ABSTRACT

Title of Document: EVALUATION OF THE INFLUENCE OF NITROGEN ON PRIMARY PRODUCTION USING RETROSPECTIVE DATA, REGRESSION ANALYSIS, AND MODELING

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Anthropogenic activities have negatively affected water quality in the Chesapeake Bay and its tributaries. The Potomac River (PR), the largest tributary, is a primary study site for water quality research and new management strategies. The Blue Plains Wastewater Treatment Plant (BP), located in the tidal fresh portion of the PR, is the largest total nitrogen (TN) point source. Retrospective examination of water quality data for the PR revealed relationships among discharge, N loading and concentration, light and primary production. Regression analysis revealed BP (TN) load was an important variable influencing production, coupled with local dissolved inorganic nitrogen concentrations and photic depth prior to installation of biological nutrient removal (BNR) at BP. After 100% BNR implementation, BP TN did not influence production. Four existing primary production models were evaluated for applicability to tidal fresh systems. Regression analysis demonstrated all models were significant but the $BZpI_0t$ model provided the most robust results.

EVALUATION OF THE INFLUENCE OF NITROGEN ON PRIMARY PRODUCTION USING RETROSPECTIVE DATA, REGRESSION ANALYSIS, AND MODELING

By

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DEDICATION

I want to dedicate this thesis to the kids in my virtue class in East Baltimore City. Thank you for helping me see clearly; I hope I encourage you the same way as you do for me.

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Chapter 1

A Retrospective Review of Water Quality Management in the Potomac Estuary and the Influence of Nitrogen on Primary Production

Introduction

Since the early 20th century, anthropogenic activities such as increased non-point nutrient runoff from terrestrial areas and point source wastewater discharges have negatively affected water quality in the Chesapeake Bay resulting in low dissolved oxygen concentrations, increased phytoplankton biomass, decreased water clarity, and loss of submerged aquatic macrophytes (Boesch et al. 2001, Hagy et al. 2004, Kemp et al. 2005). As we move into the 21st century it is pertinent to evaluate how past pollution events have altered estuarine communities and various ecosystem processes, as well as how improvements in water quality monitoring and wastewater treatment technology have aided restoration efforts. Periodic evaluation of the effectiveness of new technology, and resultant declines in pollutant loading as detected by monitoring programs, aids in increasing awareness of management successes or failures and improves future restoration strategies.

The Potomac River has been a key study site in water quality research, beginning with work to address public health concerns such as safe drinking water and waterborne disease during periods of population growth and urbanization. This tradition has continued through current water quality monitoring and management programs. Many years ago the Potomac River was thriving with fish, submerged aquatic vegetation (SAV) (Orth and Moore 1984), and other aquatic wildlife (ICPRB 2008), but as the population grew, the resulting sewage effluent was discharged directly to local waters untreated, causing severe bacterial contamination and low dissolved oxygen (DO) concentrations. In 1894 the U.S. Public Health Service considered the water unfit for humans and began efforts to define pollution and sanitary conditions that eventually influenced standards nationwide (Jaworski et al. 2007). In 1965, President Lyndon B. Johnson remarked in his State of the Union address:

> *"We will seek legal power to prevent pollution of our air and water before it happens. We will step up our effort to control harmful wastes, giving first priority to the cleanup of our most contaminated rivers. We will increase research to learn much more about the control of pollution. We hope to make the Potomac a model of beauty here in the Capital, and preserve unspoiled stretches of some of our waterways with a Wild Rivers bill."*

Growing concern for the health of the Potomac River led to increased public awareness, scientific research, policies, management strategies and monitoring efforts within the estuary (Boesch et al. 2001). The timeline of these critical management events is provided in Table 1. The Potomac River is just one example of how policy and water quality evolved over this period of intense development and population growth. The coincident development of higher population pressure, poor local water quality, and the emergence of regulatory policy to manage these water quality issues was a model system for other urban waterways, especially as the Potomac is located so close to the seat of federal government.

Recently, Jaworski et al. (2007) reviewed water quality trends in the Potomac, providing a broad historical background that is important for this study. Here I introduce my thesis research by examining retrospective data from the Blue Plains Wastewater Treatment Plant (WWTP), located in the District of Columbia (DC), in the context of the review by Jaworski et al. (2007). In particular, I was interested in exploring how nutrient concentrations and nutrient loads related to changes in primary production during the past 20 years (1985 to 2007), and how wastewater treatment, using nitrogen reduction technology, has affected the relative importance of dissolved organic nitrogen (DON) versus dissolved inorganic nitrogen (DIN) in the tidal freshwater portion of the Potomac. I also investigated whether nitrogen loads discharged from the Blue Plains WWTP were related to changes in primary production at the discharge site and downstream of the treatment plant in the tidal fresh water portion of the estuary.

History of wastewater and sewage treatment in the Washington DC metro area and development of Blue Plains Wastewater Treatment Plant

In the early 1900s, about 50 million gallons per day (mgd) of untreated sewage was discharged into the upper estuary of the Potomac. The DC sewer system carried the waste of 340,000 people to the Potomac in 1914, increasing by 60% to 575,000 people by 1932, shortly before the opening of the first WWTP. When the Blue Plains WWTP first opened in 1938 it had a capacity of 130 mgd and was only capable of primary treatment to remove floatables and sludge (DC Water 2010). The WWTP was built to serve a population of 650,000 when the average discharge was less than 100 mgd. As pictured in Figure 1, the DC metro area population doubled from 1932 to 1956, and primary treatment was inadequate as evidenced by high biological oxygen demand in local waters. Secondary treatment was added in 1959 to accommodate the growing population and industrial development. Organic materials not removed during primary treatment are degraded by bacteria in the secondary treatment process. Following secondary treatment installation, Blue Plains discharge capacity averaged 240 mgd. In 1968, chlorination was added to kill bacteria and pathogens prior to discharge in the Potomac. Shortly thereafter (1969), the DC Government collaborated with Maryland and Virginia authorities to expand the facility to address issues associated with the growing population, such as poorly treated sewage and increased nutrient pollution, and to meet the needs of the Federal Clean Water Act. Water quality studies nationwide, linked to the Clean Water Act, put in motion modified discharge requirements for wastewater effluent, first targeting phosphorus (P) as this nutrient had been strongly linked to eutrophication in freshwater lake systems (Vollenweider 1976). In 1974, Blue Plains began experimenting with phosphorus removal methods. Accelerated by regional water quality monitoring and modeling efforts, phosphorus removal was achieved by 1986 at Blue Plains and other treatment plants in the area. Dechlorination (using sodium bisulfite additions) was added in 1988 after chlorine was found to be toxic to aquatic life.

In the time period between the Clean Water Act and complete P removal, ecological studies in marine, coastal, and estuarine waters indicated that another nutrient, nitrogen (N), was also a factor causing eutrophic conditions (D'Elia et al. 1986). Management efforts related to this insight included recommendations in the Chesapeake Bay Agreement, reached in 1987, indicating the first step toward restoration was to reduce the amount of nitrogen being discharged from point and non-point sources. Wastewater effluent is high in nitrogen as it includes the waste products generated by the animal agriculture waste and humans, and has increased globally since the advent of the

Haber-Bosch process of fertilizer production (Galloway et al. 2004). In this process anhydrous ammonia, created from N_2 gas, is applied to agricultural settings and supports a vast industry that, by at least one estimate, has increased protein excretion from ~11 g N $capita^{-1}$ d^{-1} to ~16 g N $capita^{-1}$ d^{-1} during the last 100 years (Nixon et al. 2008). As the single largest point-source of nitrogen to Chesapeake Bay, the Blue Plains WWTP was a critical pollution source targeted at that time for management actions.

A critical question I considered in this study was whether nitrogen sources from the upper Potomac non-tidal basin, or Blue Plains WWTP point source discharge of nitrogen, could be linked to water quality parameters in the tidal fresh portion of the Potomac estuary. Fortunately, the United States Geological Survey (USGS) conducts extensive monitoring of stream discharge and nutrient concentrations at stream sites throughout the United States. One site is located on the Potomac River at the head of tide or "fall line" near the Chain Bridge as identified in Figure 2. This site was established in 1891 and is the oldest gauged station in the eastern United States. The Chain Bridge gauge station was used in this analysis for river discharge data and determining nutrient loading. In addition to providing a historical record of nitrogen loading to the Potomac, the Chain Bridge provides a spatial boundary distinguishing inputs from the non-tidal upper watershed versus the tidal estuary where discharge from Blue Plains enters the ecosystem.

Prior to implementation of additional nutrient removal technology at Blue Plains, a baseline study of nitrogen inputs to the Potomac River, reviewed by Buchanan (2003), showed spatial patterns of nutrient concentrations downstream of the Chain Bridge gauge station using data provided by the Chesapeake Bay Program Database. The average nitrate (NO_3) and total dissolved nitrogen (TDN) concentrations from 1990-1996 at the Chain Bridge were ~1.1 mg L^{-1} and ~1.7 mg L^{-1}, respectively. During the same time period, spatial surveys of water quality that included nutrient analyses of water downstream of the Chain Bridge site, but above Blue Plains WWTP, reported slightly lower concentrations; however at the confluence of the Anacostia River and Blue Plains discharge, concentrations nearly doubled. Concentrations then peaked above the Woodrow Wilson Bridge and decreased downstream. These patterns are displayed in Figure 3 using distance from estuary mouth to describe sampling locations for nitrate and TDN. The location of the Blue Plains discharge pipe is coincident with the peak in dissolved nitrogen, pointing to the influence of this nitrogen source on local dissolved nitrogen concentrations. During this period nitrate concentrations in the tidal fresh Potomac were much higher than those associated with limiting algal growth. Buchanan (2003) noted dilution by Chesapeake Bay water moving upstream in the bottom layer was primarily responsible for decreasing TDN and NO_3 concentrations in the lower estuary. Other reasons for reduced dissolved nitrogen concentrations are uptake by phytoplankton in warmer months, denitrification, and burial into sediments in the particulate form (Boynton et al. 1995). Denitrification may remove as much as one-third of the nitrogen loads entering the tidal fresh portion of the Potomac (Seitzinger 1986).

Based on these conditions, new denitrification systems at the Blue Plains WWTP were tested in 1996 to transform nitrate produced during nitrification to nitrogen gas (N_2), treating at least 50% of the effluent in this way from 1996 to full implementation. By 2000 Blue Plains was operating a full biological nutrient removal (BNR) system to treat all effluent and met the Chesapeake Bay Program (CBP) goal of 40% reduction in nutrients from 1985 levels; an annual average total nitrogen (TN) load of 3.9 $x10^6$ kg N yr^{-1} or a discharge concentration of 7.5 mg L^{-1} was achieved. Since implementation of complete BNR the TN load has decreased by 56% compared to years when BNR was not online at Blue Plains WWTP (Buchanan 2003).

Impact of nutrients and nutrient reduction strategies on the Potomac Estuary

As of 2010 there were 483 major (discharge greater than 1 mgd) WWTPs in the Chesapeake Bay watershed; 17 of these are in the tidal Potomac (CBP 2010). Five of the 14 WWTPs in the DC area use BNR processes to reduce nitrogen loads. Blue Plains is the largest treatment plant and point source contributor of nitrogen in the Bay and Potomac River and processes 65% of the combined WWTP flows from the DC metro area (Buchanan, 2003).

Figure 4 is taken from Jaworski et al. (2007) and chronicles estimated and actual loads of N, P, and C to the Potomac from 1900 to 2005. Phosphorus removal from detergents, changes in phosphorus fertilizers, and improvements in wastewater treatment technology have brought phosphorus levels close to what existed in the watershed in the early 20^{th} century (Figure 4); (Walker et al. 2000). Total phosphorus fluxes have been maintained at ~2 kg km^{-2} y^{-1} as normalized to watershed surface area, about a 90% reduction from levels in 1970 (Jaworski and Romano 1999). However, TN fluxes have increased approximately 95% since 1965 (Jaworski and Romano 1999). TN fluxes to the estuary from wastewater treatment have increased from 30 kg km^{-2} y^{-1}in the 1900s to above 300 kg km^{-2} y^{-1} in the mid-1990s (Figure 4). After BNR installation in early 2000 the TN fluxes were cut in half to ~150 kg km^{-2} y^{-1} (Figure 4; Jaworski et al. 2007). The average TN concentration in the early 1900s from tidal WWTPs was approximately 16.5

mg L^{-1}. These values decreased to 8.5 mg L^{-1} in 2003 when most of the WWTPs in the tidal Potomac were implementing nitrogen removal. Comparing concentrations with loading demonstrates the effect of increasing nitrogen removal at WWTPs to estimate the occurrence of lower nitrogen point-of-entry concentration than previous conditions. However, this change in concentration cannot make up for the dramatic increase in discharge rates that has occurred over the same time period as a result of increases in population size.

The relative role of WWTP inputs in comparison to other sources of nitrogen to the estuary can also be examined using Figure 5 (Jaworski et al. 2007), which includes loadings of TN into the Potomac Estuary from WWTP, river export, and atmospheric deposition (both wet and dry). The TN loadings to the entire estuary have increased from about 13.6 $x10^6$ kg y^{-1} in the early 1900s to about 43.2 $x10^6$ kg y^{-1} from the 1980s to 1998; an increase of 215% (Jaworski et al. 2007). The annual TN flux from the upper basin of the Potomac and TN from WWTPs, referred to in Figure 5 as publically operated treatment works (POTW), increased from 350 kg km^{-2} y^{-1} in 1900 to 1910s to 840 kg km^{-2} y^{-1} with a peak of 1,800 kg km^{-2} y^{-1} in 1996. TN contribution from the upper Potomac has been consistently higher than from WWTPs, except in periods of low river discharge during the droughts of the 1960s, 1999, and the early 2000s. Riverine export was, and remains, the major source of TN loading to the tidal Potomac ecosystem.

Nutrient reduction efforts and the impact on local water quality are particularly noticeable upon examination of summer surface DO concentrations estimated and measured at the Woodrow Wilson Bridge and plotted in Figure 6 (Jaworski et al. 2007). In 1912, when the population was much lower, the average summer surface DO at the

Woodrow Wilson Bridge was about 4 mg L^{-1}. As the population increased and more untreated sewage was being discharged into the river, DO levels gradually decreased. This was likely also a result of biological oxygen demand as a result of the high carbon loads from wastewater prior to primary treatment. When new wastewater treatment technologies were added, DO levels increased (Figure 6).

Present nutrient sources to the Chesapeake Bay and contribution of Blue Plains WWTP

Each year approximately 181 $x10^6$ kg y^{-1} of nitrogen are deposited from the atmosphere onto the Chesapeake Bay watershed, of which 34 $x10^6$ kg y^{-1} actually reach tidal waters (CBP 2007). An additional 8.6 $x10^5$ kg y^{-1} are directly deposited onto the tidal waters, for a total of 42.6 $x10^6$ kg y^{-1} or 33% of the TN loads to the entire Bay. About 78% of the atmospheric load comes from anthropogenic sources. WWTPs discharge about 24 $x10^6$ kg y^{-1} of nitrogen, or 19% of the TN load making it the third largest anthropogenic nitrogen source. Agriculture, the second largest source, contributes 32% of the nitrogen load. These values are compiled to provide a picture of the Chesapeake Bay N loads in Figure 7 (CBP 2007).

Blue Plains is the largest point source contributor of nitrogen to the Potomac and Chesapeake Bay and discharges an average of 3.6 $x10^6$ kg of N per year (DC Water 2010). The US Environmental Protection Agency (EPA) recently restructured Blue Plains' operating permit, reducing the allowable nitrogen discharge by 45% of past levels to help improve water quality in the Potomac River and Chesapeake Bay. Given these mandated nitrogen reductions and their associated costs, it is important to evaluate how this change in loads could impact water quality.

A single atom of nitrogen may be recycled a number of times each year to produce organic matter in an estuary, influencing both nitrogen bioavailability as well as the respiratory demand of bottom waters based on detrital inputs. This nutrient recycling is biologically mediated primarily by phytoplankton and bacterial communities and there is now a greater appreciation for the importance of DON inputs supporting phytoplankton productivity (Bronk et al. 2007). With upgrades to the biological denitrification capacity at Blue Plains, the ratio of DIN to DON will change, with the more refractory organic nitrogen likely dominating the remaining TN discharged in effluent. Understanding how this balance of DON and DIN may affect organic matter production in the estuary is an important component of this research

A major goal of my data analysis was to understand the impact of different environmental variables on primary production and understand the current contribution of Blue Plains DON as a source of nitrogen supporting primary production. In addition, a critical component of my thesis is to evaluate which TN source, Blue Plains effluent or the Potomac River at the Chain Bridge, contributed to primary production in the tidal fresh portion of the estuary. Here, I continue my review of monitoring data to evaluate existing primary production data and explore empirical relations with nitrogen loads in the Potomac and parameters influencing algal growth. Because other factors such as advection and light also affect primary production, these environmental factors were explored as well.

Methods

Retrospective Data Sites

An initial, exploratory treatment of the long term datasets was undertaken to examine change over the 1984 through 2007 time period. The focus of this exploration was the tidal fresh portion of the Potomac estuary. Relevant datasets and sampling locations are described below.

Blue Plains Wastewater Treatment Plant

The Blue Plains WWTP is operated by DC Water, previously DC WASA. It is located in the tidal fresh portion of the Potomac River approximately 2 km south of the confluence of the Potomac and the Anacostia Rivers (Figure 2).

DC Water reported monthly averages of Blue Plains flow rates, total nitrogen, total inorganic nitrogen (TIN) and total organic nitrogen (TON) concentrations, and DO levels to the Metropolitan Washington Council of Governments (MWCOG) for a dataset from January 1984 through December 2007. TIN was calculated in the database as ammonium ($NH_{4)}$ + nitrite + nitrate (NO_{2+3}) and TON = TN – TIN. MWCOG submitted the data to the CBP; it is available in the Nutrient Point Source database. Nitrogen loads were calculated using the Blue Plains effluent flow rate and the concentrations of TN, TIN or TON.

Tidal Fresh 2.3

Environmental factors at Tidal Fresh (TF) 2.3, located about 30 km downstream of the Blue Plains WWTP discharge pipe, were used in the retrospective analysis because of its proximity to Blue Plains and completeness of monitoring parameters (Figure 2).

Maryland Department of Natural Resources (MD DNR) measured data for the following TF 2.3 parameters: surface temperature, chlorophyll concentration, photic depth, surface irradiance, DON and DIN concentrations, and primary production. MD DNR collected data once a month from October to March and twice a month from April to September. The data were obtained from the CBP Water Quality database (1984-present) and the Baywide Plankton database for the time series July 1984 through October 2007. Because of differences in analytical techniques for nitrogen, I further clarify that DIN is dissolved inorganic nitrogen analytes from the MD DNR program calculated as the sum of NO_{2+3} and NH_4. DON was calculated as total dissolved nitrogen minus NH_4 and NO_{2+3}. Nitrogen data for TF 2.3 and Blue Plains flow data had several gaps; therefore, when relationships between the two parameters were statistically analyzed, the time series was May 1991 to October 2007.

Chain Bridge

The USGS Chain Bridge gauging station is located approximately 17 km upstream of Blue Plains WWTP (Figure 2); this was the closest station to Blue Plains within the USGS gauge dataset. USGS measured Potomac River discharge, TN concentration and load, and total suspended sediments (TSS) at the Chain Bridge site and monthly values were used in this analysis. Annual streamflow was calculated using monthly mean discharge data from USGS. The USGS Chesapeake Bay River Input Monitoring Program provided the data for the time series from August 1985 through October 2007

Relationship between River Discharge and Algal Biomass

Because the tidal fresh portion of the Potomac is greatly affected by freshwater discharge events, I sought to evaluate the role that advection and related hydraulic fill time plays in chlorophyll concentrations at stations TF 2.3. Hydraulic fill time represents the amount of time it would take for a given discharge rate to “fill” the volume of a portion of the estuary. As such, it is a metric that describes the relationship between basic morphology and freshwater flow effects on factors such as residence time. To examine the relationship between algal biomass and river flow, the hydraulic fill time of the tidal fresh Potomac River was calculated using data provided by Boynton et al. (1990), Cronin (1971), and Cronin and Pritchard (1975). The Potomac River was divided into 5 nautical mile segments from the mouth of the Chesapeake Bay (segment 1) and up to the fall line (segment 97); (Figure 2). The segments were used to calculate the volume of the estuary based on the surface area and volume-to-surface area ratio (mean depth). In this analysis, segments 97 through 70 were used, which encompassed the Chain Bridge, Blue Plains, and TF 2.3. I summed volume data for each segment, then divided these volumes by average daily river flow to compute hydraulic fill time for each month of the available long term dataset. A time series of hydraulic fill time for the tidal fresh Potomac was plotted with chlorophyll data. Other relationships examined using this data included fill times of greater than or less than 30 days to evaluate whether time lags were important for corresponding chlorophyll data.

Regression Analysis

I chose to evaluate which principal nitrogen source contributed to primary production at TF 2.3 using multiple regression analysis. I used an “all possible subsets” approach to rank models that include several variables affecting primary production, with the perspective that such an approach would help to determine whether TN loads from the Potomac River at the Chain Bridge gauging station and/or the Blue Plains WWTP effluent would emerge as significant explanatory variables for primary production.

The best parameters for evaluating primary production were determined using “all possible subsets regression” analysis as an alternative to step-wise regression. This method tests all possible subsets of the potential independent variable dataset, and chooses the best model based on ranking criteria using a variety of metrics and penalties for the number of variables. This analysis ranked the models according to the second-order bias correction Akaike Information Criteria for a small dataset (AICc) and the adjusted coefficient of multiple determination (adjr^2). The adjr^2 is based on the coefficient of determination, r^2, but adjusted for the number terms in the model. R2 always increases when a new term is added, but adjr2 increases only in new term improved the model more than would be expected by chance.

The AICc is derived from the original Akaike Information Criterion (AIC). It is a tool for model selection calculated from the Kullback-Leibler distance between model i and the “true” model that generated the data. The Kullback-Leibler distance is the amount of information lost when using model i to approximate the true model. The best model has the smallest Kullback-Leibler distance and thus the smallest AIC. The AIC equation (1) is below

$$\mathrm{AIC} = -2\log(L) + 2K \tag{1}$$

where L is the maximized likelihood of a fitted model and K is the number of free parameters in the model itself.

The AICc is utilized when the sample size is small with respect to the maximum K in the dataset ($n/K < 40$). Equation 2 defines the AICc

$$\mathrm{AICc} = -2\log(L) + 2K\,(n/(n - K - 1)) \tag{2}$$

Akaike weights (w_i) determined the relative support of each model. The value of w for any model i is below in equation 3

$$wi = \frac{\exp(-0.5\,\Delta i)}{\sum_{r=1}^{R} \exp(-0.5\Delta i)} \tag{3}$$

where Δi is the difference in AIC between model i and the best candidate model from the subset among the R candidates (Del Giudice 2009).

To narrow the set of explanatory variables used in the model ranking exercise, I identified a limited set of mechanistic variables known to influence primary production such as light availability, river discharge and temperature. Light availability was accounted for using TSS loads and photic depth (Zp), with the assumption that high TSS loads would lower light availability. Zp was derived from measurements of Secchi depth at TF 2.3. The vertical attenuation coefficient for light, k, was calculated using Secchi depth data (equation 4). K was then used to calculate Zp (equation 5) (Dennison et al. 1993)

$$k = 1.4/\text{Secchi measurement} \tag{4}$$

$$Zp = 4.61/k \tag{5}$$

The data for model variables of temperature, Secchi depth, and TF DIN were obtained from the Chesapeake Bay Program Water Quality database (1984-present). TN loads for the Blue Plains WWTP effluent were calculated using Blue Plains effluent flow and TN concentration data provided by the Chesapeake Bay Program Nutrient Point Source database. TN load data for the Chain Bridge gauging station were obtained directly from the USGS Chesapeake Bay River Input Monitoring Program. Rather than including chlorophyll as another independent variable, primary production was normalized to chlorophyll concentrations as the dependent variable, transforming the dependent variable into what is frequently considered a measure primary production efficiency. Chlorophyll is a proxy for biomass, and because I was most interested in the role of nitrogen, light, and temperature, using chlorophyll-normalized primary production measurements narrowed the model selection to a more streamlined set of variables that is generally recommended for this type of model ranking analysis (Burnham and Anderson 2010). Normalization to primary production also eliminated the interaction between chlorophyll and all of the other independent variables, which would have complicated interpretation. A complete table of the variables is presented in Table 2.

TSS loads and TN loads are a function of discharge rate. However, loadings and discharge can influence primary production in different ways through decreased light (TSS loads), nitrogen availability (TN load), and flow rates/salinity (discharge). The variables of TSS loads and TN loads at the Chain Bridge gauging station were separately regressed on Potomac River discharge rate. Model residuals were used as an indicator of the additional effects of TSS load or TN load after controlling for discharge. Discharge was included as a separate term in the analysis. Additional independent variables included year and month.

The data were divided into pre-BNR (1990-1999) and post-BNR (2000-2007) time periods to examine how the model and specific nitrogen sources changed when BNR, the breakthrough technology for nitrogen removal, was installed at the Blue Plains WWTP. Only data for the months of May through September were used. These months are the growing season for phytoplankton, and therefore capture critical information on primary production without inducing error from colder months when phytoplankton populations are smaller. The narrowed set of independent variables included Blue Plains TN loads, TF2.3 water temperature, TF2.3 *in situ* DIN, TF2.3, Z_p, Chain Bridge discharge, and the residuals for TSS and TN Chain Bridge loads. To carry out the all possible subsets regression, I used the R-statistical package (http://www.r-project.org/), and specifically the "leaps" and "cards" libraries. AICc values for each possible model were computed using R- generated values of the Residual Sum of Squares (RSS). RSS values divided by the number of samples can be used in place of maximum likelihood values (L) in equation 2.

Results

TF 2.3 Retrospective Data Perspective

Long term datasets are presented here using either plots of variables against time, or univariate scatterplots to explore possible relationships between two variables. This initial exploration allowed us to visualize the potential impact of management actions in time (BNR implementation between 1996 and 2000) or possible dependencies between two variables.

Analysis of the long term dataset of nitrogen concentrations from Blue Plains' effluent illustrates how improvements in wastewater treatment technology have reduced effluent TIN concentrations from 15 mg L^{-1} in 1985 to approximately 5 or 6 mg L^{-1} in 2007; TON concentrations have remained below 2 mg L^{-1} with the exception of concentrations during 2004 at Blue Plains as shown in Figure 8. Blue Plains' effluent TON levels have increased slightly compared to those measured at TF 2.3 since implementation of BNR.

Blue Plains' effluent data are reported as TIN and TON concentrations, creating a challenge of "apples and oranges" comparisons with the traditional DIN and DON pools computed in estuarine studies and for TF 2.3. To permit direct comparisons, I computed corresponding TIN and TON concentrations for TF 2.3, with particulate and organic and inorganic analytes pooled using the Maryland DNR data. Comparisons revealed decreasing TIN concentrations at TF 2.3 from 3.5 mg L^{-1} in 1991 to 0.5 mg L^{-1} in 2007, a similar pattern to the change in effluent concentrations during the same time period. TF 2.3 TON concentrations have remained approximately 0.5 mg L^{-1} (Figure 9). The difference in TIN between TF 2.3 and Blue Plains' effluent was approximately 12 mg L^{-1} in 1991 and declined to 2 mg L^{-1} in 2007. A dilution effect was not observed with organic nitrogen concentrations downstream from Blue Plains to TF 2.3. Because DIN and DON concentrations are more commonly used in estuarine studies, I present these concentrations at TF 2.3 in Figure 10, where inorganic and organic dissolved analytes show the same changes as TIN and TON (Figure 9). TF 2.3 nitrogen concentrations were lower compared to Blue Plains from 1991 to 2007. MD DNR did not begin measuring nitrogen until 1991 at TF 2.3, creating a gap in comparison with Blue Plains' data from 1985 to 1990.

TON concentrations have remained stable at TF 2.3 since 1991, averaging less than 2 mg N L^{-1} at the study site (Figure 11). Figure 11 also illustrates how Blue Plains TON levels are easily influenced by changes in flow; when flows were high in 2003 and 2004, because of increased rainfall, TON concentrations at Blue Plains increased in response because treatment capacity was exceeded. The ratio of TIN:TON at Blue Plains has decreased from 25 – 40, to about 5 in 2007 (Figure 12). The ratio is useful in evaluating the increasing relative importance of organic nitrogen at Blue Plains as technological advances in optimizing nitrogen reduction have reduced inorganic nitrogen. The ratio at TF 2.3 decreased from approximately 8 to below 5; the decline is not as evident at Blue Plains but still demonstrates the increasing influence of organic nitrogen (Figure 12).

Blue Plains TN concentration increased dramatically in 2003 and 2004 compared to previous five years. Monthly discharge was also higher during this time period. Hurricane Isabel (category 5) hit the Atlantic coast in September 2003, with detrimental effects in the Washington DC area. The surge of added rainfall and additional mixing from winds and runoff created additional internal nutrient cycling and possibly altered the ecosystem (Roman et al. 2005). The year 2004 had higher than normal precipitation and was the fourth most active season for hurricanes on record with five affecting the Washington DC metro area and Maryland. The DC combined sewer system, which directs wastewater to Blue Plains for treatment, exceeded flow during this period of heavy rainfall. When this occurs, the combination of sewage and stormwater runoff is discharged into the Potomac, or other tributaries, untreated. This event, referred to as combined sewer overflow (CSO), results in additional nutrients and pollution in the receiving water body (DC Water 2011). Monthly discharge rates and monthly average precipitation over time for the Potomac River Basin near DC are discussed further below.

Abiotic and Biotic Changes

The average discharge for the Potomac River from 1985 to 2007 was 290 $m^3 s^{-1}$. Streamflow into the Potomac River was above average in 1993, ’94, ’96, 98’, 2003, and’04; it was below average in 1985, ’88, ’92, ’95, ’99, 2001, and ’02 (USGS 2010). Peaks in discharge for the analyzed data were observed in 1993, ’94, ’98, ’03, ’04, and ’06-‘07 (Figure 13). However, the high discharge rates did not always correspond with increased precipitation (USGS 2010). USGS has observed above normal river flows despite below normal local precipitation, suggesting higher flows were observed after spring freshet events, or rainfall in the upper basin increased discharge downstream (ICPRB 2004).

Chlorophyll concentrations, shown in Figure 14, fluctuate with changes in nitrogen load or discharge levels. The highest chl-a concentrations (above 59 $\mu g\ L^{-1}$) were observed in the summers of 1994-95 and 1997-2001 in the Potomac River.

Primary production, shown in Figure 15 plotted against time, also fluctuated with changes in nitrogen load or discharge levels. Strong seasonal patterns are clear from this time series.and there appears to be some decline in summer maximum rates beginning in

2001. The highest primary production rate (above 2,000 mg C m^{-2} d^{-1}) in the Potomac River was observed in 1999.

Primary Production

Increasing river flow appears to impact phytoplankton growth in the estuary, mainly by decreasing the rate of primary production as seen in Figure 16. However, dilution effects from increased discharge were not observed in TN concentrations at the Chain Bridge gauge station. The highest TN concentrations were observed in winter or spring, when primary production was low or in initial growth stages. WWTP nitrogen loads are higher in the colder months due to decreased BNR removal efficiency as a result of lower temperatures, and in spring, the flush of fresh water from upstream added large amounts of nitrogen to the system downstream. Blue Plains' TN loads did not show obvious patterns related to primary production at TF 2.3 (Figure 17a). TN loads were between 1,000 and 21,000 kg d^{-1}, with variable primary production observed at each load level. Primary production at the Chain Bridge gauge station gradually decreased as TN load increased up to 150,000 kg d^{-1} (Figure 17b). The same pattern was observed with chlorophyll plots (Figure 17c, d). Chlorophyll concentrations were not related to Blue Plains' TN load. Chlorophyll concentrations gradually decreased as the Chain Bridge gauge station TN load increased up to 150,000 kg d^{-1}, suggesting phytoplankton production is potentially being limited by river discharge, regardless of the environmental nitrogen concentrations.

An examination of the relationship between Potomac River flow and algal growth for the tidal fresh portion segments (97 -70) is shown in a time series plot using hydraulic fill times to explore the impact of discharge rates on productivity (Figure 18). Using these segments (see Figure 2 for details), results indicate increasing chlorophyll concentrations with increasing hydraulic fill time and decreasing chlorophyll concentrations when fill time is low. When chlorophyll data were plotted with hydraulic fill times of less than 30 days in Figure 19, chlorophyll increased with increasing fill times. When chlorophyll concentrations were plotted with hydraulic fill times of greater than 30 days (Figure 20), chlorophyll peaked when fill time was in the range of 45 and 75 days then decreased with increasing fill time. Very long hydraulic fill times are likely associated with periods of drought during the time series, possibly indicating a decline in available nutrients that could have contributed to reduced growth.

An examination of TSS loads in the Potomac River suggest increasing discharge rates were associated with increasing sediment loads as shown in Figure 21, potentially limiting the amount of available light for phytoplankton growth within the water column. As TSS loads increased, primary production decreased (Figure 22).

Discharge permits for Blue Plains mandate low nitrogen loading during summer months when phytoplankton growth rates are higher and higher nitrogen loading rates in winter, when phytoplankton growth is suppressed by low temperature and light limitation and reduced residence time in the upper estuary due to higher river flow. Potomac River nitrogen loads were considerably greater than those from Blue Plains, illustrating that nitrogen loads from BP have decreased over time, and the Potomac River nitrogen load had stronger impact on the system than in the past.

Regression Analysis

While the exploratory analysis revealed some possible relationships among variables, I also conducted a more rigorous statistical analysis to quantitatively evaluate the role of nitrogen in Potomac tidal fresh primary production rates. Because univariate plots between two variables did not reveal clear relationships, a multiple regression approach was necessary to further tease apart the numerous factors that influence primary production rates. The “all possible subset regression” model ranking exercise produced 56 different subset models for the pre-BNR data and 57 subset models for post-BNR data. The pre-BNR and post-BNR sample size was 37 and 27, respectively. The models with the lowest AICc criterion with a corresponding high adj r^2 value were selected as the best fit. The top ten models for both time period datasets are presented in Table 3.

Pre-BNR Primary Production Regression Analysis

The four models below were selected as the best models for primary production from the variables we used for this analysis. Model 4 was not evaluated for statistical significance because Year was the only variable. The TF 2.3 DIN concentrations and Zp measurements were identified in several of the models for primary production in the pre-BNR models. The Blue Plains TN load was also amongst the top ranked models of primary production for this time period. The Chain Bridge TN load term was not a component of the top ten models (Table 3). Models below report linear model estimates of intercepts and beta coefficients.

$$PP/chl = 19.429 + 5.222*TF\ DIN \qquad \text{(Model 1)}$$

$$PP/chl = 12.893 + 6.070*Zp \qquad \text{(Model 2)}$$

$$PP/chl = 9.155 + 0.001*BP\ TN\ Load \qquad \text{(Model 3)}$$

$$PP/chl = 12.512 + 4.093*Zp + 3.680*TF\ DIN \qquad \text{(Model 5)}$$

All of the variables in the above models were statistically significant ($\alpha < 0.05$) except for Zp in Model 5 (Table 4). The above models were statistically significant according to the probability value of the F-statistic (Table 5).

Post-BNR

The four models below were chosen as the best models for primary production after implementation of BNR. Model 3 was not evaluated for statistical significance because the $adjr^2$ value was extremely low. Burnham and Anderson (2010) recommend consideration of other metrics such as $adjr^2$ in conjunction with AICc for model ranking exercises. The TF 2.3 DIN concentrations, Zp measurements, and water temperature explanatory variables emerged in top-ranked models for the data collected in the post-BNR time period. Neither the Blue Plains TN load nor the Chain Bridge TN load variables were included in the top ten models (Table 3), suggesting these TN sources did not contribute greatly to explanatory models of primary production following BNR implementation after 2000. As in the pre-BNR models above, the equations below include predicted y-intercepts and beta coefficients for the top 4 models.

$$PP/chl = 12.648 + 16.893*TF\ DIN \qquad \text{(Model 1)}$$

$$PP/chl = 54.462 - 1.014*T \qquad \text{(Model 2)}$$

$$PP/chl = 5.828 + 15.202*TF\ DIN + 4.781*Zp \qquad \text{(Model 4)}$$

$$PP/chl = -2332.541 + 14.739*TF\ DIN + 1.172*Year \qquad \text{(Model 5)}$$

The variables in the above models were statistically significant ($\alpha < 0.05$) except for Zp in Model 4 and Year in Model 5 (Table 6). The models, except Model 2, were statistically significant based on the probability value of the F-statistic. The probability value of Model 2 was above 0.05 (Table 7).

<u>Discussion</u>

Improvements in Wastewater Treatment and the Corresponding Nutrient Reduction

Efforts to reduce nutrient loading into the Chesapeake Bay and its tributaries have been ongoing since 1985. A primary example is phosphorus, which once abounded in freshwater due to its use in detergents and inadequate removal during wastewater treatment. As a result, phytoplankton were supplied with a significant amount of a limiting nutrient (Paerl 1997), causing large algal blooms. Improved wastewater treatment technology and detergent bans eventually resulted in low phosphorus loads (Boesch et al. 2001).

WWTP effluent discharged into freshwater or estuarine systems supplies algae with nutrients to support growth. Algae in fresh and fresher estuarine waters are typically limited by phosphorus, so under P-limited conditions, nitrogen that was unable to cycle through phytoplankton is transported downstream, stimulating algal growth in the mesohaline regions of the estuary (Kemp et al. 2005, Paerl 1997). Improved management strategies and improvements in wastewater treatment, such as BNR implementation, have reduced nitrogen loads into the fresh and estuarine water bodies (Boesch et al. 2001).

Advances in wastewater treatment locally in waterways such as the Potomac and Patuxent Rivers during the past 20 years have improved water quality, mainly in the upper (tidal fresh and oligohaline) portions of these Chesapeake Bay tributaries. This reduction in vital nutrients for phytoplankton growth has helped mitigate the negative effects of the growing human population within the watershed. Regulations, enforcement programs, and advanced technology applications along with financial investments have reduced the impact of point sources on the watershed. Currently, Blue Plains, while still the largest point source in the Chesapeake Bay, contributes less than 20 percent of the total nitrogen load to the Potomac estuary. The majority of the nitrogen load comes from atmospheric deposition and non-point sources such as agricultural and urban-suburban development (CBP 2007).

Comparison of Relative Size of Nitrogen Loads from Blue Plains versus Potomac River Loads

Over the past 100 years, riverine exports from above and below the fall line of the Potomac River have contributed 2-3 times more nitrogen than from direct WWTP discharge, except during periods of low river discharge. In the early 1980s, input sources above the Potomac River fall line contributed 62% and 57% of TN loads to the tidal freshwater and estuary, respectively. WWTPs located below the fall line contributed 28% and 26% of TN loads to tidal freshwater and estuary, respectively (Hickman 1987). The Potomac River TN load was significantly higher than what was observed at Blue Plains with yearly averages of 93,000 kg d^{-1} and 14,000 kg d^{-1}, respectively (Jaworski et al. 2007). Since the 1990s, tidal WWTP TN loading has decreased approximately 50% as a result of improved nutrient regulations and upgrades in wastewater treatment technology

(Jaworski et al. 2007). TN loading percentages from atmosphere, river export, and WWTP from 1980 to 2004 are presented in Table 8 (adapted from Jaworski et al. 2007).

The drainage area of the Potomac River located above the fall line is 29,940 km^2, which is considerably larger than the estuary below (8,055 km^2) (Jaworski et al. 2007). As a result, the majority of the nutrient loads come from riverine inputs located in this upper basin area (Boynton et al. 1995). Therefore, freshwater inflow has a significant influence on the hydrodynamics and chemistry of the estuarine portion of the Potomac River. The only instance where river flow and nutrient input are dominated by WWTP effluent occurs when overall flow is low, (e.g. low precipitation, seasonal) and effluent is not being diluted by river flow.

Variability in nutrient loads and concentrations may be due to both external (climate and anthropogenic factors) and internal factors (biogeochemical processes). An increased nutrient load frequently occurs when river runoff is higher and creates subsequent water quality issues (Hagy et al. 2004). Streamflow seasonality is important in regulating nutrient flow into the Bay from all sources. An increased nutrient load frequently occurs when river runoff is higher and creates subsequent water quality issues. Spring freshets, hurricanes, and other episodic hydrological events cause higher freshwater inputs, increasing flushing rates and contributing new nitrogen inputs to the system and make more organic matter available for recycling from sediments (Hagy et al. 2004). However, these pulsed events are also associated with advection of phytoplankton biomass and mixing of the water column, which may temporarily reduce primary production and hypoxia. Recycling of nitrogen is much larger than new inputs, providing nitrogen the opportunity to stay within the system, continuously refreshing the availability of recycled N to phytoplankton. Phytoplankton take up the nitrogen, transforming it to the particulate form, which then settles to the bottom sediments when blooms die. Bacterial communities, with some loss due to denitrification or burial, then remineralize this particulate material in the sediments before fluxes of nitrate and ammonium are returned to support phytoplankton uptake in the water column. Because loss terms are associated with this cycle, internal sources of recycled DIN are eventually limited in relationship to the efficiency of denitrification and burial.

Factors Impacting Phytoplankton Growth in the Tidal Fresh Potomac River

The change in nitrogen loads from Blue Plains and Chain Bridge had different effects on observed primary production data at TF 2.3. Chlorophyll and primary production at TF 2.3 peaked at 70 µg L^{-1} and 1,500 mg C m^{-2} d^{-1}, respectively, when Chain Bridge nitrogen loading was less than 50,000 kg d^{-1} (Figure 17b, d). However, both response variables decreased when nitrogen loading increased above 60,000 kg d^{-1} suggesting a threshold related to the high discharge rates associated with very high TN loads. Chlorophyll and primary production at TF 2.3 were below 70 µg L^{-1} and 1,500 mg C m^{-2} d^{-1}, respectively, when Blue Plains nitrogen loading was less than 20,000 kg d^{-1}.

The National Oceanic and Atmospheric Administration's Estuarine Eutrophication Survey (NOAA 1997) determined phytoplankton growth in the Mid-Atlantic tidal freshwaters, especially the Potomac River, are limited mainly by nitrogen, phosphorus, light, and flushing. Discharge from above the fall line of the Potomac River delivers large amounts of freshwater and sediments to the tidal portion, resulting in higher flow rates and decreased photic depths. This increased flow can flush phytoplankton downstream, resulting in reduced growth and productivity. The relationship between hydraulic fill time and phytoplankton supported the observation that increased flow rates decreased phytoplankton growth at station TF 2.3 and vice versa. Longer hydraulic fill times coincided with increasing chlorophyll levels and are likely indicative of longer phytoplankton residence times; this pattern was prominent when fill times were in the range of 1 to 70 days. However, above 75 days, the chlorophyll levels declined, which could be attributed to reduced resources during periods of drought.

High flow rates also influence light availability in the water column. When the flow rates are low, turbidity is typically lower and therefore more light is available in the water column for phytoplankton growth. Increasing flow is associated with increased sediment load, which decreases the photic depth, limiting the amount of light that is available for growth (Cloern 1987). Wofsy (1983) determined that waterbodies with high TSS concentrations have higher extinction coefficients on average, indicating a more rapid decline in light availability with depth in the water column. The relationship has been observed over a range of mixed layer depths and chlorophyll concentrations in a variety of environments such as rivers, tidal areas, and upwelling zones. When suspended solid loads are reduced, phytoplankton biomass increases.

Another explanation for reduced productivity, is higher nitrogen loads usually occur in late fall and winter when temperatures were colder. Wastewater treatment plant efficiency is reduced during the colder months, because the biological activity necessary to reduce nitrogen concentrations is unable to function at full capacity (DC Water 2010, Reeves 1972). Phytoplankton and bacterial growth are greatly reduced during the winter months, resulting in low production rates and decreased efficiency during microbial nitrogen removal processes, resulting in higher nitrogen loads to the receiving waterbody. Some phytoplankton blooms were observed during winter and fall; however, bloom density was smaller than what is observed in spring and summer, which is characteristic of the tidal fresh portion of the Potomac (MD DNR 2010, NOAA 1997).

The consequences of these patterns further down the Potomac estuary were not explored, but presumably the nitrogen loads are eventually used by phytoplankton either further downstream or within the main stem of Chesapeake Bay. Source tracking and rate studies of these processes by collaborators S. Kaushal and M. Niesen are ongoing.

Effluent Organic Nitrogen

For many years, the availability of organic nitrogen for uptake by phytoplankton in the aquatic environment was considered to be insignificant (Sedlak and Pehlivanoglu 2004); however more recent studies have revealed a higher bioavailability of DON (Bronk et al. 1998, Bronk et al. 2007). It is now recognized that DON contributes to plankton nutrition directly (Antia et al. 1991, Bronk et al. 1994, Stensel et al. 2008).

Effluent ON can account for about 25% of the TN from wastewater, depending on the type of ON and technology used in the treatment system. Average concentrations of DON in the environment range between 1.0 and 1.5 mg L^{-1} (Mulholland et al. 2007). Other studies of organic nitrogen concentrations reveal similar concentrations. Seitzinger and Sanders (1997) examined the contribution of DON to estuarine eutrophication in the Delaware and Hudson Rivers. Average DON concentrations for the Delaware River ranged from 0.066 – 0.64 mg L^{-1} and 0.39 – 0.47 mg L^{-1} for the Hudson. Organic nitrogen concentrations at Blue Plains and TF 2.3 have been relatively constant throughout the analysis period. The consistently low concentrations of DON across these estuarine systems may indicate a lower baseline value representing truly recalcitrant DON in the estuary. Organic nitrogen removal from WWTPs is less efficient than inorganic nitrogen removal. ON in wastewater is composed of colloids and low and high molecular weight compounds, which are difficult to completely break down during treatment (Mulholland et al. 2007). When NH_4^+ binds to effluent ON within the treatment plant, it may not be removed by nitrification/denitrification process because adsorption processes prevents further breakdown of ON substances (Stensel et al. 2008).

Regression Analysis

Despite consideration of a variety of environmental variables in the all possible subsets regression analysis, local DIN concentrations, Zp, and Blue Plains TN loads emerged as prominent drivers of chlorophyll corrected spring/summer primary production rates at station TF 2.3 prior to BNR implementation. The Chain Bridge TN load was ranked number 17 out of the 57 possible models ranked in this exercise. The resulting adjr^2 was -0.0276, respectively, and therefore too low to justify inclusion in the best fit models. Based on this model ranking exercise, the influence of Chain Bridge TN was apparently low in the pre-BNR years, while Blue Plains TN loads appeared to have a greater localized impact on primary production rates.

The prominent factors driving chlorophyll corrected primary production after implementation of BNR were local DIN concentrations, Zp, and temperature. Neither the Blue Plains nor Chain Bridge TN loads were included in the top ranked ten models, indicating that local DIN concentrations were the main nitrogen source supporting primary production. This finding further emphasizes that Blue Plains nitrogen was a more relevant explanatory variable prior to implementation of BNR treatment technology. The post-BNR primary production was mainly supported by local DIN concentrations.

Evaluations of the role different nitrogen sources have on chlorophyll corrected primary production yielded interesting results relevant to evaluating the effectiveness of point source nutrient management. Prior to upgrades in nitrogen removal technology at Blue Plains, this point source stimulated significant water quality issues and high levels of primary production. The original goal of installing BNR was to meet a goal of less than 8 mg L^{-1} TN discharged into the Potomac River as outlined in the 1987 Chesapeake Bay Agreement. Blue Plains achieved this goal by 2000 after installation of nitrogen removal technology, then a 100% operational BNR system. The impact of Blue Plains TN on production would likely have increased with the growing user population if this goal had not been met. However, as illustrated in the post-BNR model evaluation, the impact of nitrogen from Blue Plains on primary production has declined significantly.

Broader applications

Water quality in other estuaries has improved because of advancements in wastewater treatment technology. Kemp et al. (2005) noted changes in nitrogen levels from the 1950s to 1990s in the Patuxent. Increased nitrogen inputs in the Patuxent River were observed between 1950 and 1985, but declined in the early 1990s after advancements in nutrient removal technology in the discharging treatment plants. In 1988, EPA conducted a quantitative synthesis of before-and-after case studies of 27 waterbodies that were affected by the Clean Water Act and had both minor and major facilities (with the exception of the Potomac Estuary and Hudson River). Water quality data sets including pollutant loading showed that 23 of the water bodies had moderate improvements in water quality conditions after upgrades in WWTPs. Improvements included increased DO levels, reduced algal biomass, reduced nutrient concentrations, TSS levels and the return of fish and SAV.

As of September 2010, the EPA reissued the operating permit for Blue Plains WWTP, finalizing the nitrogen discharge load to the Potomac River to 1.7 $x10^6$ kg per year (EPA 2010). A recently released 17-year long study of submerged aquatic vegetation in the Potomac River illustrates the effects of nutrient reduction on aquatic organisms. The study by Ruhl and Rybicki (2010) revealed that native species of submerged aquatic vegetation (SAV) are outgrowing the non-natives and nutrients from sewage are on a long term decline. My statistical analysis provides a nuanced examination of the impact of BNR implementation on organic matter production by phytoplankton. In particular, this study provides insight into the mechanisms and factors affecting a rate process like primary production that ultimately impacts water quality through secondary effects on dissolved oxygen concentrations and light availability.

While improvements in water quality have been observed in the Potomac and other tributaries, impacts from upgrades at Blue Plains WWTP have not been observed in the lower Potomac or in other parts of the Chesapeake Bay. Watershed allochthonous nutrient loads and internal autochthonous nutrient cycling control nutrient stoichiometry in estuarine systems. The impacts of TN loads on phytoplankton are region specific, as some areas of the estuary are either N or phosphorus limited. Integrated nutrient management approaches focus on nitrogen reduction practices upstream in non-tidal freshwater riverine zones, while maintaining low phosphorus inputs in the oligo- and mesohaline regions. This strategy was successful in the Patuxent River, where parallel reductions in nitrogen and phosphorus improved water quality throughout the estuary (Prasad et al. 2010)

Based on the estimated nitrogen budget for the Potomac, it appears that the large contribution by non-point sources have been slowing progress in meeting nitrogen reductions that would result in widespread improvements to water quality. Controls on non-point sources have reduced phosphorus, but have not impacted nitrogen (Boesch et al. 2001). I suggest that the export of non-point source nutrients from the Potomac watershed as well as additional nutrients fluxes into the Chesapeake Bay from other tributaries, combined with internal recycling of nitrogen from sediments to the water column, have prevented the Chesapeake Bay from experiencing the improvements seen upstream.

Conclusions

The addition of BNR in 2000 to Blue Plains has made a significant impact on nutrient levels in the upper Potomac River estuary and resident aquatic organisms. Phytoplankton blooms have decreased and SAV are returning to the area. Nitrogen from wastewater treatment plants decreased by 17 $x10^6$ kg from 1985 levels, in effect reducing the overall nitrogen pollution attributed to wastewater in the Bay from 26% in 1985 to 19% in 2009 (EPA 2010).

While the effects have been seen directly at the discharge site, in order to continue the decrease in nutrient concentrations, non-point sources need to be addressed. Seasonal impacts, such as increased river flow in the spring, also play an important role in regulating nutrient loads within the system, and should be considered in management strategies.

Decreases in nutrient discharge from WWTP and new regulations for non-point sources could benefit the entire Chesapeake Bay watershed. The improvements to the world's largest advanced WWTP coupled with improvements in aquatic vegetation health and reduced nutrient loads serve as an ideal model for the watershed. If similar measures are taken throughout the watershed, and non-point sources are addressed, the Chesapeake Bay could be improved and environmental improvements in other waterbodies should follow.

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Table 1. Timeline of major water quality monitoring and management actions taken in the Potomac River from 1894 to 2009. Information was obtained from Jaworski et al. (2007) and the Interstate Commission on the Potomac River Basin website (http://www.potomacriver.org/cms/).

Date	Organization	Milestone
1894	US Public Health Service	Sanitary surveys begin in DC
1897	US Geological Survey	First water quality survey of entire Potomac
1940	Interstate Commission of Potomac River Basin	Helped basin states and federal government work together to address water quality and resource problems
1956	Congress	Passage of Federal Water Pollution Act; increased water quality research
1957	Potomac Washington area enforcement conference	Addressed declining water quality in upper estuary
1965	Water Quality Act	Established water quality standards for interstate waters
1970	US Environmental Protection Agency	Developed national water quality improvement programs; formalized water quality requirements and wastewater treatment goals
1972	Clean Water Act	Developed National Pollutant Discharge Elimination System (NPDES)
1975	US EPA, DC, and Bay states	Multi-year study and monitoring program initialized
1983	Chesapeake Bay Agreement (CBA)	Bay states and DC work together to address water quality issues; restore living resources
1987	Revised CBA	Reduce nitrogen and phosphorus loads entering the Bay at least 40% by the year 2000
2009	EPA, senior representatives from departments of Agriculture, Commerce, Defense, Homeland Security, Interior, Transportation	Executive Order, signed by President Barack Obama, which requires the federal government to lead a renewed effort to restore and protect the Chesapeake Bay Watershed. Goals include new actions to restore water quality and update management practices and regulations; improve stormwater management; and assess impact of climate change.

Table 2. Variables and their units used in the all possible subset regression analysis

Variables	Abbreviation	Units	Notes
Chlorophyll normalized to primary production	PP/Chl	mg C mg Chl-a^{-1} d^{-1}	
Year	Y	Y	
Photic depth	Zp	m	
Temperature	T	°C	
Potomac River discharge	Discharge	m^{3} s^{-1}	
Tidal Fresh DIN	TF DIN	mg L^{-1}	
Blue Plains TN load	BP TN Load	kg d^{-1}	Residuals from BP TN Load and discharge used
Chain Bridge TN load	CB TN Load	kg d^{-1}	Residuals from CB TN Load and discharge used
Chain Bridge sediment load	CB Sed Load	kg d^{-1}	Residuals from CB Sed Load and discharge used

Table 3. Top ten all possible subsets for potential models evaluating primary production pre and post BNR implementation. The models are listed according to their suitability. The Chesapeake Bay Program Water Quality database (1984 to present) provided all the data. The models with an asterisk were chosen as the best fit models to evaluate primary production. Adjr^2 is the coefficient of determination adjusted for the number of variable, the AIC is the Akaike Information Criterion, the AICc is the Akaike Information Criterion for a smaller dataset, ΔAIC is the difference between the AIC of the best model and the minimum value of AIC in the set, and w_i is the Akaike weights.

Model Number	Model Variables	Adjr^2	AIC	AICc	ΔAIC	w_i
Pre-BNR						
Model 1*	TF DIN	0.139	62.693	62.808	0	0.085
Model 2*	Zp	0.131	62.857	62.972	0.163	0.078
Model 3*	BP TN Load	0.130	62.867	62.981	0.173	0.078
Model 4	Year	0.124	62.969	63.083	0.275	0.074
Model 5*	Zp + TF DIN	0.174	63.585	63.938	1.130	0.048
Model 6	Year + Zp	0.173	63.602	63.955	1.147	0.048
Model 7	Zp + BP TN Load	0.170	63.649	64.002	1.194	0.047
Model 8	TF DIN + CB Sed Load	0.162	63.811	64.164	1.356	0.043
Model 9	Year + TF DIN	0.155	63.943	64.296	1.488	0.040
Model 10	Discharge + TF DIN	0.149	64.063	64.416	1.607	0.038
Post-BNR						
Model 1*	TF DIN	0.199	55.600	55.760	0	0.132
Model 2*	T	0.078	57.248	57.408	1.647	0.058
\Model 3	Year	0.070	57.344	57.504	1.744	0.055
Model 4*	Zp + TF DIN	0.204	57.021	57.521	1.761	0.055
Model 5*	Year + TF DIN	0.202	57.048	57.548	1.788	0.054
Model 6	TF DIN + CB Sed Load	0.202	57.121	57.621	1.861	0.052
Model 7	Discharge + TF DIN	0.195	57.151	57.651	1.891	0.051
Model 8	Zp	0.054	57.544	57.704	1.944	0.050
Model 9	Year + Discharge	0.167	57.550	58.050	2.289	0.042
Model 10	T + TF DIN	0.167	57.561	58.061	2.301	0.042

Table 4. Best fit models and their coefficients as determined by "all possible subset regression" for the pre-BNR dataset. T value is the t-statistic from a t-test and Pr is the probability that the t value is significant.

Model 1	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance (α<0.05)**
Intercept	19.429	2.732	7.112	2.34e-08	0
TF DIN	5.222	1.975	2.644	0.0121	0.01
Model 2	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	12.893	5.256	2.453	0.019	0.01
Zp	6.070	2.371	2.560	0.015	0.01
Model 3	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	9.155	6.704	1.366	0.181	0.1
BP TN Load	0.001	0.0004	2.555	0.015	0.01
Model 5	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	12.512	5.129	2.440	0.020	0.01
Zp	4.093	2.588	1.581	0.123	0.1
TF DIN	3.680	2.167	1.698	0.098	0.05

Table 5. Residual statistics for the best fit models in the pre-BNR dataset. DF represents degrees of freedom. The F statistic is the result of an F test and residual standard error is the square root of the quotient of the residual sum of squares and degrees of freedom.

	Adjr^2	**F statistic (DF*)**	**p-value (α = 0.05)**	**Residual Standard Error (DF*)**
Model 1	0.139	6.989 (1 and 36)	0.012	6.701 (36)
Model 2	0.131	6.553 (1 and 36)	0.015	6.735 (36)
Model 3	0.130	6.529 (1 and 36)	0.015	6.737 (36)
Model 5	0.174	4.890 (2 and 35)	0.013	6.566 (35)

Table 6. Best fit models and their coefficients as determined by "all possible subset regression" for the post-BNR dataset.

Model 1	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance (α<0.05)**
Intercept	12.648	6.545	1.932	0.065	0.05
TF DIN	16.893	6.298	2.682	0.013	0.01
Model 2	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	54.462	14.433	3.774	0.001	0
Temperature	-1.014	0.575	-1.762	0.091	0.05
Model 4	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	5.828	9.082	0.642	0.527	0.1
TF DIN	15.202	6.469	2.350	0.028	0.01
Zp	4.781	4.430	1.079	0.292	0.1
Model 5	**Estimate**	**Std. Error**	**t value**	**Pr (>|t|)**	**Significance**
Intercept	-2332.541	2227.266	-1.047	0.306	0.1
TF DIN	14.739	6.609	2.230	0.036	0.01
Year	1.172	1.113	1.053	0.303	0.1

Table 7. Residual statistics for the best fit models in the post-BNR dataset. DF represents degrees of freedom.

	$AdjR^2$	F statistic (DF*)	p-value ($\alpha = 0.05$)	Residual Standard Error (DF*)
Model 1	0.199	7.195 (1 and 24)	0.013	10.430 (24)
Model 2	0.078	3.106 (1 and 24)	0.910	11.190 (24)
Model 4	0.204	4.204 (2 and 23)	0.028	10.390 (23)
Model 5	0.202	4.168 (2 and 23)	0.029	10.400 (23)

Table 8. Fluctuation in percent contribution of atmospheric deposition, WWTP effluent, and river export to the total nitrogen load every 5yr from 1980 to 2004. Nitrogen loads from atmospheric deposition directly onto the Potomac Basin were used. All WWTPs in the Potomac Basin for the particular time period were included in the computation. Percentages may not equal 100 due to rounding differences. The table was adapted from information provided in Jaworski et al. (2007).

Year	% Atmosphere	% WWTP	% River
1980-84	1.5	21.9	76.5
1985-89	1.3	25.8	72.8
1990-94	1.2	25.8	73.1
1995-99	1.2	20.6	78.2
2000-04	1.2	19.1	79.6

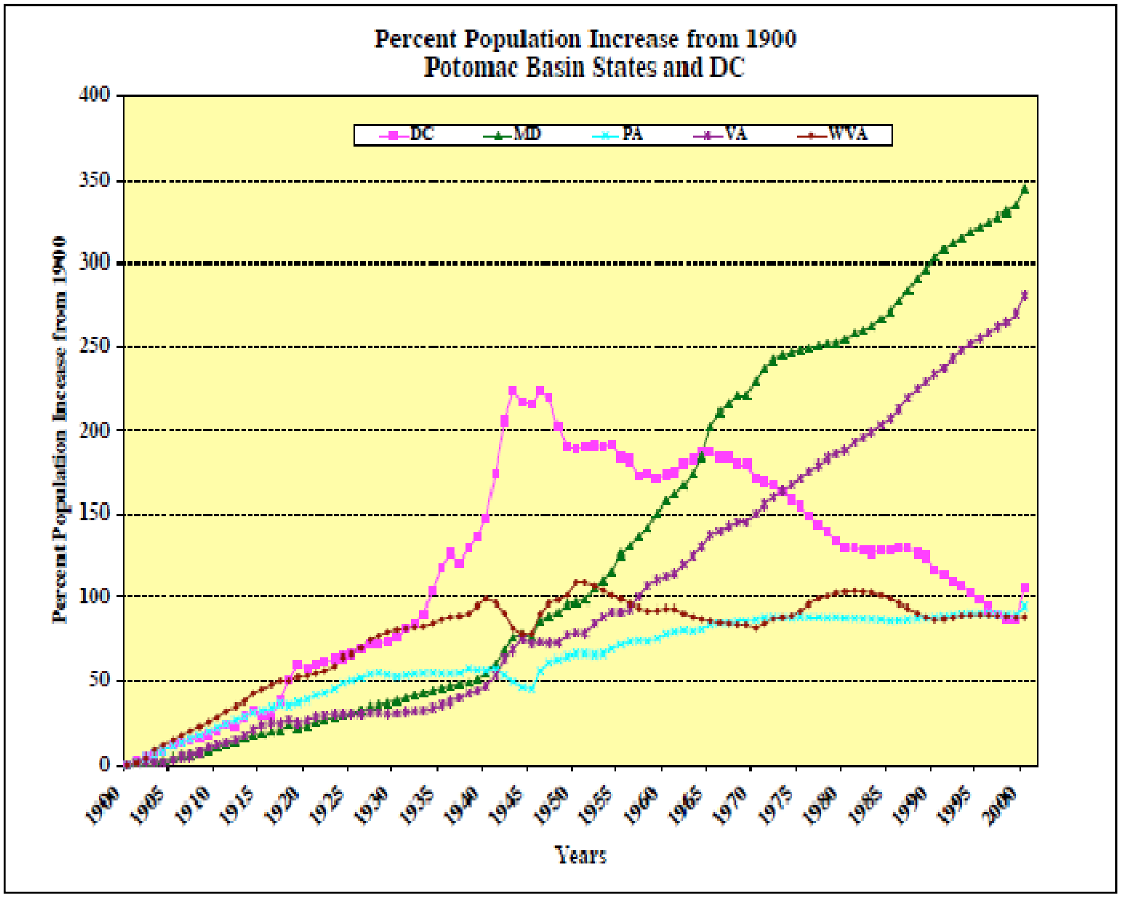

Figure 1. Percent increase in population in the District of Columbia and the states within the Potomac Basin from 1900 to 2000. Figure is from Jaworski et al. (2007).

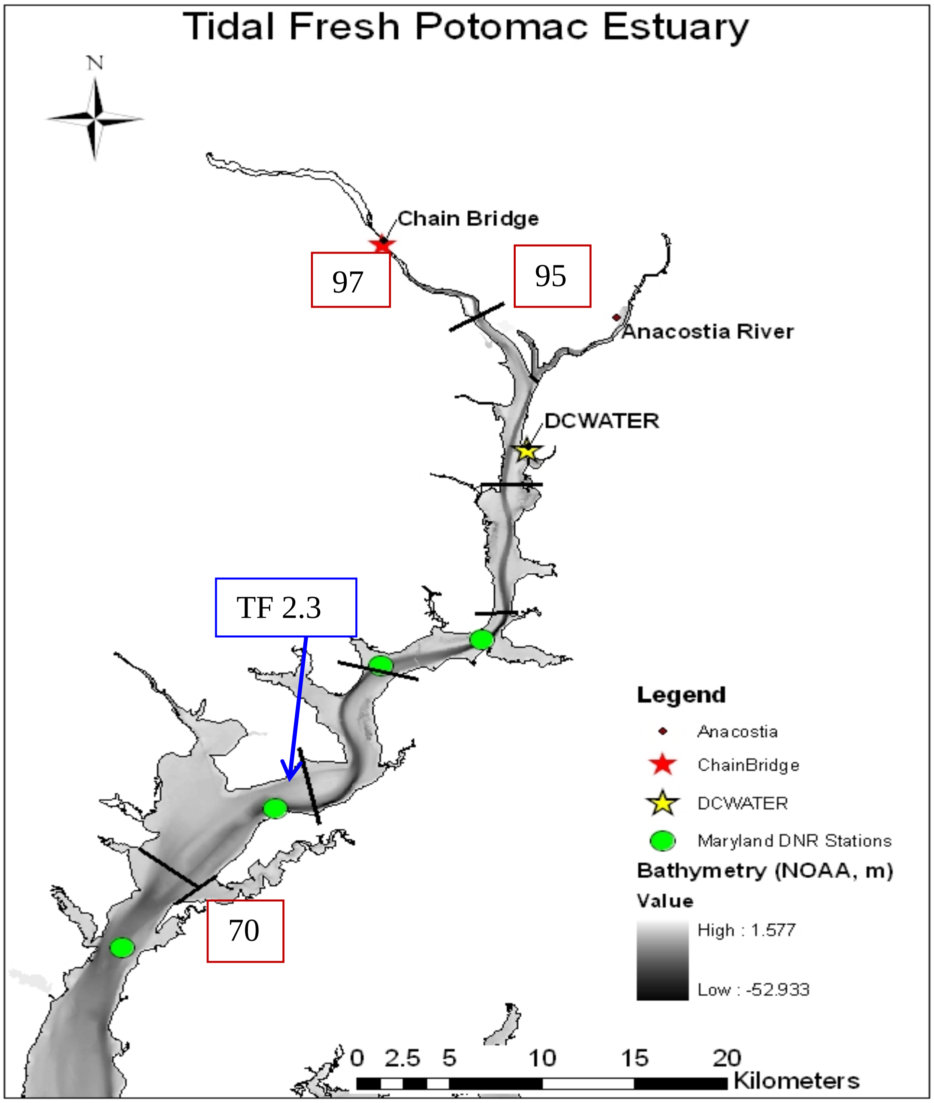

Figure 2. Map of the tidal fresh Potomac River including DC Water, MD DNR sampling stations, and USGS Chain Bridge Gauge station. The black lines across the river represent segment distances of 5 nautical miles. Segments 97 is the head of the tidal fresh area and is located 2 nautical miles north of Segment 95. Segment 70 represents the last segment where the influence of both Chain Bridge and Blue Plains TN loads are prominently represented. The area between segments 97 and 70 was used to calculate hydraulic fill time using the volume for each segment and the daily flow rate. DC Water represents the location of Blue Plains WWTP. TF 2.3 is located at the third circle below Blue Plains and is marked with an arrow.

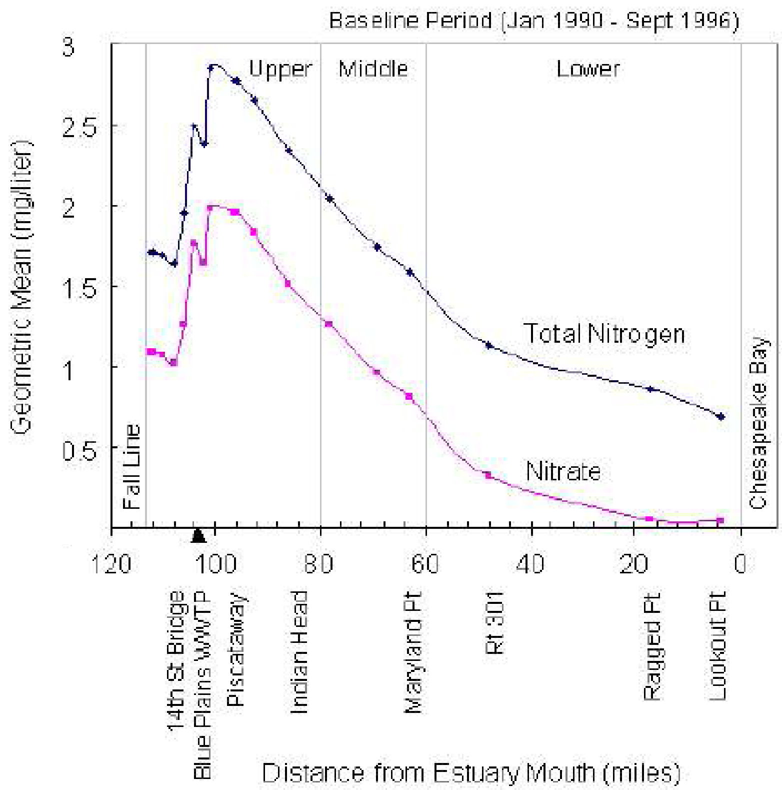

Figure 3. Mean total nitrogen and nitrate concentrations from the fall line of the upper Potomac River to lower region of the river where it enters the Chesapeake Bay. Average concentrations were calculated from data collected from 1990 to 1996, representing a pre-biological nutrient removal baseline study. The 14th St. bridge station is located near the USGS Chain Bridge gauge station. Indian Head is located near TF 2.3 Figure is from Buchanan (2003). Data are from Chesapeake Bay Program Data Center.

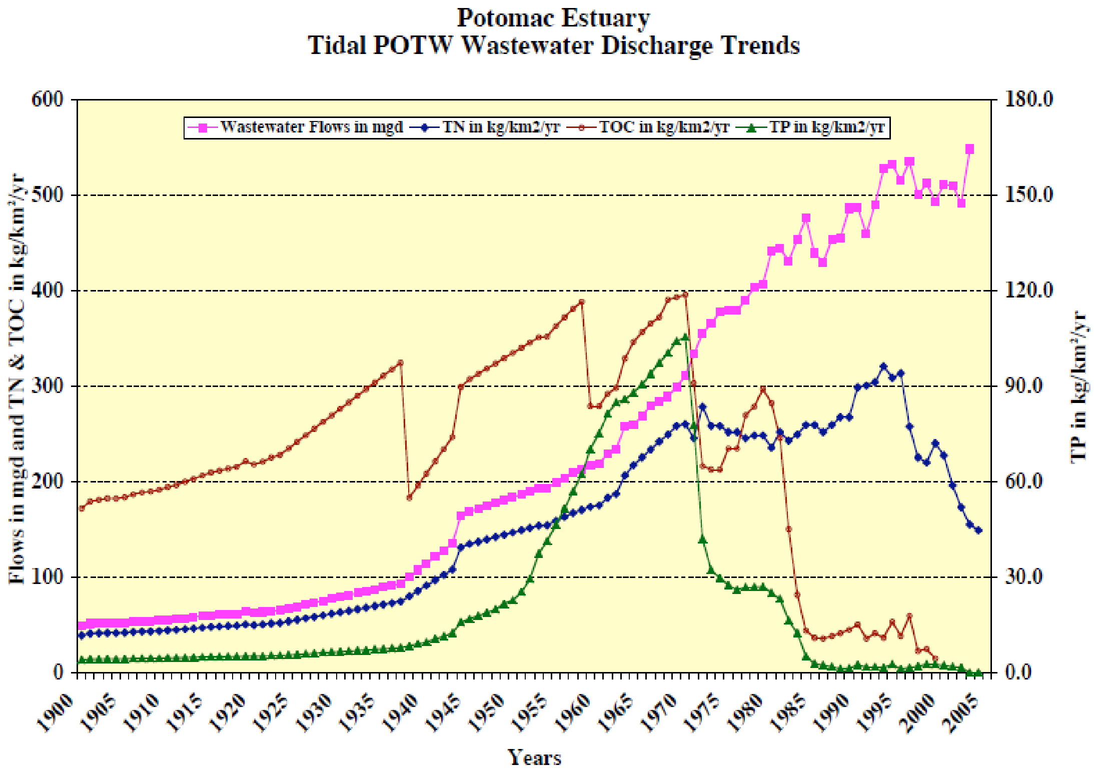

Figure 4. Average annual flux trends of nitrogen, carbon, and phosphorus sourced from wastewater discharge into the Potomac River Basin from 1900 to 2005. Nutrient data for wastewater discharge were unavailable prior to the 1960s; therefore these data were estimated using yearly population data, typical water use per capita, and typical effluent nutrient concentrations. POTW represents publically operated treatment works, also known as WWTP. Figure and methods for estimates from Jaworski et al. (2007).

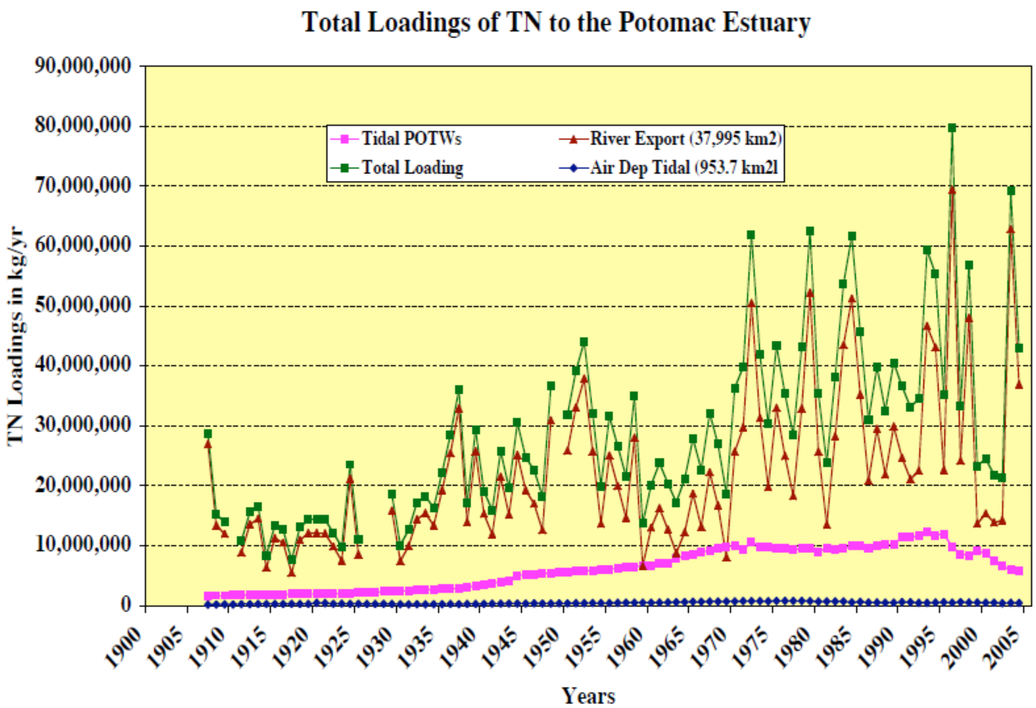

Figure 5. Total nitrogen loadings estimates for the entire Potomac Estuary from 1907 to 2005. Estimates included inputs from direct air deposition on the tidal waters (954 km^2), from direct tidal WWTP (here POTW), and from riverine export to the entire 37,995 km^2 drainage basin. Figure from Jaworski et al. (2007).

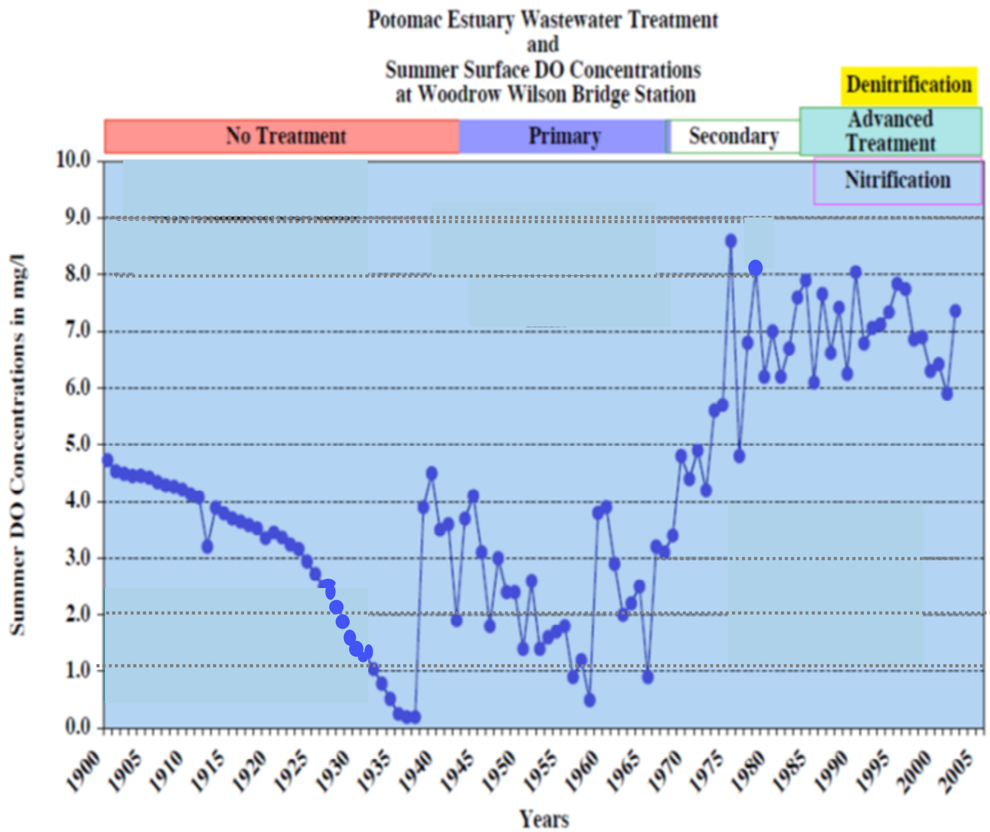

Figure 6. Fluctuations in summer dissolved oxygen concentrations as wastewater technology improved from 1900 to 2005 at the Woodrow Wilson Bridge station located below Blue Plains WWTP. Data from 1900 to 1930s were estimated from wastewater total organic carbon/biological oxygen demand data. Figure from Jaworski et al. (2007).

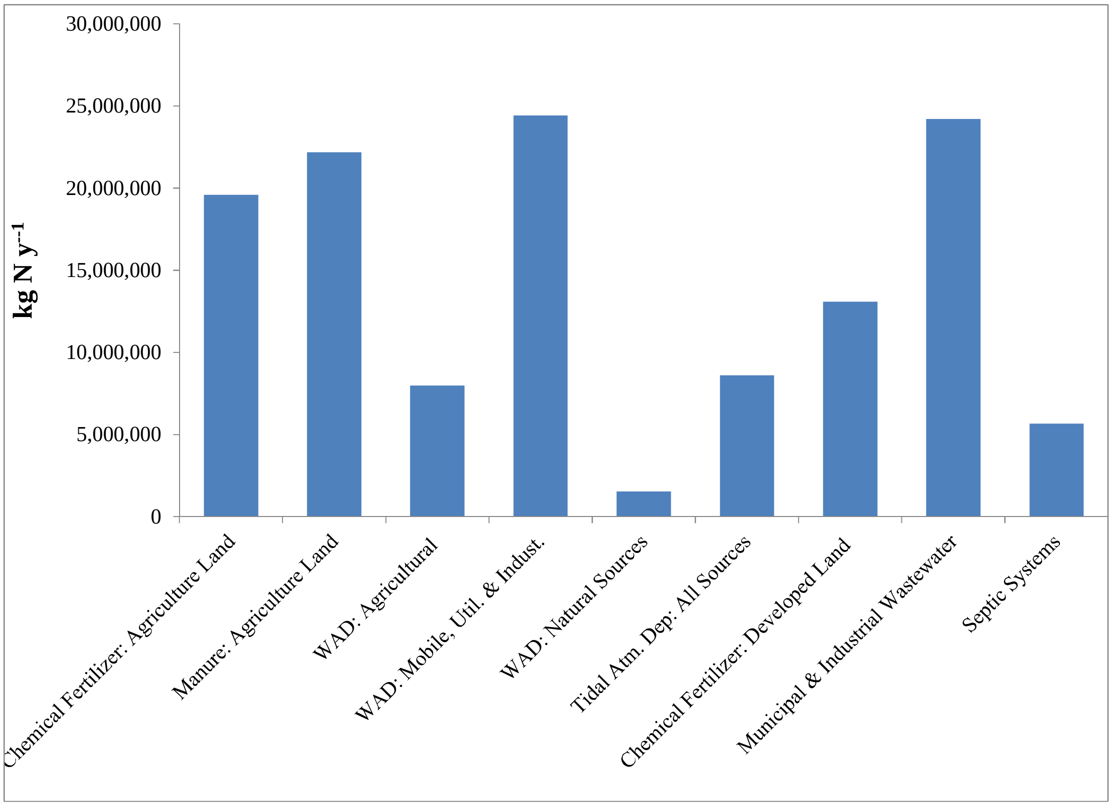

Figure 7. Nitrogen loads entering the Chesapeake Bay Watershed per year from naturally occurring and anthropogenic sources. Amount of nitrogen from watershed atmospheric deposition (WAD) depend on the originating source such as agricultural, industrial, or natural. Wastewater loads were based on measured discharges. Other loads calculated on an average hydrology year using the Chesapeake Bay Program Watershed Model Phase 4.3. Data and model from the Chesapeake Bay Program (www.chesapeakebay.net).

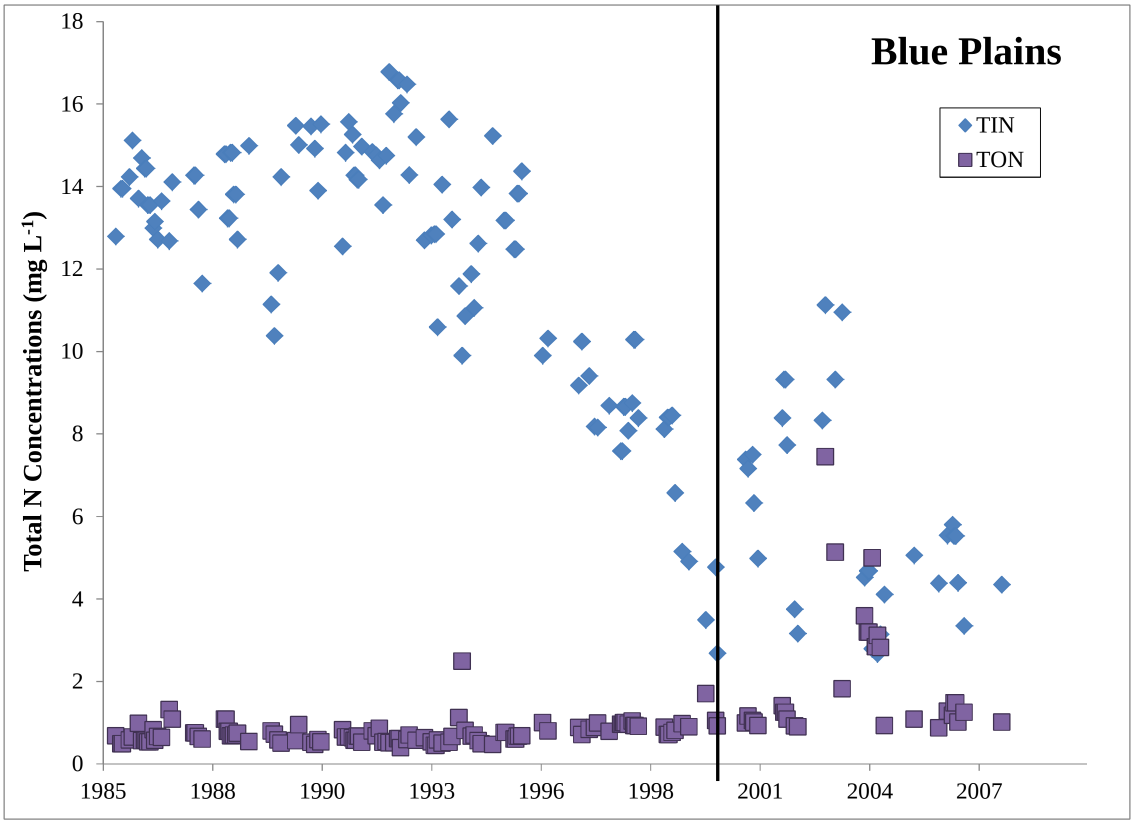

Figure 8. Time series (1985-2007) of monthly averaged total inorganic (TIN) (♦) concentrations and organic (TON) (■) concentrations in Blue Plains WWTP effluent. Data are from the Chesapeake Bay Program Nutrient Point Source database (www.chesapeakebay.net). DC Water and MWCOG supplied the data to the Chesapeake Bay Program. The line in the middle of the graph indicates initiation of BNR at Blue Plains.

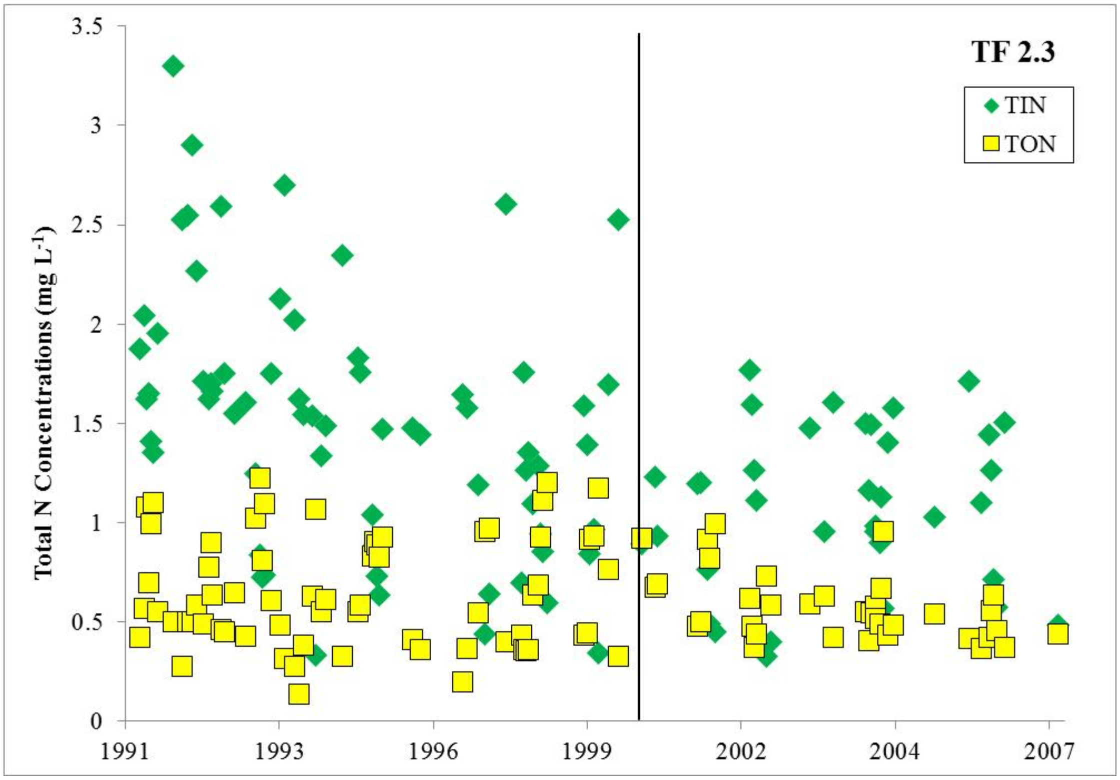

Figure 9. Time series (1991-2007) of nitrogen concentration in total inorganic (TIN) and organic (TON) fractions at TF 2.3. TIN (♦) and TON (■) concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Sampling was occasionally disrupted or not completed due to weather or mechanical factors, which prevented observational points from being equally distributed through the measurement period. The Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) provided the nitrogen data based on measurements from MD DNR. The line in the middle of the graph indicates initiation of BNR at Blue Plains.

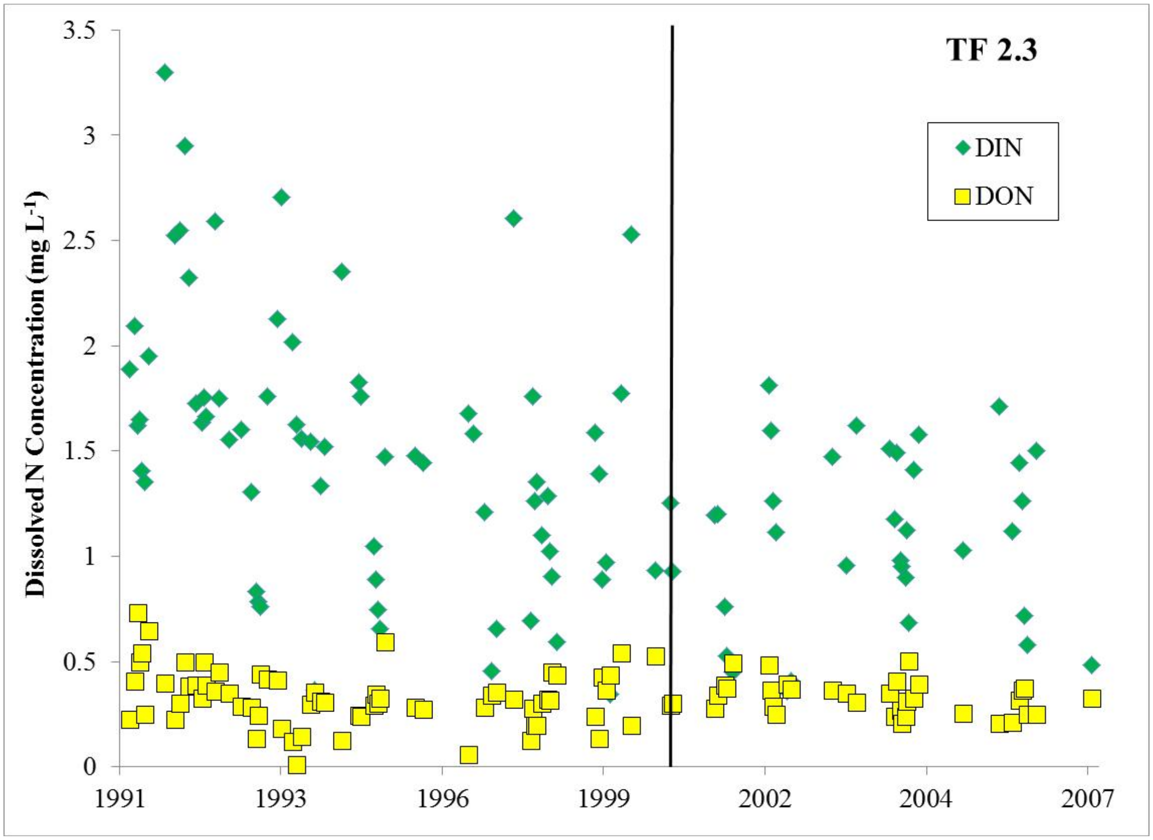

Figure 10. Time series (1991-2007) of nitrogen concentration in dissolved inorganic (DIN) and organic (DON) fractions at TF 2.3. DIN (♦) and DON (■) concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Sampling was occasionally disrupted or not completed due to weather or mechanical factors, which prevented observational points from being equally distributed through the measurement period. The Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) provided nitrogen data based on measurements from MD DNR. The line in the middle of the graph indicates initiation of BNR at Blue Plains.

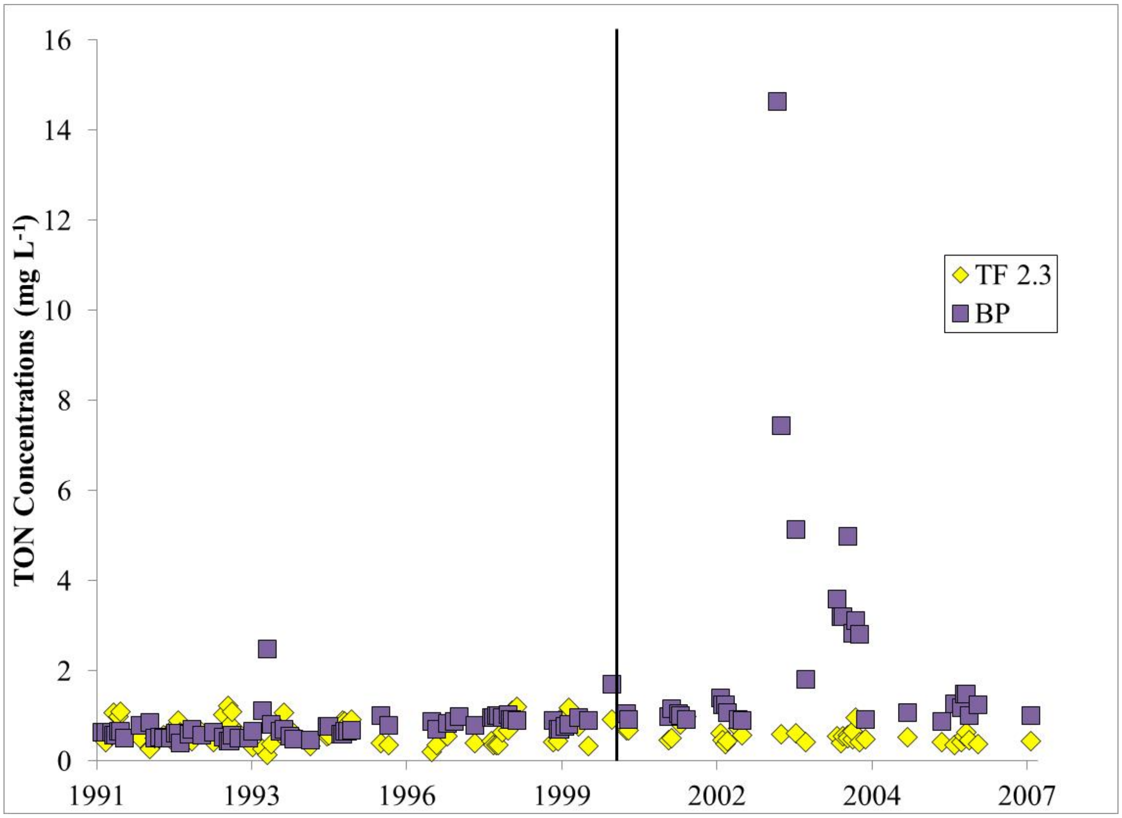

Figure 11. Times series (1991-2007) of total organic nitrogen data from both Blue Plains WWTP effluent (■) and TF 2.3 (♦). Blue Plains effluent TON concentrations were based on monthly averages. TF 2.3 TON concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Sampling frequency was occasionally disrupted or not completed due to weather or mechanical factors. Blue Plains data are from the Chesapeake Bay Program Nutrient Point Source database. DC Water and MWCOG supplied the Blue Plains effluent data to Chesapeake Bay Program. TF 2.3 data are from the Chesapeake Bay Program Water Quality database (1984-present). MD DNR supplied TF 2.3 data to Chesapeake Bay Program. The line in the middle of the graph indicates initiation of BNR at Blue Plains. All data are available at www.chesapeakebay.net.

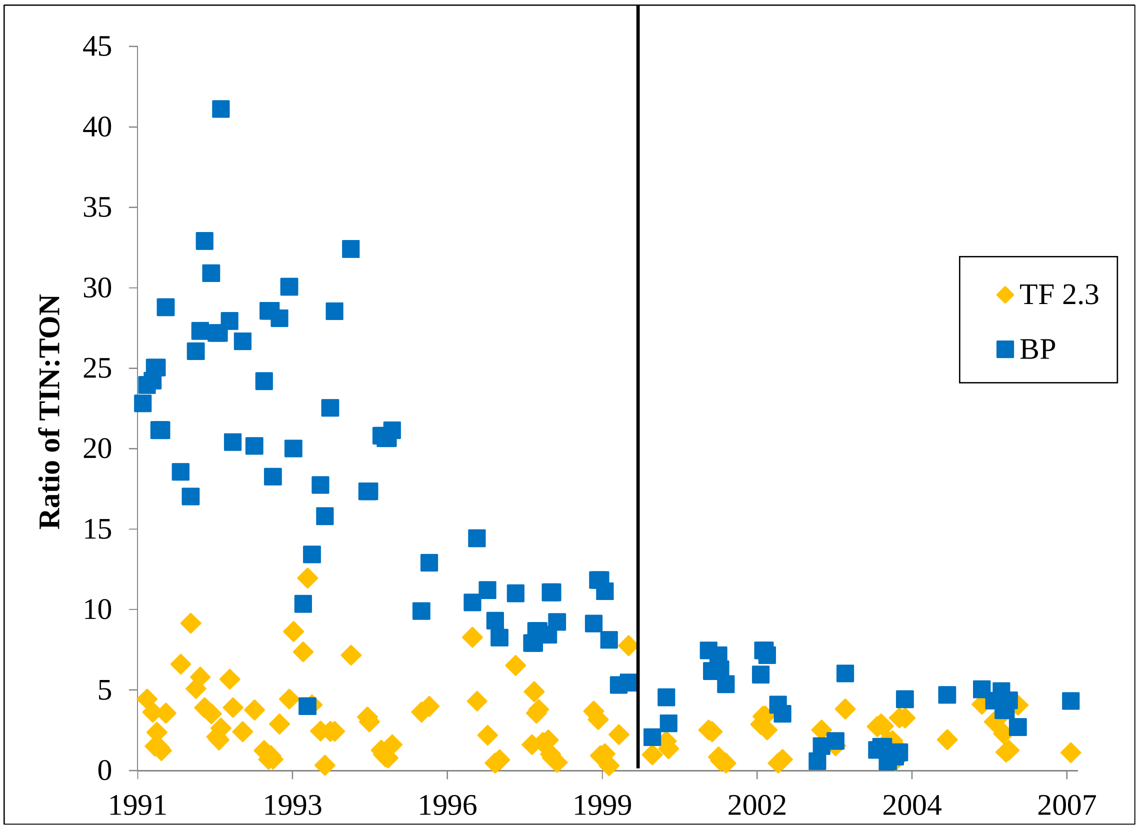

Figure 12. Ratio of TIN:TON from 1991-2007 at Blue Plains WWTP effluent (■) and TF 2.3 (♦). Blue Plains effluent data were based on monthly averages. TIN and TON concentrations at TF 2.3 were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Sampling frequency was occasionally disrupted or not completed due to weather or mechanical factors. Blue Plains data are from the Chesapeake Bay Program Nutrient Point Source database. DC Water and MWCOG supplied the Blue Plains effluent data to Chesapeake Bay Program. TF 2.3 data are from the Chesapeake Bay Program Water Quality database (1984-present). MD DNR supplied TF 2.3 data to Chesapeake Bay Program. The line in the middle of the graph indicates initiation of BNR at Blue Plains. All data are available at www.chesapeakebay.net.

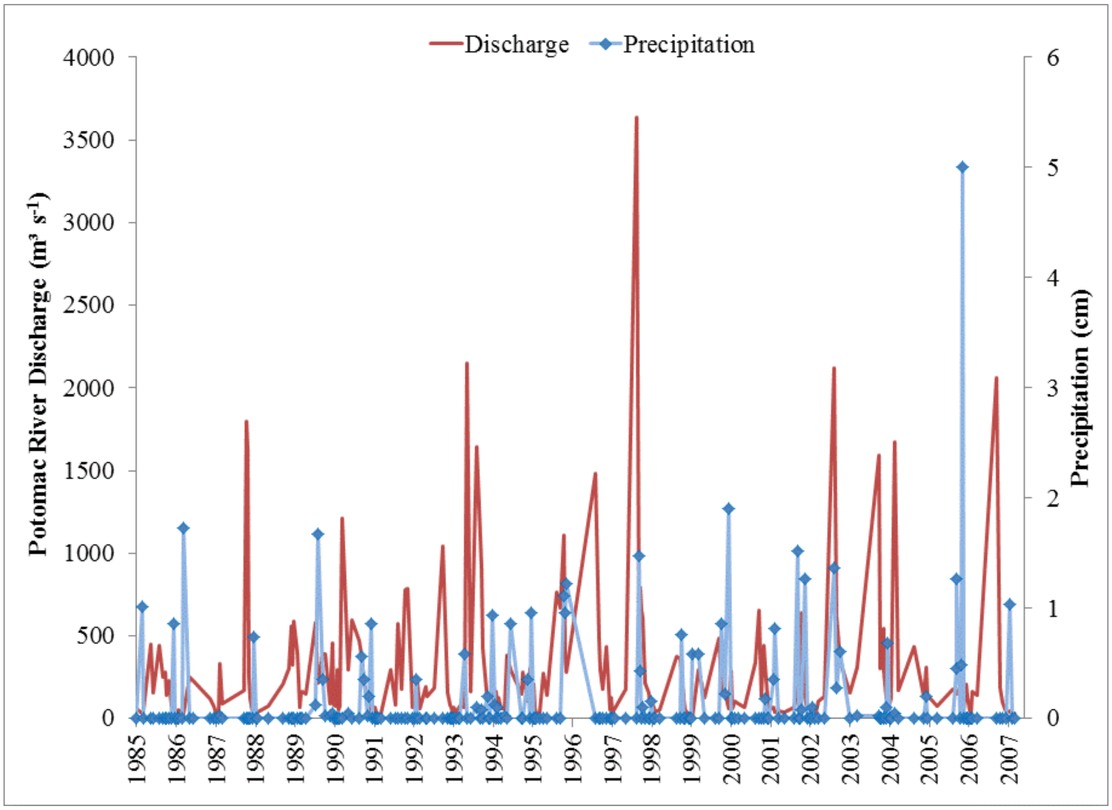

Figure 13. Time series (1985-2007) of the relationship between Potomac River discharge levels and precipitation measurements for the Washington DC metro area. Discharge data were obtained from USGS Chain Bridge gauge station and calculated as monthly average and submitted to the USGS Chesapeake Bay River Input Monitoring Program (2011) (http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html). Precipitation data were from monthly averages for the DC metro area, which included both Blue Plains WWTP and TF 2.3 within the observational range.

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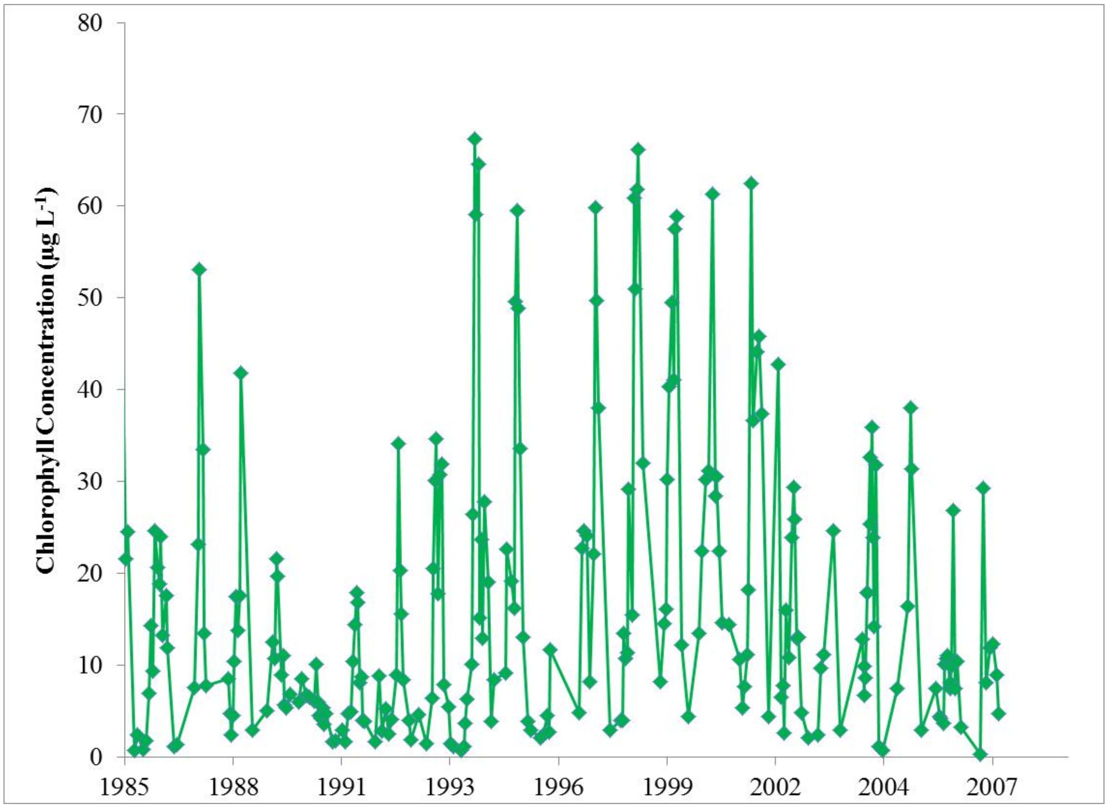

Figure 14. Time series (1985-2007) of chlorophyll concentration at TF 2.3. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Sampling frequency was occasionally disrupted or not completed due to weather and mechanical factors. Data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR.

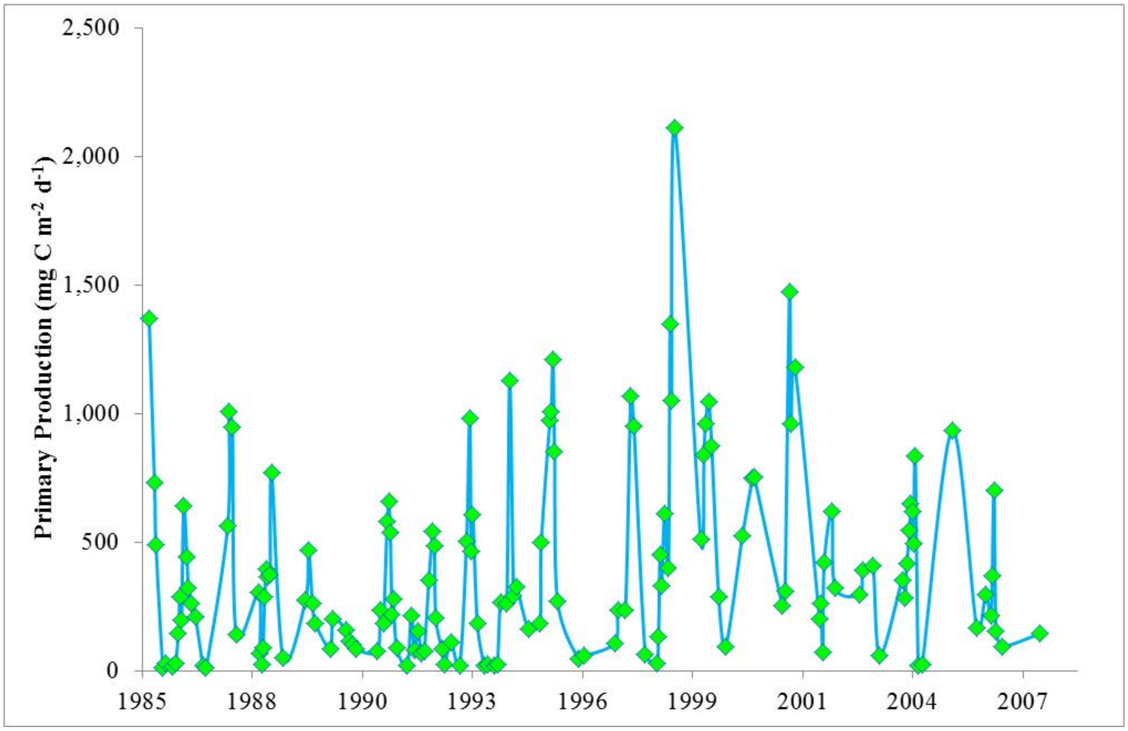

Figure 15. Time series (1985-2007) of primary production at TF 2.3. Primary production was measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Primary production data were acquired from Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) based on measurements from MD DNR. Sampling frequency was occasionally disrupted or not completed due to weather and mechanical factors. Data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR.

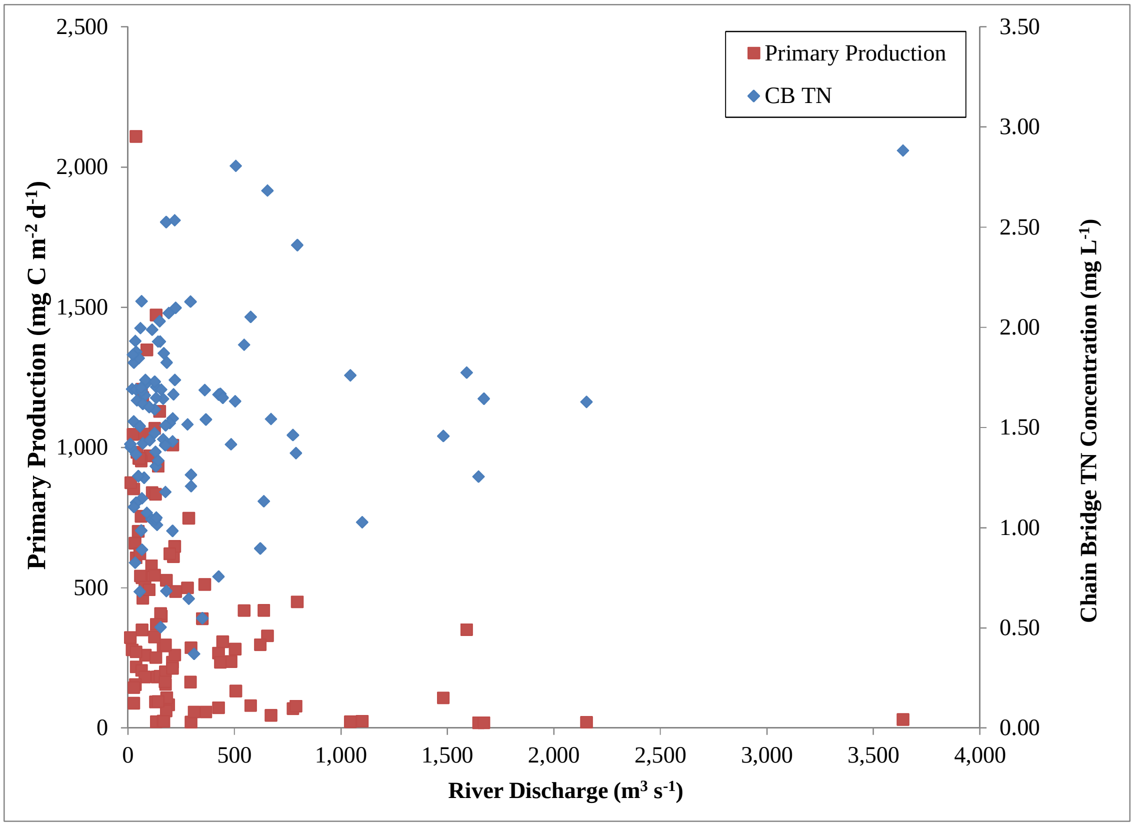

Figure 16. Influence of Potomac River discharge at Chain Bridge gauge station on Chain Bridge TN (♦) concentrations and primary production (■) at TF 2.3. Primary production was measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Primary production data were acquired from Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) based on measurements from MD DNR. The USGS Chesapeake Bay River Input Monitoring Program (2011) (http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html) provided discharge and TN data.

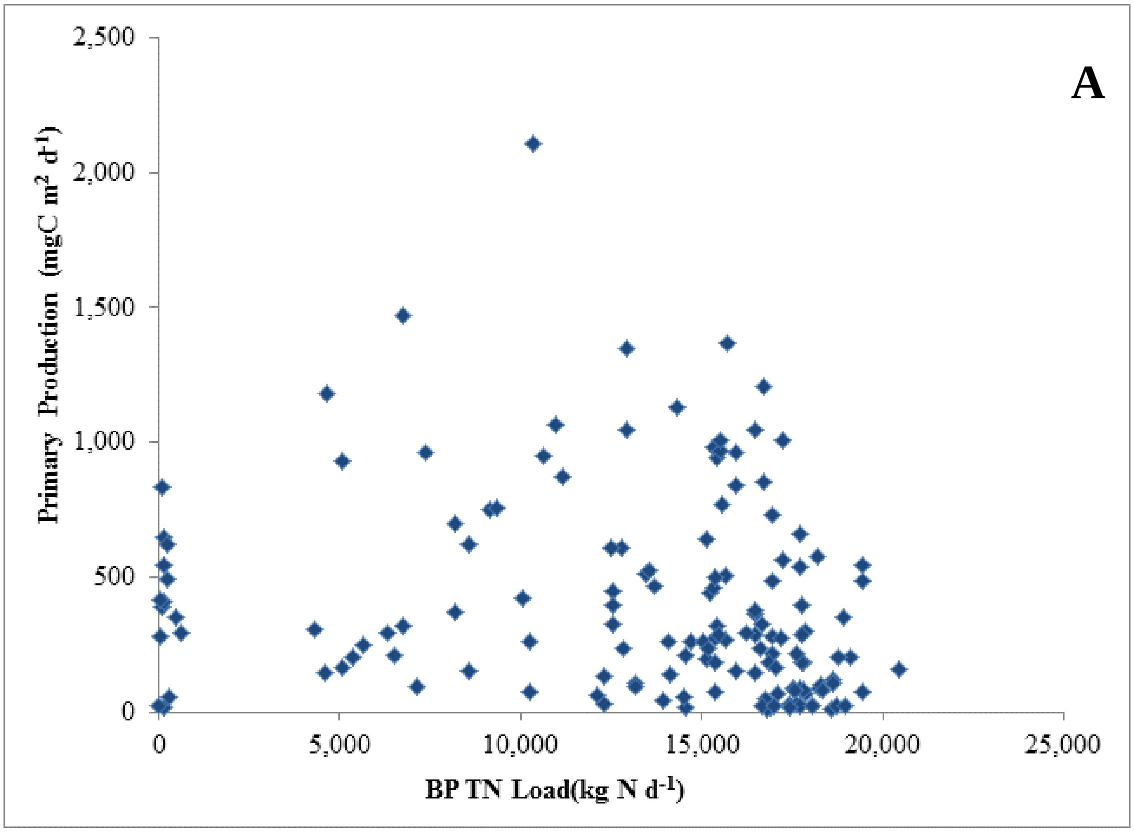

Figure 17a. Correlation between TN loads from Blue Plains effluent and primary production measured at TF 2.3. TN loads were calculated from monthly averages of Blue Plains flow data and TN concentrations. Primary production was measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. The Chesapeake Bay Program Nutrient Point Source database provided the TN load data for Blue Plains. DC Water and MWCOG supplied the Blue Plains data to Chesapeake Bay Program. Primary production data are from the Chesapeake Bay Program Baywide CBP Plankton database based on measurements from MD DNR. All data are available at www.chesapeakebay.net.

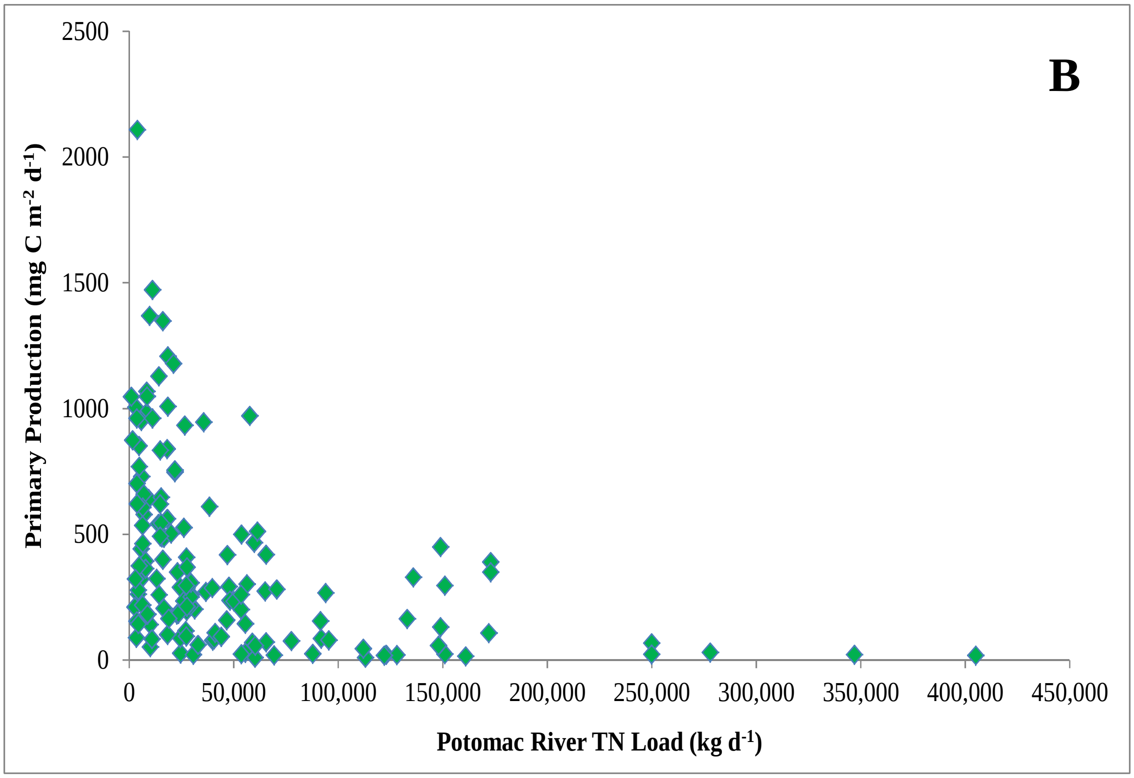

Figure 17b. Correlation between Potomac River TN loads and primary production measured at TF 2.3. Primary production was measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Primary production data are from the Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) based on measurements from MD DNR. The USGS Chesapeake Bay River Input Monitoring Program (2011)(http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html) provided the TN load data.

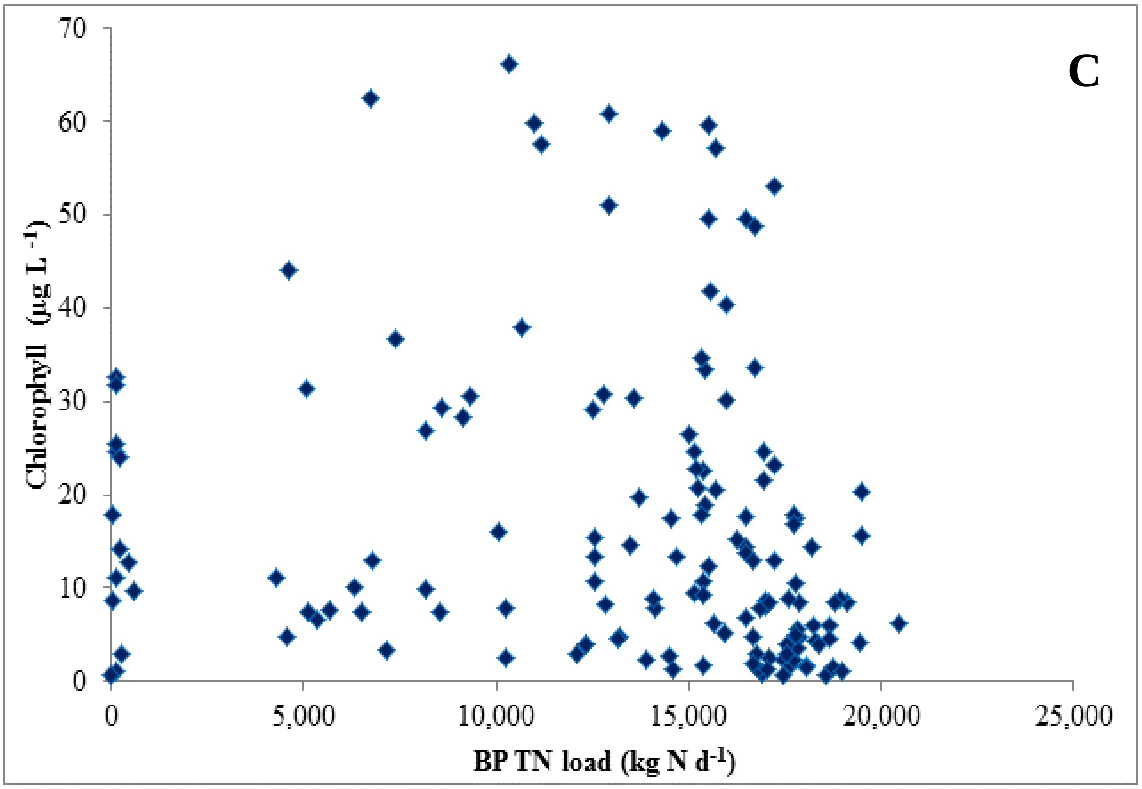

Figure 17c. Correlation between TN loads from Blue Plains effluent and chlorophyll concentrations measured at TF 2.3. TN loads were calculated from monthly averages of Blue Plains flow data and TN concentrations. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Chlorophyll data are from the Chesapeake Bay Program Water Quality database (1984-present) based on measurements from MD DNR. The Chesapeake Bay Program Nutrient Point Source database provided TN loading data for Blue Plains. DC Water and MWCOG supplied the Blue Plains data to Chesapeake Bay Program. All data are available at www.chesapeakebay.net.

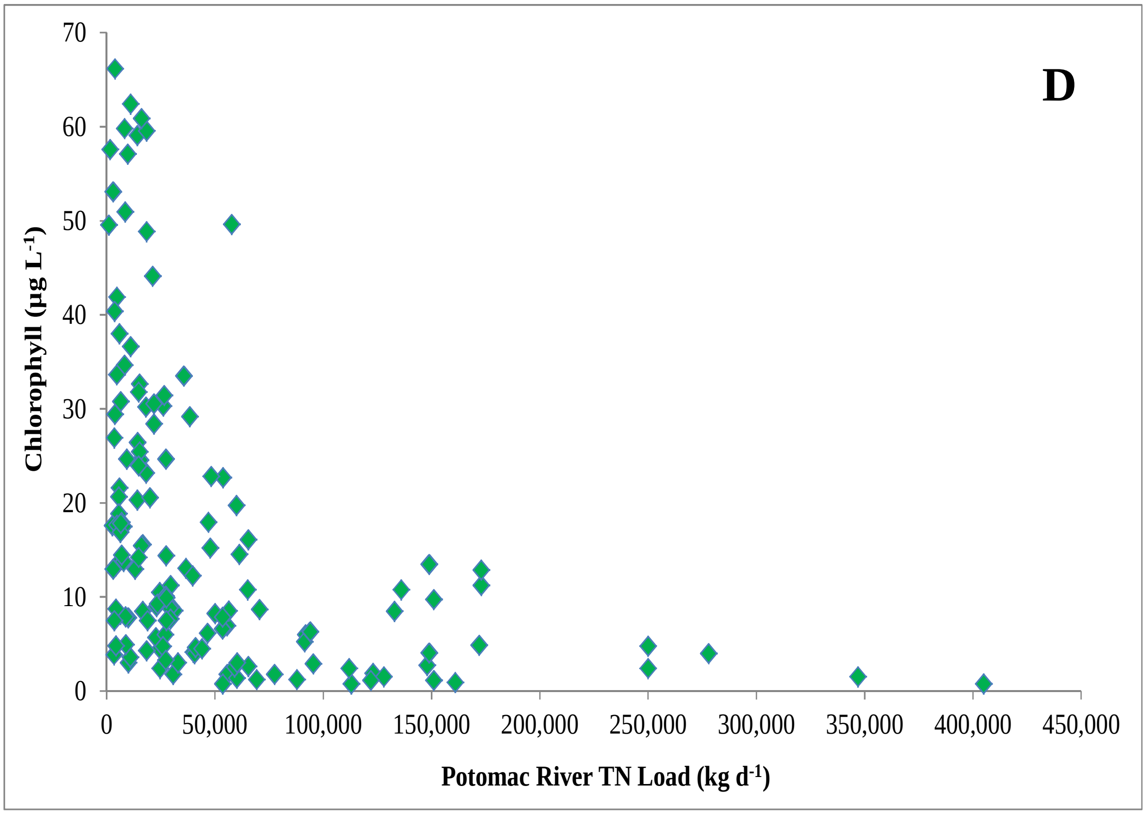

Figure 17d. Correlation between Potomac River TN loads and chlorophyll concentration measured at TF 2.3. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Chlorophyll data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR. The USGS Chesapeake Bay River Input Monitoring Program (2011) (http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html) provided discharge data.

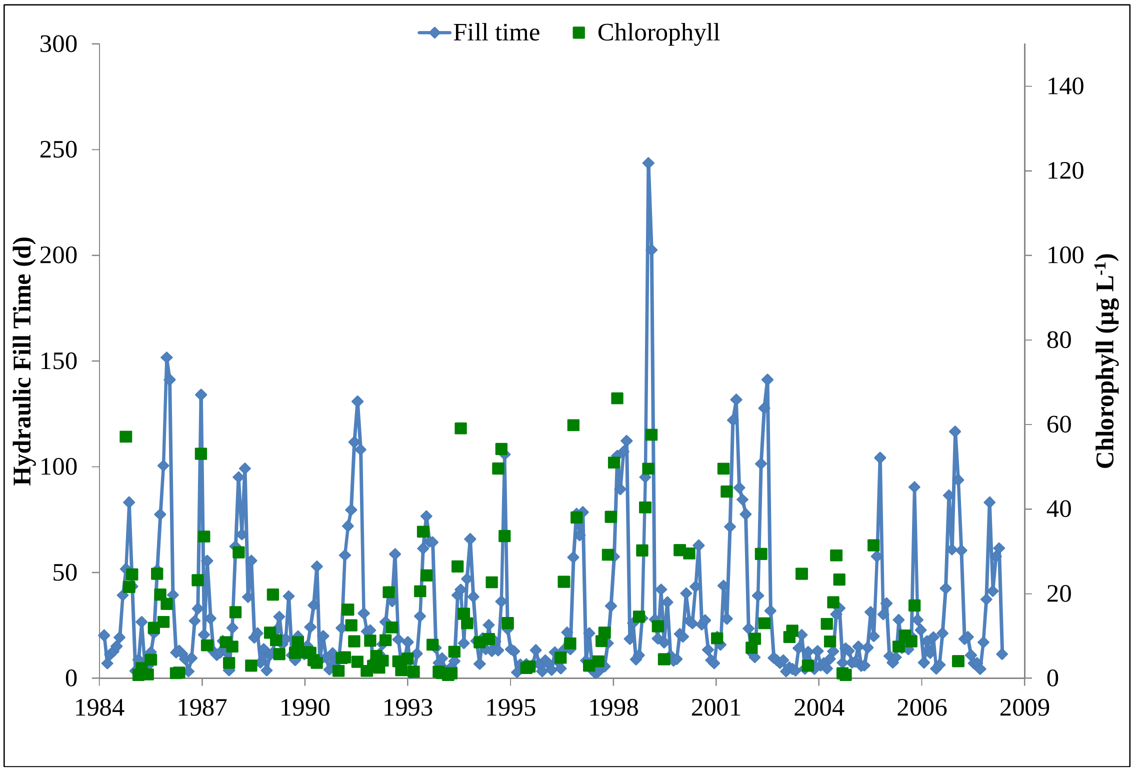

Figure 18. Time series (1984-2008) of hydraulic fill time and chlorophyll for segments 97 to 70. Hydraulic fill time was based on a monthly average. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Chlorophyll data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR. Boynton et al. (1990), Cronin (1971) and Cronin et al. (1975) provided the hydraulic fill time data.

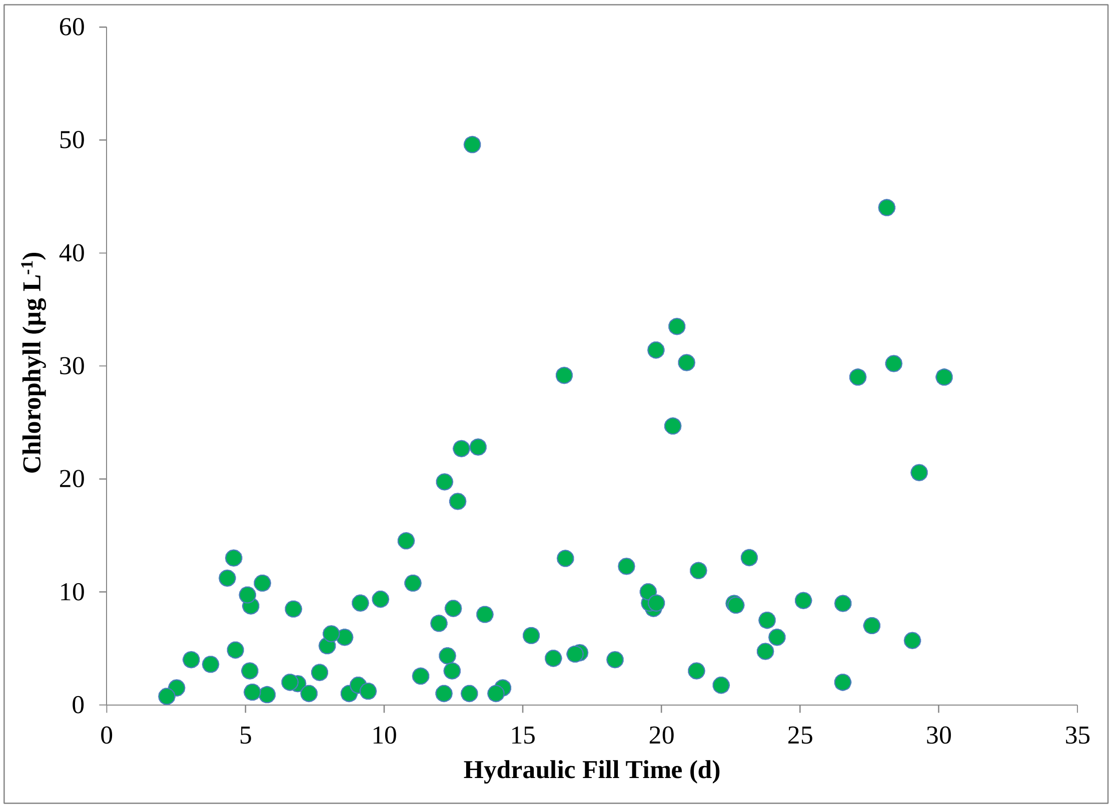

Figure 19. Time series (1984-2008) of hydraulic fill time of less than 30 d and chlorophyll for segments 97 to 70. Hydraulic fill time was based on a monthly average. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Chlorophyll data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR. Boynton et al. (1990), Cronin (1971) and Cronin et al. (1975) provided hydraulic fill time data.

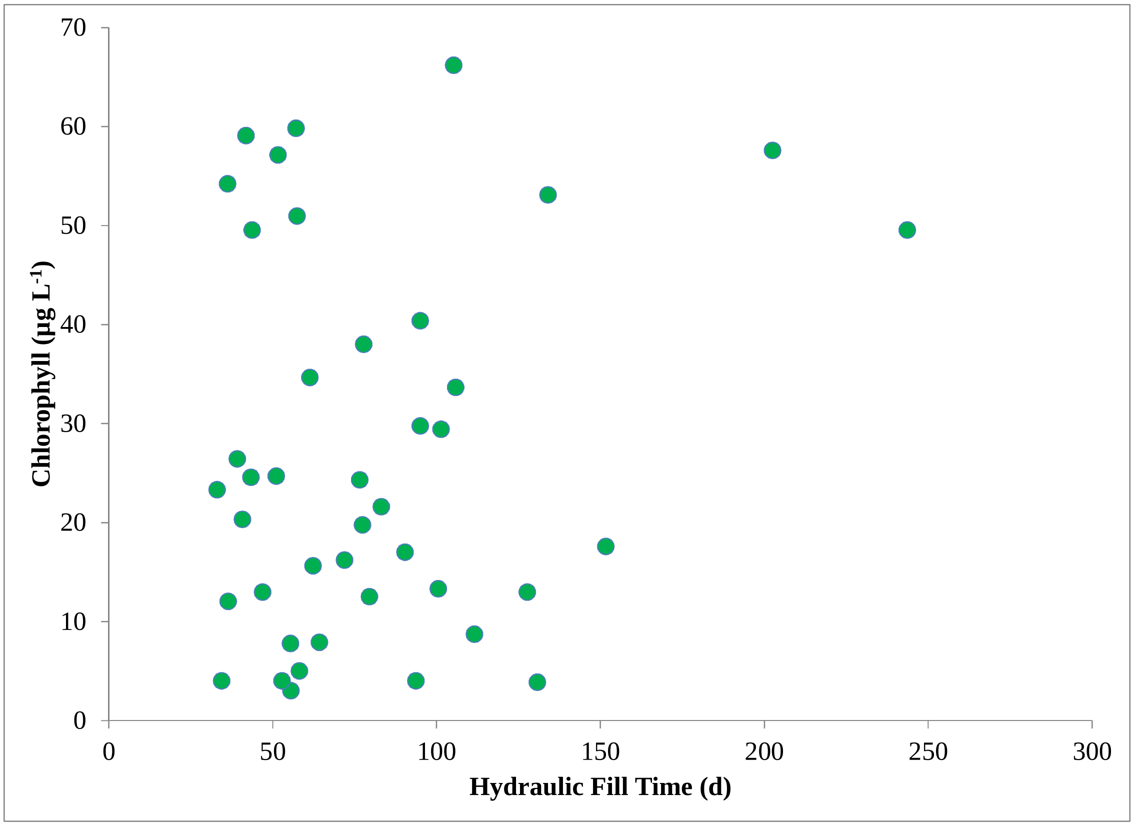

Figure 20. Time series (1984-2008) of hydraulic fill time of greater than 30 d and chlorophyll for segments 97 to 70. Hydraulic fill time was based on a monthly average river flow. Chlorophyll concentrations were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Chlorophyll data are from the Chesapeake Bay Program Water Quality database (1984-present) (www.chesapeakebay.net) based on measurements from MD DNR. Boynton et al. (1990), Cronin (1971) and Cronin et al. (1975) provided the hydraulic fill time data.

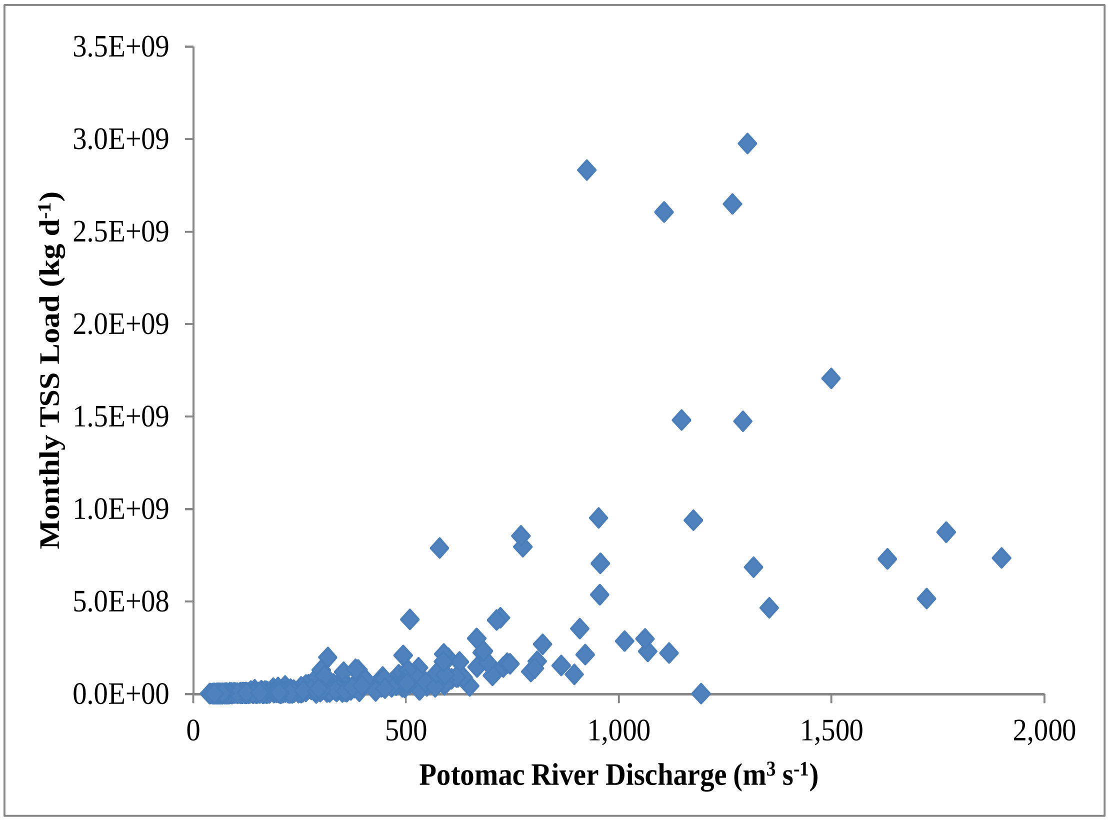

Figure 21. Correlation between monthly total suspended sediment (TSS) load at the Chain Bridge gauge station and Potomac River discharge. TSS load and Potomac River discharge data are based on monthly averages. USGS Chesapeake Bay River Input Monitoring Program supplied both datasets (2011) (http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html).

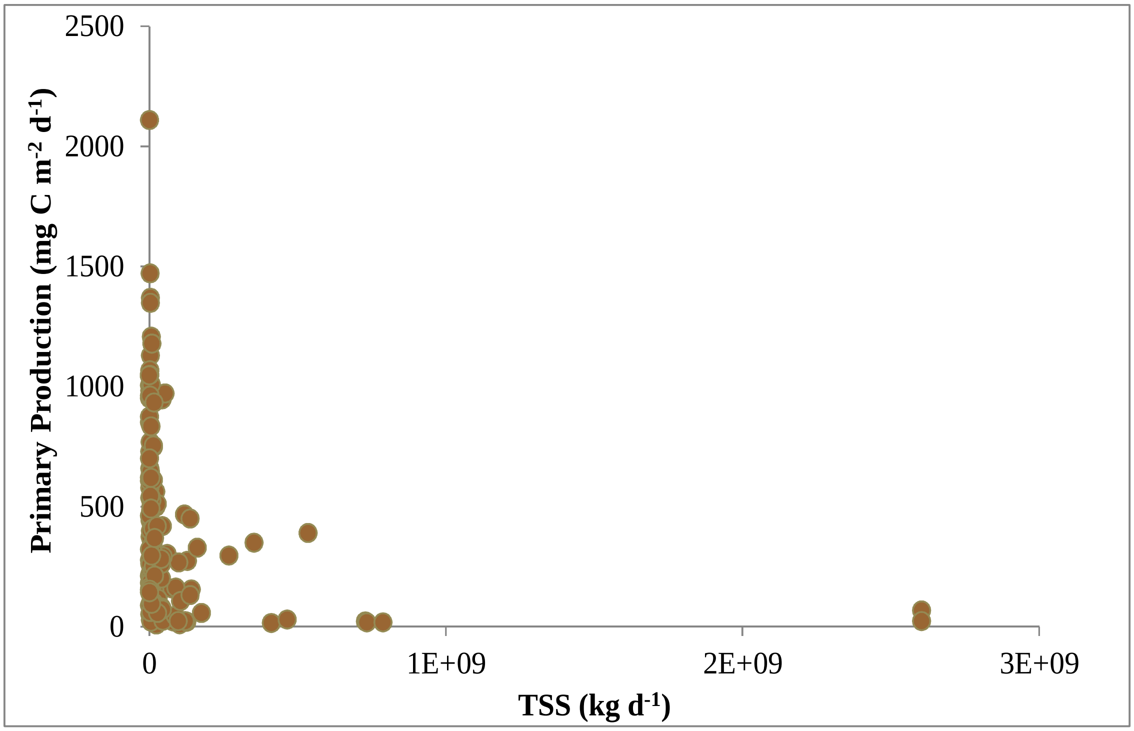

Figure 22. Correlation between monthly total suspended sediment (TSS) load at the Chain Bridge gauge station and primary production in the Potomac River. TSS loads were based on monthly averages. USGS Chesapeake Bay River Input Monitoring Program supplied the TSS data (2011) (http://va.water.usgs.gov/chesbay/RIMP/dataretrieval.html).
Primary production was measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. Primary production data are from the Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) based on measurements from MD DNR.

Chapter 2

Modeling Primary Production in the Tidal Fresh Portion of the Potomac River

<u>Introduction</u>

Phytoplankton are an essential component of a productive aquatic ecosystem. They are the base of the food chain and are the most abundant organisms involved in primary production. Primary production gives insight into the trophic status of an ecosystem and indicates responses to changes in basic parameters such as nutrient loads, light conditions, grazing, and temperature.

Chemical and physical parameters such as nitrogen, phosphorus, temperature, light availability and advective processes such as flow, tides, and flushing control the rate of primary production. Nutrients are essential for a healthy, productive system, but increased loads from anthropogenic sources can stimulate excessive phytoplankton growth resulting in high levels of organic matter, better known as eutrophication. Nixon (1995) defined eutrophication as an increase in the rate of supply of organic matter within an ecosystem, emphasizing that the process changes under varying environmental conditions and the autochthonous versus allochthonous source of carbon. Eutrophication in estuarine waters is encouraged by excessive nutrient enrichment, which can increase the rate of phytoplankton growth, leading to more *in situ* organic matter production in the environment. Other events associated with phytoplankton growth include changes in species composition, sometimes toxic, resulting in sustained blooms (Anderson et al. 2002). Bloom events increase turbidity, preventing sunlight from penetrating to greater depths, depriving submerged aquatic vegetation and benthic microalgae of light energy

(McGlathery et al. 2007). Excessive production beyond the ecosystem assimilation capacity has caused oxygen levels to decline, increasing the volume of ecosystem waters experiencing hypoxic or anoxic events (Hagy et al. 2004). When blooms start to decay, bacteria decompose the organic carbon produced by phytoplankton and in the process consume available oxygen in the environment. When oxygen concentration is low (hypoxic) or completely depleted (anoxic) fish, crabs, and other aquatic organisms cannot survive forcing them to move from their habitat or perish.

Nixon (1995) developed a productivity scheme for estuaries based on organic supply and resultant trophic status (Table 1). The organic carbon can be supplied by phytoplankton fixation (autochthonous) or input of organic matter from outside the system (allochthonous). In this scheme, estuaries exhibit the highest rate of organic production and are high in autochthonous carbon as a result of being nutrient rich and serving as a habitat for primary producers. Allochthonous sources also contribute carbon; however in the Chesapeake Bay watershed external carbon inputs are of less importance than autochthonous sources. Kemp et al. (1997) developed an organic carbon budget for the Chesapeake Bay using a mass balance approach of estimated annual means for major carbon fluxes in the mainstem of the Bay to quantify major sources and sinks of carbon. They found that the largest input and output fluxes were primary production and water column respiration, respectively. These findings support the idea that phytoplankton activity plays a crucial role in organic carbon levels and ecosystem trophic status in the Chesapeake Bay.

The balance between primary production and respiration indicates the relative heterotrophic or autotrophic characteristic of the estuarine metabolism, as well as the availability of autochthonous organic matter. An autotrophic system has more primary production than respiration. This stems from a higher inorganic to organic nutrient load, which fuels phytoplankton activity and overall net ecosystem metabolism. A heterotrophic system has more respiration than primary production activity and can be supported by allochthonous nutrient sources or an excess of autochthonous production. On the relatively short annual time scales that trophic status is typically measured (i.e., months to years), autotrophic coastal and estuarine ecosystems either bury excess organic carbon in the sediments or export it to the ocean. Heterotrophic systems either import or store organic carbon so heterotrophic organisms can use it for respiration and growth (Kemp et al. 1997, Odum 1956). Kemp et al. (1997) observed changes in the ratio of dissolved inorganic nitrogen to total organic nitrogen (TON) through the estuary with a higher ratio in autotrophic regions and lower in heterotrophic areas. These patterns were attributed to higher (or lower) inorganic nutrient loading associated with higher (or lower) primary production. Knowledge of how primary production plays a role in connecting nutrient inputs and trophic status to the ecosystem provides insight into how to improve water quality.

Unfortunately, the Chesapeake Bay Program (CBP) halted monitoring of primary production in 2009 (MD DNR 2010), making it challenging to monitor how changes in nutrient reduction strategies. Models, however, can be used to study ecosystem functions where data are missing or incomplete. Most models are intended to predict or extrapolate information on standing stocks rather than rate processes. However, in order for models to be applicable across a variety of ecosystem conditions, both state variables and rate processes should be considered. Measurements of state variables such as chlorophyll and environmental parameters controlling growth rate (e.g. light availability and nutrient concentration) can be used to develop models intended to estimate growth rates *and* primary production (Cloern et al. 1995). For example, phytoplankton biomass, represented as chlorophyll, is readily measured rather than rates of primary production (Brush et al. 2002) and models that can predict primary production from chlorophyll measurements are useful tools for mangers faced with reduced monitoring programs. In this practical class of primary production models or algorithms, two different modeling approaches exist: empirical/statistical and mechanistic/theoretical.

Mechanistic models use fundamental knowledge of interactions among process variables to define model structure, relying on first principles such as the relationship between temperature and growth rate. Mechanistic models develop physiological relationships to explain phytoplankton chemical composition and growth rate under defined conditions. The goal is to predict a rate process through representation of causal mechanisms underlying system behavior. Parameters values, rather than data, are used as inputs, as they as can be adjusted to a specific observation outside of their original context (Brush et al. 2002, Cloern et al. 1995).

Empirical models are formulated to estimate phytoplankton growth rates in numerical models of ecosystem dynamics and are largely based on observations or existing data. They describe and summarize a set of relationships, based on actual measurements, with a goal of prediction. Empirical models use site specific measurements of productivity and related variables to develop simple, practical models. Empirical models of primary production are typically based on simple linear relationships and are reasonably accurate because primary production is largely regulated by variables that are simple to measure such as irradiance and phytoplankton biomass (Brush et al. 2002, Cloern et al. 1995)

Development of primary production models for the Chesapeake Bay has been ongoing for several decades; however, they have not been developed for the tidal fresh portion of the ecosystem. The lowest salinity recorded for existing models of primary production is 2.2 (± 0.84) (Harding et al. 2002), while the site used to test the models in my analysis had an average salinity of 0.15. This caveat for existing Chesapeake Bay primary production models affects our ability to predict primary production in the area surrounding the Blue Plains Wastewater Treatment Plant (WWTP). As the largest point source in the Chesapeake Bay watershed, this WWTP frequently changes its management strategies to reflect changes in water quality rules and regulations. The Clean Water Act has developed regulatory strategies, such as the Total Maximum Daily Load, to control nutrient loading. Modeling primary production and incorporating it into management strategies provides information about whether water quality goals can be accomplished and trophic status altered in the future as a result of technological advances at the WWTP.

A key difference between the evaluation of primary production measurements in Chapter 1 and the work I present here needs clarification. The all possible subset regression analysis in Chapter 1 evaluated the effects of Blue Plains versus Chain Bridge nitrogen on primary production normalized to chlorophyll concentrations. While the regression analysis provided a model ranking of possible models to explain the variability in the primary production dataset, the ability of any of those models to predict primary production was generally poor (top model pre-BNR adjr^2 0.139; top model post-BNR adjr^2 0.199).

Here, the formulations of the primary production models are either mechanistic in nature, for example characterizing temperature dependence using the Arrhenius equation, or have been broadly applied in other ecosystems and as such merit investigation of their predictive power in the tidal fresh Potomac. A primary goal is to use chlorophyll biomass as an explanatory variable so that monitoring data may continue to be used to estimate primary production rates.

Here I evaluate existing primary production data from Potomac River site Tidal Fresh (TF) 2.3 to explore the applicability of a suite of primary production models previously developed for other, more saline estuarine systems. These models include two versions of the Vertically Generalized Production Model (VGPM-a and VGPM-b), Chesapeake Bay Production Model (CBPM), and the Light-Biomass Model with the Metabolic Theory of Ecology (MTE) (BZ_pI_0t) to estimate primary production for available CBP data collected for TF 2.3. I then use appropriate primary production models that include the effects of environmental controls on productivity such as light, temperature, and photic depth to estimate missing productivity rates from available data during time periods when monitoring of primary production rates did not occur.

Methods

Long Term Monitoring Database

The CBP database of monitoring measurements was used to develop the models for the Potomac River. I selected TF 2.3, located about 30km downstream of the Blue

Plains Wastewater Treatment Plant's discharge pipe, as it is the most comprehensive site within close proximity (Figure 1). The CBP Water Quality database (1984 to present) includes data provided by Maryland Department of Natural Resources (MD DNR) for the following variables: surface temperature, chlorophyll concentration, photic depth, surface irradiance, and primary production. When surface irradiance measurements were not available in the CBP database, data for Cambridge, MD (provided by Dr. Tom Fisher of the UMCES, Horn Point Laboratory) were used. The United States Geological Survey (USGS) Chesapeake Bay River Input Monitoring Program provided discharge, total suspended sediment load (TSS), and total nitrogen load data for the Potomac River Chain Bridge gauging station, located 17 km north of Blue Plains (Figure 1). This site was used due to its proximity to Blue Plains and TF 2.3 and because it represents nitrogen loads from the upper Potomac watershed. Blue Plains contributed information on effluent discharge rates, as part of their reporting requirements to the Metropolitan Washington Council of Governments.

Primary production data were provided by the CBP database (CBP 2010). The CBP measured production using the carbon-14 (^{14}C) fixation method, which measures the rate of radioactive carbon uptake by phytoplankton to quantify primary production. Radioactively labeled carbonate ($^{14}CO_3^{2-}$) is added as a tracer to a natural sample of phytoplankton; after a cycle of photosynthesis occurs, the sample is filtered capturing all autotrophic organisms. This method assumes the activity of phytoplankton and amount of $^{14}CO_3$ added measure total C assimilation and total C available, with a constant to correct for isotope fractionation. The data were presented in $\mu g\ C\ L^{-1}\ h^{-1}$; in order to compare models, the CBP data were converted to $mg\ C\ m^{-2} d^{-1}$ using information provided by CBP for photic zone depth (m) and day length (hours of light per day). Vertically integrated water samples were use in these computations; water samples from individual depths were not available. Samples were taken above the pycnocline, or density gradient, defined here as water taken between 0.5 m below surface and 0.5 m above the depth used as a cutoff between upper and lower layers during sampling events.

Models

Phytoplankton biomass is insufficient to predict primary production; other environmental parameters such as irradiance and photic depth need to be incorporated into the analysis to improve estimation abilities (Carr et al.2006). In an effort to find a model suited to adequately predict primary production in the tidal fresh Potomac River, I used new and existing models of primary production and implemented those using data from the CBP database, as described above. The models are described in the following sections.

Vertically Generalized Production Model - A

Behrenfeld and Falkowski (1997 a,b) developed the light-dependent, depth resolved Vertically Generalized Production Model (VGPM) using remote sensing data from shelf and slope waters of the West Atlantic Ocean to determine the environmental parameters required to accurately predict primary production. The VGPM is a depth-integrated primary production (PP) model relating surface phytoplankton biomass (chl-a, mg m^{-3}), a photoadaptive variable ($P^{B}_{opt,}$ mg C (mg Chl-a)$^{-1}$ h^{-1}) and its coefficient

(0.66125), photic depth ($Z_{p,}$ m, defined as the depth of the 1% light level), a surface irradiance-dependent function ($I_{0,}$ PAR, micro Einstein m^{-2} d^{-1}), and day length (D, h).

The original VGPM (equation 1) was published as below:

$$\widehat{PP} = 0.66125 * P^{B}_{opt} * [I_0 / (I_0 + 4.1) * Zp * \text{chl-a} * D \qquad (1)$$

where $\widehat{PP}$ is the estimated, dependent variable primary production and not designated as net or gross. The independent variables were P^{B}_{opt}, I_0, Z_p, chl-a, and D.

The original VGPM model for carbon fixation focuses on the variables influencing the vertical distribution of primary production and those controlling the optimal assimilation efficiency of productivity in the water column (P^{B}_{opt}). P^{B}_{opt} represents the maximum chlorophyll-specific carbon fixation rate observed within a water column as a function of surface temperature. In an effort to develop a model for primary production in the Chesapeake Bay, Harding et al. (2002) examined the effectiveness of the VGPM to predict primary production in estuaries. This original investigation into the Behrenfeld-Falkowski model overestimated net ^{14}C primary production (^{14}C-PP) by approximately 30%.

This prompted an adjustment to the VGPM model to improve its performance using Chesapeake Bay data. Data were collected along the main stem of the Bay, including the oligohaline, mesohaline, and polyhaline regions, with salinities ranging from 2.2 (±0.84) to 24.6 (±0.60) and included remote sensing data for temperature and occasionally chlorophyll. Using the Behrenfeld-Falkowski model, Harding et al. (2002) employed logarithmic transformations on both the data and model equation after it was noted that variances in net and gross estimates of ^{14}C-PP increased in proportion to the means, and the variances were more uniform on a logarithmic scale. After log transformation the y-intercept was $\log_{10}$ 0.66125 = - 0.1796, representing a change in that coefficient in the original equation. The log transformation preserved the structure of the original model and better met the least squares assumption of homogeneity in regression analysis. Harding et al. (2002) used this information to create a zero-intercept model with non-unity slope (equation 2) which was then log-transformed (equation 3) where $PP(i)_{VGPM}$ is equal to estimated PP from the original VGPM.

$$PP(i)_{VGPM\text{-}a} = ß * PP(i)_{VGPM} \quad (2)$$

$$\log(PP(i)_{VGPM\text{-}a}) = \log(ß) + \log(\widehat{PP}\ (i)_{VGPM}) \quad (3)$$

The adjusted model has a y-intercept of log (ß) estimated by least squares and a slope constrained to equal unity. The anti-log of the intercept of the regression was used to adjust VGPM. Calculating ß from the antilog yielded equation 4.

$$PP(i)_{VGPM\text{-}a} = 0.7577 * \widehat{PP}(i)_{VGPM} \quad (4)$$

This adjusted the output of the original VGPM to produce estimates of PP for the Chesapeake Bay data. In essence, Harding et al. (2002) multiplied the original coefficient of the Behrenfeld-Falkowski model (0.66125) by 0.7577 to yield the new coefficient of P^B_{opt}, 0.5010.

By thus adjusting the original VGPM, Harding et al. (2002) obtained a new equation to estimate net primary production in the Chesapeake Bay. It is represented by equation 5 and will be referred to as VGPM-a.

$$\widehat{PP} = 0.5010 * P^b_{opt(net)} * [I_0/(I_0 + 4.1)] * Zp * chl\text{-}a * D \quad (5)$$

Vertically Generalized Production Model - B

An additional model, the VGPM-b, was based on VGPM-a, but was multiplied by 3.3247 to perform a linear correction on equation 5 to improve its performance within the study region used by Harding et al. (2002).

The antilog of the intercept of the regression was used to adjust the VGPM giving the VGPM-b. Estimating the antilog of the intercept term yielded equation 6.

$$\widehat{PP} = \text{VGPM-b} = \text{VGPM-a}*3.3247 \tag{6}$$

Chesapeake Bay Production Model

The Chesapeake Bay Production Model (CBPM) was created by Harding et al. (2002) based on the VGPM. The CBPM relaxed constraint of the original VGPM which considered the exponents of the independent variables, equivalent to coefficients of logarithms of the independent variables in log-linear form, equal to unity. In other words, in the original VGPM, each variable within the model equation was given equal weight. For the CBPM, Harding et al. (2002) estimated optimal coefficients for each independent variable using stepwise and multiple, linear regression of the logarithmic form of the VGPM. The observed Chesapeake Bay net ^{14}C-PP data used in VGPM-a development, acted as the dependent variables. The independent variables outlined in the VGPM-a were used, which preserved the basic form and mechanistic framework of the VGPM-a. In order to determine the relative importance of independent variables, a step-wise regression analysis followed by recovery of parameter estimates was used to produce equation 7 with the CBP datasets.

$$\log \widehat{PP} = 0.1329 + 0.9064 \log P^{b}_{opt} + 1.0265 \log \text{chl-a} + 0.9710 \log Zp + 1.4260 \log I_0 + 0.6645 \log D \quad (7)$$

The final equation weighted the independent variables according to their predictive capability, as opposed to placing all of the weight on a single coefficient. This model estimates net production, distinguishing it from gross production, which was also estimated by Harding et al. (2002) but not discussed here.

Biomass, Photic Depth, Irradiance Model

The BZ_pI_0 model was originally developed by Cole and Cloern (1987) and was based on actual measurements of phytoplankton production from San Francisco Bay. They observed a strong linear relationship ($r^2 = 0.82$) between daily primary production measured using ^{14}C and the composite parameter BZ_pI_0. In this case, phytoplankton biomass (B) is multiplied by light availability in the water column, which is represented as the product of Z_p and I_0. Additional parameters include α and β as linear regression fitted coefficients as formulated in equation 8.

$$PP = \alpha + \beta\,(BZ_pI_0) \quad (8)$$

BZ_pI_0 with Metabolic Theory of Ecology

Harris and Brush (in review) adjusted the original BZ_pI_0 model to include temperature and the metabolic theory of ecology (MTE) as shown in equation 9

$$PP = \alpha + \beta\,(BZ_pI_0)e^{-E/kT} \quad (9)$$

where E is the activation energy, representing the exponential effects of temperature on biochemical reaction rates (Allen et al. 2005), k is the Boltzmann constant (8.62×10^{-5} eV

K^{-1}), and T is absolute temperature in Kelvin. This version includes characteristics of both empirical and mechanistic models.

This modification of the original Cole and Cloern (1987) model incorporates the Boltzmann-Arrhenius term $e^{-E/kT}$ to account for predictions provided by the MTE regarding thermodynamic constraints on metabolic rates. It combines Boltzmann's (1870) general theory of chemical reaction kinetics and the empirically determined activation energies of respiratory reactions originally proposed by Crozier (1924).The MTE is based on three basic parameters controlling metabolic rate: body size, body temperature, and resource availability. The activation energy for photosynthesis ranges from 0.33 to 0.7 eV depending on whether net or gross primary production is being measured, and the degree of photorespiration by the photosynthesizing organism. Plant respiration is ultimately controlled by photosynthesis and the "effective" activation energy of carbon photosynthesis is lower (~0.33 eV) because carbon fixation by Rubisco is less efficient at higher temperatures due to photorespiration (Allen and Gillooly 2007).

Because values of measured primary production are reported in the CBP datasets on a daily time scale, I selected activation energy of 0.33 eV for use in this study. The MTE creates a quantitative framework based in first principles to understand how these variables combine to affect metabolic rate, and how metabolic rate influences the ecology and evolution of populations, communities, and ecosystems. This modification will be referred to as the "BZ_pI_0t" model in subsequent descriptions.

Model Parameters

The primary variables, P^B_{opt}, chl-a, Z_p, D, and I_0, used to estimate primary production in VGPM-a, VGPM-b, and CBPM are discussed below. These basic, measurable factors control growth rate and have been used in other models to estimate primary production (Cloern et al. 1995). Phytoplankton response is light dependent, which is reflected in these models in the Z_p, D, and I_0 variables that incorporate the entire photic zone, as opposed to just surface light. P^B_{opt} incorporates T to express optimal photosynthesis in the water column. Phytoplankton biomass, expressed as chl-a, provides an estimate of the abundance of phytoplankton. These collective parameters are useful to explain temporal and spatial variations in primary productivity (Harding et al. 2002). Past studies of model development have included nutrient concentrations, a limiting factor in phytoplankton growth, which slightly improved the fits. However, a nutrient parameter is not included because of high seasonal and inter-annual variability, making it challenging to adequately represent the variable (Harding et al. 2002).

P^B_{opt}, a photoadaptive yield term, is the optimal chlorophyll-based carbon fixation rate in the water column recovered from *in situ* or simulated in-situ incubations in sunlight and chlorophyll measurements. P^B_{opt} corresponds to primary production per unit chlorophyll, the superscript B indicates normalization to biomass, which is typically parameterized as chl-a concentrations. Some models of primary production first determine an absolute maximum rate of photosynthesis (P^B_{max}) which is then multiplied by limitation factors for temperature, light, or nutrients. In contrast, the formulation of the VGPM class of models provides for a P^B_{opt} value that is determined as a function of temperature. Behrenfeld and Falkowski (1997a) used sea surface temperature (SST) as their corresponding variable. It is a good variable from a physiological perspective as P^B_{opt} varies as a function of $P^B_{max,}$ (the light saturated photosynthetic rate) which is regulated by Calvin cycle enzymatic activity and is temperature dependent (Harding et al. 2002).The near surface location of P^B_{opt} estimate ensures SST measurements are within an optimal range for growth. Behrenfeld and Falkowski (1997a) and Harding et al. (2002) selected SST because the data are easily available from remote sensing satellites. Behrenfeld and Falkowski (1997a) calculated the median value of P^B_{opt} for each 1°C temperature increment from -1 to 29°C for their 1,041 stations which had temperature information using a seventh order polynomial fit (equation 10).

$$P^B_{opt} = -3.27\times10^{-8}T^7 + 3.4132\times10^{-6}T^6 - 1.348\times10^{-4}T^5 + 2.462\times10^{-3}T^4 - 0.0205T^3 + 0.617T^2 + 0.2749T + 1.2956 \quad (10)$$

Harding et al. (2002) derived their equation for P^B_{opt} using a simple linear regression,. Harding et al. (2002) utilized the Chesapeake Bay dataset for observed P^B_{opt} from measurements of net ^{14}C primary production data and sea surface temperature to estimate $P^B_{opt\ (net)}$ based on the approach of Behrenfeld and Falkowski (1997a) to yield a simple linear regression (equation 11). Equation 11 was utilized to determine P^B_{opt} for our dataset.

$$P^B_{\ opt} = -0.056 + (0.202 * \text{water temp}) \quad (11)$$

Additional variables in the models include Z_p, I_0, and chlorophyll biomass. The variable Z_p was not directly available from the CBP database; therefore, it was calculated from Secchi disk measurements, which determine the depth of the photic zone within the water column. A Secchi disk was used to calculate k, the vertical attenuation coefficient for light (equation 12); (Dennison et al. 1993).

$$k = 1.4/\text{Secchi measurement} \tag{12}$$

From this, Z_p was calculated with meters (m) as the unit in equation 13 (Dennison et al. 1993).

$$Z_p = 4.61/k \tag{13}$$

Irradiance (I) is the total daily surface photosynthetically active radiation (PAR) (micro Einstein m^{-2} s^{-1}) and can be expressed as either a flux of energy per unit area per unit time, or as a flux of photons per unit area per unit time. Chlorophyll biomass (chl-a, mg m^{-3}) was provided by the CBP database and measured using fluorometric analysis. Daylength (D, h) is equal to the amount of day light hours in each day.

The BZ_pI_0t model defines Z_p and I_0 in the same manner as the VGPM and CBPM variables, with B representative of chlorophyll biomass. However, this model also incorporates the Boltzmann-Arrhenius term, which characterizes the exponential effect of temperature, where E is the average activation energy (eV), and k is the Boltzmann constant (8.62 x 10^{-5}eV K^{-1}). This term yields quantitative predictions of metabolic rates such as photosynthesis based on data for a variety of different taxonomic groups (Allen and Gillooly 2007).

Statistical Evaluation of Models

A least squares linear regression was performed on the modeled and TF 2.3 observations taken from the CBP dataset. Primary production data were available from 1984 to 2009. The observed data were plotted against the primary production data calculated using each model equation. A t-value and F-test statistic were used to assess whether the data were comparable at a significance level of 0.05. The VGPM-a, VGPM-b, and CBPM had a sample size of 262 observations. The BZ_pI_0t sample size was 263 observations.

Model Validation at an Additional Freshwater Location

All of the models were tested for performance with data from the Chesapeake Bay database for site CB 1.1. This verifies the universal applicability of the intercept and coefficient terms estimated from the TF 2.3 data. The CB 1.1 site is located in the upper Chesapeake Bay near the mouth of the Susquehanna River and monitored by MD DNR. Observations of chl-a, T, daylength, Z_p, and I_0 were obtained from 1990 through 2007. Evaluations were conducted for the entire data set.

Results

Models

Comparison of VGPM-a, VGPM-b, CBPM, and BZ_pI_0t with observed Chesapeake Bay data are shown in Figures 2 a, b, c, and d, respectively. All regressions were significant and r^2 values, slopes, and intercepts are presented in Table 2a. The primary production data were underestimated in the VGPM-a and CBPM, as most observations were above the 1:1 line. The VGPM-b and BZ_pI_0t slightly over estimated primary production data; however, data were dispersed almost evenly above and below the 1:1 line. Despite poor suitability of the original BZ_pI_0 model for grouped Chesapeake Bay dataset (Harding et al. 2002, Brush et al. 2002), the BZ_pI_0t performed with greater effectiveness compared to the VGPM-a and CBPM. This suggests the modifications to the Cole and Cloern (1987) model with the Boltzmann-Arrhenius term is a way to improve use of this model in the tidal freshwater portion of the Potomac River.

A comparison of slopes predicted by the least squares linear regression analyses revealed values over 2 for the VGPM-a and CBPM, while the BZ_pI_0t and VGPM-b had slopes of less than 1. The slopes of the VGPM-b and BZ_pI_0t were similar to Harding et al.'s (1986) empirical model for the original BZ_pI_0 (equation 14).

$$PP = 176 + 0.74\ (BZ_pI_0) \tag{14}$$

Other examinations of the BZ_pI_0 regression model, outlined in Brush et al. (2002), show consistent slopes of less than 1, with average slope of 0.64 ± 0.23.

A critical issue with the BZ_pI_0t model is that it consistently predicts the presence of phytoplankton growth, which is a factor of the y-intercept term for the regression equation. The y-intercept suggests there is net production in the absence of chlorophyll and/or light (Brush et al. 2002). These regressions should be forced through a zero-value y-intercept. When the BZ_pI_0t was forced through zero, performance improved as indicated in Table 2b.

When the VGPM-a and CBPM were modeled with TF 2.3 primary production data, the regressions were comparable. The BZ_pI_0t performance with TF 2.3 data were comparable to studies outlined in Brush et al. (2002). VGPM-b performed similarly to BZ_pI_0t.

Statistics

The observed F was consistently higher than the critical level of F (3.92) in all the models tested, and therefore it is unlikely the F value occurred by chance and the observed and modeled data are related. The t-values were also significant for each of the models. The p-value was <0.001, which is less than the normally defined value of $p \leq 0.05$; therefore, the models are considered as being statistically significant.

Model Validation

Comparisons of model output from the VGPM-a, VGPM-b, CBPM, and BZ_pI_0t with measured primary production at station CB 1.1 are pictured in Figures 3 a, b, c, and d. The VGPM-a and CBPM underestimated primary production at this station as the majority of the data are above the 1:1 line. The r^2 value for VGPM-a and CBPM were significant (0.63 and 0.62, respectively). The VGPM-b overestimated primary production as the data were below the 1:1 line. The r^2 value was 0.63. The BZ_pI_0t model underestimated primary production and was able to characterize primary production, however not as successfully as the previous models. All of the models were statistically significant based on the t-value and F-statistic (Table 3).

Discussion

Model Performance

The VGPM-a and CBPM performed similarly to each other, however both underestimated primary production (Figures 2a and 2c), where the highest productivity predicted was approximately 5,500 mg C m^{-2} d^{-1}. Harding et al. (2002) concluded the best model fit for the Chesapeake Bay was the VGPM-a formulation, which was improved over the original VGPM, which overestimated primary production in the Chesapeake Bay. CBPM performed similarly to VGPM-a with only a slight improvement in prediction capabilities.

Harding et al. (2002) suggested using the VGPM-a or CBPM for future calculations of primary production in the Chesapeake Bay given they are simple and useful when information on chl-a and SST are gathered from remote sensors and P^B_{opt} - data are available. The VGPM-a, VGPM-b, and CBPM models were developed using remote sensing data on phytoplankton pigments and temperature. Behrenfeld and Falkowski (1997a) state that obtaining measurements of photosynthesis using pigmentation have misled modeling efforts due to their reliance on light harvesting potential. VGPM-b (Figure 2b) performed similarly to the BZ_pI_0t (Figure 2d); however, its incorporation of the P^B_{opt} variable makes this model less attractive for our application as it can be a significant source of error as discussed below.

The original BZ_pI_0 model did not successfully model primary production for the Chesapeake Bay when evaluated by Harding et al. (2002) for stations in the main stem of the Bay. The updated BZ_pI_0t adequately represented estimates of primary production in the fresher system at station TF 2.3. This model performs better under estuarine conditions where phytoplankton growth is limited by light (Brush et al. 2002), as was observed at the TF 2.3 site. BZ_pI_0t has advantages over the other models, as it does not rely on a calculation of P^B_{opt}, as discussed below. In turbid estuarine conditions that are typical of tidal fresh tributaries, the emphasis on light limitation in this formulation may be advantageous.

Factors Influencing Model Application

Many empirical models, such as those used in remote sensing algorithms, estimate time and depth integrated primary production as a function of sea surface chlorophyll. The introduction of additional factors into the model formulations, such as photic depth, enhances our ability to predict productivity using this empirical approach. An understanding of irradiance behavior within estuaries aids in model application. Recent developments to provide a theoretical framework for empirical equations, such as the BZ_pI_0 class of models, allows us to predict primary production with a greater degree of confidence that relevant environmental factors are appropriately characterized in the numerical formulation.

Considerations to Select the Best Model for the Tidal Fresh Potomac River

P^B_{opt} vs. BZ_pI_0t Boltzmann-Arrhenius term

Models use algorithms to link parameters commonly measured in monitoring to ones that are more challenging to measure, such as primary production. The main difference between the VGPM-a, VGPM-b and CBPM versus BZ_pI_0t are the variables P^B_{opt} and the Boltzmann-Arrhenius term. P^B_{opt} is derived from measurements of SST, which from a physiological perspective is justified as the maximum rate of C fixation is regulated by Calvin cycle enzymatic activity and therefore temperature dependent (Behrenfeld and Falkowski 1997a). Productivity performance of this algorithm is dependent on the ability to represent spatial and temporal variability in P^B_{opt} as well as having a representative dataset for the modeled ecosystem to calculate a well parameterized value. Differences among the models to reproduce estimates of primary production are primarily related to the method used to estimate $P^B_{opt,}$ including errors in chlorophyll measurements and whether P^B_{opt} is estimated directly using an equation with SST or indirectly as a product of maximum photosynthesis. The Behrenfeld and Falkowski (1997a) calculation of annual primary production P^B_{opt} varied because of different geophysical characteristics controlling SST distribution, such as coastal location, wind, and water column dynamics; therefore, P^B_{opt} may require recalculation in order to accurately represent the ecosystem data. Harding et al. (2002) performed a linear regression of past P^B_{opt} data and Chesapeake Bay SST data to establish an equation for P^B_{opt} in the Bay; this linear equation was used in this analysis. Another factor to consider is changing atmospheric temperatures as climate change dynamics continue to influence ecosystems and increase temperatures. Under this likely scenario of future change, we can expect that P^B_{opt} would need to be recalculated to reflect the change of temperature within the reference dataset, as the previous regression equation with SST would not be applicable.

In models containing $P^B_{opt,}$ accurate representation of this variable is the main component determining how well the model predicts primary production as it is used to model phytoplankton primary production and trends in the vertical distribution of primary production (Harding et al. 2002). P^b_{opt} acts as the physiological input term, expressing optimal photosynthesis in the water column normalized to chl-a. Inaccurate estimates of this variable can skew the results of the entire model. Harding et al. (2002) and Behrenfeld and Falkowski (1997a) both concluded that most errors were attributed to the determination of $P^b_{opt.}$ Improvements would require establishing parameters for relationships between P^b_{opt} and various environmental factors focusing on mechanistic rather than statistical relationships in order to foster enhanced predictive capacity of productivity algorithms.

The Boltzmann-Arrhenius term provides a mathematical representation of the thermodynamic processes for photosynthesis and aerobic respiration that are the same biochemical reactions regardless of the size of the organisms. Allometric relationships describing how body size relates to metabolism were used to develop the MTE that is grounded in first principles. The laws of thermodynamics govern the quarter power scaling that underlies the MTE as described by West et al. (1997) and Gillooly et al. (2001). While other mechanistic variables, such as nutrient resource limitation, may be missing from the BZ_pI_0t model formulation, the successful application of this model to the tidal fresh Potomac provides an alternate modeling approach for primary production that moves us from empirical foundations to those grounded in the MTE. In essence, the Boltzmann-Arrhenius term incorporates the general theory of chemical reaction kinetics and characterizes the exponential effects of temperature and biochemical reaction rates (Allen and Gillooly 2007). The inclusion of these principles of thermodynamics provides an advantage over the other models used in this analysis. The Boltzmann constant relies on characteristics of phytoplankton, which are less likely to be influenced by climate change; thus, this calculation is more relevant over an extended period of time than estimates of P^B_{opt}, and therefore BZ_pI_0t is a better candidate for predicting primary production in this study.

A recent study on the application of activation energy and its effect on biological systems reported systematic variation in the distribution of rise and fall activation energies for all levels of organization, taxa, trophic groups, and habitats. Rise activation energy indicates an increase in physiological or ecological trait values with increasing temperature. Falls indicate a decrease in trait value at higher temperatures. Analysis of the mean rise activation energy within intraspecific species response revealed that 87% are well fit to the Boltzmann-Arrhenius term with a mean of 0.66±0.05 eV. However, right skewness was observed around the median activation energy of 0.55 eV. The mean fall activation energy for intraspecific response was 1.15±0.29 eV; right skewness was also observed (Dell et al. 2011). Right skewness for rises indicates the majority of trait responses have activation energies below 0.66 eV (Dell et al. 2011).

The activation energy for important metabolic reactions vary from 0.2 to 1.2 eV, with 0.65 eV is the median value. For the majority of trait rises where the relationship to metabolic rate is obvious, relationships can be significantly fit by the Boltzmann-Arrhenius term. However, traits less clearly linked to metabolism, such as conversion efficiencies; do not fit as well to the Boltzmann-Arrhenius term (Dell et al. 2011). This recent revelation of patterns observed in activation energy suggests the current MTE is limited in its precision, power and utility. Dell et al. (2011) recommend a reassessment of the MTE to determine whether it needs to be modified in order to explain these variances, and here I suggest that application to other freshwater tidal systems involve a thorough parameter estimation exercise that considers these findings before arbitrarily assigning an activation energy value.

Comparisons of predictability using the VGPM-a and the basic BZ_pI_0 model, have supported the usage of the BZ_pI_0t. Goebel et al. (2006) compared the Harding et al. (2002) VGPM-a model with the original BZ_pI_0 model to test whether using a physiological variable, such as P^B_{opt}, improved predictions of primary production using data from the Long Island Sound. The VGPM-a improved prediction by less than 10% over the BZ_pI_0 model. They concluded that difficulty in measuring the physiological variable and limited improvements in predictive ability support the need for models that do not rely on these variables. They note that the BZ_pI_0 model requires only readily available variables, thus providing an advantage over the VGPM-a.

Optimum Temperature Range

The maximum temperature for biological activity in phytoplankton ranges from 25° to approximately 35°C (Figure 4); (Canale and Vogel, 1974). The Boltzmann factor predicts a 3.8 fold increase in the rate of photosynthesis over the temperature range of 0 – 30°C (Allen et al. 2005). The chemical reaction and metabolic rates increase exponentially with temperature, which is described in the Boltzmann factor. The relationship between biological rates and temperature only applies when the temperature is between 0° and 40°C (Brown et al. 2004).

When Behrenfeld and Falkowski (1997a) developed the relationship between P^B_{opt} and SST, the median value of P^B_{opt} was calculated at each 1° C increment from -1 to 29°C for each of the study sites with SST data. Median P^B_{opt} was lowest at <1°C and peaked at 20°C. Above 20°C there was an unexpected sharp decline in P^B_{opt}. It was proposed that high SST was associated with regions of strong vertical stratification and nutrient limiting conditions for phytoplankton growth, which impacted the results.

The potential inability of P^B_{opt} to increase above 20°C prevents it from capturing the maximum photosynthetic rate of many phytoplankton species that peak at temperatures between 25° and 35°C. The Boltzmann factor is able to predict increases in photosynthetic rate at much higher temperatures than P^B_{opt}. This quality may increase the ability to accurately model primary production.

Slope and intercept comparison

Other regressions with BZ_pI_0 produced similar slopes to our regressions at TF 2.3 with BZ_pI_0t. The average slope in the study conducted by Brush et al (2002) was 0.64 ± 0.24 and represents maximum available light (Cole and Cloern 1987). The slopes are influenced by available light, with lower slopes found in highly turbid systems (Brush et al. 2002). The slopes of the BZ_pI_0t and VGPM-b (0.81 and 0.73, respectively) were indicative of a turbid system, which is characteristic of an estuary. The VGPM-a and CBPM did not coincide with what is observed in an estuary, as the slopes were much higher (2.42 and 2.23, respectively). Seasonal differences in phytoplankton speciation may require the slope to be modified to reflect the change in community composition; steeper slopes have been observed in summer, as opposed to non-summer communities (Pennock and Sharp 1986, Keller 1988, Brush et al. 2002). Consistent slopes computed for different waterbodies indicate the model can be applied to predict estimates of primary production in other ecosystems.

The y-intercepts are an artifact of linear regression and curve fitting; therefore predicting positive primary production when chl-a or irradiance equal zero (Brush et al. 2002). The models should be forced through the origin during simulation to prevent overestimation of primary production when BZ_pI_0t equals zero. Removing the y-intercept requires increasing the slope, as a result of forcing the regression through zero, such as the model developed by Cloern (1991) for San Francisco Bay, which showed a slope increase of 40% when the y-intercept was removed (Brush et al. 2002). The slope for BZ_pI_0t increased from 0.81 to 0.96 (Tables 2a and 2b) when a zero intercept was invoked in this study.

Benefits of BZ_pI_0t

The BZ_pI_0t model worked well to simulate primary production in the tidal fresh system. The BZ_pI_0t has applicability across a variety of ecosystem types, during different seasons, and with a variety of environmental parameters such as photic depth (Brush et al. 2002, Goebel et al. 2006). As discussed above, including the Boltzmann-Arrhenius term characterizes the exponential effects of temperature and biochemical reaction rates (Allen and Gillooly 2007) and relies on physiological characteristics of phytoplankton, which are less likely to change over time. In addition, the BZ_pI_0t model does not include the P^B_{opt} term, which past studies have found to be the largest source of error (Behrenfeld and Falkowski, 1997a, Harding et al. 2002).

The original BZ_pI_0 model developed by Cole and Cloern (1987) was useful in mesohaline conditions where incident radiation and phytoplankton biomass influence temporal and spatial variations in phytoplankton productivity. The same theory can be applied for the BZ_pI_0t in the oligohaline region where surface irradiance is a limiting factor in phytoplankton growth. Although untested here, I propose that the BZ_pI_0t be tested in mesohaline conditions as well to determine if incorporating temperature improves model fit.

Application to Monitoring

Freshwater estuarine systems are typically very turbid because of river flow and high sediment loads, thus preventing phytoplankton from having access to all available light and limiting primary production (Cloern 1987). These systems are usually limited by light, due to higher turbidity. Phosphorus is typically a limiting nutrient in fresher systems, and higher salinity regions can be limited by nitrogen, as freshwater inputs have high N:P and seawater often has low N:P ratios (Fisher et al. 1999). Nutrient availability may control the upper limit of bloom productivity, but seasonal and interannual variability of estuarine phytoplankton production is better predicted using empirical data on phytoplankton biomass and irradiance (Cole and Cloern 1987). The absence of a nutrient term in the regressions does not remove its influence on primary production. High nutrient loads can increase chlorophyll biomass, thus decreasing the amount of available light because of increased shading from biomass (Figure 5). Another possibility is high nutrient loads can be associated with high sediment loads, which would also decrease Zp, thus reducing light availability in the water column (Figure 6).

As discussed in Chapter 1, the importance of predicting primary production response to organic nitrogen is increasing, and this behavior will be critical for future issues regarding organic nitrogen reductions from the Blue Plains Wastewater Treatment Plant and many other WWTPs. To properly understand phytoplankton dynamics and behavior with changing resources, models help to inform our understanding of the rate processes that determine factors affecting water quality. Environmental conditions impact primary production by influencing phytoplankton photosynthesis. The photochemical energy obtained from the natural environment dictates the maximum possible growth rate (Behrenfeld and Falkowski 1997a).

Model Shortcomings

Models are important tools for understanding how ecosystems respond to different environmental conditions. However, over- or under-estimating production reduces a model's ability to be utilized in management scenarios and other applications. Improvements in understanding phytoplankton ecology and photo-physiology can enhance model predictive ability.

Previous studies which used the models assessed here underestimated primary production across a variety of sampling dates and times (Brush et al. 2002, Harding et al. 2002). Phytoplankton loss processes (a large component of plankton dynamics) such as respiration, flushing, grazing by zooplankton, and sinking are underestimated or not included in empirical models like those described here, potentially contributing to overall underestimation of primary production. An alternative would be to simulate primary production in ecosystem models that include zooplankton grazing terms and hydrodynamics; however, these processes vary among ecosystems and would require consistent monitoring, causing data to be insufficient to incorporate into simple algorithms (Brush et al. 2002).

Other errors in predicting primary production are found in methodological differences in ^{14}C measurements and errors in ^{14}C data. Models can predict the data from which they are derived very well, however once they are applied to other datasets, the prediction capabilities decline, especially when chl-a concentrations are low. Primary production and chl-a are local variables, as their magnitudes can vary over short scales of time and space. Variations in measurements of biomass yield are the main cause of variability in photosynthetic rate, thus normalization to biomass yields a property $P^B{}_{opt}$ of more general significance than biomass alone. Variation between regions and seasons can be analyzed without complications that might arise from chance fluctuations in biomass. $P^B{}_{opt}$ is an intrinsic property of the sample, or of the sampling location.

Increasing the number of variables within a model can help improve predictions. Chl-a and Z_p are not entirely independent because phytoplankton contribute to the attenuation of light, but this effect is usually small compared to that of other suspended particles (~5%, Cole and Cloern 1987). During model development Behrenfeld and Falkowski (1997a) included Z_p, which accounted for 38% of the variability, after the addition of $I_{0,}$ the model improved by 42%. Accounting for Z_p and I_0 resulted in consistent patterns in normalized productivity with depth, emphasizing the importance of irradiance and light availability. Developing an irradiance dependent function helps to describe the relative vertical distribution of production. Once Z_p, chl-a, and photoperiod are accounted for, the relative vertical distribution of PP can be modeled with a simple formulation consisting of a highly constrained, light limited slope and a variable, light dependent photoinhibition term.

Accounting for incident irradiance and light attenuation coefficients when developing models is pertinent to ensure close approximations to measured rates of primary production. High concentrations of suspended particulate matter attenuate light rapidly in the water column, confining primary production to a small section of the photic zone. Application of the BZ_pI_0t model in nutrient rich estuaries and freshwater systems, which are primarily limited by light, is the ideal choice for this dataset, as the other models discussed have not been as successful in nutrient rich, turbid systems; and the BZ_pI_0 model has been successfully applied in tidal fresh estuaries (Brush et al. 2002).

Cole and Cloern (1987) attributed significant amounts of variability in primary production rates in mesohaline water bodies to strong influence of incident radiation and phytoplankton biomass. Adjusting I_0 and Z_p in models using a method similar to Harding et al. (2002), where the relative importance of independent variables was determined using step-wise regression analysis, could help develop a model for freshwater if data from a fresh or tidal fresh system were used.

Model Validation

Attempts to validate the models with data from CB 1.1 were successful with the VGPM-a, VGPM-b, and CBPM using data that had not been used previously in model analysis. The models were statistically significant (Table 3). These results were similar to Harding et al.'s (2002) validation of VGPM-a, -b, and CBPM, which effectively predicted primary production in the Chesapeake Bay. However, Harding et al. (2002) noted the models are reliable when data for P^B_{opt} or a related measurement are available.

The BZ_pI_0t model was able to predict primary production, however not as successfully as the VGPM-a, VGPM-b, or CBPM. This may have been a result of the characterization of the activation energy used. The average activation energy of respiration is approximately 0.65 eV when temperature dependence of metabolic rate is equivalent to hours (Allen and Gillooly 2007). The activation energy used in this assessment was 0.33 eV. This value is suited for long term temperature dependence, such as daily rates. Future studies of the BZ_pI_0t model should compare the different activation energies to understand which is best suited for the estuarine environment.

Conclusions

Phytoplankton are the base of the food chain and directly related to carbon, nutrient, and oxygen cycling. They are an essential component of the aquatic ecosystem, and therefore, the ability to accurately predict primary production can aid in predicting ecosystem processes such as response to sediment and nutrient loading management and changes in discharge rates.

The models tested here were originally developed for predicting production in oceanic and estuarine waters. The original VGPM-a was derived from multiple oceanic sources, the updated version and CBPM model were developed from main-stem Chesapeake Bay data. The original BZ_pI_0 was designed for San Francisco Bay. A model has not been developed or tested for tidal fresh waters. The revelations from the application of tidal fresh data to the BZ_pI_0t model demonstrate its ability to predict productivity in turbid systems and suggest that it may be suitable for future use in developing models of primary production for other tributaries or freshwater locations where light is limiting.

Additional studies on the applicability of the models discussed here should focus on other tidal fresh sites, not just ones that are light limited. Suggested areas are the San Francisco Bay, Delaware River Estuary, Hudson River Estuary, and the northern Adriatic. These would cover a significant range of different datasets for the primary variables discussed here, thus providing an extension of the models suitability.

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Table 1. Trophic classification system proposed by Nixon (1995) to describe supply rate of organic carbon in an ecosystem.

Trophic Status	Organic Carbon Supply ($g\ C\ m^{-2}\ y^{-1}$)
Oligotrophic	< 100
Mesotrophic	100-300
Eutrophic	301-500
Hypertrophic	>500

Table 2. Linear regression analyses of the four primary production models used to describe the tidal fresh Potomac River. The coefficient of determination is R^2; the regression coefficient is slope, or the amount that primary production increases with unit increases in independent variables; the intercept is value of y where the best fit regression model crosses the y-axis; and N is the number of sampling dates used in analysis.

Table 2a. Linear regression results for the four primary production models used in analysis. The coefficient estimate predicts how much dependent variable increases when the independent variable increases; std. error is the standard error of the least square estimate; T-value is the computed t-statistic; Pr (>|t|) is the p-value; significance indicates whether the p-value is significant. RSE is the residual standard error; DF is degrees freedom; r^2 is the coefficient of determination; adjr^2 is adjusted coefficient of determination which adjusts for the number of variables in the model.

Model	Coefficient Estimate	Std. Error	t-value	Pr (>|t|)	Significance
VGPM-a	2.424	0.102	23.685	7.237 e-67	0
- **Intercept**	536.972	141.401	3.798	0.0002	0
VGPM-b	0.729	0.031	23.685	7.24 e-67	0
- **Intercept**	536.972	141.401	3.798	0.0002	0
CBPM	2.233	0.095	23.562	1.83 e-66	0
- **Intercept**	551.831	141.591	3.897	0.0001	0
BZ_pI_0t	0.809	0.038	21.166	1.43 e-58	0
- **Intercept**	901.003	143.436	6.282	1.39 e-09	0

Model	RSE (DF)	r^2	Adjr^2	F-stat (DF)
VGPM-a	1,714.576 (260)	0.683	0.682	561.0 (1 and 260)
VGPM-b	1,714.576 (260)	0.683	0.682	561.0 (1 and 260)
CBPM	1,720.689 (260)	0.681	0.680	555.2 (1 and 260)
BZ_pI_0t	1,847.893 (261)	0.632	0.630	448.0 (1 and 261)

Table 2b. Results of linear regression model for BZ_pI_0t when forced through the y-intercept.

Model	R^2	Slope	Intercept	N
BZ_pI_0t	0.77	0.96	0	263

Table 3. Linear regression results of the model validation using the dataset for CB 1.1 in the upper Chesapeake Bay. The coefficient estimate predicts how much dependent variable increases when the independent variable increases; std. error is the standard error of the least square estimate; T-value is the computed t-statistic; Pr (>|t|) is the p-value; significance indicates whether the p-value is significant. RSE is the residual standard error; DF is degrees freedom; r^2 is the coefficient of determination; adjr^2 is adjusted coefficient of determination, which adjusts for the number of variables in the model.

Model	Coefficient Estimate	Std. Error	t-value	Pr (>|t|)	Significance
VGPM-a	2.210	0.080	27.670	<2 e-16	0
- Intercept	440.708	75.290	5.853	9.19 e-09	0
VGPM-b	0.665	0.024	27.670	<2 e-16	0
- Intercept	440.708	75.290	5.853	9.19 e-09	0
CBPM	2.282	0.084	27.303	<2 e-16	0
- Intercept	423.464	76.588	5.529	5.42 e-08	0
BZ_pI_0t	1.542	0.066	23.340	<2 e-16	0

Model	RSE (DF)	r^2	Adjr^2	F-stat (DF)
VGPM-a	1,098 (458)	0.626	0.625	765.5 (1 and 458)
VGPM-b	1,098 (458)	0.626	0.625	765.5 (1 and 458)
CBPM	1,108 (458)	0.619	0.619	745.5 (1 and 458)
BZ_pI_0t	1,801 (459)	0.543	0.542	544.9 (1 and 459)

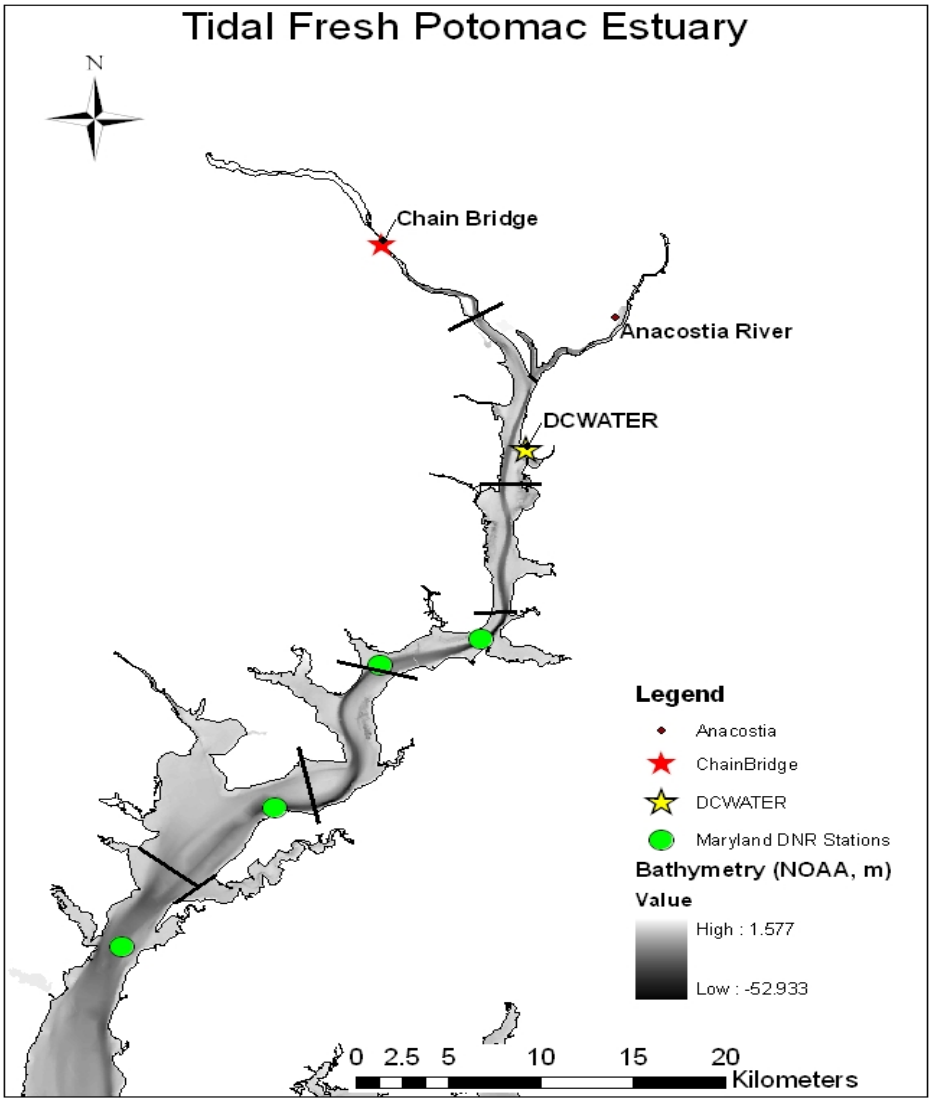
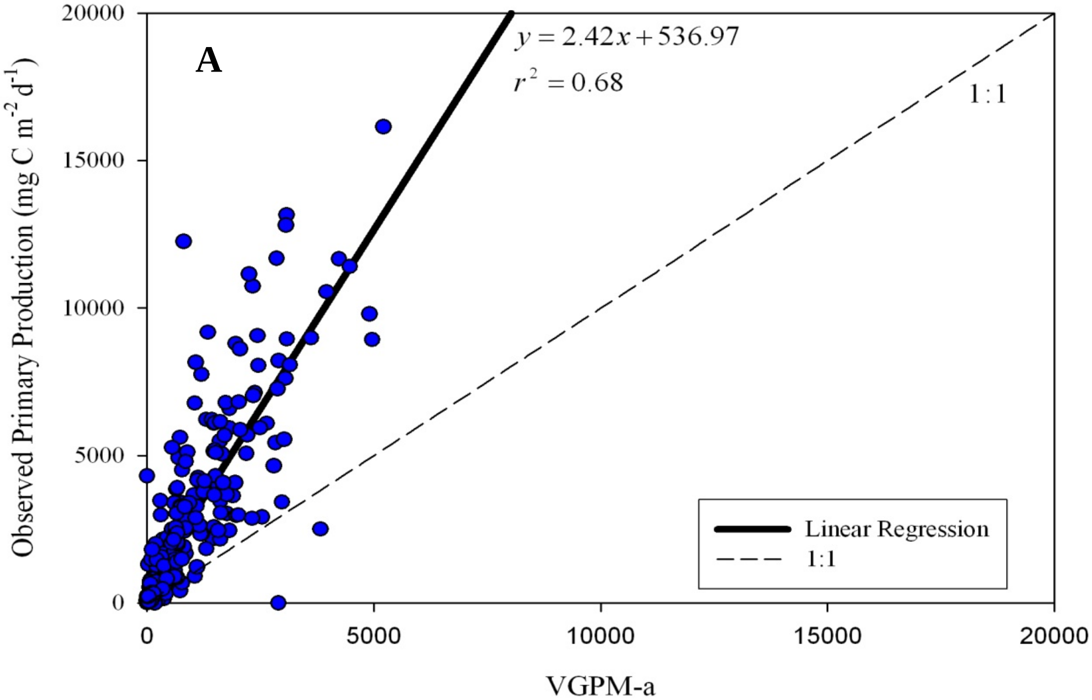


Figure 1. Map of the tidal fresh Potomac River including DC Water, MD DNR sampling stations, and USGS Chain Bridge Gauge station. The black lines across the river represent segment distances of 5 nautical miles. DC Water represents the location of Blue Plains WWTP. TF 2.3 is located at the third circle below Blue Plains and is marked with an arrow.



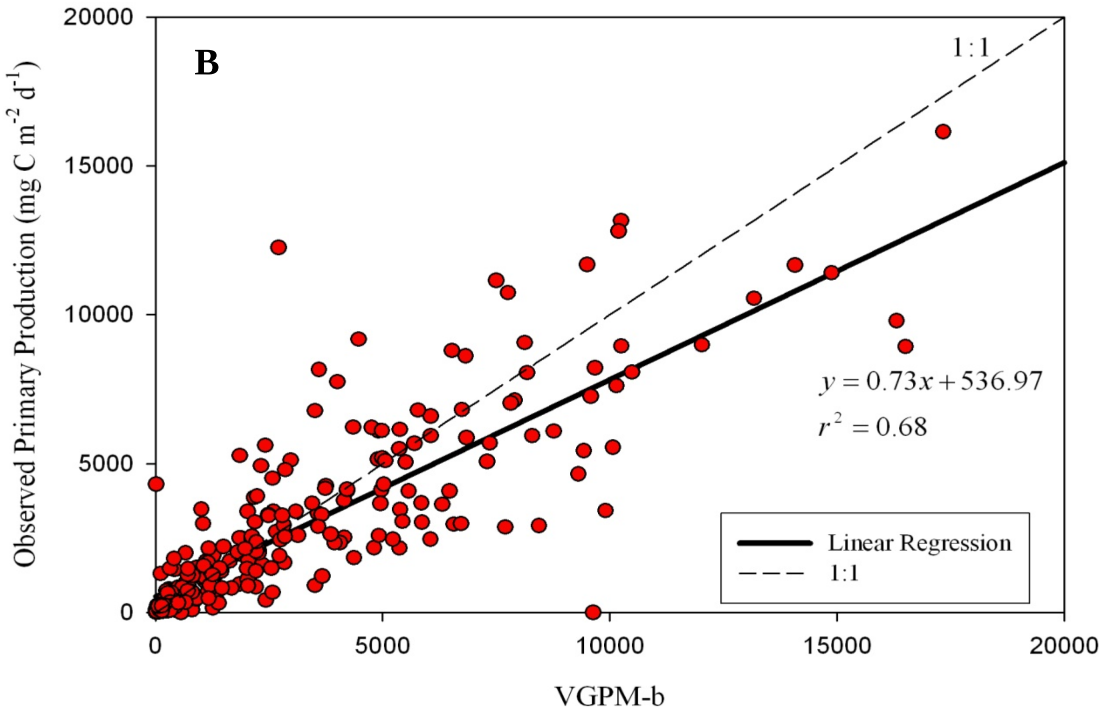
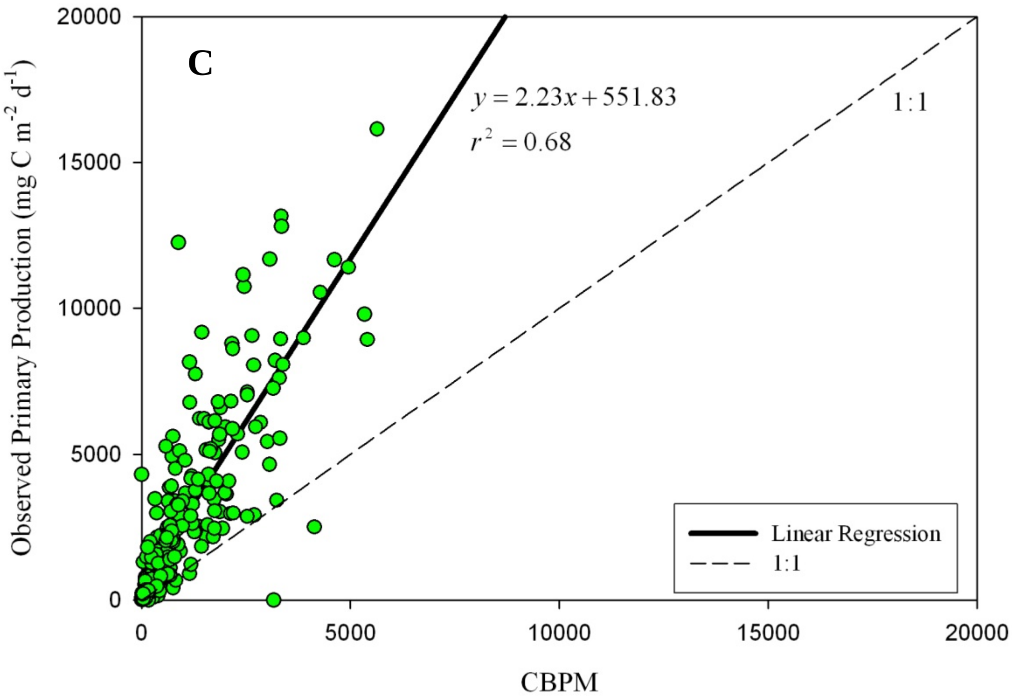


Figure 2 a, b. Linear regression of observed primary production from TF 2.3 site in the Potomac River and estimates of primary production using the a) VGPM-a, b) VGPM-b, c) CBPM, d) BZ_pI_0t. The Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) provided the TF 2.3 primary production data.



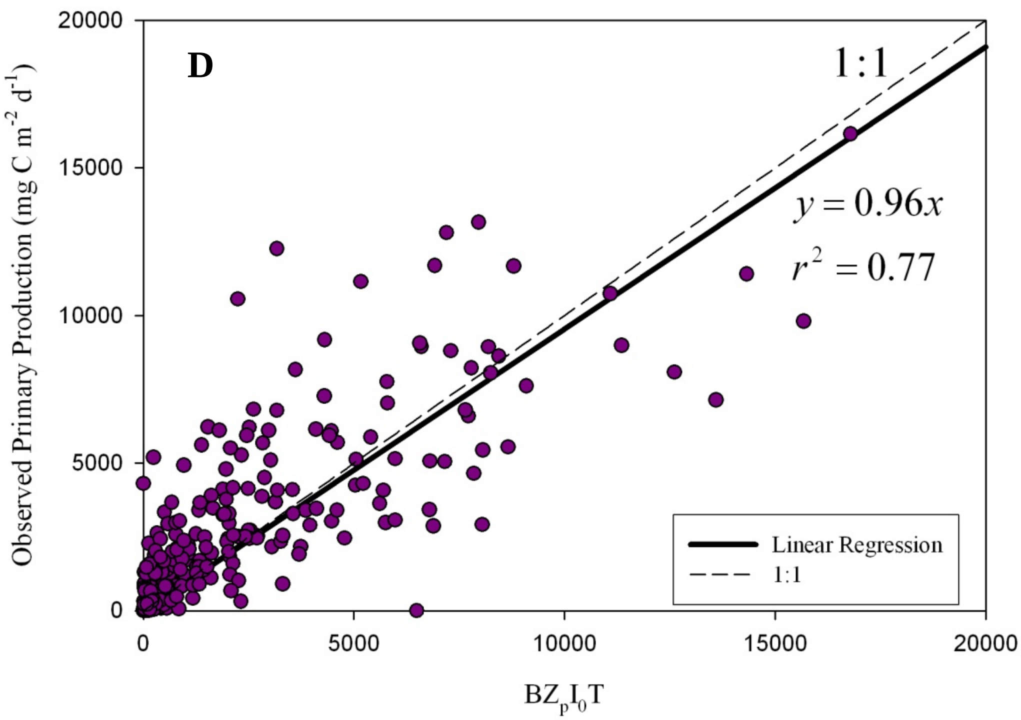


Figure 2 c, d. Linear regression of observed primary production from TF 2.3 site in the Potomac River and estimates of primary production using the a) VGPM-a, b) VGPM-b, c) CBPM, d) BZ_pI_0t. The Chesapeake Bay Program Baywide CBP Plankton database (www.chesapeakebay.net) provided the TF 2.3 primary production data.

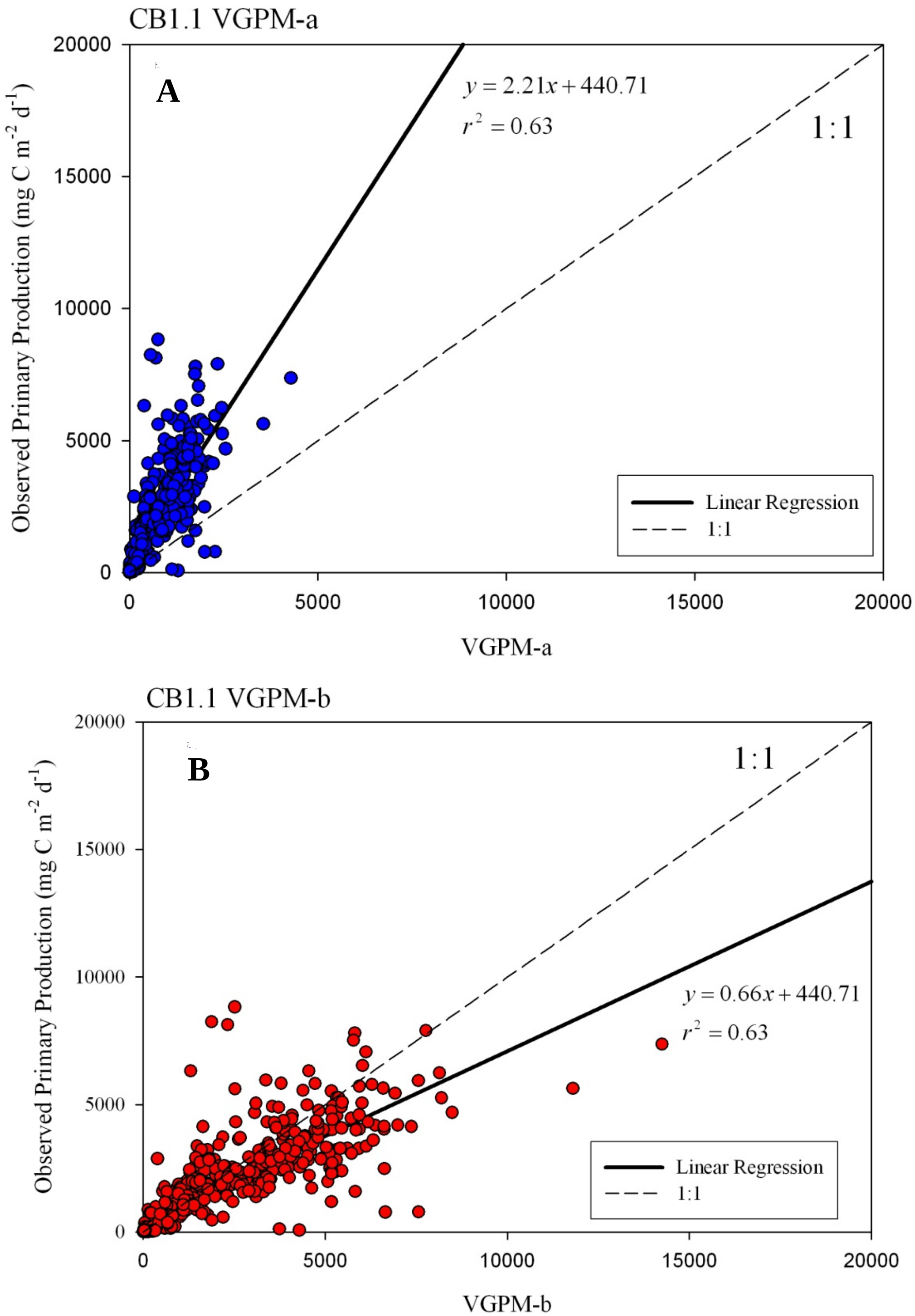


Figure 3 a, b. Model validation using data from Chesapeake Bay Program database for site CB 1.1. Comparisons included a) VGPM-a, b) VGPM-b, c) CBPM, and d) BZ_pI_0t. The Water Quality (1984-present) and Baywide CBP Plankton databases provided the data (www.chesapeakebay.net).

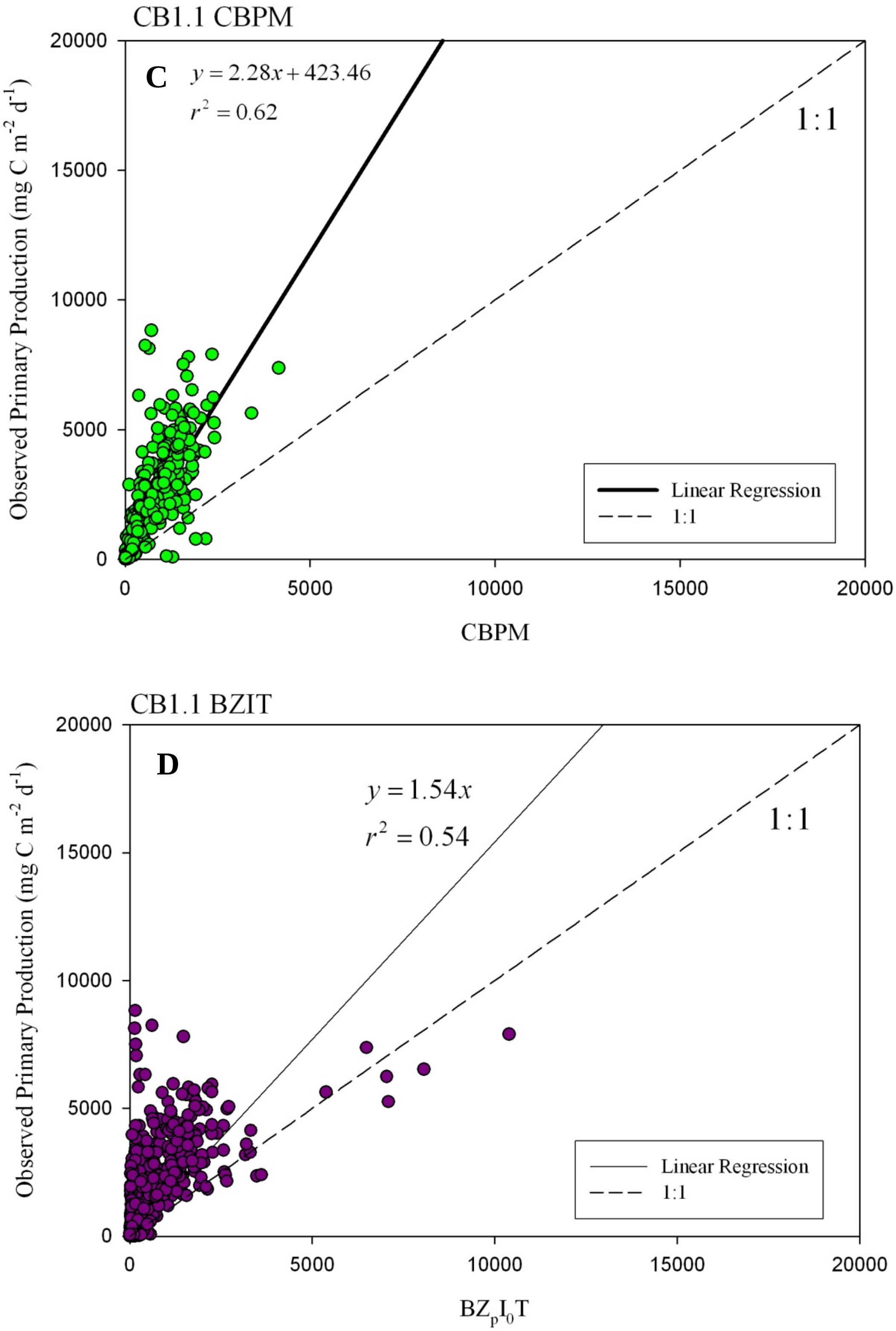


Figure 3 c, d. Model validation using data from Chesapeake Bay Program database for site CB 1.1. Comparisons included a) VGPM-a, b) VGPM-b, c) CBPM, and d) BZ_pI_0t. The Water Quality (1984-present) and Baywide CBP Plankton databases provided the data (www.chesapeakebay.net).

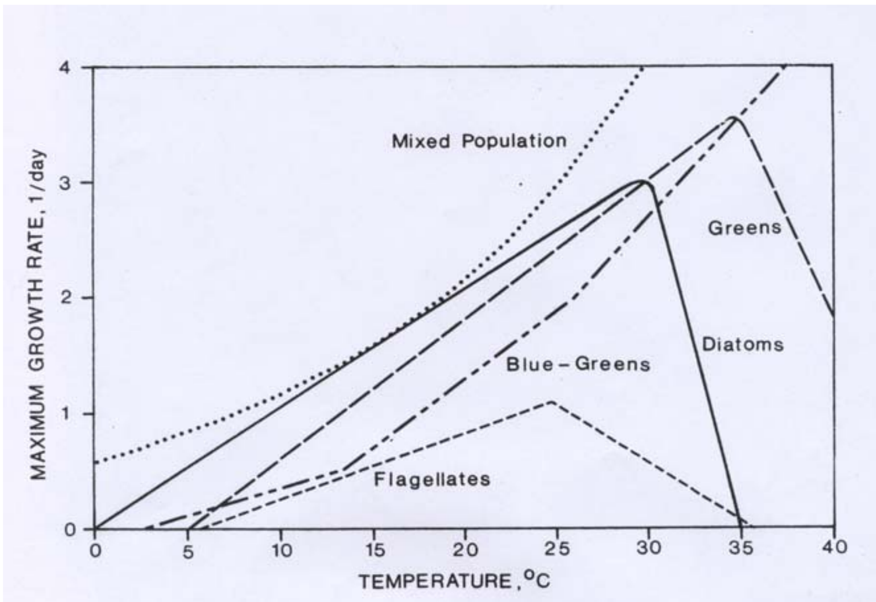


Figure 4. Temperature-growth curves for major algal groups. Figure from Canale and Vogel, 1974.

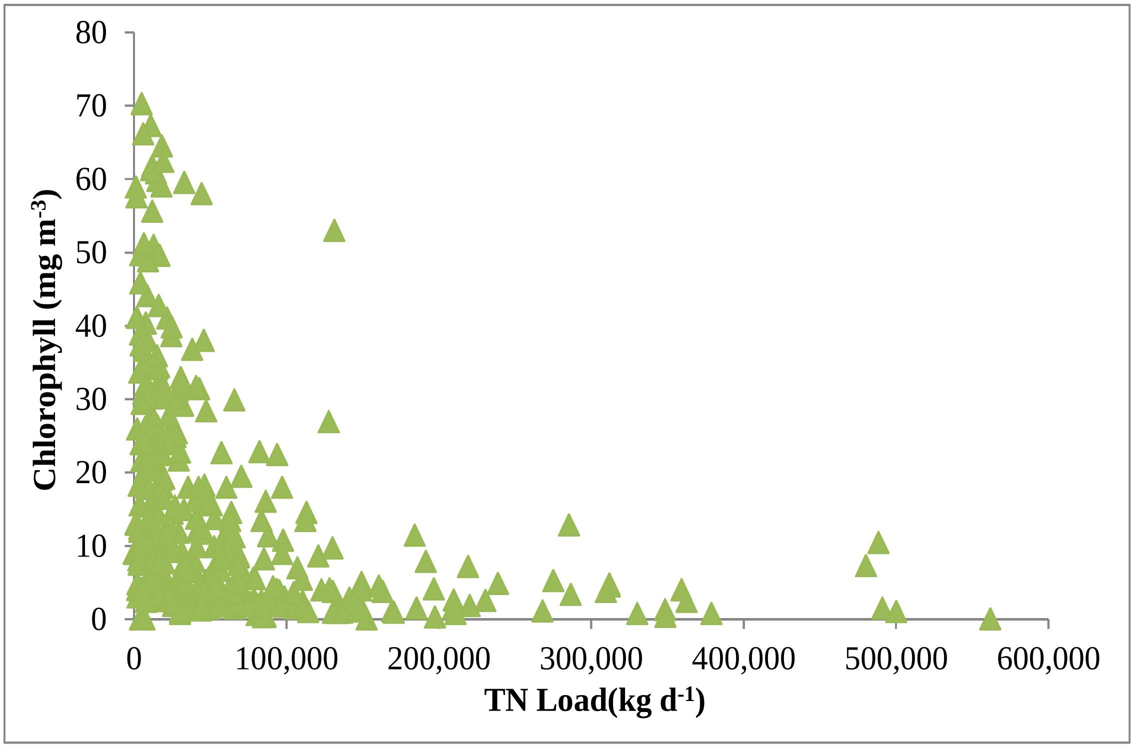


Figure 5. Relationship between chlorophyll concentrations at TF 2.3 and TF 2.3 total nitrogen (TN) loads. Chlorophyll concentrations and TN loads were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. The Chesapeake Bay Program Water Quality database (www.chesapeakebay.net) provided the chlorophyll concentration and TN load data based on measurements from MD DNR.

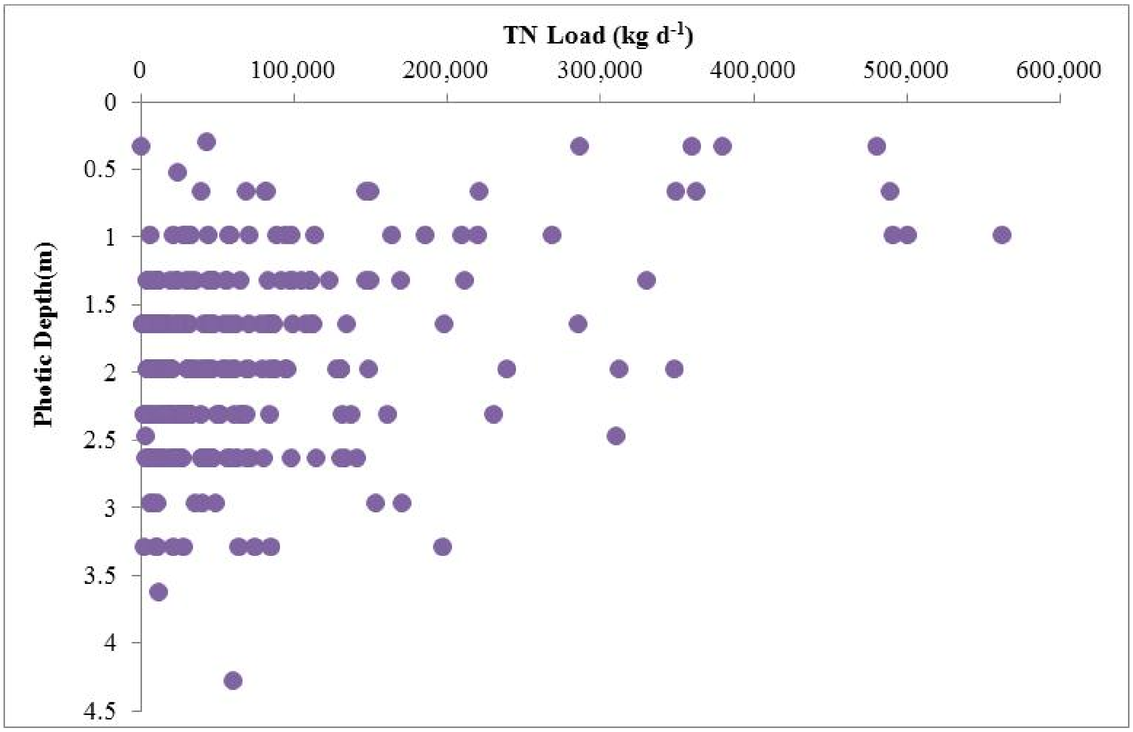


Figure 6. Correlation between photic depth (Zp) at TF 2.3 and TF 2.3 total nitrogen (TN) loads. Zp was measured monthly by MD DNR. TN loads were measured once a month from October to March and twice a month from April to September; both data points were included in analysis when applicable. The Chesapeake Bay Program Water Quality database (www.chesapeakebay.net) provided the surface irradiance and TN load data based on measurements from MD DNR.

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