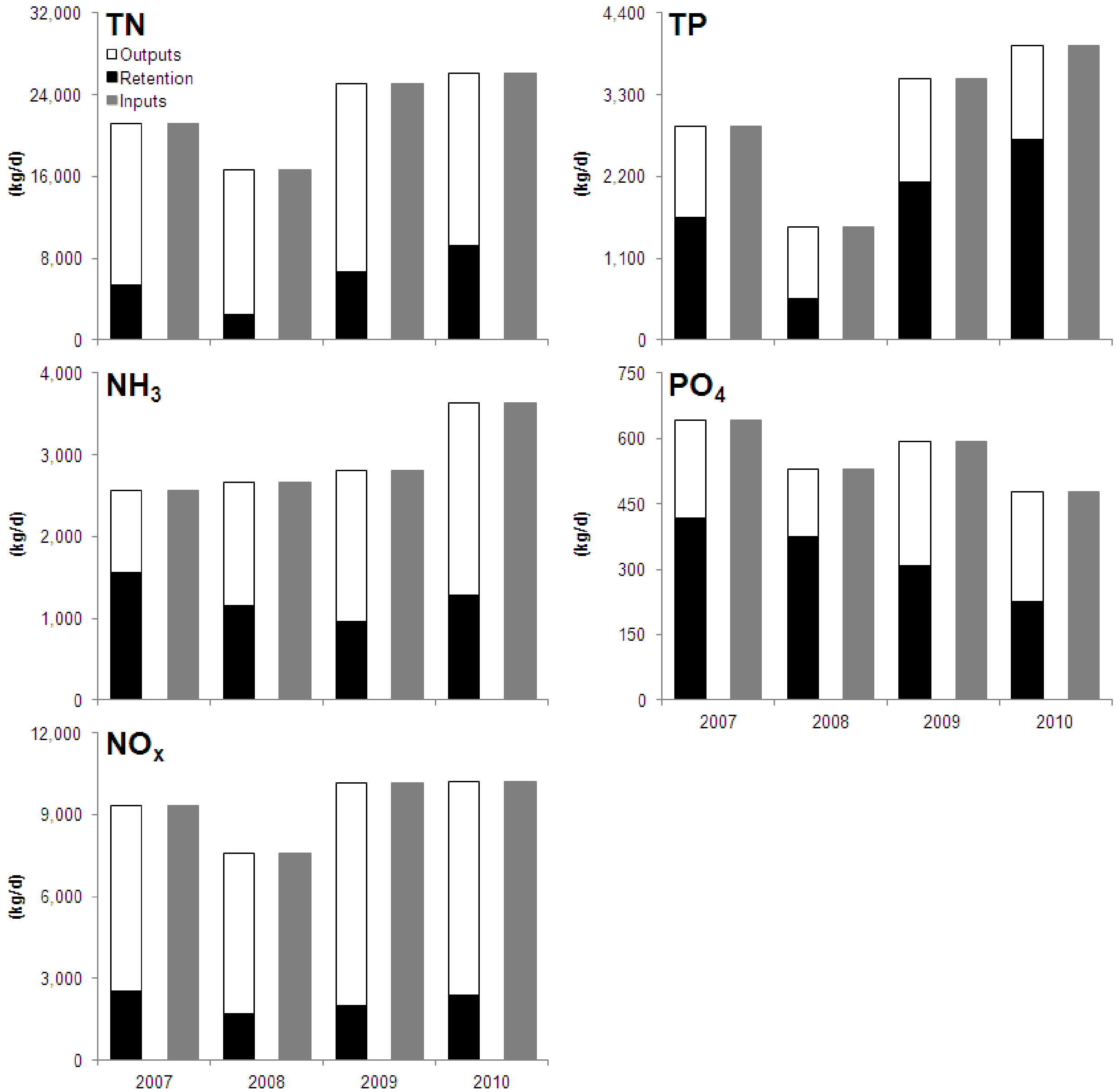

Figure 5. Interannual variation in annual nutrient inputs, outputs, and retention in the tidal freshwater James River during 2007-2010.

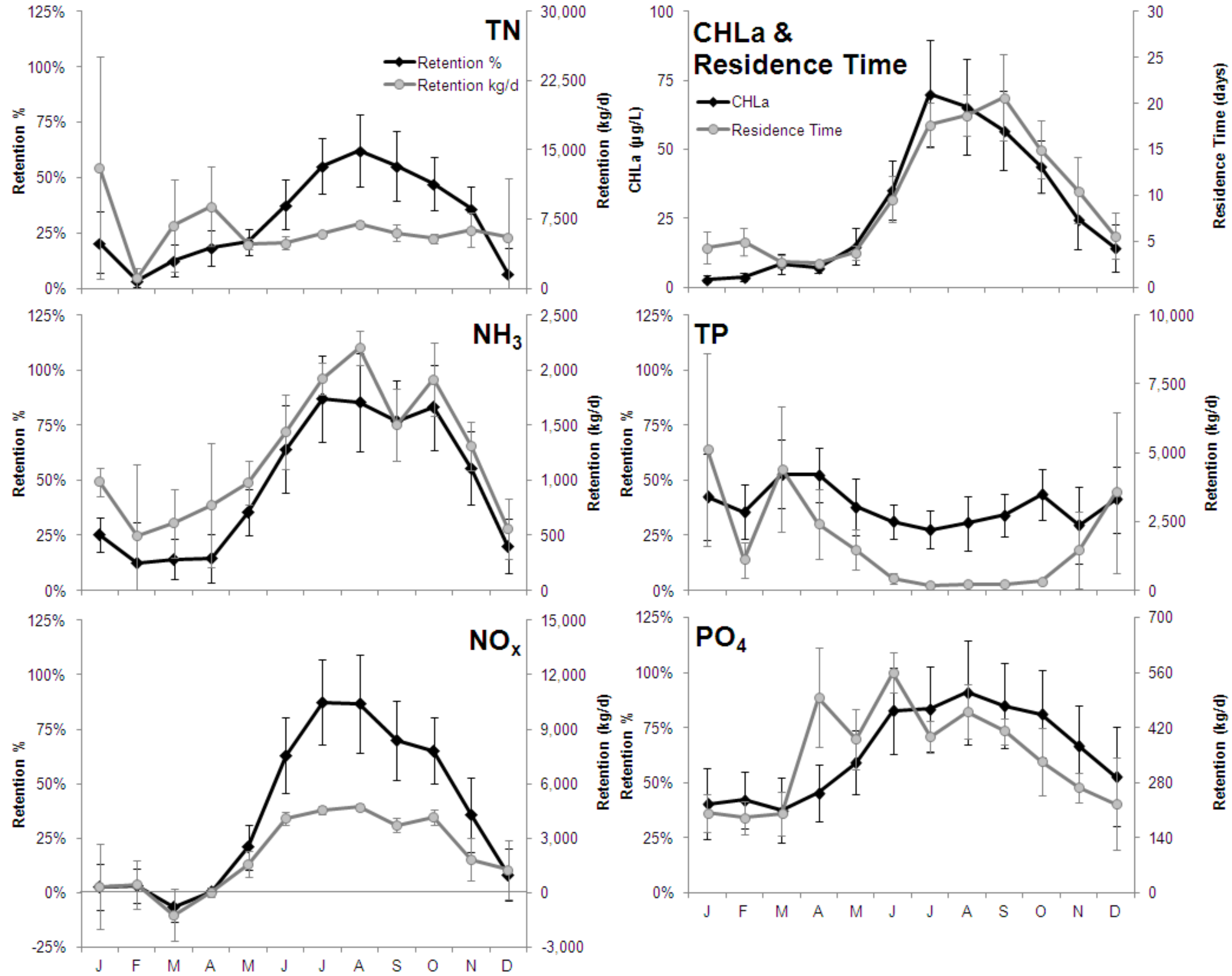

Figure 6. Seasonal variation in proportional retention (% of inputs), absolute retention (kg/d), chlorophyll-a, and residence time in the tidal freshwater James River. Mean and SE are based on monthly values for 2007-2010. Residence time is based on the freshwater replacement time.

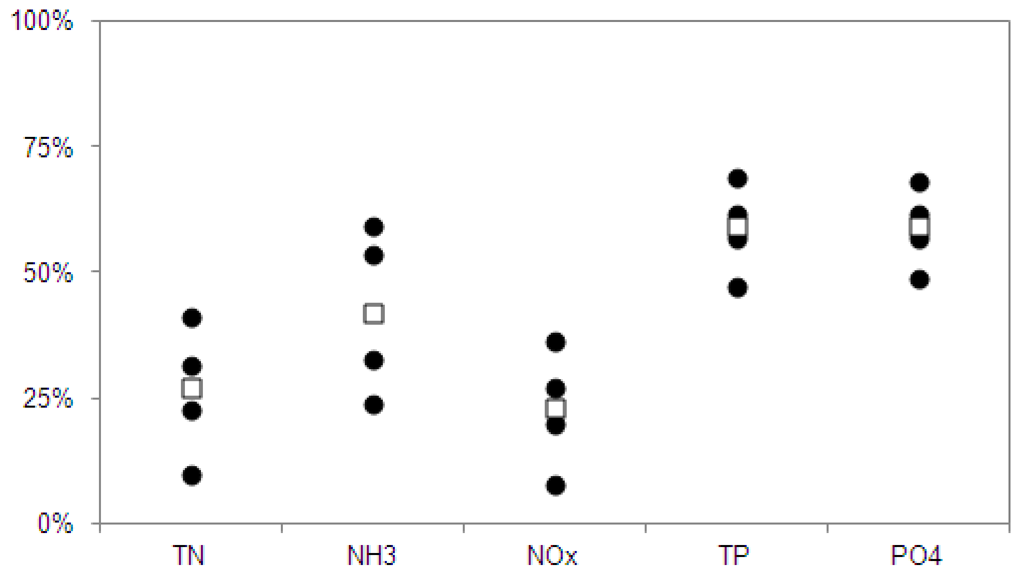

Figure 7. Ranges (closed circles) of annual mean retention as a percent of inputs for all five nutrient fractions. Ranges are based on adjustment of derived fluxes by their budget term errors (Eyre et al., 2011), and are plotted about the actual (open squares) estimated retention.

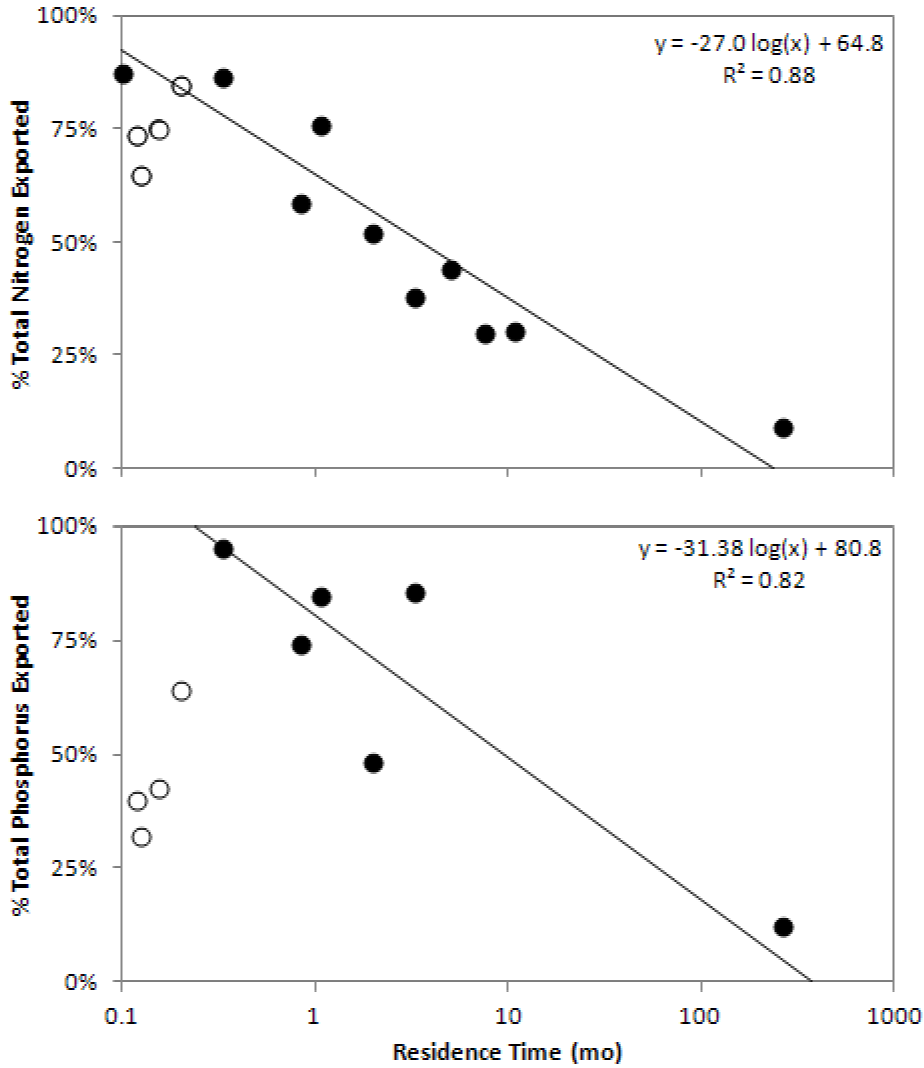

Figure 8. Comparison of residence time and percent of TN and TP inputs that were exported from different estuaries (Nixon et al. 1996). Closed circles, regression lines, and regression equations are from Nixon et al. 1996, with open circles representing the tidal freshwater James River during 2007-2010. Estuaries from Nixon et al. 1996 include the Baltic Sea , Chesapeake Bay (TN only), Delaware Bay, Narragansett Bay, Guadalupe Estuary in a dry (1984) and wet (1987) year, Potomac Estuary (TN only), Ochlockonee Bay (TN only), Boston Harbor, and Scheldt Estuary.

APPENDIX

Table 1. Mean nutrient concentrations for four CSO events monitored in 2009 by the Richmond Department of Public Utilities and the mean (±SE) of all four events. TN was calculated by the sum of total Kjeldahl nitrogen and NO_x.

Date	TN	NH_3	NO_x (mg/L)	TP	PO_4
9/9/2009	6.6	3.4	0.7	0.5	0.4
9/28/2009	4.4	0.9	N/A	0.4	0.3
10/25/2009	7.2	2.9	0.6	1.6	0.3
11/11/2009	13.4	7.4	0.6	1.3	0.5
Mean	7.9±1.9	3.7±1.4	0.6±0.03	1.0±0.3	0.4±0.05

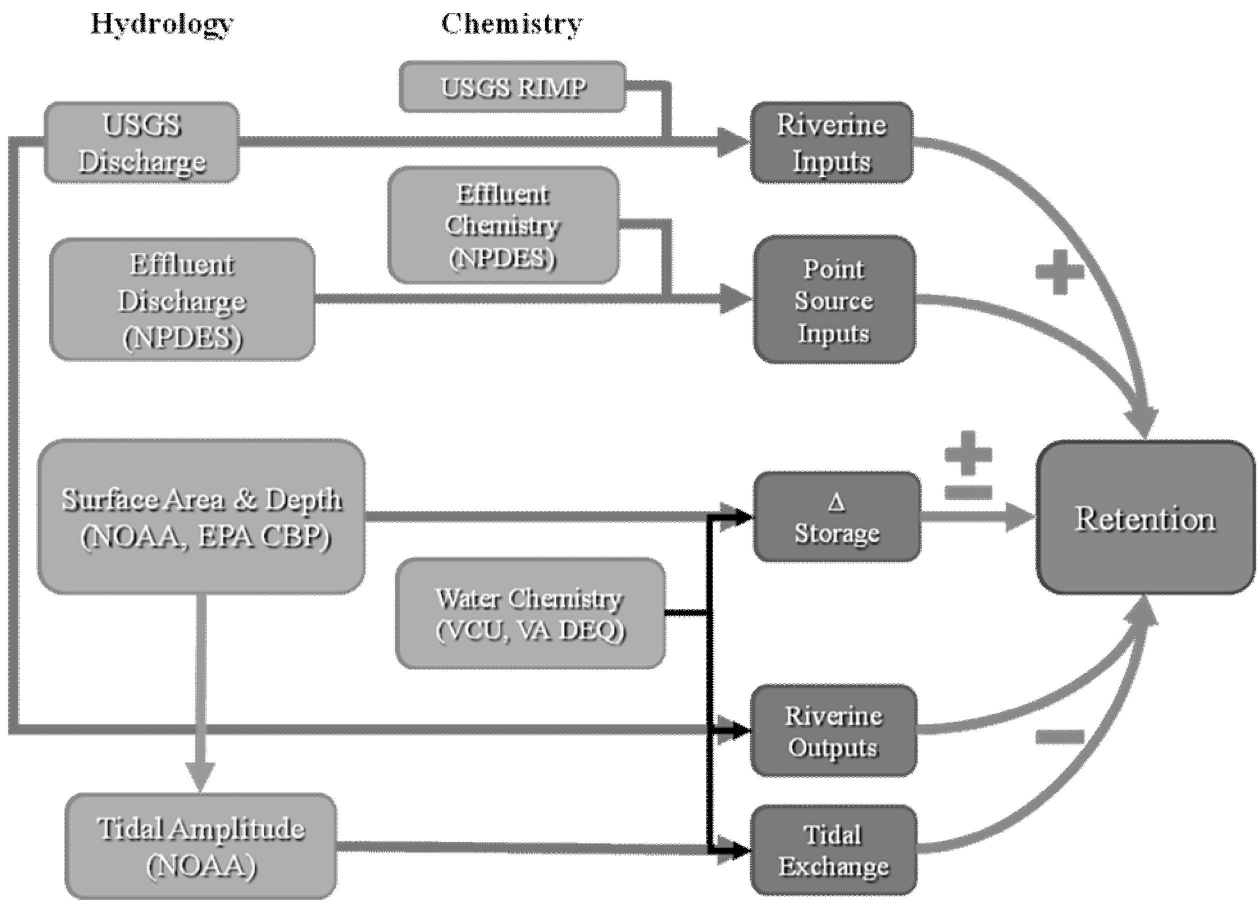

Figure 1. Flow chart indicating the use of different data sources (light grey) to derive the budget terms (dark grey).

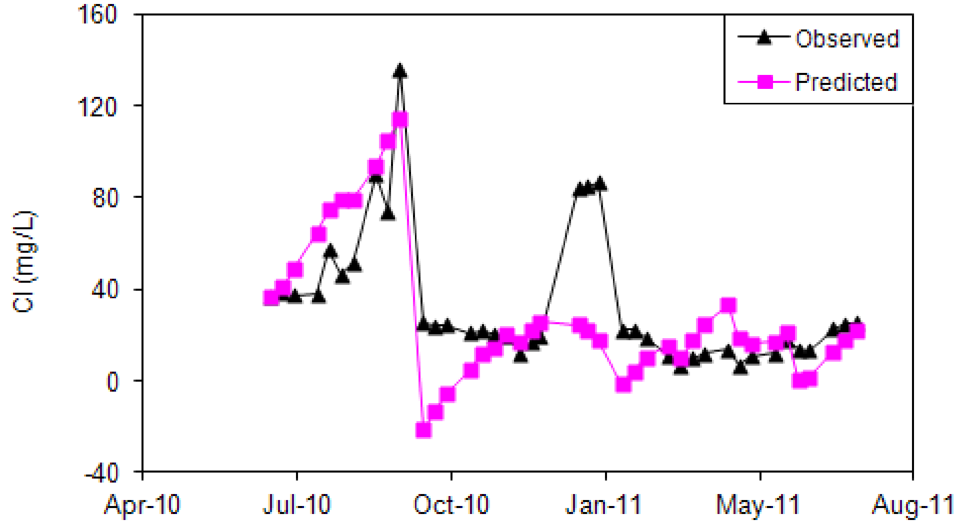

Figure 2. Observed and predicted volume weighted chloride concentrations for the study reach from July 2010 to June 2011.

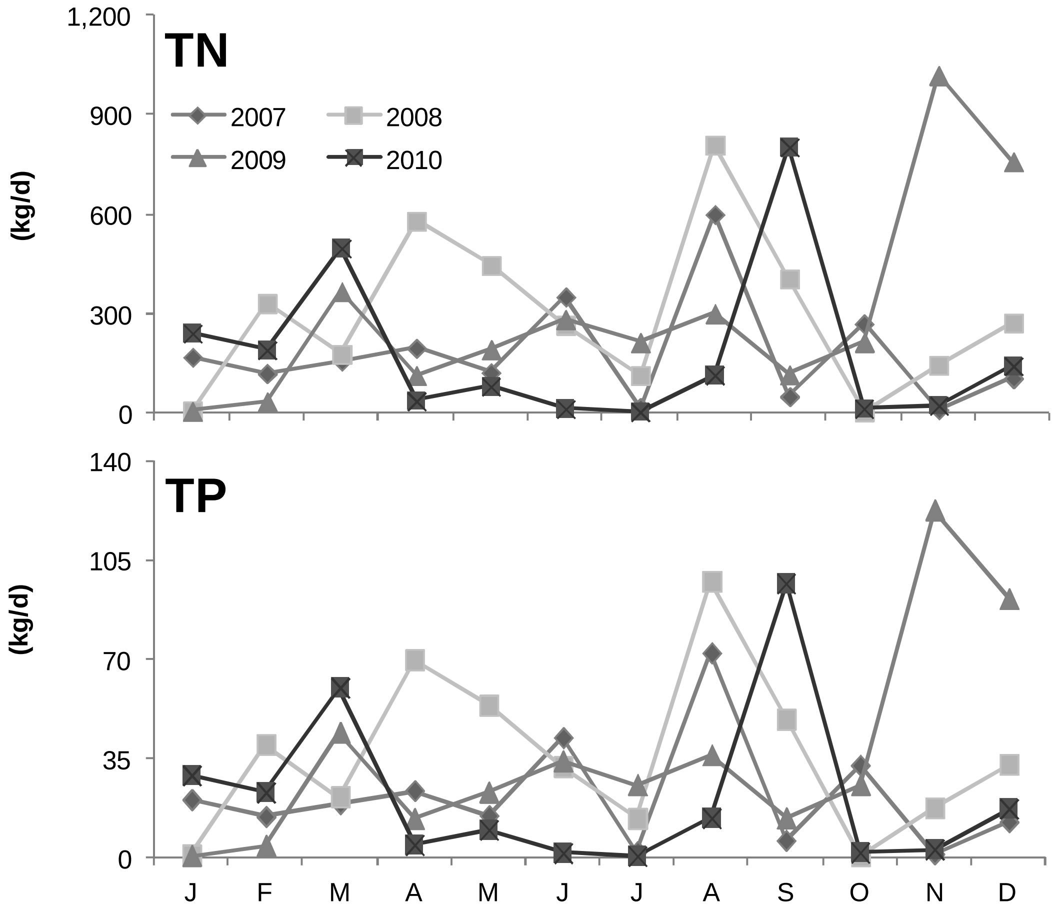

Figure 3. CSO event monthly TN and TP fluxes from the Richmond Combined Sewer System for 2007-2010.

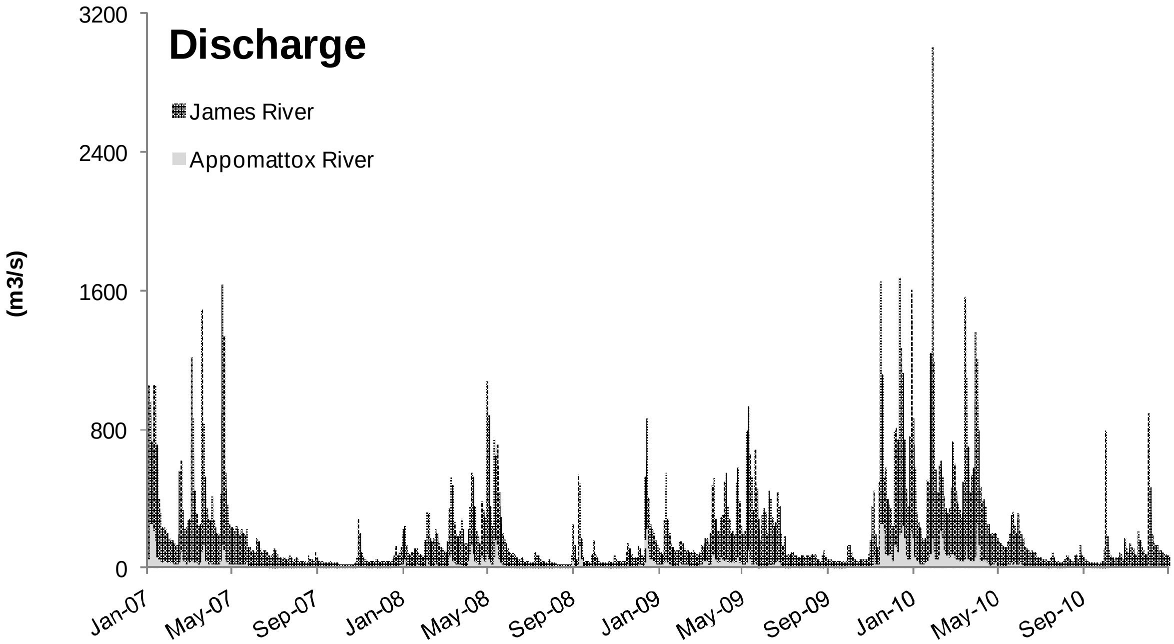

Figure 4. Four year (2007-2010) time series of average daily discharge for both the James and Appomattox Rivers. Discharge values are plotted as stacked bars in order to show the total daily average.

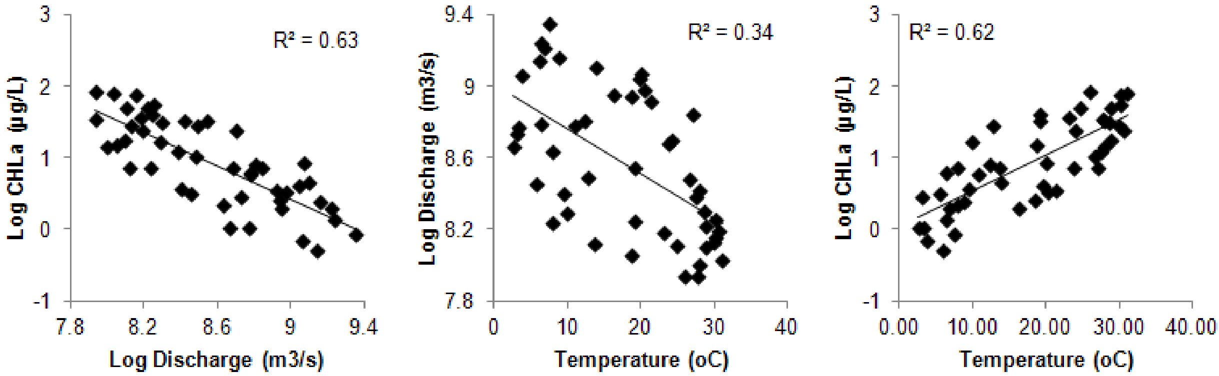

Figure 5. Relationships between discharge, chlorophyll-a, and estuarine water temperature for the tidal freshwater James River during 2007-2010. All relationships are significant.

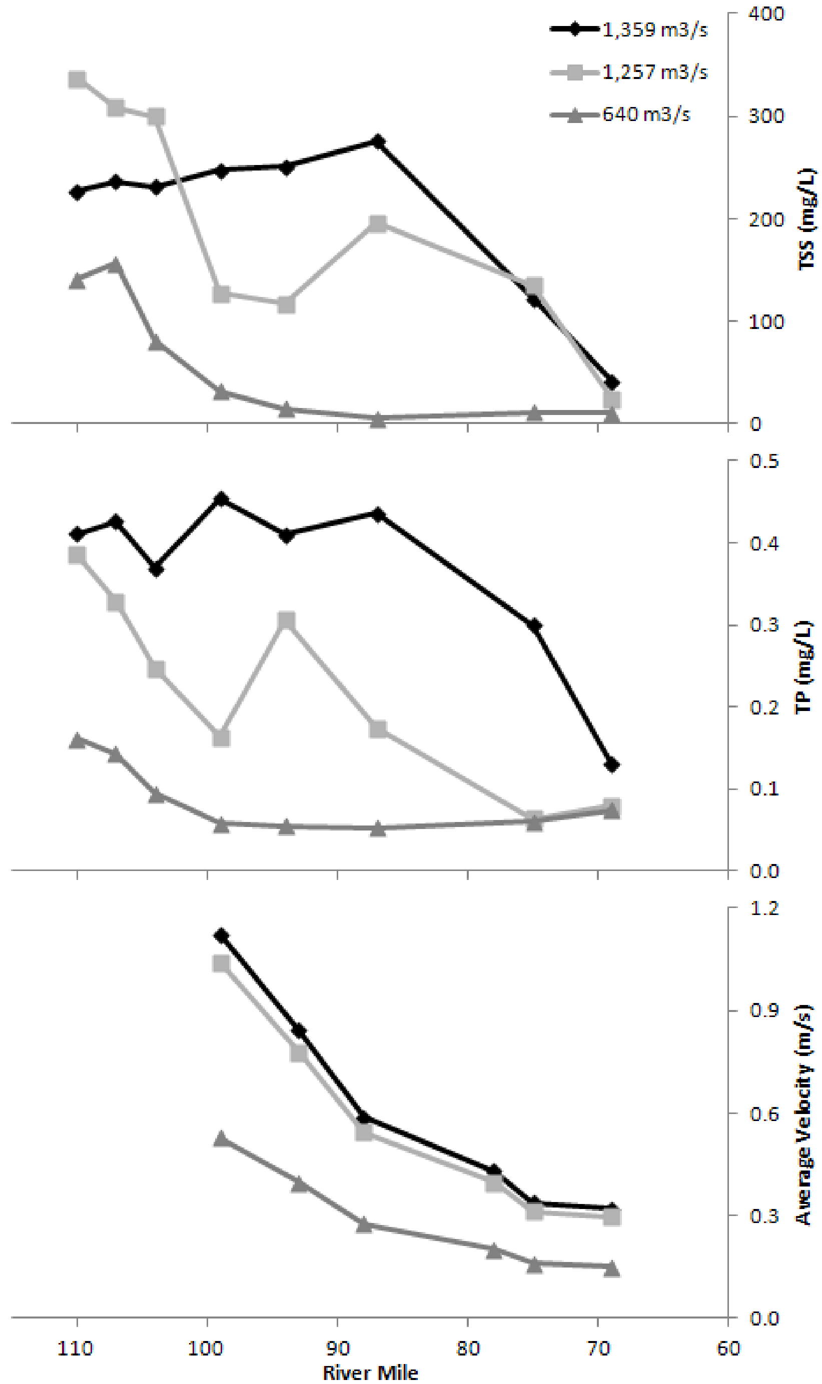

Figure 6. Longitudinal profiles of TSS, TP, and average water velocity in the tidal freshwater James River during three high discharge events. The 1359 m3/s, 1257 m3/s, and 640 m3/s events occurred on 4-19-2011, 3-8-2011, and 12-1-2011, respectively. Average velocity was derived from average discharge divided by river cross-sectional area.

VITA

William Isenberg was born in Miami, FL on January 27th, 1988. After graduating Palmer Trinity High School in 2006, he moved to Richmond, VA where he started his college career at Virginia Commonwealth University as a Jazz Performance Major. In 2007 he switched major to Environmental Studies, and graduated in 2010 summa cum laude with a B.S. in Environmental Studies. Through his time in the Center for Environmental Studies, he received a teaching assistantship and was a water quality technician on the James River water quality cruises that were funded by the City of Richmond Department of Public Utilities. Starting in August 2012, he will be teaching middle school science in Huntingtown, Maryland.