ABSTRACT

Title of Thesis: DEVELOPING NUMERIC NUTRIENT CRITERIA FOR STREAMS ON THE DELMARVA PENINSULA.

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To better address stream impairments due to excess nitrogen and phosphorus and to accomplish the goals of the Clean Water Act, the U.S. Environmental Protection Agency (EPA) is requiring states to develop numeric nutrient criteria. An assessment of nutrient concentrations in streams on the Delmarva Peninsula showed that nutrient levels are mostly higher than numeric criteria derived by EPA for the Eastern Coastal Plain, indicating widespread water quality degradation. Here, various approaches were used to derive numeric nutrient criteria from a set of 52 streams sampled across Delmarva. Results of the percentile and y-intercept methods were similar to those obtained elsewhere. Downstream protection values show that if numeric nutrient criteria were implemented for Delmarva streams they would be protective of the Choptank River Estuary, meeting the goals of the Chesapeake Bay Total Maximum Daily Load (TMDL).

DEVELOPING NUMERIC NUTRIENT CRITERIA FOR STREAMS ON THE DELMARVA PENINSULA

By

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Dedication

To my mother, who always encouraged me to seek a career I would love.

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Chapter 1: An Introduction to Numeric Nutrient Criteria

Consequences of Nutrient Pollution

Nutrient pollution (nitrogen and phosphorus) of streams and rivers has increased significantly during the last century due to increasing human populations and production of synthesized fertilizers (e.g., Galloway et al. 1995, 2003, 2004, Vitousek et al. 1997). This has led to the degradation of streams, estuaries, and other aquatic systems due to excess algal growth (e.g., Mitsch et al. 2001, Kemp et al. 2005). As a result, nutrients are responsible for 25 to 50% of stream impairments in the United States (U.S, Faustini et al. 2009). Of Maryland's more than 22,500 km of freshwater streams (Smith 2005), 4,784 km (21%) are considered impaired by phosphorus, more than 5,000 km (22%) have impaired benthic and fish communities due to unknown causes, and many lack sufficient data to be assessed (MDE 2010a). Problems continue downstream, as there are more than 400 estuarine systems worldwide with documented hypoxia, including the Chesapeake Bay (Diaz and Rosenberg 2008).

High nutrient levels may have an immediate local impact within the stream, as well as effects further downstream. Nitrogen is often the limiting nutrient in estuarine systems (Fisher et al. 1999), and phosphorus is commonly limiting in freshwater systems (Wetzel 2001, Dodds 2002, and others); however, exceptions occur. For example, the Choptank River Estuary, a tributary of the Chesapeake Bay, experiences phosphorus limitation during spring flows (Fisher et al. 2006), and streams may also be limited by nitrogen or light (Dodds and Welch 2000, Dodds 2002). The response of streams to nutrients may vary across a gradient from upstream to downstream and may depend on various factors, such as light availability, flow, and grazing (Dodds and Welch 2000). For instance, in phosphorus limited or low phosphorus streams nitrate may be transported downstream without negative impacts. It is when this nitrate reaches estuarine and coastal systems that the effects are exacerbated. Excess nutrients in streams can result in increases in algae (sestonic, epilithic, and filamentous), large diel oxygen fluctuations, and changes in species diversity (Dodds and Welch 2000). Although nitrogen may not have immediate local impacts in non-tidal streams, it is often carried downstream where it enters coastal and estuarine systems, resulting in algal blooms, hypoxia, and loss of aquatic life. Therefore, reductions in both nitrogen and phosphorus are necessary to control eutrophication and help restore aquatic systems (Paerl 2009).

Water Quality Standards and Criteria

The Clean Water Act (1972) requires states to assess water quality, identify impaired waters, and implement steps to improve overall water quality. In Maryland, the Chesapeake Bay, many of its tributaries, including the Choptank River Estuary on the Delmarva Peninsula, and several segments of freshwater streams are impaired (not meeting designated uses) due to high nutrient levels. Designated uses for Maryland waters include water contact recreation, protection of aquatic life, support of estuarine and marine aquatic life, shellfish harvesting, recreational trout fisheries, and public water supplies (COMAR 26.02.08). When these uses are no longer supported the water body is considered impaired. Water quality criteria and standards help identify when designated uses are violated and provide steps for remediation, such as stricter permit discharge limits or identification of the amount of a pollutant that waters are able to assimilate and still maintain uses, a Total Maximum Daily Load (TMDL). To better address stream impairments due to excess nutrients and accomplish the goals of the Clean Water Act, the U.S. Environmental Protection Agency (EPA) is requiring states to develop numeric nutrient criteria. Currently, many states rely on qualitative, narrative criteria to determine if a stream is impaired due to nutrients.

The distinction between narrative and numeric criteria is important. Narrative criteria are qualitative, commonly referred to as "free-from" criteria, and are very often left open to interpretation. For example, the Code of Maryland Regulations (COMAR) states that waters may not be polluted by substances that "create a nuisance", "interfere directly or indirectly with designated uses", and "are harmful to human, plant, or aquatic life" (COMAR 26.02.08). Narrative criteria are a catch-all for various pollutants and other factors leading to impaired water quality. Numeric criteria on the other hand are quantitative, less open to interpretation, and include specific numeric targets. For instance, Maryland has a set numeric criterion for dissolved oxygen—the dissolved oxygen concentration may not be below 5 mg L^{-1} at any time for non-tidal streams with warm water aquatic life (COMAR 26.02.08). In addition to narrative and numeric criteria, biological criteria may also be used to identify impairment. In Maryland, the water quality standards state that "quantitative assessments of biological communities in streams" may be used to determine if waters are meeting uses (COMAR 26.02.08).

Approaches to Develop Numeric Nutrient Criteria

EPA has recommended several approaches to develop numeric nutrient criteria, which include using percentiles, reference or least-impacted streams, models, and other scientifically defensible methods (EPA 2000b). In 2000, EPA identified numeric nutrient criteria for streams and rivers in the U.S. using an ecoregion approach to account for natural variation (EPA 2000a). Using the 25th percentile of available data from a ten-year period (1990 to 1999), EPA developed nutrient and response criteria, including total phosphorus (TP), total nitrogen (TN), chlorophyll *a*, and turbidity for 14 ecoregions in the U.S. as well as subecoregions (EPA 2000a). This approach takes into account varying geology, land use, and other factors (EPA 2000a) by using Level III ecoregions originally developed by Omernik (1987) that were aggregated into 14 nutrient ecoregions (Omernik 2000). In Maryland three aggregate nutrient ecoregions were identified: the Southeastern Temperate Forested Plains and Hills (IX), Central and Eastern Forested Uplands (XI), and Eastern Coastal Plain (XIV) (EPA 2000a). The Eastern Coastal Plain extends from Maine to Georgia and includes the Delmarva Peninsula and small portions of Maryland's western shore, Figure 1-1 (EPA 2000a). It is comprised of three Level III ecoregions or subecoregions: the Middle Atlantic Coastal Plain, Atlantic Coastal Pine Barrens, and Northeastern Coastal Zone. Delmarva is located in the Middle Atlantic Coastal Plain (Figure 1-1). In this part of the Middle Atlantic Coastal Plain soils are not as poorly drained and there is a higher percentage of cropland (EPA 2000a). The Eastern Coastal Plain is dominated by woodland, marshland, urban areas, and some cropland and pastureland (Rohm et al. 2002). Many streams in these low gradient areas are tidally influenced and soils are often poorly-drained (Rohm et al. 2002).

Using this method, EPA derived numeric nutrient criteria for nitrogen and phosphorus concentrations in streams across the Eastern Coastal Plain (Table 1-1). Both causal and response variables were identified. Causal variables are the cause of the impairment (high nitrogen and phosphorus) that can manifest in responses (the response variable), such as increases in algae and decreases in clarity and dissolved oxygen that result in the non-attainment of designated uses (EPA 2000a). The criteria calculated by EPA were 0.031 mg P L^{-1} for TP and 0.71 mg N L^{-1} for TN. Response criteria were also calculated for turbidity and chlorophyll *a* for which the values were 3.04 Formazin Turbidity Units (FTU) for turbidity and 3.75 µg L^{-1} chlorophyll *a*. In addition to ecoregion criteria, data from the smaller subecoregions were assessed. Nutrient criteria calculated for the Middle Atlantic Coastal Plain subecoregion by EPA were higher than those calculated for the Eastern Coastal Plain ecoregion (Table 1-1). Additional quantitative criteria or thresholds, as discussed further in the paragraphs below, have been identified based on a variety of approaches. These values range from 0.01 to 0.14 mg P L^{-1} for TP and 0.2 to 3.0 mg N L^{-1} for TN. The lowest are based on concentrations from forested watersheds, and the highest are based on the Maryland Department of Environment (MDE) biological threshold. Most are < 0.06 mg P L^{-1} for TP and < 1.0 mg N L^{-1} for TN (Table 1-1).

EPA also assessed and compared using the 75th percentile of nutrient concentrations in reference streams. A similar statistical approach that uses the 80th percentile of nutrient concentrations (during flow periods with a high likelihood of algal growth) is applied to least disturbed watersheds by the Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand to identify streams with a high risk of ecological changes (Chambers et al. 2012). Although EPA observed that the 75th percentile of reference sites and 25th

percentile of all samples yielded similar results, Herlihy and Sifneos (2008) found that the 25th percentiles were two to six times lower than the reference site 75th percentile approach. The 75th percentiles for TP and TN are often greater than the 25th percentile estimates, potentially due to reference streams being minimally impacted (Evans-White et al. 2014). This was also observed by Heatherly (2014) who noted that 75th percentiles, as well as regression model results, were slightly higher than the 25th percentile calculated across Nebraska.

Some authors have questioned the 25th percentile method (e.g. Herlihy and Sifneos 2008, Dodds and Oakes 2004, Smith and Tran 2010). For instance, Herlihy and Sifneos (2008) described the 25th percentile as a "moving target" that 75% of streams would not meet, and noted that water quality samples are often taken from areas in which there is some environmental concern and may not be representative of the true population. This statistical approach is also not tied to the health or designated uses of the stream (Smith and Tran 2010). Therefore, the 25th percentile may be overly protective or not protective enough of water quality (Suplee et al. 2007). In a review of existing literature, Evans-White et al. (2014) noted that EPA-suggested criteria were often more conservative than those identified in regional studies. For example, a study of the Red River Basin in the south central U.S. found that 25th percentiles for TN were similar but that the 25th percentile of TP was often greater than EPA recommendations (Longing and Haggard 2010). On the other hand, the 25th percentiles found by Herlihy and Sifneos (2008) using Wadeable Stream Assessment data from across the U.S. were lower than the EPA 25th percentiles in most instances, as was the case in the Eastern Coastal Plain (Table 1-1).

There is also large variation between TN and TP background concentrations within ecoregions (Smith et al. 2003), and ecoregions often do not explain variation in stream phosphorus concentrations (Dodds et al. 2002). Herlihy and Sifneos (2008) observed that more variation may occur within ecoregions than is accounted for by the ecoregion delineation used by EPA by assessing data from surveys in the Pacific Northwest. Similarly, Wickman et al. (2005) found more variation in nutrient concentrations (six times for nitrogen and three times for phosphorus) due to land-cover composition within ecoregions than between ecoregions when re-analyzing the 1977 EPA National Eutrophication Survey data. Because of this variation within ecoregions it is important to assess streams on a regional level (Clark et al. 2000, Evans-White 2014), and EPA encouraged states to evaluate and possibly develop alternative delineation schemes, as well as site-specific criteria when necessary (EPA 2000b).

There are various methods that have been proposed and are being explored to develop numeric nutrient criteria in addition to the 25^{th} percentile approach taken by EPA, such as identification of reference or background conditions (Clark et al. 2000, Dodds and Oakes 2004, Smith et al. 2003) and linking nutrients to the biological condition of the stream (e.g. Smith et al. 2007, Smith and Tran 2010, Wang et al. 2014, Zheng et al. 2008, Ashton et al. 2014, Black et al. 2011).

One approach to developing numeric nutrient criteria is based on identifying nutrient concentrations for reference streams or least-impacted systems. For example, Clark et al.

(2000) assessed nutrient concentrations from 85 streams in undeveloped watersheds. These streams generally showed low nutrient concentrations, (ranges of 0.01 to 2.6 mg N L^{-1} and < 0.01 to 0.20 mg P L^{-1}; median values of 0.26 mg N L^{-1} and 0.022 mg P L^{-1}). The 75th percentile of phosphorus (0.091 mg P L^{-1}) was three times greater than that recommended by EPA for Eastern Coastal Plain streams (0.031 mg P L^{-1}); however, the 75th percentile of nitrogen (0.72 mg N L^{-1}) was nearly identical to that recommended by EPA (0.71 mg N L^{-1}), Table 1-1. These values are for all stream basins across the U.S. and are not segregated by region.

Using minimally impacted streams throughout the U.S., Smith et al. (2003) modelled background concentrations using the U.S. Geological Survey (USGS) Spatially Referenced Regressions on Watershed attributes (SPARROW). The modeled background concentrations were lower than suggested EPA criteria in some instances. This was true for the Eastern Coastal Plain, where modeled results were lower (0.015 mg P L^{-1} and 0.56 mg N L^{-1}) than EPA-proposed values (0.031 mg P L^{-1} and 0.71 mg N L^{-1}), Table 1-1. However, background concentrations of TP in nearly half of the streams exceeded the EPA-proposed criteria (Smith et al. 2003) suggesting that these values may be, in some instances, over protective.

Some researchers and managers suggest that nutrient criteria should ideally be based on nutrient concentrations of undisturbed systems (Herlihy and Sifneos 2008); however, undisturbed and minimally impacted streams are often hard to find (Dodds and Oakes 2004), especially on a regional level. Smith et al. (2003) stated that "pristine reference sites are essentially nonexistent in most regions…" In the absence of minimally disturbed streams, Dodds and Oakes (2004) proposed modeling nutrients and land use using multiple linear regression, where the y-intercept represents the reference value in the absence of anthropogenic land use. The TP criterion calculated by Dodds and Oakes (2004) for the Eastern Coastal Plain falls between the EPA ecoregion and subecoregion criteria, and TN was about half that of the EPA criterion (Table 1-1). Although this method requires extrapolation, the authors cite many advantages such as not requiring data from a large number of reference sites and identifying anthropogenic land use practices that may guide management (Dodds and Oakes 2004).

This method has been applied to agriculturally dominated watersheds across the U.S., including Maryland. Using multiple linear regression, Morgan et al. (2013) identified a set of reference criteria based on land uses variables (agricultural and urban) for various regions in Maryland, including the Middle Atlantic Coastal Plain using Maryland Biological Stream Survey (MBSS) data (Table 1-1). This state-wide monitoring program managed by the Maryland Department of Natural Resources (DNR) collects and analyzes water chemistry samples during the spring, avoiding sampling after heavy rains (Stranko et al. 2010).

While the use of background concentrations or reference concentrations can help guide nutrient criteria development, the data is not connected to the designated uses and biological responses in streams (Smith and Tran 2010). Some researchers propose that nutrient criteria should be related to designated uses and the causes of impairments—

excess algae or low biological diversity or abundance. Biotic indices take into account species diversity and population numbers and can be useful tools in assessing water quality. Several studies have focused on linking nutrient impairment to stream biological conditions to identify thresholds and set numeric nutrient criteria. If an ecological threshold can be detected, a stressor-response relationship may then be used (Zheng et al. 2008). Although difficult to identify due to the presence of multiple stressors and other variables, relationships between nutrients and macroinvertebrates (e.g. Smith et al. 2007, Smith et al. 2013, Robertson et al. 2006, Zheng et al. 2008, Ashton et al. 2014), as well as algae (e.g. Van Nieuwenhuyse and Jones 1996, Lohman and Jones 1999, Pan et al. 1999, Ponader et al. 2008) have been documented. However, these apply only to local impairments and do not address downstream impairments of coasts or estuaries.

For example, Van Nieuwenhuyse and Jones (1996) found a strong relationship between TP and suspended chlorophyll *a* in the U.S. and European streams. A positive correlation between TP and suspended chlorophyll *a* was also documented in Missouri streams (Lohman and Jones 1999), and Pan et al. (1999) found relationships between benthic algae and nutrient enrichment in mid-Atlantic streams. However, algal abundance may not be directly related to nutrient concentrations due to light limitation and scouring (Dodds et al. 2002). Other factors, such as grazing and temperature can affect algal growth and various forms of algae may show different responses (Royer et al. 2008). For instance, Morgan et al. (2006) found that chlorophyll *a* (filamentous, sestonic, and periphitic algae) did not give a good estimate of nutrients in small agriculture streams in Illinois, possibly due to factors such as light and hydrology, although there were some weak relationships between nutrients and algal types. Royer et al. (2008) suggested that sestonic chlorophyll *a* may be more useful for larger Illinois rivers with open canopy cover and large drainage areas.

Many of the relationships between macroinvertebrate communities and nutrients are also indirect. Macroinvertebrate communities can be impacted due to multiple stressors, and it is difficult to identify causes in declines and shifts in diversity and link these changes to increases in nutrient concentrations. For these reasons, macroinvertebrates may not be good indicators of nutrient concentrations (Friberg et al. 2010, Ashton et al. 2014), and nutrients often do not explain all the variability in biological communities (Wang et al. 2007, Friberg et al. 2010). However, a variety of statistical techniques are now being utilized to identify such relationships (Dodds et al. 2010), and researchers have identified several metrics with strong relationships to nutrients.

For example, Smith et al. (2007) developed a Nutrient Index of Biological Integrity for New York streams. Further, Smith et al. (2013) identified nutrient thresholds for wadeable streams in New York, including streams in New York's Eastern Coastal Plain (0.017 mg P L^{-1} and 1.1 mg N L^{-1}), by evaluating biological community metrics, marcoinvertebrates, and diatoms. It has been suggested that diatom assemblages may be used as indicators of nutrient enrichment in streams (Ponader et al. 2008). Ponader et al. (2008) observed a strong relationship between TP, but not TN concentrations, and algal assemblages on artificial substrate in New Jersey's Coastal Plain streams. The authors then created a TP inference model and index to help identify stream trophic states to aid with nutrient criteria development in the state. Further, Black et al. (2011) utilized algal metrics (abundance and taxa richness) to identify thresholds for TN and TP for agricultural streams in the western U.S. While TP was the most statistically important variable in most instances, overall TN was not a good indicator for explaining the variation in algal metrics (Black et al. 2011).

In Wisconsin wadeable streams, Robertson et al. (2006) found that biotic indices change with increasing nutrient concentrations, and that the threshold response to changes in nitrogen concentration were about 0.5 mg N L^{-1} for fish and 0.9 to 1.2 mg N L^{-1} for diatom and microinvertebrate indices. However, once streams are above reference conditions, phosphorus was found to have a greater effect on biotic communities. Zheng et al. (2008) identified a threshold for nitrate plus nitrite in relation to benthic macroinvertebrate communities and diatom communities in the Eastern Ridge and Valley ecoregion. In another study, Friberg et al. (2010) found a relationship between macroinvertebrate communities and ammonia and TP (but not TN) in Danish streams; however, they suggest that biological oxygen demand (BOD) is actually the primary driver.

In Maryland, MDE has identified thresholds for nutrients and other water chemistry parameters which it uses to assess and identify impaired waters for its *Integrated Report of Surface Water Quality* (MDE 2009a). A TP threshold of 0.14 mg P L^{-1} was identified for the coastal plain using benthic macroinvertebrate and fish indices of biological integrity (MDE 2009a). While a threshold was found for TP, there was no statistical difference between biological integrity at sites in regards to TN in coastal plain streams. MDE chose to use the threshold identified for the highland region of 3.0 mg N L^{-1} for the entire state (MDE 2009a). These nutrient thresholds are greater than most of the numeric nutrient criteria values derived for the region (Table 1-1).

Ashton et al. (2014) also examined the benthic index of biotic integrity (BIBI) and macroinvertebrate taxa for Maryland streams to identify biologically protective nutrient criteria. While correlations between macroinvertebrate taxa and the TN benchmark chosen for the study were found, these taxa did not accurately predict whether a stream would exceed the chosen benchmark (1.68 mg N L^{-1}). The authors determined that further investigation is necessary to understand the relationships between nutrients and biological integrity. A study was also completed by the Interstate Commission on the Potomac River Basin (Mandel et al. 2011) to develop and evaluate stressor-response indices for macroinvertebrate, periphyton, and phytoplankton communities to aid in the development of nutrient criteria for the state of Maryland. This report identified a range of thresholds (0.012 to 0.087 mg P L^{-1} and 0.58 to 2.67 mg N L^{-1}; Table 1-1) protective of high quality biological communities. Results varied by physiographic region, and for the Middle Atlantic Coastal Plain nutrient thresholds for TN based on phytoplankton (2.15 to 2.36 mg N L^{-1}) were higher than those calculated for macroinvertebrates (0.58 mg N L^{-1}). Threshold values associated with TP ranged from 0.012 to 0.030 mg P L^{-1}.

Because of the varying techniques proposed to develop numeric nutrient criteria and the need to ensure scientific defensibility, a weight-of-evidence approach can be taken

(Smith and Tran 2010, Chambers et al. 2012, Huang et al. 2010). Combining various methods and identifying overlap between derived criteria can help support decisions and provide confidence for adoption of numeric nutrient criteria (Chambers et al. 2012). For instance, Smith and Tran (2010) combined several methods using a weight-of-evidence approach for large rivers in New York. In Canada, Chambers et al. (2012) found overlap between criteria statistically derived from nutrient concentrations and biologically derived criteria.

While application of various biological indices and other statistical methods may prove useful for developing numeric nutrient criteria for streams and identifying local nutrient impairments, they do not take into account downstream impacts. Assessing the impact any proposed criteria have on downstream water quality and uses is important to ensure the criteria are protective of downstream water quality (EPA 2000a). Because the Chesapeake Bay is not meeting water quality standards, it is considered impaired and a multi-state TMDL was developed to reduce pollution entering the bay (EPA 2010). As part of this process, nutrient endpoints and nutrient loading allocations were determined for smaller watersheds within the Chesapeake Bay watershed (EPA 2010). Assessing whether the proposed EPA criteria, as well as other numeric nutrient criteria, will be protective of designated uses in the Chesapeake Bay is essential.

Maryland has yet to adopt nutrient criteria for non-tidal streams (MDE 2009b), and the state is not alone. As of 2008, 36 states have not adopted any numeric nutrient criteria for streams and rivers (EPA 2008). MDE is in the process of developing candidate criteria for non-tidal streams (MDE 2009b). In 2003 the *Preliminary Draft Plan for Development of Nutrient Criteria in Maryland* was released (Beaman and Eskin 2003) which states that MDE will use other scientifically defensible methods in the creation of nutrient criteria because the measured percentiles of concentrations do not correlate well to aquatic life use support. The scientifically defensible methods Maryland plans to use include empirical approaches (directly measured relationships between nutrient indicators and impacts), loading models, and/or cause and effect based studies and relationships (Beaman and Eskin 2003). It is suggested that nutrient criteria will be developed using the three EPA nutrient ecoregions, although in some instance site-specific criteria could be used (Beaman and Eskin 2003). As Maryland moves forward with development and adoption of numeric nutrient criteria the applicability of the EPA-suggested criteria should be examined on the agriculturally dominated Delmarva Peninsula.

Nutrient Concentrations in Maryland Streams

A review of nutrient data from a subset of streams in one Delmarva watershed, the Choptank River Basin (Figure 1-2), shows that nutrient concentrations are mostly higher than the suggested EPA numeric nutrient criteria. Comparison of the EPA-suggested criteria for the Eastern Coastal Plain with nutrient data from subwatersheds within the Choptank River Basin (Sutton et al. 2010) indicate that nutrient levels in the basin's streams are mostly higher than the EPA-suggested numerical criteria (Fisher et al. 2006, 2010). This is consistent with observations of degrading water quality in the Choptank River Estuary (Fisher et al. 2006, 2010). For example, 95% of samples collected during baseflow in fall 2009 (Fisher et al. unpublished) from 78 stream sites exceeded the total nitrogen Eastern Coastal Plain criterion, and 91% exceeded the subecoregion criterion (Figure 1-3). Phosphorus values were also higher than the criteria, with 85% greater than the regional and 68% greater than the subecoregional criterion (Figure 1-3).

Nutrient concentrations in a first-order stream with a forested watershed (Marshy Hope forested reference site) just outside the Choptank River Basin (Figure 1-2) exceed suggested criteria during baseflow conditions on some occasions (6 to 39%, Figure 1-4). However, all nitrogen data is < 1.0 mg N L^{-1} and all but one of the TP concentrations is < 0.06 mg P L^{-1}. Many small forested watersheds may have nitrogen and phosphorus concentration which exceed the recommended EPA criteria (Ice and Binkley 2003). Currently the site is thought to be minimally disturbed, although it has a history of timber harvest, and it has not been completely determined whether groundwater is entering the watershed from adjacent farmland (T. Fisher 2010, pers. comm.). If the site is an appropriate reference site, this suggests that the subecoregion criteria calculated by EPA (which is slightly lower than the ecoregion criteria) may be more appropriate for the Delmarva Peninsula; however, more data and analysis is necessary. It should also be noted that the EPA criteria did not distinguish between samples taken at baseflow and storm flow (EPA 2000a), and all data in Figure 1-3 and Figure 1-4 were taken under baseflow conditions. Nitrogen and phosphorus concentrations usually increase during storm flows, sometimes by as much as an order of magnitude, particularly for TP, because of the erosion and re-suspension of sediments (Fisher et al. 2006, Koskelo 2008). This has been observed in the Choptank River Basin, and while most forms of nitrogen increased during storm events, nitrate decreased due to dilution of high-nitrate groundwater (Koskelo 2008).

Assessing the application of numeric nutrient criteria on a regional level, as well as the relationships to downstream estuarine uses will help ensure the adoption of realistic and attainable numeric nutrient criteria protective of streams and the Chesapeake Bay. It is also important to keep in mind that the goal of nutrient criteria is not to restore streams to a pristine state but to aid in the identification of waters that are impaired (not supporting designated uses) due to elevated nutrient levels. EPA recognizes this and acknowledges that some anthropogenic loading cannot be avoided nor will it necessarily result in adverse responses (EPA 2000b), although in some instances it may be necessary (Dodds and Welch 2000). In general, nutrient criteria can help identify goals and set load reductions in Maryland's non-tidal streams and are another tool that can be utilized to help manage, restore, and reduce pollution in aquatic systems, including the Chesapeake Bay.

Research Goals

The overall goal of this thesis research is to explore numeric nutrient criteria on the Delmarva Peninsula. The ranges of nutrients on the Delmarva Peninsula were first examined, with an emphasis on the Choptank River Basin, relative to suggested criteria. In addition, a set of reference conditions were identified using methods proposed by Dodds and Oakes (2004), specifically focusing on the role of land use and hydric soil, known to reduce nitrogen concentration through denitrification (Fisher et al. 2010, Fox et al. 2014). In Chapter 3, numeric nutrient criteria were evaluated for consistency with TMDL goals for the Chesapeake Bay using the Choptank River Estuary as a case study, and numeric nutrient criteria were identified that would be protective of downstream water quality. While assessment of the biological condition of streams is important to the development of nutrient criteria on Delmarva, it was not included in the scope of this research.

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Tables

Table 1-1: Total phosphorus (TP) and total nitrogen (TN) concentrations take from literature for the Eastern Coastal Plain and Maryland region.

Source	Location	Method	TP (mg L^{-1})	TN (mg L^{-1})	Chl *a* (*µg* L^{-1})	Turbidity (FTU / NTU)
EPA, 2000a	Eastern Coastal Plain Ecoregion (IIV)	25th Percentile	0.031	0.71	3.75	3.04 / 1.94
EPA, 2000a	Middle Atlantic Coastal Plain Subecoregion	25th Percentile	0.053	0.87	3.75	4.50 / 3.89
Herlihy & Sifneos, 2008	Eastern Coastal Plain	25th Percentile	0.023	0.62		
Morgan & Kline, 2011	Maryland	25th Percentile	0.025 – 0.037	1.34 – 1.68		
Morgan et al., 2013	Middle Atlantic Coastal Plain	25th Percentile	0.094	0.93		
Morgan et al., 2013	Middle Atlantic Coastal Plain	75th Percentile of Reference Streams	0.065	2.5		
Morgan et al., 2013	Middle Atlantic Coastal Plain	Modelled Reference Concentration	0.044	0.45		
Dodds & Oakes, 2004	Eastern Coastal Plain	Modelled Reference Concentration	0.040	0.36		
Smith et al., 2003	Eastern Coastal Plain	Modelled Background Concentration	0.015	0.56		
Clark et al., 2000	United States	Concentration in Undeveloped Watersheds	0.020 – 0.037	0.24 – 0.32		
MDE, 2009a	Maryland Coastal Plain	Biological Threshold	0.14	3.0		
Mandel et al., 2011	Maryland	Biological Threshold	0.012 – 0.087	0.58 – 2.67		
		Range	**0.012 – 0.14**	**0.24 – 3.0**		
		Median	**0.042**	**0.79**		

Figures

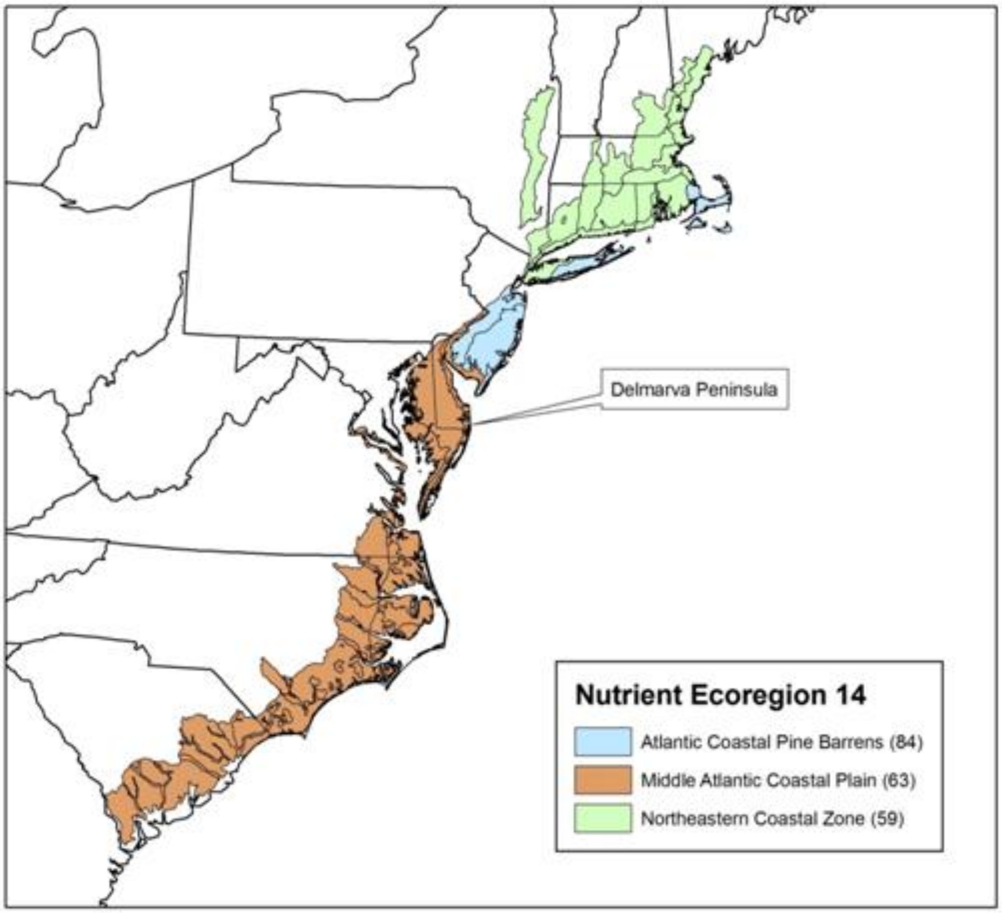


Figure 1-1: Region XIV, Eastern Coastal Plain, and subecoregions used for nutrient criteria development by EPA.

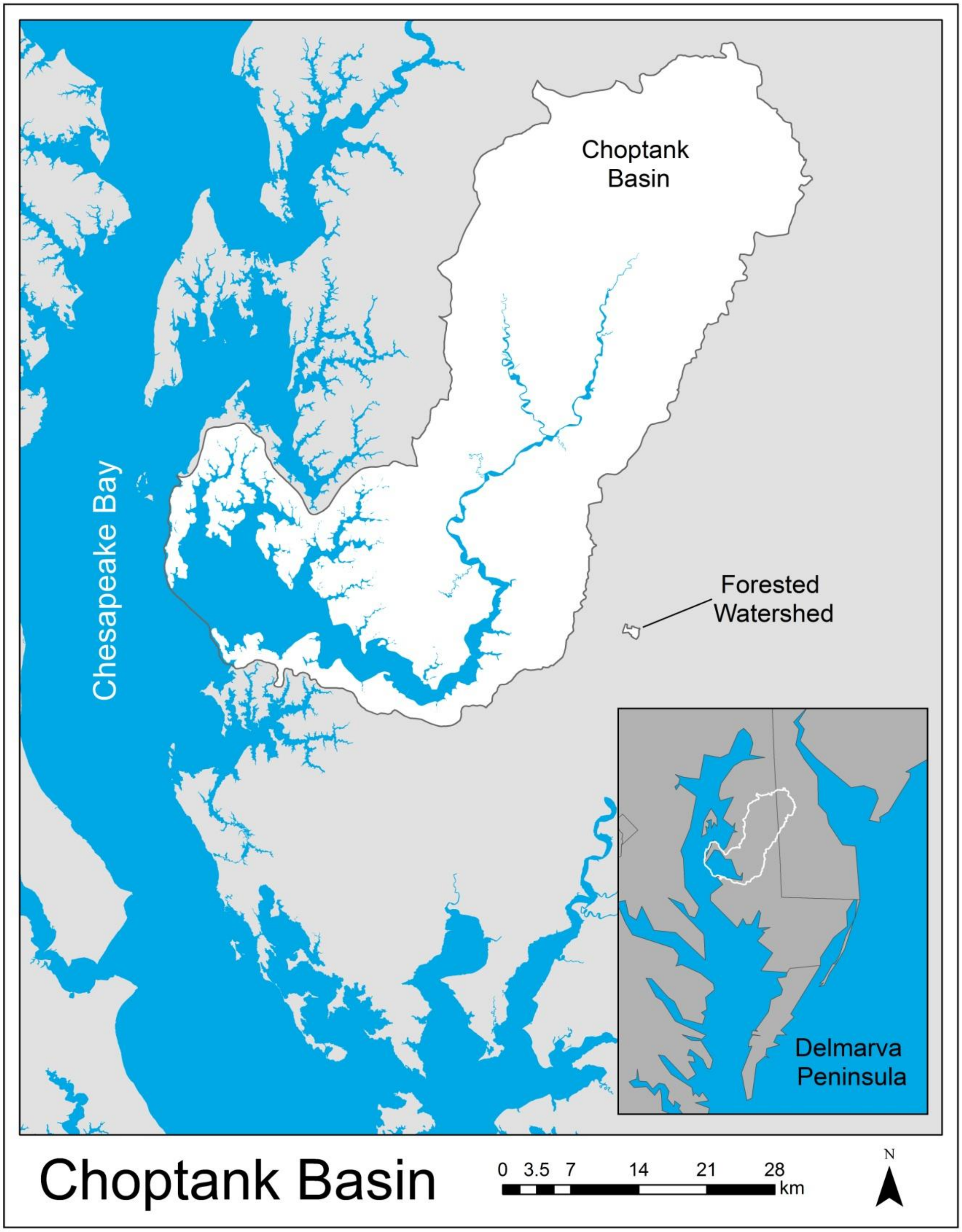
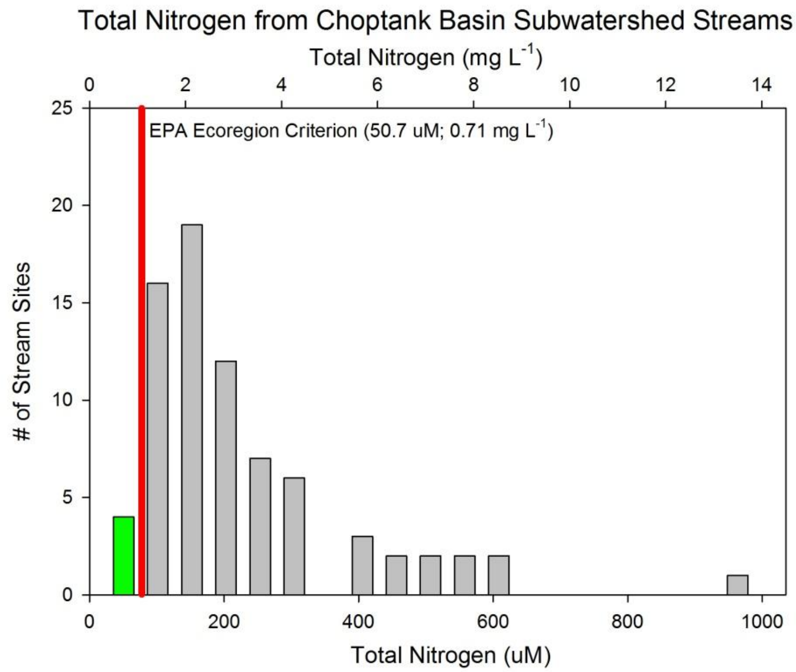


Figure 1-2: Location of the Choptank River Basin on the Delmarva Peninsula. Also shown is the watershed for the Marshy Hope forested reference site.



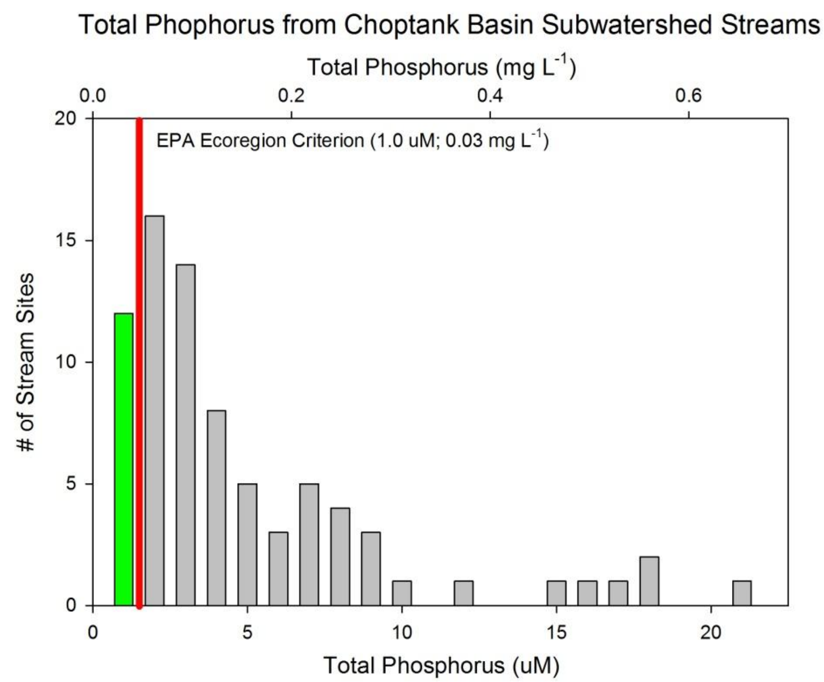
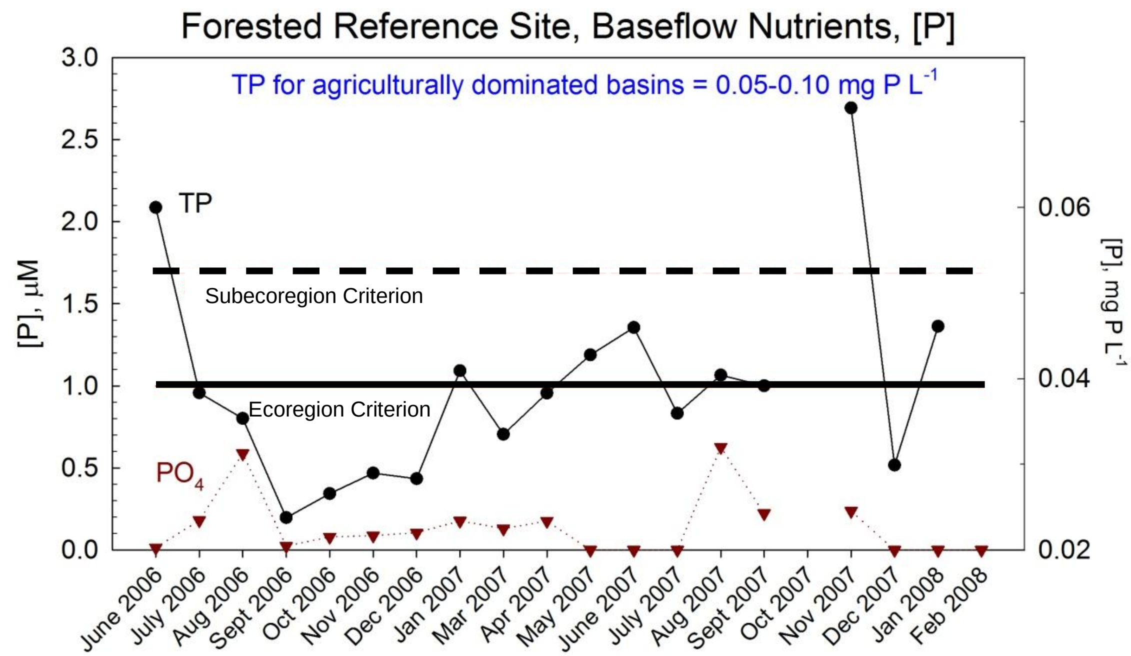


Figure 1-3: Total nitrogen (TN) and total phosphorus (TP) concentrations from 78 stream sites within five Choptank River Basin subwatersheds sampled during fall of 2009 (Fisher et al. unpublished). Ninety-five percent exceed the Ecoregion XIV criterion for TN and 85% for TP.



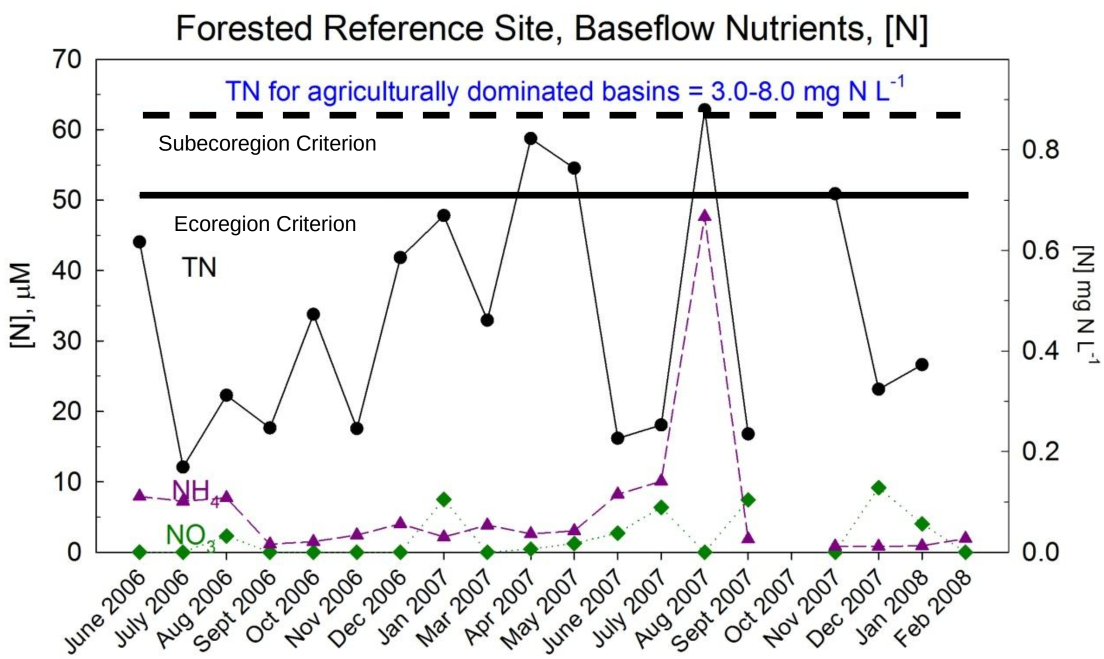


Figure 1-4: Baseflow nutrients at a forested reference site, Marshy Hope, just outside the Choptank River Basin (Fisher et al. unpublished). Nutrient concentrations exceed both the ecoregion and subecoregion criteria recommended by EPA on occasion.

Chapter 2: The Variation of Nutrients with Land Use and Hydric Soils on the Delmarva Peninsula

Abstract

Watershed land use and soil properties are known to be important determinants of nitrogen and phosphorus concentrations in streams and can be useful in the development of numeric nutrient criteria. Nutrient concentrations in 52 streams sampled on the Delmarva Peninsula (mid-Atlantic region of North America) typically varied over several orders of magnitude with TN and TP concentrations ranging from 0.2 to 20.2 mg N L^{-1} and 0.01 to 1.64 mg P L^{-1}, respectively. In this dataset, more than 95% of streams failed nutrient criteria recommended by EPA for the Eastern Coastal Plain, and 88% exceeded one or both of the criteria by a factor of two, indicating widespread water quality degradation on the Delmarva Peninsula. Percentages of land uses, population density, and hydric soils in the surrounding watersheds were calculated and combined in a multiple linear regression to derive a set of reference criteria for nutrients in Delmarva streams. Several significant correlations were found between nutrients, land use, hydric soils, and other parameters sampled. Combining percent agriculture land and hydric soils in a multiple linear regression resulted in a significant relationship to TN (adjusted r^2 = 0.62, $p < 0.001$), with the intercept yielding a reference criterion (zero agriculture, no hydric soils) of 1.6 mg N L^{-1}. Agriculture alone gave a reference criterion of 0.62 mg N L^{-1}. TP was best predicted by the presence of hydric soils, developed land, population density, and agriculture (adjusted r^2 = 0.39, $p < 0.001$) and provided a reference criterion (no hydric soils, zero developed land, zero population density) of 0.007 mg P L^{-1}. These reference criteria for TN and TP can be used to assess the degree of anthropogenic enhancement of streams on Delmarva and are comparable to results obtained elsewhere.

Introduction

In order to better address impairments due to excess nutrients, the U.S. Environmental Protection Agency (EPA) is requiring states to develop numeric nutrient criteria for streams. Excess nutrient loading can significantly degrade aquatic systems. In streams, increased nutrients, especially phosphorus, can result in excess algal growth, large diel oxygen fluctuations, and changes in species diversity (Dodds and Welch 2000). When these nutrients enter downstream estuarine and coastal systems, they can cause algal blooms, hypoxia, and loss of aquatic life. A prime example of this is the Chesapeake Bay which experiences algal blooms and hypoxia due to excess nutrients. Many streams on the agriculturally dominated Delmarva Peninsula, Figure 2-1, drain to the Chesapeake Bay, making managing and reducing nutrient concentrations in these streams not only important to support the health of the streams but vital to bay restoration.

Numeric nutrient criteria can help identify goals, set load reductions in streams, and are another tool that can be utilized to manage, restore, and reduce pollution in aquatic systems. When developing numeric nutrient criteria, there are multiple factors that influence stream water quality that should be considered. These include nutrients, other pollutants, hydrology, rainfall and climate, geology and soils, land use, and trophic structure (EPA 2000a). In order to account for some of the variation in these factors, assessing streams on a regional level is often beneficial. EPA recognized the impact these variables have on nutrient concentrations in streams when developing numeric nutrient criteria and used a series of aggregated ecoregions (Omernik 2000) originally derived by Omernik (1987) to create regional criteria for total phosphorus (TP) and total nitrogen (TN) (Table 2-1), as well as chlorophyll *a* and turbidity (EPA 2000a). While this approach takes into account varying geology, physiography, vegetation, climate, soils, land use, wildlife, and hydrology (EPA 2000a), there is still the potential for high variation among streams within nutrient ecoregions (Herlihy and Sifneos 2008, Heatherly 2014). EPA used the 25th percentile of nutrient concentrations in streams to derive numeric nutrient criteria for 14 ecoregions (EPA 2000a), but several additional approaches have been proposed by researchers. These include identifying reference conditions from least-impacted streams or models, as well as biological thresholds and indices as discussed in Chapter 1 of this thesis.

Reference conditions for nutrient concentrations under anthropogenically undisturbed conditions can be difficult to identify. There is a lack of relatively undisturbed streams for comparison, natural variation among streams, and the presence of multiple stressors (Dodds and Oakes 2004, Chambers et al. 2008). Nearly all streams have experienced some level of alteration, and even minimally disturbed streams are impacted by atmospheric deposition (Smith et al. 2003). On the Delmarva Peninsula, changes in land use such as agriculture and urbanization are often cited sources of nutrient pollution (Fisher et al. 2010). Ranges of nutrient concentrations proposed for Maryland and the coastal plain are shown in Table 2-1. These include concentrations of nutrients from a sampling of undeveloped watersheds across the U.S., 0.02 to 0.037 mg P L^{-1} and 0.24 to 0.32 mg N L^{-1} (Clark et al. 2000), and modeled background concentrations for coastal plain streams, 0.015 mg P L^{-1} and 0.56 mg N L^{-1} (Smith et al. 2003).

In the absence of unimpacted streams, Dodds and Oakes (2004) presented a statistical method to identify reference criteria that can be applied to streams on the Delmarva Peninsula. This method uses multiple linear regression with anthropogenic land use as the independent variable and nutrient concentrations as the dependent variable to identify reference criteria from the resulting y-intercept. Their results showed that for the Eastern Coastal Plain, which includes the Delmarva Peninsula, the best predictive variables were percent farm land (buildings and livestock holding facilities) for TP and a combination of percent farm land, cropland (areas used for production of crops for harvest), and population density for TN. Other land use categories included in the Dodds and Oakes (2004) assessment were pasture land (land managed primarily for the production of introduced forage plants for livestock grazing), range land (plant cover that is principally grasses or small plants suitable for grazing), and urban land (residential, industrial, commercial, and institutional land). Results from Dodds and Oakes (2004) for the Eastern Coastal Plain, shown in Table 2-1, yielded TN concentrations nearly half of EPA’s recommendation but only slightly higher TP values. Although this method requires extrapolation, the authors cite many advantages such as not requiring data from a large number of reference sites and identifying anthropogenic land use practices that may guide management (Dodds and Oakes 2004). This approach, in comparison with other methods, has been used in several agriculturally dominated watersheds including Nebraska, Maryland, West Virginia, Canada, and eastern China (Heatherly 2014, Morgan et al. 2013, Zheng et al. 2008, Chambers et al. 2008, and Chen and Lu 2014). An overview of these studies follows.

In West Virginia, Zheng et al. (2008) used multiple regression to examine the relationship of nutrient concentrations and land uses, finding that agricultural and urban land uses were able to predict TN (r^2 = 0.64), NO_3 (r^2 = 0.75), and TP (r^2 = 0.43) concentrations. Also used in Nebraska, results showed a correlation between percent row crop and TN, with a TP correlation being found only in the north-central ecoregion of the state (Heatherly 2014). Heatherly (2014) also assessed various row crop percentages to factor in some level of agricultural production. Morgan et al. (2013) used Maryland Biologic Stream Survey (MBSS) data to derive numeric nutrient criteria using the regression method and also calculated the 25th and 75th percentile from Maryland stream data for comparison. Regression model results were 0.45 mg N L^{-1} and 0.044 mg P L^{-1} ; results from the 25th and 75th percentile analysis were higher (0.93 mg N L^{-1} and 0.094 mg P L^{-1}; 2.5 mg N L^{-1} and 0.065 mg P L^{-1}, respectively) (Table 2-1). Both TN and TP were best predicted by agriculture, and urban land use was not significant (Morgan et al. 2013). While the model predicted $\log_{10}$ (TN) with moderate strength (adj. r^2 = 0.43), for $\log_{10}$ (TP) it was extremely weak (adj. r^2 = 0.013) (Morgan et al. 2013). Similarly, the results from Dodds and Oakes (2004) show that land use was better at predicting TN (r^2 = 0.53) than TP (r^2= 0.19) for the Eastern Coastal Plain.

The regression approach (Dodds and Oakes 2004) has also been used to assess streams in other countries. For instance, using a variety of approaches, including the y-intercept method, Chambers et al. (2008) identified TN and TP targets ranging from 0.44 to 1.19 mg N L^{-1} and 0.013 to 0.055 mg P L^{-1}, respectively, for agricultural watersheds comprised of less than 10% urban land in Ontario, Canada. The y-intercept method yielded the lowest nutrient concentrations of the methods used by Chambers et al. (2008), with r^2 values of 0.39 (TP) and 0.53 (TN). The regression approach was also applied in an agricultural region of eastern China by Chen and Lu (2014). Taking cropland slope into account, they found the best predictor for $\log_{10}$ (TN) to be percent urban land plus cropland with slopes less than 8%. For $\log_{10}$ (TP) the best model included livestock and poultry waste, urban land, and crop land with slopes less than 8%. The r^2 of both models was high (0.90 and 0.80, respectively). Chen and Lu (2014) then compared their modeled results to percentile calculations. The TN reference criterion Chen and Lu (2014) generated using the regression model, 1.78 mg N L^{-1} was in line with values obtained using the 25th percentile approach (1.83 mg N L^{-1}) and the 75th percentile reference stream approach (1.59 mg N L^{-1}). The lowest TP value they obtained was from the regression approach (0.049 mg P L^{-1}), with the 25th and 75th percentile approaches yielding slightly higher results (0.059 mg P L^{-1} and 0.056 mg P L^{-1}, respectively) (Chen and Lu 2014).

Generally, relationships between nutrients and land use derived using the y-intercept approach in the literature were good. The exception was the TP model on Maryland's coastal plain, which showed a weak predictive relationship (Morgan et al. 2013, Dodds and Oakes 2004) and TP in some regions of Nebraska (Heatherly 2014). Overall, in the studies to date, land use was better able to predict TN concentrations than TP. It is possible that other factors, such as slope, soil type, and rainfall may have a stronger influence on phosphorus delivery to streams. Also, phosphorus is inadequately sampled in many instances because stormflow, which transports large quantities of phosphorus, is under sampled (Correll et al. 1999).

Relationships between watershed land use and nutrient concentrations in streams have been well documented (e.g. Beaulac and Recklow 1982, Likens and Bormann 1974, Jordan et al. 1997, Beckert et al. 2011, Dodds and Oakes 2014). Anthropogenic land use such as agriculture and urbanization can contribute to stream nutrient loading. Fertilizer use in agricultural and urban areas, wastewater from humans and livestock, and atmospheric deposition serve as nutrient sources. Other natural land uses also act as sinks, such as forests, grasslands, and wetlands, and may take up and transform nutrients to organic forms or trap phosphorus in particulate forms (Lowrance et al. 1984, Richardson 1989, Mitsch and Gosselink 2000).

The eastern shore of Maryland is predominately agriculture with small grain production (corn, soybean, wheat) and poultry farms (Jordan et al. 1997, Staver and Brinsfield 2001). Studies of streams on the Delmarva Peninsula have shown that cropland is correlated with higher nitrogen concentrations (Ritter and Harris 1984, Jordan et al. 1997, Norton and Fisher 2000, Fisher et al. 2006, 2010, Sutton et al. 2010, Beckert et al. 2011, Hively et al. 2011). Relationships have also been found between phosphorus and agricultural land uses (Hively et al. 2011, Sutton et al. 2010); however, soils type, stream slope, and runoff potential also play a significant role (Norton and Fisher 2000, Hively et al. 2011, Koskelo et al. 2012).

The presence of hydric soils can impact nutrient delivery to streams. Hydric soils are defined as those "that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part" (Mid-Atlantic Hydric Soils Committee 2011). The low oxygen conditions of hydric soils can promote increased denitrification rates, decreasing available nitrogen (e.g., Lee et al. 2000, Fox et al. 2014). Hydric soils can also lead to decreased baseflow (Koskelo 2008), and on the Delmarva Peninsula well-drained (non-hydric) soils yield some of the highest nitrogen export coefficients (Ritter 1986). On the other hand, hydric soils can potentially increase available phosphorus due to the reduction of metals, especially iron-phosphate complexes (Dodds 2002) or erosion of sediment bound with phosphorus during storm events (Seltzer and Wang 2004). Most phosphorus is transported to streams in particulate form during storm events (Correll et al. 1999, Koskelo et al. *in press*). Phosphorus binds to soil particles and elements such as iron (Fe), magnesium (Mn), aluminum (Al), and calcium (Ca) (Jordan et al. 2008). Compton et al. (2000) estimates that more than half of all particulate phosphorus entering rivers is bound to ferric iron. Under low oxygen conditions ferric iron (Fe^{3+}) is reduced, releasing phosphate and soluble ferrous iron (Fe^{2+}) (Jordan et al. 2008). When these ions are later exposed to air, the reduced iron is often re-oxidized resulting in $Fe(OH)_3$ precipitate, or rust. Ritter (1986) found that "higher phosphorus loading rates occurred during storm events on watersheds with poorly drained soils than with well drained soils." In contrast, Koskelo (2008) and Koskelo et al. (2012) observed that hydric soils were unrelated to stormflow in several Choptank River watersheds and that transport was instead driven by topography. Nonetheless, because of the impact hydric soils can have on nutrient transformation, this factor, along with watershed land use, should be considered when deriving numeric nutrient criteria for Delmarva streams.

In this chapter, nutrient concentrations in Delmarva streams are evaluated in relation to criteria proposed by EPA. The relationships of soil and land use to water quality in these streams are also explored. Parameters used to quantify water quality included pH, conductivity, turbidity and total suspended solids, dissolved oxygen, and nutrient concentrations (TN, TP, PO_4, NO_3, and NH_4). In addition, a technique similar to that of Dodds and Oakes (2004) is applied to derive local nutrient criteria while also considering hydric soils in the assessment. Data collected locally from Delmarva streams was used to test the following **hypotheses**:

1) Nitrogen and phosphorus concentrations in streams will increase with anthropogenic land uses, such as agriculture and urban land use, or population density.

2) Nitrogen concentrations in streams will decrease with the presence of hydric, water-saturated soils in the watershed, while phosphorus concentrations will increase.

3) Nutrient concentrations in a majority of Delmarva streams will be greater than the proposed EPA criteria during baseflow conditions.

Methods

Study Area

The study area included 52 streams across the Delmarva Peninsula and their surrounding watersheds (Figure 2-1). A majority of these sites were located in the Choptank River Basin, and included the Choptank River near Greensboro, MD (United States Geological Survey [USGS] gaging station 01491000), 15 streams sampled through the U.S. Department of Agriculture (USDA) Conservation Effects Assessment Program (CEAP), and 20 subwatershed sites located within five CEAP watersheds. Additional locations spatially distributed throughout the Delmarva Peninsula were sampled; including four MBSS sentinel sites, one small forested watershed, and 11 other sites with no known available data.

Sample Collection and Analysis

Each location was sampled quarterly during summer and fall of 2011 and winter and spring of 2012 during baseflow conditions (Figure 2-2). Dissolved oxygen, pH, temperature, and specific conductivity were measured in the field using portable meters and probes (YSI 85, Symphony SP70P, VWR Traceable, and Yokogawa SC82, respectively).

As conductivity increases with temperature, field-measured temperature (T) and specific conductivity (cond) results were used to calculate conductivity at 25 °C [cond(25)] using an equation derived by Fisher et al. (1998) using samples from the Greensboro, MD USGS gauging station (eq. 2-1).

$$cond(25) = cond(T) * exp\ (0.023 * 25) / exp\ (0.023 * T) \qquad \text{(eq. 2-1)}$$

where T = temperature and $cond$ = specific conductivity.

Dissolved oxygen concentrations are also influenced by temperature, and solubility decreases as temperature increases. To account for this, an exponential function fitted to oxygen solubility data from Colt (1984), eq. 2-2, was used. Subsequently, the solubility of oxygen in freshwater, percent oxygen saturation, was calculated using eq. 2-3.

$$[O_2] = 138.4 + 317.1 * exp\ (-0.03918*T) \qquad \text{(eq. 2-2)}$$

$$\%\ oxygen\ saturation = 100 * observed\ O_2\ /\ solubility \qquad \text{(eq. 2-3)}$$

In addition to field measurements, a whole water grab sample was taken from each stream for nutrient analyses (unless there was no visible flow) and transported to Horn Point Laboratory (HPL) in coolers on ice. To evaluate analytical variance, duplicate samples and analyses were performed on approximately 10% of these samples. Samples were filtered within 36 hours for total suspended sediment (TSS), and the filtrate was saved for dissolved nutrient analyses (see below). Both whole and filtered water samples were stored in freezers at -5.0 °C until analyzed in the laboratory for TN, TP, NO_3, NH_4, and PO_4.

Both turbidity and TSS were measured for each water sample. Turbidity was measured using an Orbeco-Hellige portable turbidimeter (model 969), and samples were filtered for TSS (Strickland and Parson 1972) using pre-weighed Whatman GF/F glass microfibre filters (47 mm). Duplicate TSS analyses were done for each sample, and at least 10% of each set were blanks (filtered deionized water) to estimate a correction factor to account for weight changes in the filter due to the filtration process. The filters were then placed in plastic containers in a drying oven at 40 °C. Once dry, the filters were re-weighed and TSS (mg L^{-1}) was calculated using eq. 2-4.

$$TSS = (W_f - W_i - C) / V \qquad \text{(eq. 2-4)}$$

where W_f = final weight (mg), W_i = initial weight (mg), C = correction factor, the initial minus final weight of blanks (mg), and V = volume of water filtered (L).

Samples for CEAP sites were sent to USDA's Beltsville, MD laboratory for nutrient analysis. All other samples were analyzed colorimetrically for nutrients (TN, TP, NO_3, NH_4, and PO_4) at HPL. A statistical test of 171 split samples (Fisher et al., unpublished) showed no significant bias between the two laboratories, except for TP. Analysis of TP by the USDA laboratory was 81% of analysis of TP by HPL. Whole water samples were analyzed to determine TN and TP as described in Strickland and Parsons (1972) and Lane et al. (2000). This consisted of adding persulfate, followed by placing the samples in an autoclave for 30 minutes to transform all forms of nitrogen and phosphorus into NO_3 and PO_4. Filtrate was also analyzed for NO_3, NH_4, and PO_4. During NH_4 analysis, several June samples sat in the refrigerator for multiple days while resolving issues with blanks. This could have led to increased ammonium, and results from all June ammonium samples were excluded from analysis. Minimum detection limits were 0.005 mg N L^{-1} and 0.003 mg P L^{-1}. Minimum detection limits for CEAP samples analyzed at USDA laboratory were 0.01 mg N L^{-1} and 0.01 mg P L^{-1}. No TN or TP samples were lower than the minimum detections limits.

Determination of Watershed Characteristics

Watershed boundaries were delineated in ArcGIS v9.3 using stream layers from USGS National Hydrology Dataset, 1-meter resolution geo-referenced areal imagery (National Agricultural Imagery Program [NAIP] 2009 and 2011) for Maryland and Delaware, and topography from the USGS 7.5 minute maps. Where appropriate, existing watershed boundaries (USGS hydrological units or HUCS) were used for all or parts of boundaries. Once the watershed boundaries were determined, land use (forest, agriculture, developed, and poultry houses) was visually interpreted and digitized using NAIP imagery for 2009 or 2011. Population density of each watershed was estimated using 2010 census data for zip code zones in the study area (U.S. Census Bureau 2012). The Soil Survey Spatial and Tabular Data (SSURGO 2.2) were used to determine soil characteristics for each watershed. Soil characteristics calculated included percentages of: hydric classification (presence of hydric plus partially hydric soils), drainage class under dominant conditions (very poorly drained, poorly drained, and somewhat poorly drained), and hydrologic group under dominant conditions (C, D, C/D, and B/D), which represents the runoff potential of the soil. In addition, the three dominant soil types and their parent material were determined for each watershed. The attributes of land use, soil, and population polygons that were only partially intersected by watershed polygons were apportioned by areas inside and outside the watershed boundary. For population, the distribution was assumed to be evenly distributed across the census block. Stream order was determined visually from the USGS National Hydrology Dataset (NHD) using the Strahler stream order scheme (Strahler 1957). Sampling sites on stream segments that did not have visible flowlines in the NHD shapefile were classified as zero order. A common projection (Universal Transverse Mercator [UTM]) and datum (North America Datum [NAD] 83, Zone 18N) was used for each data layer.

Statistical Methods

The statistical package SigmaPlot 11.0 was used for data analysis. Pearson's Product-Moment Correlation was used to determine if significant correlation was present among normally distributed data. Normality was assessed through visual interpretation of the data and a Shapiro-Wilk normality test. Non-normal data was transformed to determine if normality could be met. For data where no transformation to normality could be found, non-parametric procedures such as Spearman Rank Correlation were used. Averages of the concentration data for each site were used when running correlations with land use, population density, and hydric soils.

Multiple linear regression was applied to the logarithms of averaged TN and TP, as the data was not normal without transforming. Land use (% Agriculture, Poultry, Developed), % Hydric Soils, and population density were the independent variables. Co-linearity between the independent variables was assessed using the Variance Inflation Factor (VIF). Because of inverse co-linearity with % Agriculture, % Forest was not included as an independent variable. A regression between forest and nutrients was run to determine nutrient concentrations under 100% forested conditions. While there were some weak correlations found between other variables, such as % Agriculture and %

Hydric Soils and % Developed and Population Density, these did not meet the criteria used for exclusion (VIF > 8). To determine the best fit model, the Akaike information criterion (AIC) (Akaike 1973) was applied.

$$AIC = n * ln\ (SSerror/n) + 2K \qquad \text{(eq. 2-5)}$$

where n is sample size, *SSerror* is the regression sum of squares error term, and K is the number of model parameters +1. This takes into account the model complexity and degrees of freedom to determine the best model. The model with a significant model fit ($p < 0.05$) and the lowest AIC score was chosen as the best model. If a simple and complex model both had similar AIC values (± 7) the less complex model was chosen (Burnham and Anderson 2002).

Results

Water Quality

Comparison of Nutrient Concentrations to Criteria

Water quality parameters from 52 stream sites across Delmarva typically varied over several orders of magnitude. Only three individual samples of 200 had nutrient concentrations that met both the EPA-proposed nutrient criteria for TN and TP. These were the December samples for the Marshy Hope forested reference site and SF12 and the March sample for LM1. No site had a geometric mean that met both criteria, but the geometric means of three sites (SF12, LM1, and Marshy Hope forested reference site) were less than the nitrogen criterion and four (SF1, Owens, Tull, and an unnamed Trib. to

Marshy Hope) met the phosphorus criterion (Figure 2-3, Table 2-2). The 25th percentiles calculated with this data were 0.052 mg P L^{-1} and 1.44 mg N L^{-1} (Table 2-1). Below are details on the ranges and statistical distributions of each parameter, which influenced how measures of central tendency and variance were used for subsequent statistical tests.

Nitrogen and Phosphorus

Median, average, and geometric mean for TP and TN by site are shown in Table 2-2. Both nitrogen and phosphorus concentrations in Delmarva streams ranged over several orders of magnitude (0.24 mg N L^{-1} to 20.2 mg N L^{-1} and 0.01 to 1.64 mg P L^{-1}, respectively). The geometric means were 0.079 mg P L^{-1} for TP and 2.89 mg N L^{-1} for TN.

Dissolved inorganic forms of nitrogen and phosphorus were important components of TP and TN. Inorganic PO_4 (soluble reactive phosphorus) comprised anywhere from nearly 100% of the TP values to less than 5%. The remaining phosphorus is dissolved and particulate organic phosphate. A few outliers were observed, including KT16 which had an extremely high TN concentration for March (20.2 mg N L^{-1}) and LM17 and Back Creek which had very little NO_3 but higher TN. Concentrations of PO_4 ranged from 0.001 mg P L^{-1} to more than 1.0 mg P L^{-1} with a geometric mean of 0.028 mg P L^{-1}. As expected, PO_4 and TP values were highly correlated ($r = 0.84$, $p < 0.001$; Figure 2-4). Dissolved inorganic nitrate (NO_3) was the dominant form of TN and was highly correlated with TN ($r = 0.93$, $p < 0.001$; Figure 2-4). The minimum NO_3 concentration was close to zero (non-detectable) and the maximum was 14.1 mg N L^{-1}. The sites with the highest average concentration of NO_3 were SF1, the unnamed Trib. to Marshy Hope, Tull, KT16, Oaklands, Dukes, Piney, and GB16. All other sites had average NO_3 concentrations measuring below 5.0 mg N L^{-1}. Ten sites had a NO_3 concentration below 0.001 mg N L^{-1}, including the Marshy Hope forested reference site, Back, Corkers, Milleville, Ellendale, Nassawango, LM17, SF12, LM9, and LM1. In most instances ammonium only comprised a small amount (< 10%) of the TN and ranged from less than 0.10 mg N L^{-1} to 4.8 mg N L^{-1}. Sites KT4, SF1, SF12, and the unnamed Trib. to Marshy Hope all had average ammonium concentration at or below 0.01 mg N L^{-1}. TN, TP, and PO_4 were normally distributed when log transformed, but transformation did not normalize NO_3 and NH_4 data.

Dissolved Oxygen

Dissolved oxygen saturation varied seasonally and was generally higher during March and December at lower temperatures than during warmer months. For instance, in September, 33% of streams sampled had a dissolved oxygen concentration below 5.0 mg O_2 L^{-1}, the state standard, with several below 1.0 mg O_2 L^{-1}. In June 29% were also lower than the state standard. This compares with the March and December sampling, where < 10% of sites sampled had dissolved oxygen below the Maryland state standard (5.0 mg O_2 L^{-1}). Dissolved oxygen values ranged from less than 1.0 mg O_2 L^{-1} to 13.7 mg O_2 L^{-1} with oxygen saturations of 3% to 135%. Dissolved oxygen and oxygen saturation were not normally distributed and could not be transformed into a normal distribution.

Turbidity & Total Suspended Solids

Spearman Rank Correlation showed that TSS and turbidity were correlated, $r = 0.72$, $p < 0.001$ (Table 2-3). Individual turbidity measurements ranged from less than 1 Nephelometric Turbidity Units (NTU) to more than 90 NTU at Back Creek, with a median of 4.6 NTU. The range for TSS was 0.2 mg L^{-1} to 126 mg L^{-1} with one extremely high measurement of 725 mg L^{-1} at site GB8. Median TSS was 5.6 mg L^{-1}. When the individual TSS and turbidity measurements were log transformed only turbidity passed normality, but both turbidity and TSS passed normality tests when the averages were log transformed.

Conductivity & pH

Normally distributed when averaged by site, conductivity (cond [25]) ranged from 37 µS cm^{-1} at site LM9 to 543 µS cm^{-1} at Back Creek. The mean value for conductivity was 165 µS cm^{-1}. Not normally distributed, the range of pH was 4.18 to 7.51. Thirty-two streams had an average pH below 6.5, Maryland's minimum value for stream pH.

<u>Watershed Characteristics</u>

Watersheds ranged in size from less than 1 km^2 to 293.3 km^2 for the Choptank River at Greensboro, MD (Table 2-4). Average watershed size was 18.3 km^2. Half of the streams sampled were small zero to first order streams. There were 16 second order, 8 third order, and 1 fifth order (Choptank River at Greensboro, MD) streams sampled (Figure 2-5).

Land use varied from almost 100% agriculture to a few watersheds dominated by forest (Table 2-4). Agriculture and forest were co-linear and had a strong negative correlation ($r = -0.97$, $p < 0.001$). Average watershed land use was 53% agriculture, 42% forest, 6% developed, and <1% poultry. The metric % Agriculture was normally distributed, but % Forest, % Developed, and % Poultry were not normally distributed when log transformed.

Few watersheds had greater than 10% developed lands ($n = 7$). The watershed with the highest percent of developed lands was Sandy Branch at 27% which had a population density of 62.6 people km^{-2}. Population estimates within watersheds ranged from zero to more than 10,000 people for the Choptank River at Greensboro, MD (Table 2-4). Census data for approximately 17% of the watersheds showed zero human population, and population density was not normally distributed. Population density ranged from zero in several watersheds to 171 people km^{-2} in the unnamed Trib. to Marshy Hope watershed. Leonard Pond Run near Salisbury, MD also had one of the higher population densities (141 people km^{-2}) of the study watersheds. Population density and total population showed a weak positive correlation to the percentage of developed land ($r = 0.39$, $p = 0.005$; $r = 0.41$, $p = 0.003$, respectively). Removing outliers from the data set (unnamed Trib. to Marshy Hope and Leonard Pond Run for population density; Leonard Pond Run and Greensboro for total population) only slightly improved the correlation ($r = 0.44$, $p = 0.002$) for population density and resulted in a lower r ($r = 0.35$, $p = 0.01$) for total population, Figure 2-6.

Many of the watersheds sampled were dominated by hydric, water-saturated soils. The presence of hydric soils ranged from 13% to nearly 100% with an average of 66% (Table 2-4). The primary soil type in many of the watersheds was Fallsington, a loamy, poorly drained soil found throughout the coastal plain (USDA 2015), followed by Corsica and Hambrook (Table 2-5). A description of the drainage class and parent material is provided in Table 2-7.

Hydric soil data was normally distributed. There was a significant negative correlation between presence of hydric soils and agriculture ($r = -0.54$, $p < 0.001$) and a positive correlation with forest ($r = 0.66$, $p < 0.001$) (Figure 2-7, Table 2-8), indicating that hydric soils tend to remain in forest land uses. There was also a weak correlation between hydric soils and developed land ($r = -0.34$, $p = 0.015$).

Nutrients and their Relationship to Presence of Hydric Soils

When transformed, both TN and TP concentrations were correlated with the amount of hydric soils, Figure 2-8. The metric % Hydric Soils showed a better relationship with TN ($r = -0.58$, $p < 0.001$) than did drainage class or hydrologic group ($r = -0.49$, $p < 0.001$; $r = 0.40$, < 0.001, respectively), and hydrologic group only had a slightly better correlation than % Hydric Soils for TP ($r = 0.54$, $p < 0.001$; $r = 0.51$, $p < 0.001$, respectively); therefore, % Hydric Soils was used for all subsequent statistics. TN and NO_3 had a weak to moderate negative correlation with % Hydric Soils ($r = -0.58$, $p < 0.001$; $r = -0.62$, $p < 0.001$, respectively). Likewise, TP and PO_4 showed a weak positive correlation with % Hydric Soils ($r = 0.51$, $p < 0.001$; $r = 0.44$, $p = 0.001$, respectively). The results of the correlations are provided in Table 2-9.

Nutrients and their Relationship to Land Use

Several significant correlations were also found between nutrients and land use (Table 2-9). The amount of forest and agriculture in watersheds was strongly correlated to the amount of TN and NO_3 in the stream. There was a positive correlation between $\log_{10}$ (TN) and % Agriculture in watersheds ($r = 0.76$, $p < 0.001$) and a negative correlation between $\log_{10}$ (TN) and % Forest ($r = -0.76$, $p < 0.001$) (Figure 2-7). NO_3 showed slightly better correlations with % Agriculture ($r = 0.77$, $p < 0.001$) and % Forest ($r = -0.78$, $p < 0.001$), whereas no correlations were found between ammonium and land use. Despite the strong correlations between nitrogen and land use, there were no such correlations for TP and PO_4. A Spearman Rank Correlation did show significant but weak to moderate negative correlation between TP and population density ($r = -0.42$, $p = 0.002$), and a similar negative correlation was found between PO_4 and population density ($r = -0.43$, $p = 0.002$). There were no significant correlations between nutrients and % Developed or % Poultry.

<u>Relationships of Oxygen Levels with Nutrients, Land Use, and Hydric Soils</u>

TN, NO_3, TP, and PO_4 values were all significantly correlated with oxygen levels measured in streams. Results of Spearman Rank Correlation, Table 2-3, show that both TN and NO_3 are positively correlated with dissolved oxygen ($r = 0.35$, $p < 0.001$; $r = 0.50$, $p < 0.001$, respectively), whereas TP and PO_4 showed an inverse relationship ($r = -0.58$, $p < 0.001$; $r = -0.43$, $p < 0.001$, respectively).

Dissolved oxygen levels were also positively correlated with % Agriculture ($r = 0.48$, $p < 0.001$) and negatively correlated with % Forest ($r = -0.48$, $p < 0.001$) in the watershed. A significant negative relationship was also present between % Hydric Soils in the watershed and dissolved oxygen ($r = -0.42$, $p = 0.002$), as well as oxygen saturation ($r = -0.36$, $p < 0.001$). While all seasons independently showed a significant relationship with the percentage of hydric soils in the watershed ($p < 0.05$), each relationship was weak ($r < 0.39$) except in September ($r = 0.60$), under low flows, with hydric soils explaining about 35% of the variation in dissolved oxygen levels and percent oxygen saturation.

Relationships of Turbidity and TSS with Nutrients, Land Use, and Hydric Soils

Nutrient concentrations were correlated with turbidity and TSS, shown in Figure 2-9. TN and NO_3 had a weak negative correlation with both turbidity ($r = -0.37$, $p < 0.001$; $r = -0.42$, $p < 0.001$, respectively) and TSS ($r = -0.30$, $p < 0.001$; $r = -0.39$, $p < 0.001$, respectively), while ammonium showed a weak positive relationship with turbidity and TSS ($r = 0.42$, $p < 0.001$; $r = 0.25$, $p = 0.002$, respectively). TP and PO_4 were positively correlated with both turbidity and TSS. TP was moderately correlated with turbidity, Figure 2-9, ($r = 0.65$, $p < 0.001$) and also TSS ($r = 0.57$, $p < 0.001$). The relationships between PO_4, turbidity, and TSS were weaker ($r = 0.39$, $p < 0.001$; $r = 0.29$, $p < 0.001$, respectively). Both turbidity (Figure 2-9) and TSS were positively correlated with the amount of hydric soils in the watershed ($r = 0.54$, $p < 0.001$; $r = 0.46$, $p = 0.002$, respectively), and turbidity showed a weak, positive correlation with % Forest ($r = 0.34$, $p = 0.013$).

Other Correlations

Additional correlations found are shown in Table 2-3. TN and NO_3 showed a moderate positive correlation with conductivity ($r = 0.65$, $p < 0.001$; $r = 0.70$, $p < 0.001$, respectively) and a weak positive correlation with pH ($r = 0.35$, $p < 0.001$; $r = 0.44$, $p < 0.001$, respectively). Conductivity was also positively correlated with pH ($r = 0.65$, $p < 0.001$), and pH was weakly correlated with dissolved oxygen ($r = 0.30$, $p < 0.001$). Dissolved oxygen was negatively correlated with turbidity and TSS, although weak ($r = -0.38$, $p < 0.001$; $r = -0.40$, $p < 0.001$, respectively).

Multiple Linear Regressions to Determine Reference Criteria

Results of the multiple linear regression to determine reference nutrient criteria are discussed below and provided in Table 2-10. Looking at land use alone, the best predictor of $\log_{10}$ (TN) in this data set is % Agriculture, eq. 2-6. Transforming the y-intercept yields a reference criterion of 0.62 mg N L^{-1} with zero agriculture. When hydric soil is included in the model, eq. 2-7, the adjusted r^2 increases from 0.56 to 0.60 which yields a reference criterion of 1.61 mg N L^{-1} with no hydric soil or agriculture. This is more than twice the derived criterion using agriculture only. However, results of the AIC show that the best model is the simpler model that includes only agriculture. Using land use only, modeled results yielded criteria ranging from 0.53 to 0.62 mg N L^{-1}, while models that included hydric soils ranged from 1.1 to 1.8 mg N L^{-1}.

$$\log_{10} (TN) = -0.210 + (0.0124 * \%\ Agriculture) \qquad \text{(eq. 2-6)}$$

adj. $r^2 = 0.56$

$$\log_{10}(TN) = 0.207 + (0.0102 * \%\ Agriculture) - (0.00454 * \%\ Hydric\ Soils) \quad \text{(eq. 2-7)}$$

adj. $r^2 = 0.60$

For $\log_{10}$ (TP) the best predictor for all land use (agriculture, developed, and poultry) and population density models, although weak, is population density, eq. 2-8. This yields a reference criterion of 0.094 mg P L^{-1} at zero population density. Presence of hydric soils was a better predictor of $\log_{10}$ (TP) than population density (adj. $r^2 = 0.24$, <0.001), eq. 2-9. This would yield a lower reference criterion of 0.024 mg P L^{-1}. The range of the transformed y-intercept for all significant models with % Hydric Soils included was lower (0.007 to 0.032 mg L^{-1}) than those that only included land use and population (0.082 to 0.095 mg L^{-1}). When all parameters were run the best model, with the lowest AIC (9.2 units higher than the simplest model) included all independent variables except poultry, eq. 2-10. This gives a much lower criterion of 0.007 mg P L^{-1} under no developed land, zero population density, no agriculture, and no hydric soils.

$$\log_{10}(TP) = -1.027 - (0.00391 * Population\ Density) \quad \text{(eq. 2-8)}$$

adj. $r^2 = 0.12$

$$\log_{10}(TP) = -1.616 + (0.00791 * \%\ Hydric\ Soils) \quad \text{(eq. 2-9)}$$

adj. $r^2 = 0.24$

$$log_{10}(TP) = -2.165 - (0.00279 * Population\ Density) + (0.0114 * \%\ Hydric\ Soils) + (0.00457 * \%\ Agriculture) + (0.0221 * \%\ Developed) \quad \text{(eq. 2-10)}$$

adj. $r^2 = 0.39$

Further, 100% forest was used to derive criteria as shown in the equations below (eq. 2-11 and 2-12). However, the relationship between phosphorus and % Forest was not significant.

$$log_{10}(TN) = 0.932 - (0.0118 * \%\ Forest) \quad \text{(eq. 2-11)}$$

adj. $r^2 = 0.58$

$$log_{10}(TP) = -1.105 + (0.000320 * \%\ Forest)\text{\^{}} \quad \text{(eq. 2-12)}$$

adj. $r^2 = 0.00$ (^ not significant, $p = 0.74$)

Discussion

Watershed Characteristics and Stream Nutrient Concentrations

Results of this study indicate that both land use and presence of hydric soil in surrounding watersheds are predictors of nutrient concentrations in Delmarva streams and that a majority of nutrient streams had nutrient concentrations higher than EPA-suggested numeric nutrient criteria. Results were used to test the three main hypotheses:

1) Nitrogen and phosphorus concentrations in streams will increase with anthropogenic land uses, such as agriculture and urban land use, or population density.

2) Nitrogen concentrations in streams will decrease with the presence of hydric, water-saturated soils in the watershed, while phosphorus concentrations will increase.

3) Nutrient concentrations in a majority of Delmarva streams will be greater than the proposed EPA criteria during baseflow conditions.

Portions of the first hypothesis were supported by the data. Nutrient concentrations in the sampled streams varied with the land use in the surrounding watershed (Hypothesis 1). However, significant relationships were only found for nitrogen (TN and NO_3) and agriculture. Nitrogen concentrations increased with agricultural land use; however, nitrogen concentrations showed little correlation with other anthropogenic land uses. Phosphorus did not show any significant correlation with anthropogenic land uses, but phosphorus did decrease with population density. There were no significant correlations between TN or TP with % Poultry and % Developed. In most instances these land uses made up a smaller percentage of total land use, and most watersheds were dominated by agriculture and forest making it difficult to test the effects of these anthropogenic land uses.

Nutrient concentrations in streams also varied with the presence of hydric, water-saturated soils in the watershed (Hypothesis 2). Statistically significant correlations ($p < 0.05$) were found between nutrients and % Hydric Soils (eq. 2-7 and 2-9), supporting both sets of observations in the second hypothesis. There was a negative correlation between stream nitrogen concentration and % Hydric Soils, and as the percentage of hydric soils in the watersheds increased, less nitrogen was found in the streams. This was true for both TN and NO_3, although NO_3 ($r = -0.62$, $p < 0.001$) showed a marginally stronger correlation than TN ($r = -0.58$, $p < 0.001$). The decrease in nitrogen with increasing hydric soils in the watershed may be due to higher rates of denitrification in the presence of hydric soils (Fox et al. 2014). A few outliers were observed, including KT 16, Marshy Hope forested reference site, and Sandy Branch. While KT16 had a high percentage of hydric soils, it also was dominated by agriculture and had one of the highest TN concentrations observed during the study, 20.2 mg L^{-1}. Because of its high percentage of agriculture and hydric soils it was a clear outlier. There is often a relationship between hydric soils and land use because these water-logged soils are not productive for farming due to their poor drainage. However, there are many streams on the Delmarva Peninsula that have been ditched (and tile drainage installed) so the land can be more readily used for agricultural purposes, but human-induced changes do not change the hydric status of soil by USDA. Conversely, the watershed of the Marshy Hope reference site is nearly all forest despite being comprised of 47% hydric soils. Dominated by well-drained soils, Sandy Branch was another outlier and had the lowest amount of hydric soils of any watershed sampled. While most of the soils in the watersheds sampled had little to no soils with slopes greater than 5%, Sandy Branch, the most northern watershed sampled, had soils with slopes of up to 15%. These soils comprised approximately 30% of the watershed. During sampling multiple farms with horses were observed in the area, and it is possible that the type of agriculture in the watershed is dominated by pastures instead of row crops, accounting for the difference.

As the percentage of hydric soils in the watershed increased so did the phosphorus found in the streams. Phosphorus values were predicted to increase in Hypothesis 2 due to the increased presence of hydric soils. The increase in phosphorus values can be explained by either the lack of oxygen in streams draining hydric soils causing the release of bound phosphorus and/or the increased runoff potential of water-logged soils and transport of sediment bound with phosphorus to streams. As hydric soils increased turbidity also increased, which could indicate increased runoff; however, both are likely to play a role. Land surface slope was not assessed here but may be a factor. Koskelo (2008) and Koskelo et al. (2012) found that slope was a predictor of stream phosphorus levels in watersheds of the Choptank River Basin. In eastern China, Chen and Lu (2014) included slope in their regression model to identify reference nutrient criteria, finding that nutrient levels were better predicted using crop land with slopes less than 8%. Again Sandy Branch, having high slopes and horse farms, was an outlier with low % Hydric Soils and a slightly higher phosphorus value. Other outliers included unnamed Trib. to Marshy Hope, Owens, and SF1, three of the four sites that would meet the TP criterion proposed by EPA. While the unnamed Trib. to Marshy Hope and SF1 watersheds were dominated by well-drained soils, the Owens and Ellendale watersheds are dominated by poorly drained, hydric soils and are mostly forested.

The majority of streams sampled here exceed EPA-suggested numeric nutrient criteria supporting Hypothesis 3. Even minimally impacted streams, such as the Marshy Hope forested reference site, exceed the criteria on occasion. Less than 10% of streams sampled had TP or TN concentrations that would meet EPA-suggested criteria (Figure 2-3). In this data set, no site had a geometric mean that met both criteria. The 25th

percentiles calculated with this Delmarva data set were 0.052 mg P L^{-1} and 1.44 mg N L^{-1}. These are consistent with results obtained in other studies (Table 2-1) and are within a factor of two of the EPA-recommended values for the Middle Atlantic Coastal Plain subecoregion. For comparison, Morgan et al. (2013) identified 25th percentiles of 0.094 mg P L^{-1} and 0.93 mg N L^{-1} using a larger dataset of MBSS data for streams on the Middle Atlantic Coastal Plain.

Nutrient concentrations ranged over several orders of magnitude and a clear outlier, the KT16 March sample, had a high TN concentration of 20.2 mg N L^{-1}. This site is a ditched stream adjacent to a farm field, and during the March sampling a large amount of filamentous algae was present with only a small trickle of water entering a nearly stagnant pool (Figure 2-10).

Of the stream samples that met the phosphorus criterion, SF1's watershed was dominated by agriculture, 97%, and the watershed of the unnamed Trib. to Marshy Hope was comprised of 72% agriculture and 28% forest. Both sites were minimally developed (< 1%) and had the least amount of development of all the sites sampled. SF1 and the unnamed Trib. to Marshy Hope also had some of the lowest PO_4 values sampled but had high concentrations of NO_3. The sites with the lowest average TN values were mostly forested and included LM1 (82%), the Marshy Hope forested reference site (98%), and Owens (85%). However, SF12 with low TN was only 60% forested and approximately 38% agricultural. There were exceptions, as two other sites with high percentage of forest (> 90%) had average TN concentrations nearly twice the EPA-recommended criterion. These sites were Ellendale at 1.6 mg N L^{-1} and Milleville at 1.4 mg N L^{-1}, but despite their high TN concentrations NO_3 was low ~ 0.002 mg N L^{-1}. These results show that land use such as forest and agricultural can help predict nutrient concentrations but is not the only factor to be evaluated.

<u>Numeric Nutrient Criteria Calculations</u>

Both land use and hydric soils are predictors of nutrient concentrations in Delmarva streams (eq. 2-6 to 2-10). Using the results of the y-intercept method, approximately 40% of streams sampled on Delmarva met the nitrogen criterion calculated (1.6 mg N L^{-1}), whereas none met the phosphorus criterion of 0.007 mg P L^{-1}. The phosphorus value is likely an unrealistic target as it is lower than both the natural background concentration modeled by Smith et al. (2003) and concentrations found in undeveloped watersheds by Clark et al. (2000). Biological assessments by Mandel et al. (2011) suggest phosphorus values as low as 0.012 mg P L^{-1} may be needed to protect stream health in Maryland's streams.

The ability of the models to predict nutrient concentrations improved with the addition of hydric soils (eq. 2-7, 2-9, and 2-10). However, it is unlikely that a stream's watershed would have no hydric soil as the range of sampled watersheds was 13 to 100% with an average of 66%. Streams with watersheds comprised of a large percentage of hydric soils may have lower background concentrations for nitrogen and higher phosphorus concentrations than those with little to no hydric soils. Table 2-11 shows several scenarios, crated from eq. 2-7 and 2-10, using different values for the percentage of hydric soil and allowing for 10% to 20% anthropogenic land use. In order to predict the nutrient concentration in streams based on reference conditions using the percentage of hydric soils in the surrounding watershed (% Hydric Soils) the following equations (eq. 2-13 and 2-14) are provided:

$$TN = 10^{(0.207 - [0.00454 * \%\ Hydric\ Soils])} \qquad \text{(eq. 2-13)}$$

$$TP = 10^{(-2.165 + [0.0114 * \%\ Hydric\ Soils])} \qquad \text{(eq. 2-14)}$$

In most watersheds, especially the agriculturally dominated Delmarva Peninsula, some anthropogenic loading cannot be avoided; therefore, the change in TN concentrations with % Agriculture (eq. 2-6) is also shown in Table 2-11. While in some instances nutrient concentrations may need to be reduced to reference or pristine conditions to protect the biologically condition of a stream (Dodds and Welch 2000), some streams are able to assimilate increased nutrient level with small increases not necessarily resulting in adverse responses. Reference criteria were also created using 100% forest, and results fall within the range of concentrations predicted by others (Table 2-1). While the TN concentration of 0.56 mg N L^{-1} is the same as that predicted by Smith et al. (2003), the phosphorus value is larger than those predicted and observed for undeveloped watersheds (Smith et al. 2003, Clark et al. 2000). However, the relationship between forest and phosphorus was not significant suggesting this value is not appropriate for a phosphorus criterion.

Stream Health

Several other water quality parameters measured in this study can also provide insight into overall stream health. These parameters include dissolved oxygen, turbidity and TSS, conductivity, and pH. Table 2-12 shows desired levels for many of these parameters and other water quality criteria. One of the more important parameters of stream health is dissolved oxygen which is essential to sustain aquatic life, such as fish and invertebrates. The Maryland state standard for protection of aquatic life is 5.0 mg O_2 L^{-1}, and dissolved oxygen values in most Delmarva streams were greater than 5.0 mg O_2 L^{-1}. Ten streams, or 20%, had average dissolved oxygen below 5 mg O_2 L^{-1}, but seasonal variation was observed. For example, in September and June nearly one-third of streams had dissolved oxygen levels below 5.0 mg O_2 L^{-1} with several below 1.0 mg O_2 L^{-1} in September. In May less than 10% of streams had dissolved oxygen levels below 5.0 mg O_2 L^{-1}, and only one stream had low levels in December. It is common for dissolved oxygen levels to be lower in warmer months due to increased water temperature, increased biological activity, and low flow conditions. Most of the streams with low oxygen in September and June had watersheds comprised of a high percentage of hydric soils (> 70%), probably reflecting inputs of low oxygen groundwater from hydric soils. However, low oxygen levels could also be the result of microbial respiration and increased temperature coupled with low flows.

Low dissolved oxygen is often associated with increased nutrient levels in streams, especially phosphorus. Significant relationships were found between nutrients (TN, TP, NO_3, and PO_4) and dissolved oxygen in streams, Table 2-3. As phosphorus levels increased dissolved oxygen levels decreased. However, as TN and NO_3 increased oxygen levels increased. This observation could be the result of increased denitrification in streams with low oxygen but could also be due to the presence of other limiting factors, such as phosphorus or light.

In addition to dissolved oxygen levels, turbidity and TSS were also measured. Because increased turbidity can be linked to increases in algae for slow moving streams, EPA used it as a response variable for nutrient criteria. For the Eastern Coastal Plain a criterion of 3.04 FTU was suggested. In this study, turbidity was measured in NTUs; however, the two numbers are somewhat comparable (USGS 1998). Less than a quarter of the streams sampled had average turbidity values below 3.04 NTU. Increased levels of phosphorus were correlated with increased turbidity and TSS. As phosphorus is often bound to sediment, this increase could also be the result of more phosphorus entering the stream leading to increased algal growth.

Conductivity can also indicate the presence of pollutants. High conductivity may mean an industrial or wastewater discharge is present. Low conductivity is usually associated with undeveloped or forested watersheds, as was also observed in this study. In addition, groundwater inflows, soil, and rock type impact stream conductivity levels. According to EPA, "studies of inland fresh waters indicate that streams supporting good mixed fisheries have a range between 150 and 500 μS/cm" (EPA 2012). This is also the range cited by Maryland as necessary to support healthy communities of macroinvertebrates and fish; however, the threshold identified for the Coastal Plain is less, 300 μS/cm (MDE

2009a). This is also the conductivity benchmark proposed by Cormier et al. (2013) in the Central Appalachia and Western Allegheny Plateau ecoregions of West Virginia streams. Three sites had conductivity levels above 300 μS/cm (KT16 and Cordova) with Back Creek having conductivity levels greater than 500 μS/cm. Waters with high nutrient concentrations usually have higher conductivity due to the presence of more dissolved ions such as nitrate (Dodds 2002). In this study, TN and NO_3 were positively correlated with conductivity. Increases in nutrients and runoff associated with agricultural land are likely to increase conductivity levels, although several agricultural sites sampled had low conductivity.

A range of pH between 6.5 and 8.5 is supportive of aquatic life (MDE 2009a). Acidic waters can negatively impact aquatic communities. According to Maryland stream surveys, streams with pH above 6 had more fish per mile (~9,000) compared to those with pH below 5 which usually contained no fish (Smith 2005). Five streams had individual samples with pH values below 5.0, including LM9, the Marshy Hope forested reference site, SF12, Milleville, and Ellendale, with the latter two having averages of 4.4 and 4.7. Benthic macroinvertebrates may begin to disappear when pH falls below the 4.5 to 5 range, and mayflies are even more susceptible to decreasing pH disappearing when pH is below 6.5 (Jeffries and Mills 1990). Alternatively, if pH levels rise too high aquatic life can be negatively impacted due to mobilization of toxic elements and dissolved heavy metals (MDE 2009a). Low pH can be caused by acid rain and fertilizer runoff; however, several streams on Delmarva have naturally low pH due to the presence of organic acids (Smith 2005). These “black water” streams are usually low gradient, slow flowing with decomposing leaves and other organic matter. It was noted during sampling that several of the streams, including the Marshy Hope forested reference site, had a tea-colored appearance which can denote the presence of tannins in the water from the decomposition of organic matter.

Conclusion

Few streams on the Delmarva Peninsula would meet the suggested EPA criteria and the criteria calculated here, indicating widespread water quality degradation. While the use of reference concentrations can help guide criteria development, using anthropogenic land use alone may yield nutrient criteria that are difficult to achieve on the Delmarva Peninsula and do not account for natural variation, such as the presence of hydric soils in the surrounding watershed. However, it is difficult to avoid the conclusion that there is widespread nitrogen and phosphorus contamination of streams on Delmarva.

Excess nutrients are just one cause of impairment in streams, and their health depends on many factors. As demonstrated here, there are multiple complex interactions that occur within streams that are dependent on the physical, chemical, and biological characteristics of the stream and surrounding land. This can make development of nutrient criteria challenging. On Delmarva, physical characteristics such as surrounding soil, channelization, and slope could impact nutrient concentrations as well as stream chemistry and biology. Additional approaches such as the identification of biological thresholds could be used to help develop and validate numeric nutrient criteria to ensure it is protective of aquatic life. Further assessment of macroinvertebrates, fish, and algae on Delmarva may prove beneficial especially since little to no relationship between phosphorus and anthropogenic land uses was observed here.

Another challenge is the role of nutrient limitation in streams, as not all streams will experience degradation due to high nutrient levels. Some streams, for example, with high nitrogen levels are clear with a diversity of species. It is when this nitrogen is carried downstream entering coastal and estuarine systems that problems can occur. This makes it important to assess downstream designated uses and impairments, as is done in Chapter 3 of this thesis, in an effort to help identify numeric nutrient criteria (Chambers et al. 2008, EPA 2000a).

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Tables

Table 2-1: Total phosphorus (TP) and total nitrogen (TN) concentrations take from literature for the Eastern Coastal Plain and Maryland region.

Source	Location	Method	TP ($mg\ L^{-1}$)	TN ($mg\ L^{-1}$)
EPA, 2000	Eastern Coastal Plain Ecoregion (IIV)	25th Percentile	0.031	0.71
EPA, 2000	Middle Atlantic Coastal Plain Subecoregion	25th Percentile	0.053	0.87
Herlihy & Sifneos, 2008	Eastern Coastal Plain	25th Percentile	0.023	0.62
Morgan & Kline, 2011	Maryland	25th Percentile	0.025 – 0.037	1.34 – 1.68
Morgan et al., 2013	Middle Atlantic Coastal Plain	25th Percentile	0.094	0.93
Morgan et al., 2013	Middle Atlantic Coastal Plain	75th Percentile of Reference Streams	0.065	2.5
Morgan et al., 2013	Middle Atlantic Coastal Plain	Modelled Reference Concentration	0.044	0.45
Dodds & Oakes, 2004	Eastern Coastal Plain	Modelled Reference Concentration	0.040	0.36
Smith et al., 2003	Eastern Coastal Plain	Modelled Background Concentrations	0.015	0.56
Clark et al., 2000	United States	Concentration in Undeveloped Watersheds	0.020 – 0.037	0.24 – 0.32
MDE, 2009a	Maryland Coastal Plain	Biological Threshold	0.14	3.0
Mandel et al., 2011	Maryland	Biological Threshold	0.012 – 0.087	0.58 – 2.67
		Range	**0.012 – 0.14**	**0.24 – 3.0**
		Median	**0.042**	**0.79**
This Study	Delmarva Peninsula	25th Percentile	0.052	1.44
This Study	Delmarva Peninsula	Modelled Reference Concentration, (land use only)	0.094	0.62
This Study	Delmarva Peninsula	Modelled Reference Concentration, (mean hydric soil values)	0.039	0.81
This Study	Delmarva Peninsula	Modelled Reference Concentration, (100% forest)	0.085	0.56

Table 2-2: Median, average, and geometric mean for total nitrogen (TN) and total phosphorus (TP). Values are shown in mg L^{-1}. Grey boxes represent sites that would meet suggested EPA numeric nutrient criteria.

Site	Location		TN			TP		
	Latitude	Longitude	Median	Average	Geometric Mean	Median	Average	Geometric Mean
Back	38.1336	-75.6995	1.34	1.99	1.45	0.30	0.30	0.25
Beaverdam	39.0742	-75.8660	4.80	4.93	4.90	0.06	0.07	0.06
Blockston	38.9757	-75.9636	7.45	7.29	7.20	0.04	0.06	0.05
Broadway (BW)	39.0345	-75.7758	2.20	2.13	2.08	0.07	0.09	0.08
BW1	39.0444	-75.7844	3.21	3.59	3.18	0.13	0.17	0.11
BW2	39.0428	-75.7846	4.25	4.29	3.75	0.10	0.15	0.12
BW3	39.0471	-75.7828	4.68	5.13	4.62	0.26	0.27	0.22
BW7	39.0674	-75.7960	1.40	1.33	1.30	0.16	0.15	0.13
BW8	39.0760	-75.7947	1.29	1.26	1.23	0.19	0.21	0.16
Cordova	38.8905	-75.9605	6.93	7.34	7.23	0.07	0.09	0.08
Corkers	38.1276	-75.4416	0.86	0.90	0.89	0.15	0.19	0.16
Dividing	38.2202	-75.5768	1.03	1.14	1.07	0.09	0.09	0.08
Downes	38.8822	-75.9260	8.63	8.48	8.48	0.04	0.04	0.03
Dukes	38.5923	-75.4909	9.91	9.43	9.19	0.05	0.07	0.05
Ellendale	38.7672	-75.4339	1.83	1.58	1.52	0.06	0.06	0.05
German Branch (GB)	39.0094	-75.9374	4.47	4.75	4.70	0.11	0.11	0.09
GB9	39.0876	-75.9239	1.56	2.36	1.83	0.64	0.72	0.43
GB16	39.0622	-75.9501	6.44	6.53	6.52	0.07	0.07	0.06
GB17	39.0570	-75.9480	4.70	4.60	4.59	0.10	0.10	0.09
GB24	39.0213	-75.9647	1.40	1.47	1.45	0.16	0.18	0.17
Gravelly	39.2049	-75.7434	1.46	1.54	1.52	0.10	0.14	0.12
Greensboro	38.9972	-75.7858	1.92	1.89	1.89	0.09	0.10	0.09
Jacobs	39.3643	-75.8199	5.20	5.23	5.23	0.07	0.08	0.08
Kitty (KT)	38.8113	-75.9705	3.26	3.34	3.31	0.08	0.09	0.07
KT4	38.8285	-75.9672	1.19	1.28	1.19	0.06	0.08	0.06
KT7	38.8364	-75.9991	6.59	6.30	5.92	0.23	0.22	0.20
KT15	38.8332	-75.9890	3.03	3.22	3.16	0.14	0.14	0.12
KT16	39.3641	-76.0115	13.6	14.5	13.8	0.21	0.31	0.26
Leonard Pond	38.4142	-75.5914	5.11	5.47	5.38	0.04	0.04	0.04
Long Marsh (LM)	39.0687	-75.8523	2.72	2.73	2.72	0.07	0.10	0.08
LM1	39.0695	-75.8423	0.44	0.47	0.43	0.03	0.13	0.07
LM9	39.0945	-75.8164	1.56	1.61	1.56	0.13	0.21	0.13
LM17	39.1060	-75.8157	1.22	1.80	1.57	0.21	0.39	0.27
LM29	39.1085	-75.8349	1.77	1.74	1.72	0.14	0.15	0.12
LM30	39.1087	-75.8445	1.36	1.44	1.44	0.75	0.82	0.42
Marshy Hope (forested)	38.6358	-75.8049	0.75	0.74	0.71	0.04	0.04	0.04
Milleville	38.2467	-75.4891	1.08	1.09	1.06	0.10	0.11	0.09
Nassawango	38.2633	-75.4625	1.65	1.62	1.54	0.10	0.14	0.12
North Forge	38.9855	-75.8162	2.80	2.77	2.74	0.04	0.06	0.04
Norwich	38.9239	-75.9740	3.10	3.15	3.13	0.09	0.10	0.09
Oaklands	38.9987	-75.9178	10.7	10.5	10.5	0.04	0.04	0.04
Old Town	39.0237	-75.7874	2.63	2.90	2.85	0.06	0.07	0.06
Owens	38.4932	-75.7539	0.83	0.81	0.81	0.03	0.03	0.03
Piney	38.9597	-75.9316	8.39	8.49	8.48	0.05	0.05	0.05
Sandy	39.4603	-75.7737	3.47	3.46	3.24	0.05	0.06	0.05
South Forge (SF)	38.9696	-75.8349	5.48	5.31	5.30	0.05	0.10	0.06
SF1	38.9773	-75.8378	14.4	14.3	14.3	0.01	0.01	0.01
SF12	38.9909	-75.8603	0.37	0.58	0.50	0.04	0.22	0.07
Skeleton	38.7167	-75.9643	0.92	0.91	0.90	0.16	0.14	0.13
Spring	38.9435	-75.7962	5.83	5.96	5.89	0.04	0.06	0.04
Trib. to Marshy Hope	38.6198	-75.8265	13.5	12.9	12.8	0.01	0.01	0.01
Tull	38.7195	-75.7720	9.88	9.85	9.83	0.02	0.03	0.03

Table 2-3: Results of Spearman Rank and Pearson's Product Moment Correlation. P-values less than 0.05 are significant, and boxes in light grey represent moderate (r > 0.4) to strong correlation (r > 0.7). The asterisk (*) denotes use of Pearson's Product Moment Correlation for which data was either normal or normal when log transformed.

	TN	NO_3	NH_4	TP	PO_4	DO	pH	Conductivity	Turbidity	TSS
TN		0.93 p < 0.001	0.07 p = 0.420	-0.28 p < 0.001	-0.20 p = 0.005	0.35 p < 0.001	0.35 p < 0.001	0.65 p < 0.001	-0.37 p < 0.001	-0.30 p < 0.001
NO_3	0.93 p < 0.001		0.06 p = 0.456	-0.38 p < 0.001	-0.23 p = 0.001	0.50 p < 0.001	0.44 p < 0.001	0.70 p < 0.001	-0.42 p < 0.001	-0.39 p < 0.001
NH_4	0.07 p = 0.422	0.06 p = 0.456		0.36 p < 0.001	0.22 p = 0.006	0.02 p = 0.822	0.17 p = 0.043	0.20 p = 0.021	0.42 p < 0.001	0.25 p = 0.002
TP	-0.28 p < 0.001	-0.38 p < 0.001	0.36 p < 0.001		0.84 p < 0.001*	-0.58 p < 0.001	0.08 p = 0.258	0.07 p = 0.334	0.65 p < 0.001*	0.57 p < 0.001
PO_4	-0.20 p = 0.005	-0.23 p = 0.001	0.22 p = 0.006	0.84 p < 0.001*		-0.43 p < 0.001	0.15 p = 0.040	0.14 p = 0.061	0.39 p < 0.001*	0.29 p < 0.001
DO	0.35 p < 0.001	0.50 p < 0.001	0.02 p = 0.822	-0.58 p < 0.001	-0.43 p < 0.001		0.30 p < 0.001	0.20 p = 0.006	-0.38 p < 0.001	-0.40 p < 0.001
pH	0.35 p < 0.001	0.44 p < 0.001	0.17 p = 0.043	0.08 p = 0.258	0.15 p = 0.040	0.30 p < 0.001		0.65 p < 0.001	-0.10 p = 0.181	-0.08 p = 0.311
Conductivity	0.65 p < 0.001	0.70 p < 0.001	0.20 p = 0.021	0.07 p = 0.334	0.14 p = 0.061	0.20 p = 0.006	0.65 p < 0.001		-0.15 p = 0.042	-0.05 p = 0.491
Turbidity	-0.37 p < 0.001	-0.42 p < 0.001	0.42 p < 0.001	0.65 p < 0.001*	0.39 p < 0.001*	-0.38 p < 0.001	-0.10 p = 0.181	-0.15 p = 0.042		0.72 p < 0.001
TSS	-0.30 p < 0.001	-0.39 p < 0.001	0.25 p = 0.002	0.57 p < 0.001	0.29 p < 0.001	-0.40 p < 0.001	-0.08 p = 0.311	-0.05 p = 0.491	0.72 p < 0.001	

Table 2-4: Area, stream order, population, and percent hydric soils and land use (forest, agriculture, developed, and poultry houses) in the surrounding watershed of sampled sites.

Watershed	Area (km^2)	Stream Order	Population	% Hydric Soils	% Land Cover			
					Agriculture	Forest	Developed	Poultry
Back	15.4	1	93	98	27	69	4	1
Beaverdam	23.3	3	75	84	63	32	4	1
Blockston	17.0	2	47	60	70	28	2	0
Broadway (BW)	16.2	2	140	73	53	40	7	0
BW1	0.9	1	6	81	58	33	7	2
BW2	0.2	0	15	52	82	0	18	0
BW3	0.7	0	3	52	93	0	7	0
BW7	4.2	1	11	79	50	45	4	1
BW8	1.2	1	1	68	69	28	3	0
Cordova	26.5	2	418	48	70	21	8	0
Corkers	27.7	2	315	72	31	66	3	0
Dividing	29.2	1	144	89	27	66	7	0
Downes	23.4	3	545	34	74	15	11	0
Dukes	3.3	1	43	72	60	35	4	0
Ellendale	2.0	1	13	99	7	92	1	0
German Branch (GB)	51.4	3	68	64	66	28	5	0
GB9	0.8	0	0	83	43	55	2	0
GB16	0.6	2	0	48	65	25	11	0
GB17	17.3	1	10	69	63	30	5	1
GB24	2.3	0	0	60	50	49	2	0
Gravelly	19.1	3	1063	92	43	46	11	0
Greensboro	293.3	5	10018	75	44	47	9	0
Jacobs	12.9	1	91	46	59	30	11	0
Kitty (KT)	13.5	2	46	56	62	33	4	0
KT4	0.3	0	0	71	35	63	2	0
KT7	0.9	0	0	63	78	15	5	2
KT15	7.4	2	45	59	59	36	4	1
KT16	0.01	0	0	97	99	0	1	0
Leonard Pond	63.9	3	9018	52	34	47	19	1
Long Marsh (LM)	41.3	3	328	82	53	43	3	0
LM1	0.4	0	0	76	16	82	2	0
LM9	0.9	0	1	94	15	84	2	0
LM17	0.1	0	0	51	82	9	9	0
LM29	12.1	2	121	84	42	54	3	1
LM30	1.7	0	1	83	69	31	1	0
Marshy Hope (forested)	1.4	1	10	47	0	98	2	0
Milleville	16.2	1	239	91	8	91	2	0
Nassawango	79.3	2	1156	94	22	72	6	1
North Forge	25.0	3	258	69	66	31	4	1
Norwich	24.5	3	65	67	68	29	4	0
Oaklands	10.0	2	192	27	82	10	7	0
Old Town	11.6	2	196	70	52	40	8	0
Owens	6.6	1	105	98	14	85	2	0
Piney	14.7	2	53	44	72	20	8	0
Sandy	6.9	1	432	13	55	18	27	0
South Forge (SF)	8.5	2	42	55	61	35	4	0
SF1	0.2	0	0	27	97	3	0	0
SF12	0.4	1	6	84	38	60	2	0
Skeleton	2.6	1	40	86	27	69	4	0
Spring	12.2	2	81	42	72	25	3	0
Trib. to Marshy Hope	1.7	1	290	21	72	28	0	0
Tull	12.7	2	298	54	59	34	6	1

Table 2-5: Dominant three soil types for each watershed and percent area. Grey boxes denote poorly drained soils.

Watershed	Dominant Soil Type			Watershed	Dominant Soil Type		
	Primary	Secondary	Tertiary		Primary	Secondary	Tertiary
Back %	Fallsington 43	Kentuck 37	Woodstown 7	KT15 %	Sassafras 30	Fallsington 24	Woodstown 18
Beaverdam %	Carmichael 34	Othello 15	Whitemarsh 11	KT16 %	Fallsington 79	Woodstown 18	Sassafras 3
Blockston %	Whitemarsh 20	Ingleside 15	Othello 10	Leonard Pond %	Rockawalkin 30	Lenni 19	Hurlock 7
Broadway (BW) %	Corsica 41	Fallsington 29	Hambrook 20	Long Marsh (LM) %	Corsica 27	Fallsington 19	Carmichael 12
BW1 %	Corsica 42	Fallsington 35	Hambrook 10	LM1 %	Corsica 47	Fallsington 25	Hambrook 20
BW2 %	Ingleside 48	Fallsington 43	Corsica 10	LM9 %	Corsica 62	Fallsington 28	Hambrook 6
BW3 %	Hambrook 46	Corsica 39	Fallsington 13	LM17 %	Hambrook 49	Corsica 36	Fallsington 15
BW7 %	Corsica 42	Fallsington 29	Hambrook 14	LM29 %	Corsica 25	Carmichael 20	Hurlock 16
BW8 %	Corsica 38	Fallsington 30	Hambrook 20	LM30 %	Carmichael 38	Hurlock 27	Hammonton 11
Cordova %	Sassafras 41	Woodstown 18	Fallsington 11	Marshy Hope (forested) %	Runclint 28	Hurlock 23	Pone 15
Corkers %	Fallsington 33	Kentuck 14	Mullica 9	Milleville %	Mullica 38	Hurlock 29	Berryland 9
Dividing %	Mullica 23	Hurlock 17	Berryland 13	Nassawango %	Askecksy 28	Hurlock 19	Klej 11
Downes %	Hambrook 51	Fallsington 32	Ingleside 10	North Forge %	Fallsington 39	Hambrook 22	Corsica 20
Dukes %	Hurlock 53	Pepperbox 22	Hammonton 9	Norwich %	Whitemarsh 14	Sassafras 12	Ingleside 11
Ellendale %	Fallsington 77	Hurlock 14	Klej 8	Oaklands %	Hambrook 40	Sassafras 23	Fallsington 23
German Branch (GB) %	Carmichael 19	Ingleside 16	Whitemarsh 12	Old Town %	Fallsington 34	Corsica 32	Hambrook 18
GB9 %	Hurlock 44	Ingleside 17	Whitemarsh 15	Owens %	Askecksy 47	Hurlock 32	Corsica 16
GB16 %	Ingleside 53	Carmichael 19	Corsica 10	Piney %	Hambrook 39	Fallsington 37	Ingleside 15
GB17 %	Carmichael 23	Ingleside 23	Hurlock 16	Sandy %	Reybold 46	Queponco 17	Sassafras 11
GB24 %	Whitemarsh 27	Ingleside 15	Othello 14	South Forge (SF) %	Fallsington 47	Hambrook 36	Ingleside 9
Gravelly %	Fallsington 27	Corsica 21	Hammonton 17	SF1 %	Hambrook 62	Fallsington 27	Ingleside 11
Greensboro %	Fallsington 24	Corsica 21	Othello 9	SF12 %	Fallsington 84	Hambrook 16	
Jacobs %	Matapeake 33	Sassafras 20	Fallsington 13	Skeleton %	Fallsington 49	Elkton 15	Hambrook 12
Kitty (KT) %	Sassafras 33	Woodstown 22	Fallsington 19	Spring %	Hambrook 34	Fallsington 33	Ingleside 21
KT4 %	Woodstown 50	Sassafras 29	Fallsington 21	Trib. to Marshy Hope %	Galestown 29	Fort Mott 25	Downer 13
KT7 %	Sassafras 31	Fallsington 25	Woodstown 18	Tull %	Fallsington 51	Hambrook 36	Ingleside 8

Table 2-6: Hydrologic group and drainage class under dominant conditions.

	Hydrologic Group (%)						Drainage Class (%)						
Watershed	**A**	**B**	**B/D**	**C**	**C/D**	**D**	**Excessive**	**Some-what Excessive**	**Well**	**Moderate-Well**	**Poorly**	**Very Poorly**	**Some-what Poorly**
Back	0	3	0	10	0	88	0	0	2	9	58	32	0
Beaverdam	0	28	8	3	51	10	0	0	18	17	52	14	0
Blockston	0	50	10	11	26	4	0	0	36	24	38	2	0
Broadway (BW)	0	27	0	14	0	59	0	0	26	31	19	24	0
BW1	0	19	0	8	0	73	0	0	19	8	31	42	0
BW2	0	48	0	8	0	45	0	0	48	8	35	9	0
BW3	0	48	0	3	0	49	0	0	48	3	10	39	0
BW7	0	21	0	18	0	60	0	0	19	41	19	21	0
BW8	0	32	0	17	0	51	0	0	25	48	14	14	0
Cordova	0	54	0	27	0	19	0	0	54	24	18	1	3
Corkers	8	13	45	12	17	4	2	4	7	20	53	14	0
Dividing	6	4	51	18	7	15	5	1	1	19	31	43	1
Downes	1	65	0	12	0	22	0	1	66	12	22	0	0
Dukes	4	17	0	25	0	55	1	0	3	38	55	2	0
Ellendale	0	13	0	14	0	72	0	0	0	6	3	82	9
German Branch (GB)	0	44	9	6	34	8	0	0	36	15	41	7	0
GB9	0	24	44	0	32	0	0	0	0	8	69	6	0
GB16	0	60	10	0	30	0	0	0	53	7	30	10	0
GB17	0	39	16	3	38	3	0	0	30	13	42	15	0
GB24	0	34	4	14	30	18	0	0	37	18	44	0	0
Gravelly	0	37	0	12	0	52	0	0	8	37	30	25	0
Greensboro	5	23	0	13	1	58	1	2	21	19	31	24	3
Jacobs	3	55	13	17	9	3	0	3	58	13	25	0	0
Kitty (KT)	0	44	0	24	0	31	0	0	43	25	28	3	1
KT4	0	29	0	50	0	21	0	0	29	50	21	0	0
KT7	0	37	0	25	0	38	0	0	37	25	35	4	0
KT15	0	41	0	21	0	38	0	0	41	20	33	5	1
KT16	0	3	0	17	0	79	0	0	3	17	79	0	0
Leonard Pond	1	15	0	35	0	30	9	0	10	43	24	9	3
Long Marsh (LM)	1	24	8	10	22	35	0	0	18	29	31	22	0
LM1	0	24	0	12	0	64	0	0	24	59	17	0	0
LM9	0	7	0	20	0	73	0	0	7	77	12	5	0
LM17	0	49	0	6	0	46	0	0	49	11	9	31	0
LM29	1	25	16	3	44	11	0	0	14	15	40	30	0
LM30	0	41	27	0	31	0	0	0	14	28	57	2	0
Marshy Hope (forested)	4	0	49	3	0	0	37	12	0	0	23	26	3
Milleville	9	1	74	9	2	6	8	1	0	9	31	51	0
Nassawango	1	30	10	17	0	33	10	0	0	7	27	45	11
North Forge	2	29	0	16	0	53	0	0	30	31	29	9	0
Norwich	0	41	6	18	23	12	0	0	33	22	38	3	3
Oaklands	0	73	0	8	0	19	0	0	73	8	18	1	0
Old Town	0	30	0	10	0	60	0	0	30	19	28	23	0
Owens	2	61	0	3	0	33	2	0	1	8	33	53	3
Piney	0	56	0	16	0	28	0	0	56	18	24	1	0
Sandy	0	91	0	1	0	8	0	0	91	1	2	6	0
South Forge (SF)	0	45	0	12	0	42	0	0	45	13	39	2	0
SF1	0	73	0	22	0	5	0	0	73	22	5	0	0
SF12	0	16	0	6	0	79	0	0	16	6	79	0	0
Skeleton	0	22	0	17	0	61	0	0	22	17	57	5	0
Spring	1	59	0	8	0	33	0	0	59	9	32	1	0
Trib. to Marshy Hope	6	18	6	10	0	6	7	29	39	5	11	0	10
Tull	1	46	0	14	0	39	0	1	46	14	37	2	0

Table 2-7: Description of drainage type and parent material for soils found within the sampled watersheds.

Soil Series	Drainage Type	Parent Material
Askecksy	Poorly drained	Sandy alluvial and marine sediments
Berryland	Very poorly drained	Sandy eolian deposits and /or fluviomarine sediments
Carmichael	Poorly drained	Loamy eolian and/or fluviomarine sediments
Corsica	Very poorly drained	Loamy fluviomarine sediments
Downer	Well drained	Loamy fluviomarine deposits
Elkton	Poorly drained	Silty eolian material underlain by loamy alluvial or marine sediments
Fallsington	Poorly drained	Loamy fluviomarine sediments
Fort Mott	Well drained	Sandy eolian deposits and/or fluviomarine deposits
Galestown	Somewhat excessively drained	Sandy eolian deposits and/or fluviomarine sediments
Hambrook	Well drained	Stratified alluvial and marine sediments
Hammonton	Moderately well drained	Loamy fluviomarine sediments
Hurlock	Poorly drained	Stratified alluvial and marine sediments
Ingleside	Well drained	Stratified loamy alluvial and marine sediments
Kentuck	Very poorly drained	Silty eolian deposits underlain by loamy alluvial or marine sediments
Klej	Somewhat poorly drained	Sandy fluviomarine sediments
Lenni	Poorly drained	Clayey fluviomarine sediments
Matapeake	Well drained	Silty eolian sediments underlain by coarser fluvial or marine sediments
Mullica	Very poorly drained	Sandy and loamy siliceous fluviomarine sediments
Othello	Poorly drained	Silty eolian deposits and/or fluviomarine sediments
Pepperbox	Moderately well drained soils	Loamy fluviomarine sediments
Pone	Very poorly drained soils	Woody organic deposits overlying unconsolidated, stratified alluvial and marine sediments
Queponco	Well drained	Loamy fluvial and eolian deposits underlain by sandy and loamy fluviomarine deposits
Reybold	Well drained	Silty eolian deposits underlain by sandy and loamy fluvio-marine sediments
Rockawalkin	Moderately well drained	Sandy eolian deposits over fluviomarine deposits
Runclint	Excessively drained	Sandy eolian deposits and/or fluviomarine sediments
Sassafras	Well drained	Sandy marine and old alluvial sediments*
Whitemarsh	Poorly drained	Silty eolian deposits over fluviomarine sediments
Woodstown	Moderately well drained	Sandy marine and old alluvial sediments

Sources: USDA Soil Series Classification Database (USDA 2015); * Soil Survey: Wicomico County, MD (USDA 1970).

Table 2-8: Results of Spearman Rank and Pearson's Product Moment Correlation. P-values less than 0.05 are significant, and boxes in light grey represent moderate (r > 0.4) to strong correlation (r > 0.7). The asterisk (*) denotes use of Pearson's Product Moment Correlation for which data was either normal or normal when log transformed.

	% Hydric Soils	**% Agriculture**	**% Forest**	**% Developed**	**% Poultry**	**Population Density**
% Hydric Soils		-0.54 p < 0.001*	0.66 p < 0.001	-0.34 p = 0.015	0.06 p = 0.690	-0.08 p = 0.553
% Agriculture	-0.54 p < 0.001*		-0.97 p < 0.001	0.17 P = 0.227	0.02 p = 0.911	-0.18 p = 0.206
% Forest	0.66 p < 0.001	-0.97 p < 0.001		-0.32 p =0.020	0.0 p = 0.997	0.11 p = 0.431
% Developed	-0.34 p = 0.015	0.17 P = 0.227	-0.32 p =0.020		0.28 p = 0.048	0.39 p = 0.005
% Poultry	0.06 p = 0.690	0.02 p = 0.911	0.0 p = 0.997	0.28 p = 0.048		0.017 p = 0.224
Population Density	-0.08 p = 0.553	-0.18 p = 0.206	0.11 p = 0.431	0.39 p = 0.005	0.17 p = 0.224	

Table 2-9: Results of Spearman Rank and Pearson's Product Moment Correlation averaged by site. P-values less than 0.05 are significant, and boxes in light grey represent moderate (r > 0.4) to strong correlation (r > 0.7). The asterisk (*) denotes use of Pearson's Product Moment Correlation for which data was either normal or normal when log transformed.

	TN	NO_3	NH_4	TP	PO_4	DO	pH	Conductivity	Turbidity	TSS
% Hydric Soils	-0.58 p < 0.001*	-0.62 p < 0.001	-0.11 p = 0.432	0.51 p < 0.001*	0.44 p = 0.001*	-0.42 p = 0.002	-0.31 p = 0.025	-0.41 p = 0.003*	0.54 p < 0.001*	0.46 p < 0.001*
% Agriculture	0.76 p < 0.001*	0.77 p < 0.001	0.17 p = 0.216	-0.03 p = 0.832*	0.04 p = 0.799*	0.48 p < 0.001	0.40 p = 0.004	0.69 p < 0.001*	-0.28 p = 0.04*	-0.18 p = 0.213*
% Forest	-0.76 p < 0.001	-0.78 p < 0.001	-0.18 p = 0.206	0.10 p = 0.483	0.02 p = 0.917	-0.48 p < 0.001	-0.42 p = 0.002	-0.67 p < 0.001	0.34 p = 0.013	0.22 p = 0.120
% Developed	0.27 p = 0.050	0.25 p = 0.072	0.11 p = 0.455	-0.11 p = 0.455	-0.11 p = 0.440	0.31 p = 0.030	0.35 p = 0.011	0.26 p = 0.069	-0.04 p = 0.773	-0.05 p = 0.748
% Poultry	0.25 p = 0.075	0.22 p = 0.121	0.12 p = 0.404	-0.02 p = 0.893	0.01 p = 0.404	0.34 p = 0.014	0.25 p = 0.079	0.15 p = 0.299	-0.17 p = 0.225	-0.17 p = 0.242
Population Density	0.06 p = 0.685	0.10 p = 0.499	0.00 p = 0.432	-0.42 p = 0.002	-0.43 p = 0.002	0.20 p = 0.155	0.10 p = 0.494	-0.01 p = 0.922	0.08 p = 0.587	-0.10 p = 0.481
Stream Order	0.16 p = 0.267	0.20 p = 0.148	0.19 p = 0.182	-0.37 p = 0.007	-0.28 p = 0.045	0.60 p < 0.001	0.45 p < 0.001	0.08 p = 0.558	-0.20 p = 0.154	-0.38 p = 0.005

Table 2-10: Results of multiple linear regressions to predict nutrient concentrations in Delmarva streams using anthropogenic land use (A), anthropogenic land use plus the addition of hydric soils (B), and forest (C) in the surrounding watersheds. Anthropogenic land use was assumed to be zero, hydric soils 66% (the mean value), and forest 100% to determine corresponding total nitrogen (TN) and total phosphorus (TP) concentrations. ^non-significant relationship.

Equations	**adj. r^2**	**TN (mg L^{-1})**
A) $\log_{10}$ (TN) = -0.210 + (0.0124 * % Agriculture)	0.56	0.62
B) $\log_{10}$ (TN) = 0.207 + (0.0102 * % Agriculture) - (0.00454 * % Hydric Soils)	0.60	1.61
C) $\log_{10}$ (TN) = 0.932 - (0.0118 * % Forest)	0.57	0.56
	adj. r^2	**TP (mg L^{-1})**
A) $\log_{10}$ (TP) = -1.027 - (0.00391 * Population Density)	0.12	0.094
B) $\log_{10}$ (TP) = -2.165 - (0.00279 * Population Density) + (0.0114 * % Hydric Soils) + (0.00457 * % Agriculture) + (0.0221 * % Developed)	0.39	0.007
C) $\log_{10}$ (TP) = -1.105 + (0.000320 * % Forest)^	0.00	0.085

Table 2-11: Various scenarios using multiple linear regression (eq. 2-7 and 2-10) to predict total nitrogen (TN) and total phosphorus (TP) concentrations and variation with hydric soils. Eq. 2-6 was used for the agricultural scenario with no hydric soils.

Agriculture	**% Hydric Soils**	**TN (mg L^{-1})**		**% Hydric Soils**	**TP (mg L^{-1})**
0%	0	1.61	**No Development, No Agriculture, Zero Population**	0	0.007
	13	1.41		13	0.010
	66	0.81		66	0.039
	100	0.56		100	0.094
10%	0	0.82			
20%	0	1.09			
40%	0	1.93			
60%	0	3.42			

Table 2-12: Select criteria for water contact recreation and protection of non-tidal warm water aquatic life in Maryland's Class I waters (COMAR 26.08.02.03-3). In addition, Maryland also has numerous numeric criteria for toxic substances, such as metals and pesticides. While no criterion exists in COMAR for conductivity, MDE uses 300 µS cm^{-1} as a threshold. Also shown are EPA's water quality criteria recommendations for chlorophyll *a*, nitrogen, phosphorus, and turbidity for Eastern Coastal Plain non-tidal streams.

Stream Health Parameter	**Numeric Criteria / Recommended Values**
Dissolved Oxygen	5.0 mg L^{-1}
pH	6.5 to 8.5
Temperature	32°C, or ambient temperature of the surface water
Turbidity	150 NTU*, 50 NTU* monthly average, or levels detrimental to aquatic life
E. coli	126 per 100 mL
Conductivity+	300 µS cm^{-1}
Chlorophyll *a*^	3.75 µg L^{-1}
Nitrogen^	0.71 mg L^{-1}
Phosphorus^	0.031 mg L^{-1}
Turbidity^	3.04 FTU

* Turbidity resulting from a discharge.
+ There is no water quality criterion for conductivity in COMAR.
^ EPA-suggested criteria for the streams in the coastal plain.

Figures

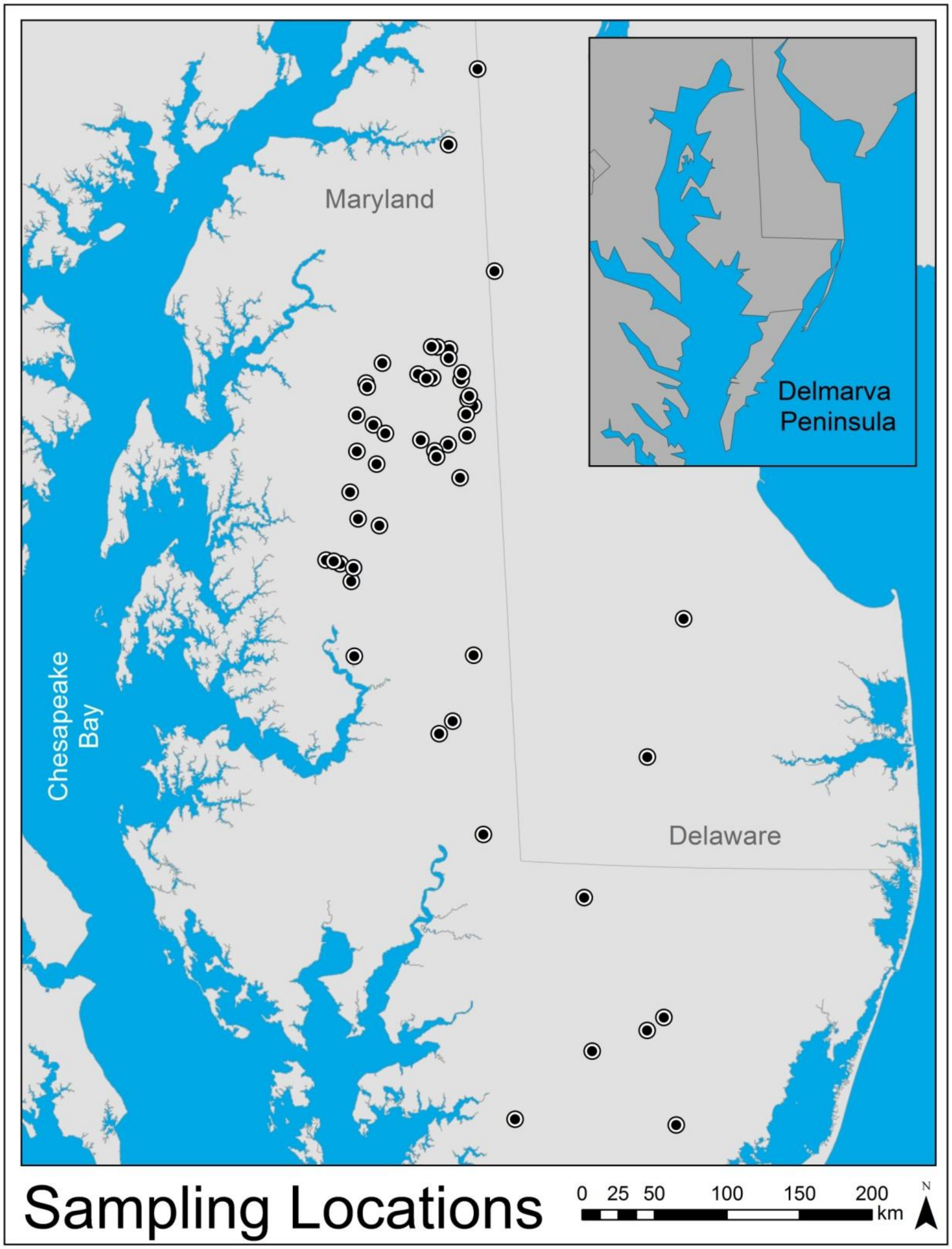


Figure 2-1: Location of 52 stream sampling sites on the Delmarva Peninsula, located between the Atlantic Ocean and the Chesapeake Bay. It is comprised of three states: Delaware, Maryland, and Virginia.

Discharge During Sampling at the Choptank River at Greensboro

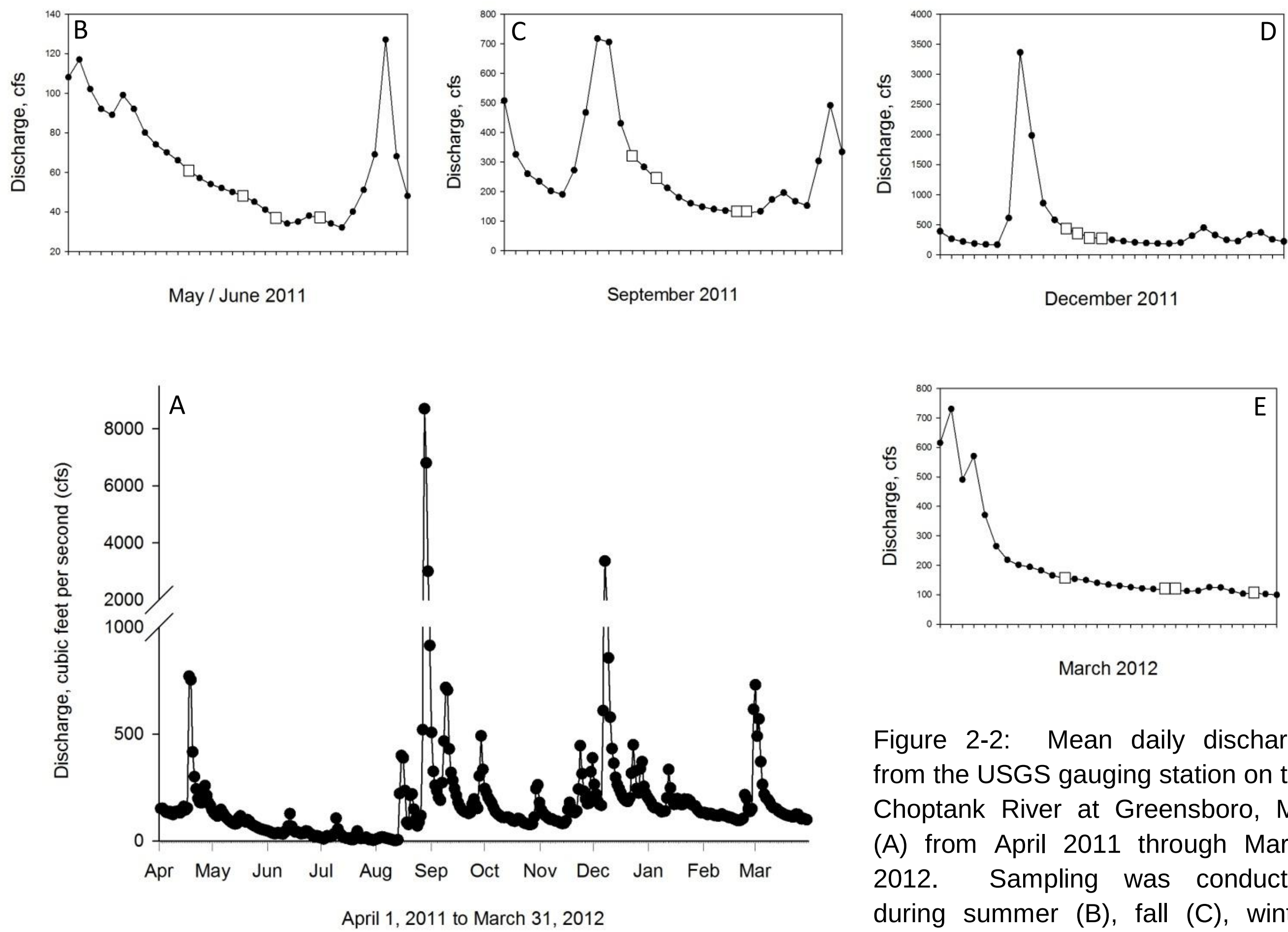
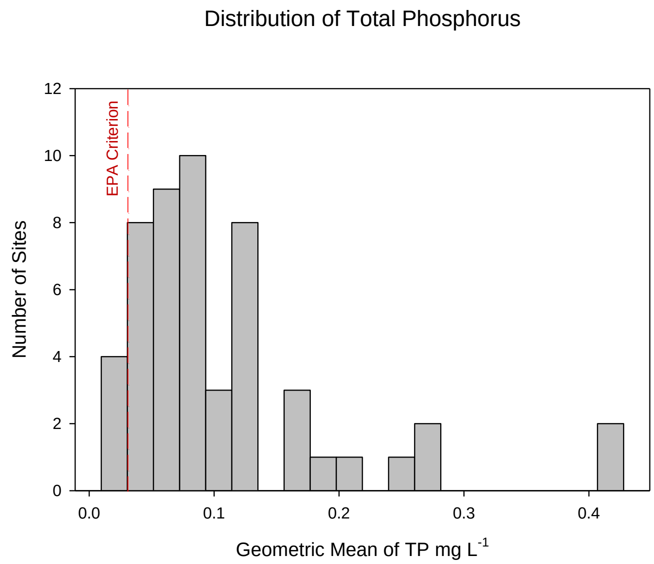


Figure 2-2: Mean daily discharge from the USGS gauging station on the Choptank River at Greensboro, MD (A) from April 2011 through March 2012. Sampling was conducted during summer (B), fall (C), winter (D), and spring (E). Most samples were taken during baseflow conditions over multiple days, shown by the squares in panels B-E.



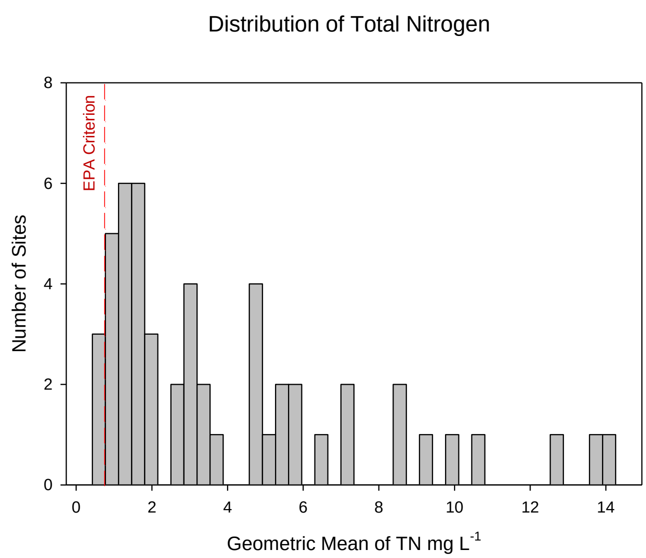


Figure 2-3: Frequency distributions of the geometric mean of total nitrogen (TN) and total phosphorus (TP). Most sites (> 90%) would not meet EPA-suggested criteria.

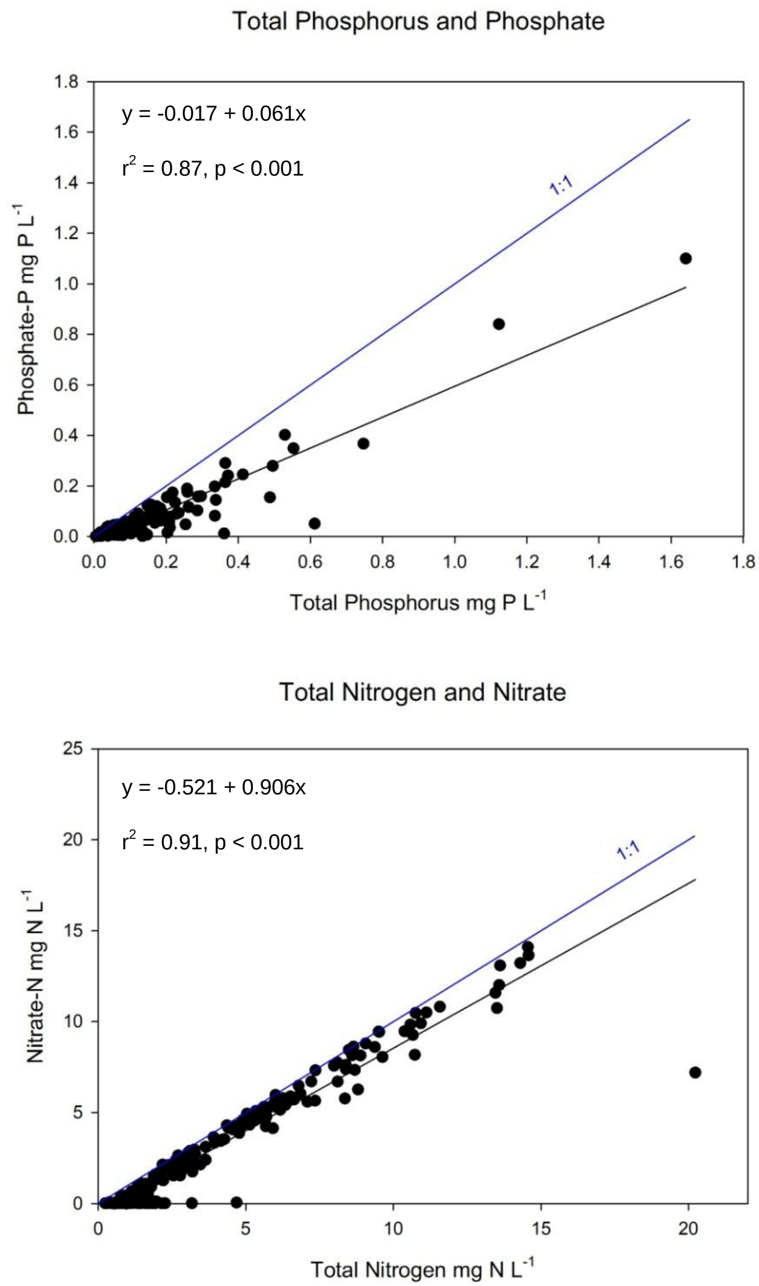


Figure 2-4: Comparison of total phosphorus (TP) and phosphate (PO_4) and total nitrogen (TN) and nitrate (NO_3).

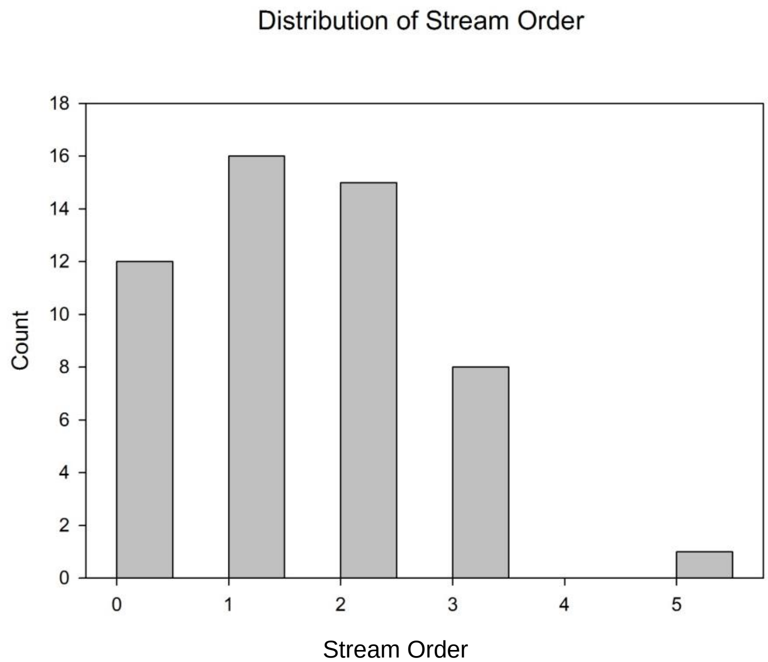


Figure 2-5: Distribution of stream order. A majority of streams sampled were small, zero order (with flowlines not mapped in NHD) to third order. The Choptank River at Greensboro, MD is a fifth order stream.

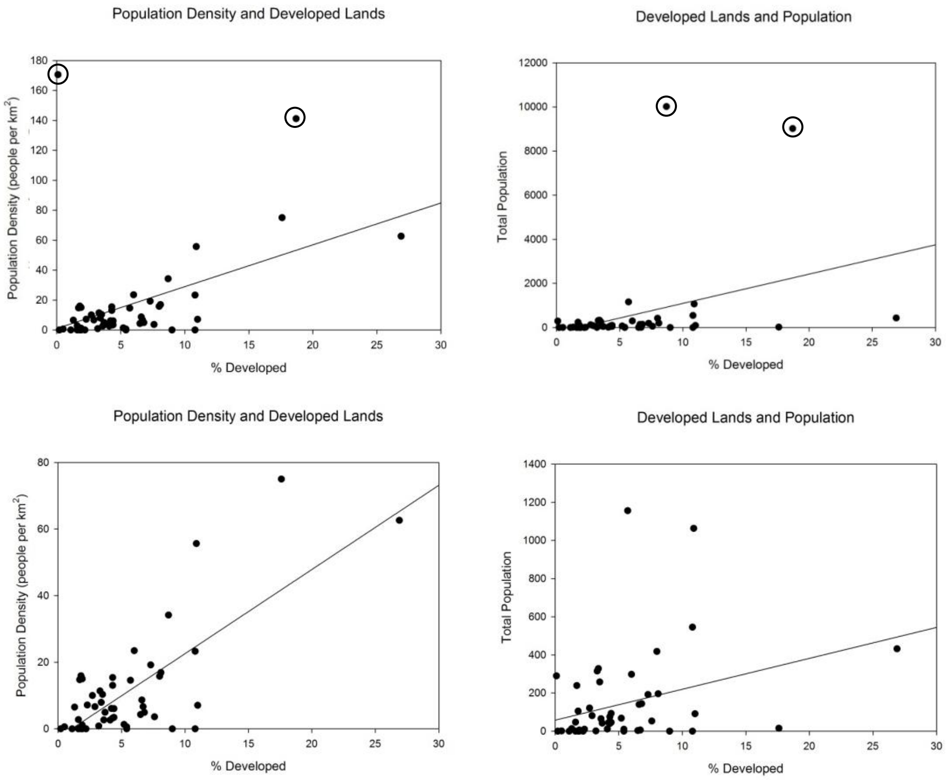


Figure 2-6: Estimated population density and the percentage of developed lands shown on the left. Outliers, unnamed Trib. to Marshy Hope and Leonard Pond Run, were removed from the bottom left figure. Population and the percentage of developed lands are shown in the graphics on the right. Leonard Pond Run (population 9,018) and Greensboro (population 10,018) were removed from the graphic on the bottom right.

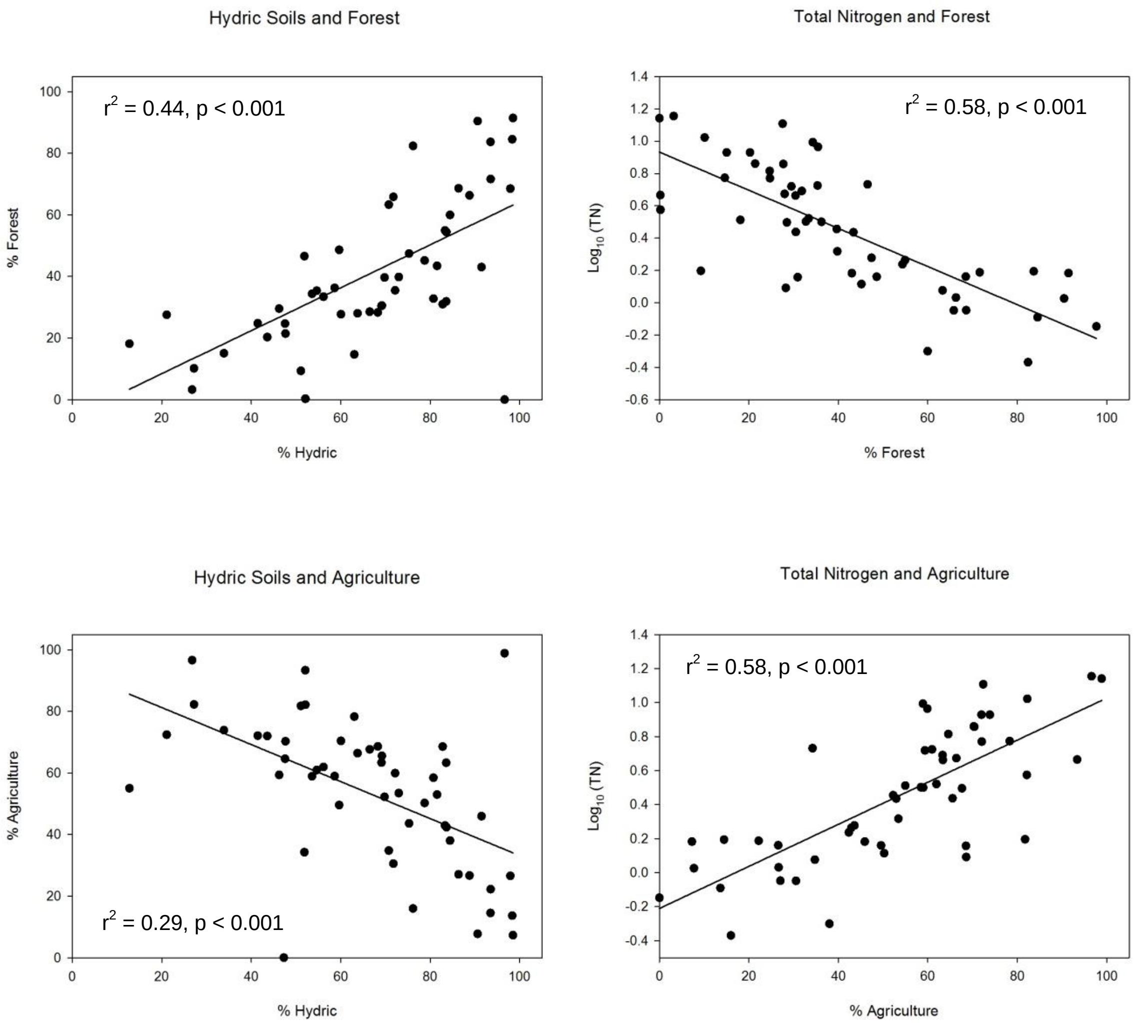


Figure 2-7: Land use was related to the presence of hydric soils within watersheds, as well as nutrient concentrations. Agriculture in watersheds decreased and forests increased as % Hydric Soils increased. Total nitrogen (TN) concentrations increased with percent agriculture in watersheds, while it decreased with increasing forest.

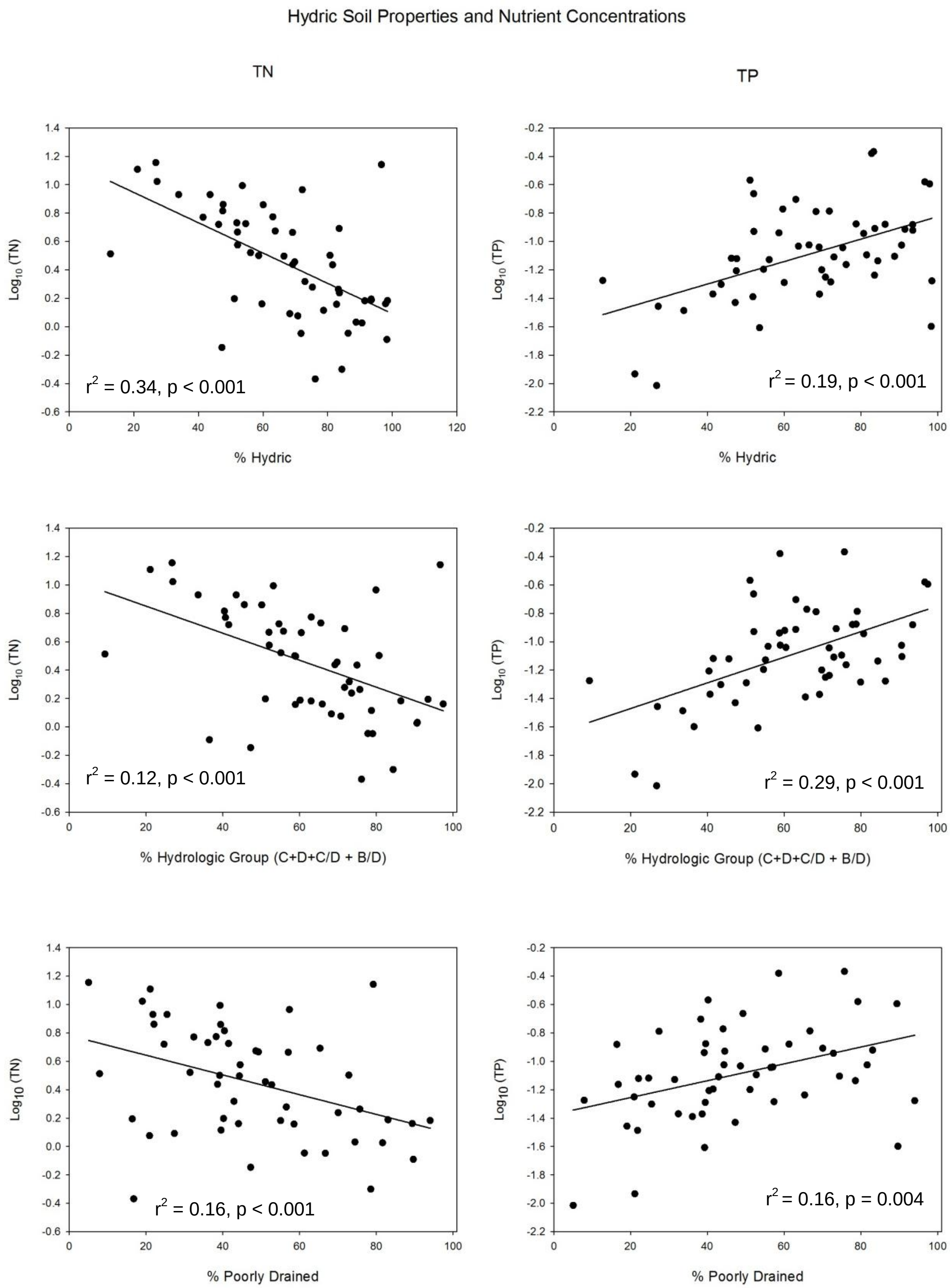


Figure 2.8: Relationship of hydric classification, hydrologic group, and drainage class with nutrient concentrations (total nitrogen [TN] and total phosphorus [TP]). Hydric soils are negatively correlated with TN but positively correlated with TP.

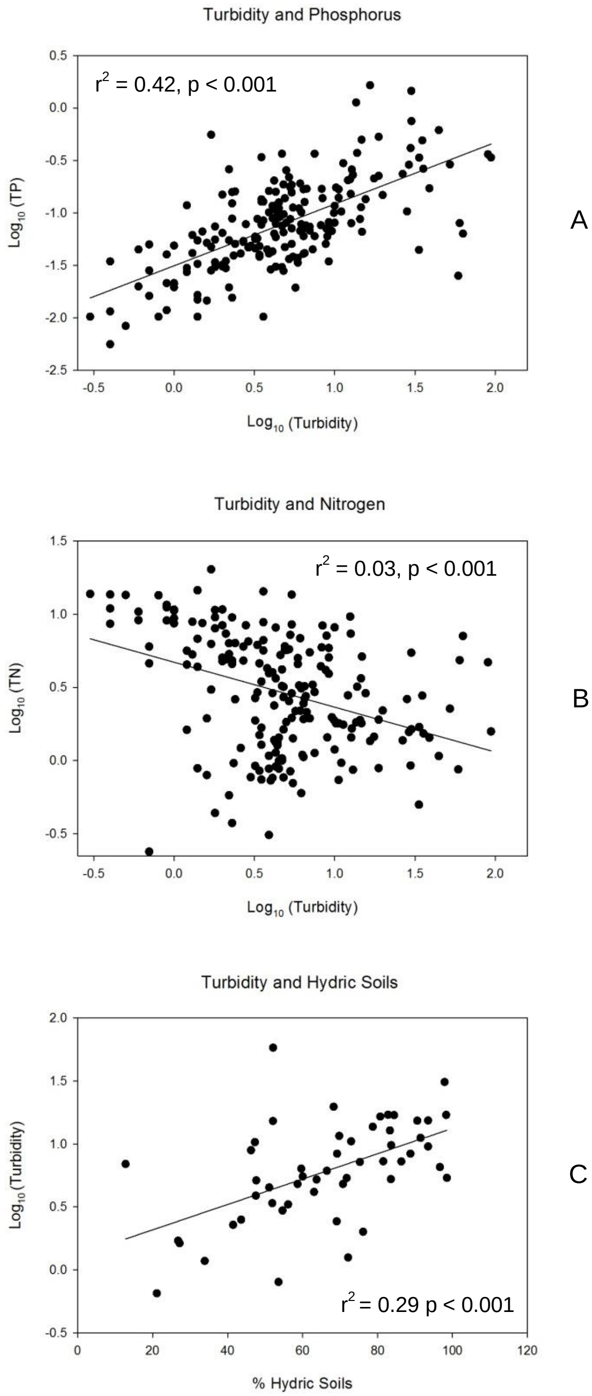
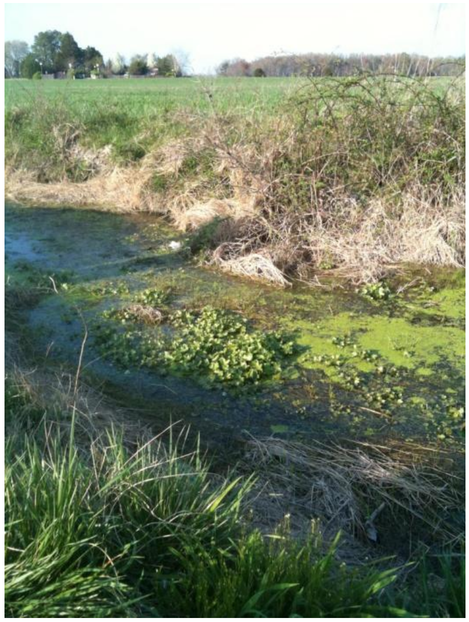
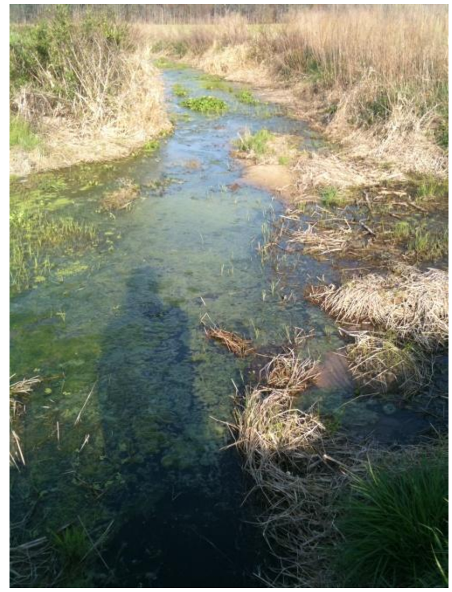


Figure 2-9: Nutrient concentrations are correlated with turbidity. Phosphorus has a positive correlation (A), while nitrogen a negative correlation (B). Stream turbidity was also correlated with % Hydric Soils in the watershed (C).



A



B

C

Figure 2-10: Site KT16 during sampling in March 2012. Filamentous algae and duckweed were present downstream (photos A and B). Upstream the stream flows through an agricultural field and through a culvert under the road (C); water also enters through a road side ditch adjacent to the road.

Chapter 3: Connecting Streams and Downstream Estuaries-- An Evaluation of the Ability of Freshwater Numeric Nutrient Criteria to Protect the Choptank River Estuary

Abstract

To determine if non-tidal numeric nutrient criteria for streams would be protective of the Choptank River Estuary, downstream protection values were derived using two approaches. The first approach used values consistent with the multi-state Chesapeake Bay Total Maximum Daily Load (TMDL). Results show that during 90% of water years, freshwater nutrient concentrations of 1.02 mg N L^{-1} and 0.11 mg P L^{-1} would meet annual TMDL goals. In addition, downstream protection values were derived using the fraction of freshwater method and a two-dimensional box model with a chlorophyll *a* endpoint of 15 µg L^{-1}, taking into account nutrient inputs from bay water and nutrient losses to sediments and intertidal wetlands. Downstream protection values for nitrogen calculated with the TMDL are in line with freshwater nutrient criteria suggested in the literature, but phosphorus is higher. Using a two-dimensional model, downstream protection values were higher than proposed by EPA but lower than those calculated using the TMDL (0.88 mg N L^{-1} and 0.081 mg P L^{-1}). These results suggests that if numeric nutrient criteria proposed by the EPA were adopted they would be more than adequate to protect the estuary; however, while TMDL loading goals may be protective of the estuary, they may not be stringent enough to protect freshwater streams. Further phosphorus reductions will most likely be necessary to meet any freshwater numeric nutrient criteria implemented on Delmarva.

Introduction

Numeric nutrient criteria for non-tidal streams have the potential to protect not only the streams themselves but also downstream water bodies such as lakes and estuaries. Nutrients from streams are transported downstream where they enter lacustrine, estuarine, and coastal systems, and when in excess levels, lead to algal blooms, hypoxia, and loss of aquatic life (e.g., Kemp et al. 2005, Diaz and Rosenberg 2008). In some instances the negative consequences of excess nutrients are not evident until the nutrients enter the downstream waters. With this in mind, viewing numeric nutrient criteria for streams and rivers in terms of downstream effects in the coastal zone is a holistic approach that can ensure that estuarine uses are protected.

It is important to assess the impacts that any proposed nutrient criteria for streams will have on downstream water quality because of the interactions between streams and estuaries (U.S. Environmental Protection Agency [EPA] 2000). The Clean Water Act (1972) states that when designating criteria the state "shall ensure that its water quality standards provide for the attainment and maintenance of the water quality standards of downstream waters." These downstream protection values, as EPA refers to them, are simply numeric water quality targets derived to ensure that downstream water quality and designated uses are protected.

Downstream protection values are especially relevant in the Chesapeake Bay region where a multi-state Total Maximum Daily Load (TMDL) has been developed to reduce nitrogen, phosphorus, and sediment loads. According to the Interstate Commission on the Potomac River Basin "it is important to anticipate both the impact of the Bay TMDLs on local water quality and the potential impact of the adoption of nutrient criteria on Bay TMDL implementation." Assessing both is valuable because the nutrient concentrations protective of the estuary may very well be different from those needed to protect streams due to water body characteristics, hydrology, and nutrient limitations. The Chesapeake Bay TMDL provides a basis for developing downstream protection values. As part of the TMDL process, nutrient loading allocations for sub-watersheds within the Chesapeake Bay watershed were developed (EPA 2010). Each state involved in the TMDL, will develop Watershed Implementation Plans in three phases to address local actions, how states will meet the loading reductions, and provide an assessment of progress.

To meet the goals of the Chesapeake Bay TMDL, significant nutrient reductions in streams will be necessary. For the state of Maryland, this equates to an overall reduction of 21% nitrogen and 18% phosphorus from the 2009 baseline load by the year 2025 (MDE 2010b). For the Choptank River Basin on Delmarva, the TMDL calls for a 22% nitrogen and 15% phosphorus reduction (EPA 2010). If freshwater numeric nutrient criteria adopted are consistent with these goals, it will help to ensure the health of downstream waters such as the Choptank River Estuary and Chesapeake Bay.

Downstream protection values are not a new concept. Several states have developed them, but they are often site specific. For example, a state may adopt a site specific downstream protection value for a stream that feeds a lake to ensure the water quality of the lake is protected. Perhaps one of the more well-known and recent examples is in

Florida where EPA promulgated numeric nutrient criteria that included downstream protection values for lakes as well as estuaries. These were later withdrawn, and instead of the EPA-promulgated values Florida's implementation plan for numeric nutrient standards addresses protection of downstream waters in more general terms: "[t]he loading of nutrients from a water body shall be limited as necessary to provide for the attainment and maintenance of water quality standards in downstream waters." Florida plans to implement this when developing TMDLs, issuing discharge permits, and evaluating trends during assessments (FL DEP 2013). While downstream protection values may not be formally adopted into state water quality standards, they can provide a goal to ensure downstream water quality is protected and act as a threshold to trigger management actions in specific watersheds.

To generate downstream protection values, EPA has identified a variety of techniques that can be employed (EPA 2014, EPA 2001). These include, but are not limited to:

- Establishing downstream protection values at strategic locations using water quality modeling applications.
- Using regression or other statistical methods to relate downstream pollutant concentrations to upstream pollutant concentrations and determine the upstream concentration protective of the downstream water quality standards.
- Using existing TMDLs on downstream waters to help determine what pollutant concentrations in upstream waters are expected to provide for the attainment and maintenance of downstream water quality standards.

In this chapter, I utilize the first and third methods suggested by EPA above using the Choptank River Estuary as a case study. First, downstream protection values for the Choptank River Estuary are derived that are consistent with the nitrogen and phosphorus loading goals of the multi-state Chesapeake Bay TMDL. Second, I examine whether upstream water quality criteria will be protective of a chlorophyll *a* value below 15 µg L^{-1} in the estuary using a modeling approach.

Hypotheses

The following hypotheses were tested to determine if EPA-suggested numeric nutrient criteria for freshwater coastal plain streams would be protective of estuarine water quality in the Choptank River Estuary:

i. Downstream protection values (freshwater nutrient concentrations necessary to protect downstream uses) for the estuary calculated using the TMDL for nitrogen and phosphorus will be higher than the suggested EPA freshwater numeric nutrient criteria (0.031 mg P L^{-1}, 0.71 mg N L^{-1}).

ii. Chlorophyll *a* values of less than 15 µg L^{-1} will be achieved at the chlorophyll maximum in the Choptank River Estuary if nutrient concentrations are less than suggested EPA numeric criteria (0.031 mg P L^{-1}, 0.71 mg N L^{-1}) in Choptank River Basin streams.

Study Area

The Choptank River, Figure 3-1, was chosen to examine the relationship of numeric nutrient criteria in streams and estuaries. The Choptank River is located on the Atlantic coastal plain of Maryland's eastern shore and is one of seven major tributaries that discharge into the Chesapeake Bay.

The 1756 km^2 watershed is rural and dominated by agriculture and forests (Fisher et al. 2006). The estuary is relatively shallow with a mean depth of 3.6 m and a length of 68 km (Fisher et al. 2006). The estuarine surface area is 280 km^2 (Lee et al. 2000), and the estuarine volume is 1,070 x 10^6 m^3 (Fisher et al. 2006). It is "comparatively well-mixed" (Ward and Twilley 1986) in fall and winter, experiencing seasonal stratification in spring and summer (Fisher 1988, Fisher et al. 2006). At monitoring station ET5.2 (Figure 3-1) stratification is common in the summer after rain events but further upstream the dissolved oxygen concentration in the lower and upper water columns are similar (Whitall et al. 2010). It is often well-mixed above the confluence with Warwick Creek (Berndt 1999).

The Choptank River Estuary and several of the basin's rivers have been placed on Maryland's 303d list of impaired waters, and the estuary is part of the Chesapeake Bay TMDL. The estuary experiences high chlorophyll *a* in surface waters and low dissolved oxygen in bottom waters associated with anthropogenic inputs of excess nitrogen and phosphorus from the watershed (Fisher et al. 2006, 2010). Lee et al. (2001) estimated nitrogen and phosphorus inputs to the estuary as 2.49 x 10^6 kg N yr^{-1} and 0.057 x 10^6 kg

P yr^{-1}. According to the Chesapeake Bay TMDL, the existing loading in 2009 was 1.49 x 10^6 kg N yr^{-1} and 0.152 kg P yr^{-1}. The EPA-estimated load for nitrogen is nearly half the load estimated by Lee et al. (2001), while the phosphorus load is double, Table 3-1. Variations in the loading rates calculated may be in part to the inclusion of stormwater samples in modeling for the Chesapeake Bay TMDL. As part of the Chesapeake Bay watershed monitoring network, samples are collected under a range of flow conditions, including stormflow (EPA 2010). This could account for the higher phosphorus load calculated by EPA.

The Chesapeake Bay TMDL sets forth loading goals for the year 2025 (Table 3-2). For nitrogen the loading goal is 1.17 x 10^6 kg N yr^{-1} (nonpoint and point), a nitrogen reduction of 22% based on EPA estimates. Using the loading values derived by Lee et al. (2001) a greater reduction (53%) would be necessary. For phosphorus the loading goal is 0.13 x 10^6 kg P yr^{-1} (nonpoint and point) and a 15% reduction necessary using EPA estimates.

The chlorophyll maximum in the Choptank River Estuary is near the Chesapeake Bay Program monitoring station ET5.2. The chlorophyll maximum occurs in shallow waters (5 to 15 m) that are weakly stratified (Berndt 1999), and annual average chlorophyll *a* concentrations range from 15 to 20 µg L^{-1} (Fisher et al. 2006, 2010). The production of phytoplankton biomass in the Choptank River Estuary is mostly nitrogen limited; however, the estuary can experience phosphorus limitation under high flow conditions (Fisher et al. 2006).

Harding et al. (2014) analyzed 20 years of Chesapeake Bay data to identify a suggested numerical chlorophyll *a* goal of 14.2 μg L^{-1} (annual geometric mean) for the Choptank River Estuary and a compliance limit of 20.1 μg L^{-1}. This compliance limit was calculated using the corresponding 90th percentile threshold of data from the 1960s and 1970s, and the authors note that it should rarely be exceeded. Based on Harding et al.'s analyses, a decline in oxygen to 3.0 to 5.0 mg L^{-1} is observed when chlorophyll *a* in the Choptank River Estuary is greater than 15 μg L^{-1}; however, oxygen did not decline below 3.0 mg L^{-1} even when the annual mean chlorophyll *a* was greater than 20 μg L^{-1}. The associated water quality criterion for dissolved oxygen in the Choptank River Estuary is 5.0 mg L^{-1}, supporting the need for a chlorophyll *a* criterion near 15 μg L^{-1}. Additional research also supports that this range would be protective of water quality. For instance, SAV regrowth has been associated with mean chlorophyll *a* values of less than 15 μg L^{-1} in the Choptank River Estuary (Stevenson et al. 1993), and 15 μg L^{-1} is the recommended habitat requirement for the mesohaline portions of the Chesapeake Bay (Batiuk et al. 2000). Here, 15 μg L^{-1} is used as an end point protective of estuarine water quality.

Methods

I utilized two endpoints, or goals, to determine if the EPA-suggested non-tidal nutrient criteria would be protective of downstream designated uses and to derive downstream protection values: (1) the Chesapeake Bay TMDL for the Choptank River Basin and (2) a 15 μg L^{-1} chlorophyll *a* concentration at the chlorophyll maximum of the Choptank

River Estuary. Once downstream protection values using these endpoints were identified, the values were compared to EPA-suggested numeric nutrient criteria.

Approach 1: Assessing TMDL Scenarios

The average stream nutrient concentration (C, g m^{-3} = mg L^{-1}) was determined using the annual TMDL goal (W, kg yr^{-1}, Table 3-2) and total annual discharge (Q, m^3 yr^{-1}) for the entire Choptank River Basin, eq. 3-1, 3-2.

$$C = W / Q \qquad \text{(eq. 3-1)}$$

$$Q = WY_{Greensboro} * A \qquad \text{(eq. 3-2)}$$

where $WY_{Greensboro}$ is the annual water yield for the Choptank River at the USGS Greensboro, MD gauging station (m y^{-1}) and A is the total watershed area (m^2). This assumes uniform hydrology throughout the basin using the gauged area as a reference station (Figure 3-1).

The loading goals for the Choptank River Basin (Table 3-2) were determined by combining the nonpoint (load allocation) and point source (waste load allocation) goals for Choptank River segments in Maryland and Delaware from the Chesapeake Bay TMDL: Choptank Mesohaline Mouth 1, Choptank Mesohaline 2, Choptank River Oligohaline, and Upper Choptank River Tidal Fresh (EPA 2010). The delivered loads for nitrogen and phosphorus were used instead of edge of stream values, as the delivered loads represent the loading that actually reaches the tidal waters. Atmospheric deposition on land was included within the total load estimate from each watershed, and EPA identified direct deposition to tidal waters as a separate estuarine input. The average stream flow per unit area or water yield ($m^3\ y^{-1}\ m^{-2} = m\ yr^{-1}$) for the Choptank River at the USGS gauging station at Greensboro, MD was determined using discharge records from 1949 to 2010 (USGS, Figure 3-2). This was extrapolated by area to the entire basin to estimate the average annual amount of freshwater flow entering the estuary (eq. 3-2).

To evaluate the impacts of wet and dry years, the minimum, 10th percentile, average, 90th percentile, and maximum annual water yields (1949 to 2010) for the watershed of the Choptank River above Greensboro, MD and corresponding discharge for the Choptank River Basin were calculated. Downstream protection values consistent with the nitrogen and phosphorus loading goals of the Chesapeake Bay TMDL were then determined using eq. 3-1. This approach assumes constant annual export of nitrogen and phosphorus and no net storage during dry years or net loss during wet years.

In addition, the total annual discharge values as determined by eq. 3.2 were used to estimate the nutrient loads using eq. 3-1 if the nutrient concentrations in streams were 0.031 mg P L^{-1} and 0.71 mg N L^{-1}, the EPA-suggested freshwater numeric nutrient criteria.

Approach 2: Modeling

The second approach used a chlorophyll *a* goal of 15 µg L^{-1} near the chlorophyll maximum (site ET5.2) in the Choptank River Estuary to derive downstream protection values. Both a two-dimensional box model and a more simplified fraction of freshwater method were used to account for nutrient removal due to burial and denitrification of freshwater inputs as well as nutrient inputs from Chesapeake Bay waters.

Determining Estuarine Nutrient Concentrations

The first step was to determine the estuarine nutrient concentrations equivalent to 15 µg L^{-1}, the chlorophyll *a* value assumed to be protective of the Choptank River Estuary. To do this, ratios of nutrients to chlorophyll *a* (elemental stoichiometry) were determined from the scientific literature. According to Parsons et al. (1984), the ratios are: 30 µg of carbon to 1 µg chl *a*, 6 µg of carbon to 1 µg nitrogen, and 40 µg of carbon to 1 µg phosphorus. These ratios are similar to those observed by Fisher et al. (1999) in the Choptank River Estuary. Dividing the ratio of carbon to chlorophyll *a* by the ratio of carbon to nutrients provides the ratio of nutrients to chlorophyll *a*. The ratios of nutrients to chlorophyll *a* in phytoplankton are calculated to be 5.0 µg N per µg chl *a* and 0.75 µg P per µg chl *a*. For the purposes of this approach, nutrient concentrations needed to protect the estuary were based on the amount equivalent to 15 µg L^{-1} chlorophyll *a*. These values (0.075 mg N L^{-1} and 0.011 mg P L^{-1}) were determined by taking the ratio of nutrients to chlorophyll *a* and multiplying it by the chlorophyll *a* goal of 15 µg L^{-1}, and were assumed to be protective of estuarine water quality.

Fraction of Freshwater - A one-dimensional model

The fraction of freshwater method (Mills et al. 1985) was used to determine the fraction of freshwater water at site ET5.2 using eq. 3-3 (below). The waters of the Choptank River Estuary at site ET5.2 are comprised of freshwater entering from the river basin and tidal, estuarine waters from the Chesapeake Bay. As salt is conservative, it can be used to estimate the fraction of freshwater at a given site (Hagy 2002). Salinity data for sites ET5.2 (S_e) and EE2.1 (S_B) were retrieved from the Chesapeake Bay Program Water Quality Database (2005 – 2014), http://www.chesapeakebay.net/data_ waterquality.aspx. The average salinity value for all depths from 2005 to 2014 was used to calculate the fraction of freshwater (f_e), eq. 3-3.

$$f_e = \frac{S_B - S_e}{S_B} \quad \text{(eq. 3-3)}$$

where f_e = the fraction of freshwater in the Choptank River Estuary at location ET5.2, S_B = salinity of bottom water in the lower Choptank River Estuary at site EE2.1, and S_e = salinity at location ET5.2. Likewise the fraction of bay water at ET5.2 may be expressed as

$$1 - f_e = \frac{S_e}{S_B} \quad \text{(eq. 3-4)}$$

The total nutrient concentration at the estuarine station is directly proportional to the fraction of freshwater and bay water at ET5.2 (Mills et al. 1985).

$$c_e = f_e * c_r + (1 - f_e) * c_B \quad \text{(eq. 3-5)}$$

where c_e = the concentration of nutrients in the Choptank River Estuary at site ET5.2, f_e = the fraction of freshwater in the Choptank River Estuary at location ET5.2, c_r = concentration of nutrients in the river flow, and c_B = concentration of nutrients in downstream bottom water moving towards ET5.2.

The fraction of biologically available nitrogen and phosphorus in Chesapeake Bay water entering the Choptank River Estuary is not negligible. While there is a net export of nitrogen and phosphorus from surface waters of the Choptank River Estuary to the Chesapeake Bay, there is also a net import of phosphorus from the Chesapeake Bay to bottom waters of the Choptank River Estuary (Boynton et al. 1995). To account for the available nitrogen and phosphorus from the bay water, dissolved inorganic nitrogen (DIN) and phosphate (PO_4) at station EE2.1 were used (Fig. 3-1). These data were downloaded from the Chesapeake Bay Program Water Quality Database, http://www.chesapeakebay.net/data_waterquality.aspx, for the time span of 2005 to 2014. The average DIN and PO_4 for the bottom waters were calculated, as this is the water that would be moving up the estuary with the net non-tidal flow. From these data, the nutrient concentration at ET5.2 from waters at EE2.1, the lower Choptank River Estuary, was determined using equation 3-6.

$$c_e = c_B * \frac{S_e}{S_B} + c_r * \frac{S_B - S_e}{S_B} \qquad \text{(eq. 3-6)}$$

Solving for c_r:

$$c_r = \frac{[(c_e * S_B) - (c_B * S_e)]}{S_B - S_e} \qquad \text{(eq. 3.7)}$$

Also, nutrients are not conservative and undergo a variety of transformations. Nitrogen and phosphorus are buried in subtidal sediments and intertidal wetlands, and nitrate is reduced to N_2 gas through denitrification (Figure 3-3). In the Choptank River these processes account for a high percentage of removal (Boynton et al. 1995, Fisher et al. 2006). As nutrient removal is often a function of the quantity of nutrient present, the percentage removal was calculated. Using the mass balance estimates by Boynton et al. (1995) and loading input calculated by Lee et al. (2001), Fisher et al. (2006) estimated that 84% of the nitrogen load is removed by denitrification and burial in the sediments of the Choptank River Estuary. While the denitrification and depositional rates per unit area are greater for the upper Choptank River Estuary, the large bottom area of the lower Choptank River Estuary represents a greater sink. Calculations of phosphorus removal by Boynton et al. (1995) exceed 100%, potentially because of a net input of phosphorus from the bay. Instead, I used values of phosphorus removal from the Patuxent River. Using a box modeling approach, Hagy et al. (2000) identified the net efflux of phosphorus for the Patuxent River, which Fisher et al. (2006) states is about 36% of the annual phosphorus input for the basin. The remaining phosphorus is buried or transformed through biological processes not considered here. Therefore, 64% was used to represent the amount of phosphorus removed in the Choptank River, and I used the 84% figure derived above for the amount of nitrogen removed.

For comparison with the TMDL, the nitrogen and phosphorus loadings (W) were also calculated, eq. 3-8, using the nutrient endpoints for nitrogen and phosphorus concentrations at site ET5.2 calculated above and estimated freshwater inflow (eq. 3-2).

$$W = \frac{Q * c_e}{f_e} \qquad \text{(eq. 3-8)}$$

where W = loading (g yr^{-1}), Q = freshwater inflow (m^3 yr^{-1}, eq. 3-2), c_e = concentration of nutrients (0.075 g N m^{-3} or 0.011 g P m^{-3}) at site ET5.2 corresponding with chlorophyll *a* of 15 µg L^{-1}, and f_e = the fraction of freshwater at location ET5.2 (eq. 3-3).

A Two-Dimensional Box Model

In order to obtain a better estimate of downstream protection values for the Choptank River Estuary, a two-dimensional box model was also developed. For this, the Choptank River Estuary was divided into two sections, or boxes: the upper oligohaline estuary (EE5.1, Box 1) and middle mesohaline estuary (ET5.2, Box 2), Figure 3-4. The lower mesohaline estuary (EE2.1) below the pycnocline was considered the downstream boundary and to be representative of water entering from the Chesapeake Bay. The middle estuary was further subdivided into an upper and lower box at the average pycnocline depth. Each box was assumed to be well-mixed.

Salt and Water Balance

The advective and non-advective exchanges between the boxes can be estimated by solving a series of linear equations describing the salt and water balance, assuming steady state (Hagy et al. 2000). To determine the freshwater inflow, average annual discharge data from two USGS gauging stations (Figure 3-4) was used: the Choptank River at Greensboro, MD (01491000) and Tuckahoe Creek near Ruthsburg, MD (01491500) for the time period of 2005 to 2014. Water inputs from the ungauged areas were estimated by using the average water yield per area of the two gauged watersheds and multiplying by the ungauged basin area (eq. 3-2). Together, with rainfall and evapotranspiration onto the estuarine surface, this is the total freshwater input entering each box, eq. 3-9 (below).

Estimates of rainfall (112 cm yr^{-1}) and evapotranspiration (62 cm yr^{-1}) in the Choptank River Basin from water year 1980 to 1996 were taken from Lee et al. (2001). For each box:

$$Q_{fw\,i} = Q_{r\,i} + (P - E) * A_i \qquad \text{(eq. 3-9)}$$

where $Q_{fw\,i}$ is the total freshwater inflow for box *i*, $Q_{r\,i}$ is the river flow entering box *i*, P is precipitation onto the estuarine surface, E evapotranspiration from the estuarine surface, and A_i is the estuarine surface area of box *i*.

The equations describing the water balance in Fig. 3-4 are:

$$Q_1 = Q_{fw1} \qquad \text{(eq. 3-10)}$$

$$Q_2 = Q_{fw2} + Q_1 + Q_{v2} \qquad \text{(eq. 3-11)}$$

$$Q_{v2} = Q'_B \qquad \text{(eq. 3-12)}$$

$$Q'_B = Q_2 - (Q_{fw1} + Q_{fw2}) \qquad \text{(eq. 3-13)}$$

where Q_{fw1} is the freshwater input into Box 1, Q_{fw2} is the freshwater input into Box 2, Q_1 = advective transport from upstream into Box 2, Q_2 = advective transport down-estuary, Q_{v2} = vertical advective transport into the box, and Q'_B = advective transport from downstream.

Salinity data for sites ET5.1, ET5.2, and EE2.1 was retrieved from Chesapeake Bay Program Water Quality Database (2005 – 2014), http://www.chesapeakebay.net/data_waterquality.aspx, to determine the average salinity of each box.

The equations describing the salt balance are:

$$E_{1,2} = (Q_1 * S_1)/(S_2\text{-}S_1) \qquad \text{(eq. 3-14)}$$

$$E_{v2} = (Q_2S_2 - Q_1S_1 - Q_{v2}S'_2)/(S'_2\text{-}S_2) \qquad \text{(eq. 3-15)}$$

where E_{v2} = vertical non-advective exchange, $E_{1,2}$ = non-advective exchange between Boxes 1 and 2, S_1 is the salinity in Box 1, S_2 is the salinity in upper Box 2A, S'_2 is the salinity in bottom Box 2B, and S'_B is the salinity at the boundary, EE2.1 (see Figure 3-4).

<u>Nutrient Concentrations</u>

A series of equations was developed to determine the nutrient concentration in freshwater (c_{fw}) if Box 2 nutrient concentrations were consistent with those assumed to keep chlorophyll *a* less than 15 µg L^{-1} at site ET5.2, taking into account nutrient losses from denitrification (k_d) and burial (k_b), nutrient input from bay water (c'_B), and atmospheric deposition directly onto the estuarine surface (W_a). The equations used to determine the freshwater nutrients concentrations protective of estuarine water quality, or downstream protection values, are as follows:

$$c_1 = \frac{Q_{fw1}c_{fw} + W_{a1} - E_{1,2}(c_2 - c_1) - (k_{d1} + k_{b1})}{Q_1} \qquad \text{(eq. 3-16)}$$

$$c_2 = \frac{Q_1C_1 + E_{1,2}(C_2 - C_1) + Q_{fw2}c_{fw} + W_{a2} + Q_{v2}c'_2 + E_{v2}(c'_2 - c_2)}{Q_2} \quad \text{(eq. 3-17)}$$

$$c'_2 = \frac{Q'_B c'_B - E_{v2}(c'_2 - c_2) - (k_{d2} + k_{b2})}{Q_{v2}} \quad \text{(eq. 3-18)}$$

where Q_{fw1} = freshwater input into Box 1, Q_{fw2} = freshwater input into Box 2, Q_1 = advective transport from upstream into Box 2, $E_{1,2}$ = non-advective exchange between Boxes 1 and 2, Q_2 = advective transport down-estuary, Q_{v2} = vertical advective transport into the box, E_{v2} = vertical non-advective exchange, Q'_B = advective transport from downstream, k_d is denitrification, k_b is nutrient burial, and W_a = atmospheric deposition onto the estuarine surface of each box (see Figure 3-4).

Losses of nitrogen and phosphorus in the estuary, including denitrification and burial in subtidal sediments and tidal wetlands, were estimated using removal rates (denitrification and burial) from the scientific literature shown in Table 3-3. Nitrogen and phosphorus burial rates from Boynton et al. (1995) were multiplied by the bottom area, excluding the wetland area, of each bottom box to determine burial in the sediments. The median value of 6.8 g N m^{-2} yr^{-1} was used for denitrification. Intertidal and tidal wetland area for the Choptank River Estuary was calculated from the GIS data layer for the National Wetland Inventory (http://www.fws.gov/wetlands/ Data/Mapper.html) and multiplied by burial rates in wetlands (22.0 g N m^{-2} yr^{-1} and 2.0 g P yr^{-1}, respectively).

Atmospheric deposition rates from Lee et al. (2001) of 5.5 kg N ha^{-1} yr^{-1} and 0.027 kg P ha^{-1} y^{-1}, respectively, were used. These were multiplied by estuarine surface area of each upper box to determine total nutrient input from atmospheric deposition. Nutrient loading from bay water was also determined by multiplying the flow calculated through the salt and water balance above (Q'_B) by the nutrient concentrations DIN and PO_4 (c'_B) below the pycnocline at EE2.1.

Results

Approach 1: Assessing TMDL Scenarios

The Chesapeake Bay TMDL sets the 2025 loading goals for the Choptank River Basin at 1.17×10^6 kg N yr^{-1} and 0.13×10^5 kg P yr^{-1} (Table 3-2). The total land area in the Choptank River Basin is 1756 km^2. Water yield for the Choptank River at the USGS gauging station at Greensboro, MD is shown in Figure 3-2, and the estimated average water yield for the basin is 0.427 m yr^{-1} for 1949 to 2014. The year on record with the lowest flow is 1966 with an estimated water yield of 0.081 m yr^{-1} and the maximum yield is 0.931 m yr^{-1} in 2003. The 10^{th} percentile is 0.215 m yr^{-1}, and the 90^{th} percentile is 0.655 m yr^{-1}, Table 3-4.

The downstream protection values needed to meet the annual TMDL goals during 90% of hydrologic years are 1.02 mg N L^{-1} and 0.11 mg P L^{-1} (Table 3-4). During a low flow year such as 1966, the maximum concentrations allowed to meet the TMDL are much higher, 8.24 mg N L^{-1} and 0.92 mg P L^{-1}. During a high flow year, such as 2003, lower nutrient concentrations are needed to meet TMDL goals, 0.72 mg N L^{-1} and 0.08 mg P L^{-1}. These calculations all assume no relationship between loading and discharge.

Using the suggested numeric nutrient criteria for freshwater streams recommended by EPA (2000a), 0.031 mg P L^{-1} and 0.71 mg N L^{-1}, nutrient loading was also determined using the calculated discharge. These results (Table 3-5) show that even during the year with the greatest water yield on record loading rates (1.16 x 10^6 kg N yr^{-1} and 0.036 x 10^6 kg P yr^{-1}) would be less than TMDL goals if streams in the Choptank River Basin met the numeric nutrient criteria suggested by EPA.

<u>Approach 2: Modeling</u>

The concentrations of 0.075 mg N L^{-1} and 0.011 mg P L^{-1} were determined to be the equivalent of 15 µg L^{-1} chlorophyll *a* and are assumed to be protective of the Choptank River Estuary. Results of the modeling approaches are shown in Table 3-8.

Fraction of Freshwater - A one-dimensional model

The average salinity at site ET5.2 (S_e) for a ten-year period was 10.2 and for the lower Choptank River Estuary, site EE2.1 (S_B), 12.4. Using eq. 3-3, the fraction of freshwater at site ET5.2 (f_e) was 0.18. Using the endpoints of 0.075 mg N L^{-1} and 0.011 mg P L^{-1}, this yields a corresponding upstream concentration of 0.42 mg N L^{-1} and 0.062 mg P L^{-1}. The corresponding loading (taking into account various water yields) ranges from 0.05 to 0.6 x 10^6 kg N yr^{-1} and 0.007 to 0.09 x 10^6 kg P yr^{-1} (Table 3-6) without accounting for nutrient removal or input from the lower estuary. Assuming 84% of nitrogen is removed and 64% of the phosphorus is removed, downstream protection values for non-tidal Choptank freshwaters would be 2.6 mg N L^{-1} and 0.17 mg P L^{-1}. Additional removal rates were calculated using loading estimates from Lee et al. (2000) for the area above ET5.2 and methods used by Boynton et al. (1995). This resulted in removal rates of 41%

nitrogen and greater than 100% phosphorus inputs from freshwater. Using these removal rates the downstream protection value for nitrogen would be 0.72 mg N L^{-1}, which is close to the EPA-suggested criterion and that calculated during the high flow year in Approach 1. As the removal rate for phosphorus is greater than 100%, it was not calculated. It is important to note that these removal values have a high degree of error associated with them.

Because of the potential for inputs from the lower Choptank River Estuary via the Chesapeake Bay, the nutrient concentration of the bottom waters at EE2.1 were used to determine the nutrient concentrations at site ET5.2 from the lower estuary. The average DIN and PO_4 of bottom waters were 0.14 mg N L^{-1} and 0.0047 mg P L^{-1}, respectively. Accounting for nutrient entering site ET5.2 from down estuary, the nutrient concentration necessary to protect water quality of the Choptank River Estuary are lower. Taking the input of nutrients from the lower estuary and removal rates (84% nitrogen and 64% phosphorus), the corresponding downstream protection value for phosphorus is 0.11 mg P L^{-1}. However, concentration of DIN from the lower bay is greater than the nitrogen endpoint, 0.075 mg N L^{-1}. Accounting for the inputs of bay water the ranges are higher, with phosphorus exceeding suggested TMDL loadings during the highest year on record, Table 3-7. To calculate these loadings, the area of the non-tidal portion of the basin upstream of site ET5.2 was used to determine flow, 1528 km^2, instead of the whole basin area.

A Two-dimensional Box Model

Results of the two-dimensional box model are shown in Figure 3-5 and Figure 3-6. The average annual discharge at the USGS gauging station on the Choptank River at Greensboro, MD is 144 x 10^6 m^3 yr^{-1} and for Tuckahoe Creek near Ruthsburg it is 98 x 10^6 m^3 yr^{-1}. The corresponding average annual water yields are 49.2 and 44.6 cm yr^{-1}, respectively. Extrapolating the average to the remaining basin area above ET5.2 while also accounting for evapotranspiration and precipitation (eq. 3-9) provided the freshwater inflow to Box 1 (Q_{fw1} = 644 x 10^6 m^3 yr^{-1}) and to Box 2 (Q_{fw2} = 141 x 10^6 m^3 yr^{-1}). Using the salt and water balance equations, eq. 3-10 to 3-15, the inflow from the lower Choptank River Estuary (Q'_B) was calculated to be 2,301 x 10^6 m^3 yr^{-1}. The non-advective exchange between the top and bottom of Box 2 is 4,836 x 10^6 m^3 yr^{-1} and between Box 1 and Box 2, 44.0 x 10^6 m^3 yr^{-1}.

The majority of the water (75%) entering ET5.2 is from the Chesapeake Bay, Figure 3-6. Corresponding loading entering ET5.2 from freshwater is 0.59 x 10^6 kg N yr^{-1} and 0.045 x 10^6 kg P yr^{-1}, Figure 3-6, with dilution from Chesapeake Bay water occurring. Current estimates of loading, including point, nonpoint, and atmospheric depositions, from hydrochemical modeling by Lee et al. (2001) were 1.70 x 10^6 kg N yr^{-1} and 0.032 x 10^6 kg P yr^{-1} for Box 1 and 0.41 x 10^6 kg N yr^{-1} and 0.02 x 10^6 kg P yr^{-1} for Box 2. Removal through denitrification and burial were: 0.15 x 10^6 kg N yr^{-1} and 0.019 x10^6 kg P yr^{-1} in Box 1 and 0.68 kg N x 10^6 yr^{-1} and 0.021 x 10^6 kg P yr^{-1} for Box 2. This accounts for approximately 77% of the current freshwater phosphorus input and 40% of the freshwater nitrogen input.

Downstream protection values were calculated to be 0.88 mg N L^{-1} and 0.081 mg P L^{-1}. These values are greater than those recommended by EPA to protect freshwater streams, which means the EPA-suggested numeric nutrient criteria would be protective of the Choptank River Estuary. It is also worth noting, that these values are similar, but less than those calculated using the TMDL during 90% of hydrologic years.

Discussion

If the numeric nutrient criteria proposed by EPA were adopted for the Choptank River Basin, these results provide evidence that they would be protective of downstream estuarine water quality. Using the Chesapeake Bay TMDL for the Choptank River, downstream protection values were estimated to be 1.02 mg N L^{-1} and 0.11 mg P L^{-1} during 90% of hydrologic years on record (Table 3-4). The corresponding loads associated with the numeric nutrient criteria would also be less than the Chesapeake Bay annual TMDL, over a range of flow (Table 3-5). As the concentration and amount of nutrients delivered is dependent on the volume of water, with more nutrients delivered during a year with greater flow, a range of flow conditions were assessed. It was determined that the EPA-suggested nutrient criteria (0.71 mg N L^{-1} and 0.031 mg P L^{-1}) would meet TMDL goals, even during high flow conditions when more nutrients are delivered into the estuary. However, the phosphorus protection value necessary to meet the TMDL in the Choptank River Estuary is higher than the majority of those proposed in scientific literature to protect Delmarva's freshwater streams (Table 3-10). In a recent report, the Interstate Commission on the Potomac River Basin poses an important question, "Are the Bay TMDL nitrogen and phosphorus allocations sufficient to protect not only the Bay but also local free-flowing rivers and streams?" Results here suggest that while the TMDL may protect the estuary and the Chesapeake Bay, reductions in phosphorus beyond those in the TMDL are likely needed to protect the health of Choptank River Basin streams, especially since phosphorus often drives nutrient impairment in streams.

Approach 2 utilized simple one and two-dimensional models to estimate dilution by Chesapeake Bay water, nutrient removal rates such as denitrification and burial, and nutrient input from lower estuarine waters. Without accounting for removal and inputs from bay water, downstream protection values were 0.42 mg N L^{-1} and 0.06 mg P L^{-1} increasing to 2.64 mg N L^{-1} and 0.17 mg P L^{-1} when removal is taken into account. A downstream protection value for Approach 2 using the fraction of freshwater method was obtained for phosphorus, 0.11 mg P L^{-1}. This is based on the nitrogen and phosphorus concentrations required to keep chlorophyll *a* in the Choptank River Estuary at ET5.2 below 15 µg L^{-1}. The phosphorus concentration is the same as the 90th percentile of flow for hydrologic years estimated in Approach 1, which suggests that the Chesapeake Bay TMDL goal for phosphorus would be protective of water quality in the Choptank River Estuary. Because the nitrogen loading from downstream bay waters alone led to concentrations greater than those estimated to be protective of the Choptank River Estuary, a downstream protection value for nitrogen was not obtained.

Results of the two-dimensional model (0.081 mg P L^{-1} and 0.88 mg N L^{-1}) also indicate that EPA-suggested numeric nutrient criteria would be protective of water quality in the Choptank River Estuary. It is likely that input of nutrients from freshwater are driving the water quality degradation in the Choptank River Estuary, as nutrients being lost from the upper box into the lower box were observed in the model.

Further refinement of this model is ongoing. The addition of more boxes and/or shorter time scales may help improve performance, providing information for the basis of a more complex model. Further, the exchanges of nitrogen and phosphorus between the Choptank River Estuary and Chesapeake Bay may fluctuate over the course of a year, and the composition of inorganic and organic nitrogen and phosphorus may vary (Fisher et al. 2006). Approach 2 also relies heavily on the assumption that the nitrogen and phosphorus endpoints chosen for this analysis are protective of estuarine water quality in terms of chlorophyll *a* greater than 15 µg $L^{-1.}$ Accuracy and variability of removal rates have large temporal and spatial variability.

Others have also estimated values protective of estuarine water quality (Table 3.8). Malone et al. (2003) identified target total nitrogen and total phosphorus values of 0.64 mg N L^{-1} (46 µM) and 0.043 mg P L^{-1} (1.4 µM) to protect the Chesapeake Bay and its tributaries (Jones et al. 2003). Kelly (2008) suggested a rough threshold for hypoxia in estuaries around 80 µM TN, or 1.12 mg N L^{-1}. Kelly (2008) also noted that chlorophyll *a* tends to increase at about 0.75 µg L^{-1} with every 1 µM increase in dissolved inorganic nitrogen (DIN), which would mean that the corresponding DIN concentration to

15 μg L^{-1} chlorophyll *a* would equal approximately 0.28 mg N L^{-1}. These values are higher than those chosen for this study, but the ratios identified to derive the endpoints used here are similar to those observed in the Choptank River Estuary by Fisher et. al (1999). Identification of the appropriate endpoint is essential and needs more exploration.

Conclusion

Downstream protection values can help guide management of waters and ensure that the criteria adopted to protect Delmarva's streams also protect the Chesapeake Bay. Although simplified, these multiple approaches to derive downstream protection values provide greater confidence that significant improvements in the Choptank River Estuary will occur if EPA-suggested numeric nutrient criteria are adopted and enforced throughout the region. Further, while nitrogen loading allocations are likely to protect Delmarva's streams, greater reductions in phosphorus may be necessary than called for in the TMDL to protect freshwater streams and meet nutrient criteria.

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Tables

Table 3-1: Comparison of loading rates (kg 10^6 yr^{-1}) calculated from various studies.

Nitrogen	Phosphorus	Study Period	Study
1.81	0.290	1976-1979	Lomax and Stevenson 1982
1.32	0.080	1980-1987	Fisher et al. 1988
1.54	0.115	1985-1986	Boynton et al. 1995
2.48	0.058	1980-1996	Lee et al. 2001
1.49	0.152	2009	EPA 2010

Table 3-2: Chesapeake Bay Total Maximum Daily Load (TMDL) allocations for nutrients in Choptank River segments (EPA 2010).

	Nitrogen (kg yr^{-1})		Phosphorus (kg yr^{-1})	
Segment	**Point**	**Nonpoint**	**Point**	**Nonpoint**
CHOMH1	4,039	128,328	763	15,074
CHOMH2	51,238	108,510	4,478	12,701
CHOOH	25,611	215,476	2,334	25,267
CHOTF	19,772	619,076	3,121	67,299
Subtotal	100,660	1,071,390	10,696	120,341
Total	1,172,050		131,037	

Table 3-3: Various burial and denitrification rates from literature.

Location	N Burial (g N m^{-2} y^{-1})	P Burial (g P m^{-2} y^{-1})	Source
Wetlands			
Choptank River Tidal and Oligohaline Wetlands	21.0	1.7	Malone et al. (2003)
Choptank River Tidal and Oligohaline Wetlands	23.0	2.0	Merrill (2000)
Choptank River Oligohaline Wetland	38.7	2.6	Traband (2003)
Tidal Marshes	13.0		Greene (2005)
Median Value	**22.0**	**2.0**	
Subtidal			
Estuaries	6.0		Green (2005)
Lower Choptank	1.7	0.3	Boynton et al. (1995)
Upper Choptank	8.1	1.9	Boynton et al. (1995)
Median Value	**6.0**	**1.1**	
	Denitrification (g N m^{-2} y^{-1})		
Wetlands			
Coastal Wetland	**6.7**		Geene (2005)
Subtidal			
Subtidal Estuary	4.9		Geene (2005)
Chesapeake Bay Sediments	7.9		Kana et al. (2006)
Lower Choptank	3.6		Boynton et al. (1995)
Upper Choptank	7.5		Boynton et al. (1995)
Choptank River Sediments	10.5		Owens (2009)
Choptank River Sediments	6.2		Owens (2009)
Median Value	**6.8**		
Global Denitrification in Estuaries	6.0		Seitzinger (2006)

Table 3-4: Estimated nutrient concentration in streams using the Chesapeake Bay TMDL (Approach 1).

	Water Yield cm yr^{-1}	Nitrogen mg L^{-1}	Phosphorus mg L^{-1}
Minimum	8.1	8.24	0.92
10th Percentile	21.5	3.10	0.35
Average	42.7	1.56	0.17
90th Percentile	65.5	1.02	0.11
Maximum	93.1	0.72	0.08
EPA Criteria		0.71	0.03

Table 3-5: Loading scenarios calculated using the EPA-suggested freshwater numeric nutrient criteria of 0.71 mg N L^{-1} and 0.031 mg P L^{-1}. If EPA-suggested criteria were adopted and met in Delmarva's freshwater streams loading would be less than the Chesapeake Bay TMDL targets for nutrients in Choptank River segments even during years with high flow.

	Water Yield cm yr^{-1}	Nitrogen kg yr^{-1}	Phosphorus kg yr^{-1}
Minimum	8.1	100,988	3,131
10th Percentile	21.5	268,053	8,310
Average	42.7	532,367	16,503
90th Percentile	65.5	816,628	25,315
Maximum	93.1	1,160,734	35,983
TMDL		1,172,050	131,037

Table 3-6: Loading scenarios derived using nutrient endpoints based on a 15 µg L^{-1} chlorophyll *a* value *not* accounting for nutrient losses in the upper Choptank River Estuary or nutrient inputs from the lower estuary.

	Water Yield cm yr^{-1}	**Nitrogen kg yr^{-1}**	**Phosphorus kg yr^{-1}**
Minimum	8.1	51,983	7,674
10^{th} Percentile	21.5	137,978	20,368
Average	42.7	274,032	40,452
90^{th} Percentile	65.5	420,353	62,052
Maximum	93.1	597,479	88,199
TMDL		1,172,050	131,037

Table 3-7: Loading scenarios derived using nutrient endpoints based in a 15 µg L^{-1} chlorophyll *a* value accounting for nutrient losses, 64% phosphorus and 84% nitrogen, in the upper Choptank River Estuary and input of nutrients from the lower Choptank River Estuary. Nitrogen inputs from the lower estuary alone were greater than the nutrient endpoints; therefore, no downstream protection value and corresponding loads were determined.

	Water Yield cm yr^{-1}	**Nitrogen kg yr^{-1}**	**Phosphorus kg yr^{-1}**
Minimum	8.1		13,614
10^{th} Percentile	21.5		36,137
Average	42.7		71,770
90^{th} Percentile	65.5		110,092
Maximum	93.1		156,482
TMDL		1,172,050	131,037

Table 3-8: Results of various model scenarios using the fraction of freshwater method, accounting for dilution and input from bay water. These results represent the necessary downstream protection values to protect the Choptank River Estuary and keep chlorophyll *a* below 15 µg L^{-1}.

TN (mg L^{-1})	TP (mg L^{-1})	Model
0.42	0.06	assuming nutrients conserved and nutrients in bay water are negligible
2.64	0.17	using removal rates of 84% N and 64% P, assuming nutrients in bay water are negligible
0.72	< 0	using removal rates of 41% N and 134% P, assuming nutrients in bay water are negligible
< 0	0.11	using removal rates of 84% N and 64% P, assuming nutrients in bay water are *not* negligible
1.02	0.11	results using TMDL, 90^{th} percentile
0.71	0.032	EPA-suggested freshwater numeric nutrient criteria for the Eastern Coastal Plain

Table 3-9: Summary of nutrient concentrations proposed to be protective of estuarine water quality.

	Nitrogen mg L^{-1}	Phosphorus mg L^{-1}
This Study	0.075	0.011
Malone et al. (2003)	0.64	0.043
Kelly (2008)	1.12	

Table 3-10: Total phosphorus (TP) and total nitrogen (TN) concentrations taken from literature for the Eastern Coastal Plain and Maryland region. Downstream protection values for the Choptank River Estuary are shown at the bottom of the table.

Source	Location	Method	TP (mg L^{-1})	TN (mg L^{-1})
EPA, 2000	Eastern Coastal Plain Ecoregion (IIV)	25^{th} Percentile	0.031	0.71
EPA, 2000	Middle Atlantic Coastal Plain Subecoregion	25^{th} Percentile	0.053	0.87
Herlihy & Sifneos, 2008	Eastern Coastal Plain	25^{th} Percentile	0.023	0.62
Morgan & Kline, 2011	Maryland	25^{th} Percentile	0.025 – 0.037	1.34 – 1.68
Morgan et al., 2013	Middle Atlantic Coastal Plain	25^{th} Percentile	0.094	0.93
Morgan et al., 2013	Middle Atlantic Coastal Plain	75^{th} Percentile of Reference Streams	0.065	2.5
Morgan et al., 2013	Middle Atlantic Coastal Plain	Modelled Reference Concentration	0.044	0.45
Dodds & Oakes, 2004	Eastern Coastal Plain	Modelled Reference Concentration	0.04	0.36
Smith et al., 2003	Eastern Coastal Plain	Modelled Background Concentrations	0.015	0.56
Clark et al., 2000	United States	Concentration in Undeveloped Watersheds	0.020 – 0.037	0.24 – 0.32
MDE, 2009a	Maryland Coastal Plain	Biological Threshold	0.14	3.0
Mandel et al., 2011	Maryland	Biological Threshold	0.012 – 0.087	0.58 – 2.67
		Range	**0.012 – 0.14**	**0.24 – 3.0**
		Median	**0.042**	**0.79**
This Study (Chap. 2)	Delmarva Peninsula	25^{th} Percentile	0.052	1.44
This Study (Chap. 2)	Delmarva Peninsula	Modelled Reference Concentration, (land use only)	0.094	0.62
This Study (Chap. 2)	Delmarva Peninsula	Modelled Reference Concentration, (mean hydric soil values)	0.039	0.81
This Study (Chap. 2)	Delmarva Peninsula	Modelled Reference Concentration, (100% forest)	0.085	0.56
This Study (Chap. 3)	Choptank River Estuary	Downstream Protection Value using Chesapeake Bay TMDL (90^{th} percentile)	0.11	1.02
This Study (Chap. 3)	Choptank River Estuary	Downstream Protection Value Fraction of Freshwater	0.11	
This Study (Chap. 3)	Choptank River Estuary	Downstream Protection Value Two-Dimensional Model	0.081	0.88

Figures

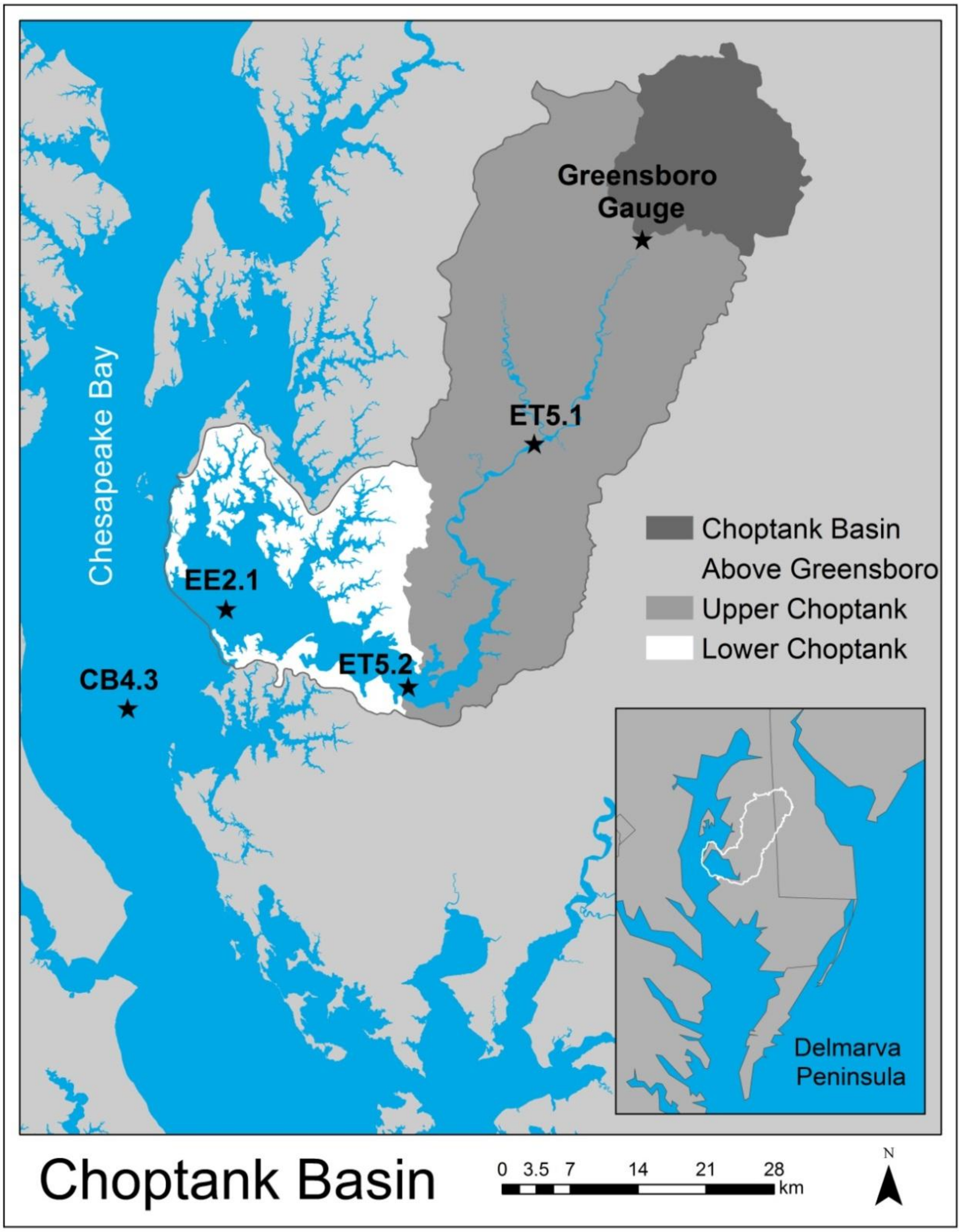


Figure 3-1: Location of the Choptank River Basin on the Delmarva Peninsula. Shown are the Choptank River USGS gauging station at Greensboro, MD and Chesapeake Bay Program sample sites CB4.3, EE2.1, ET5.2, and EE5.1.

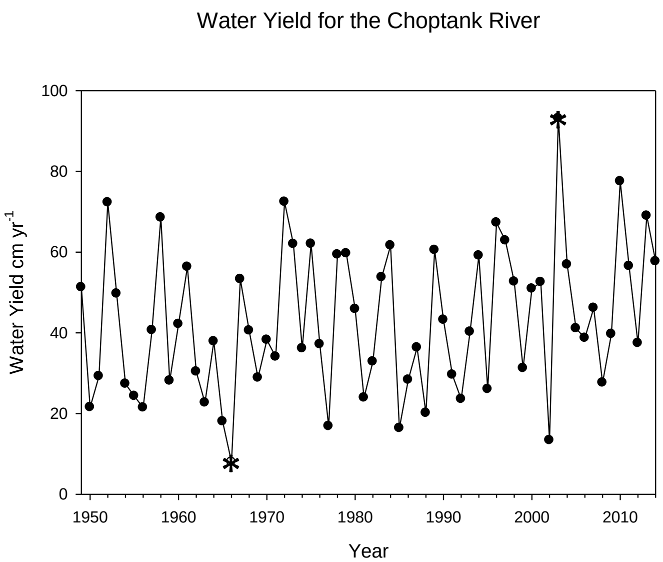


Figure 3-2: Annual water yield for the Choptank River at Greensboro, MD for water years 1949 to 2014. The maximum and minimum water yields are denoted with asterisks. Water yields are discharge (m^3 yr^{-1}) normalized to basin area (m^2).

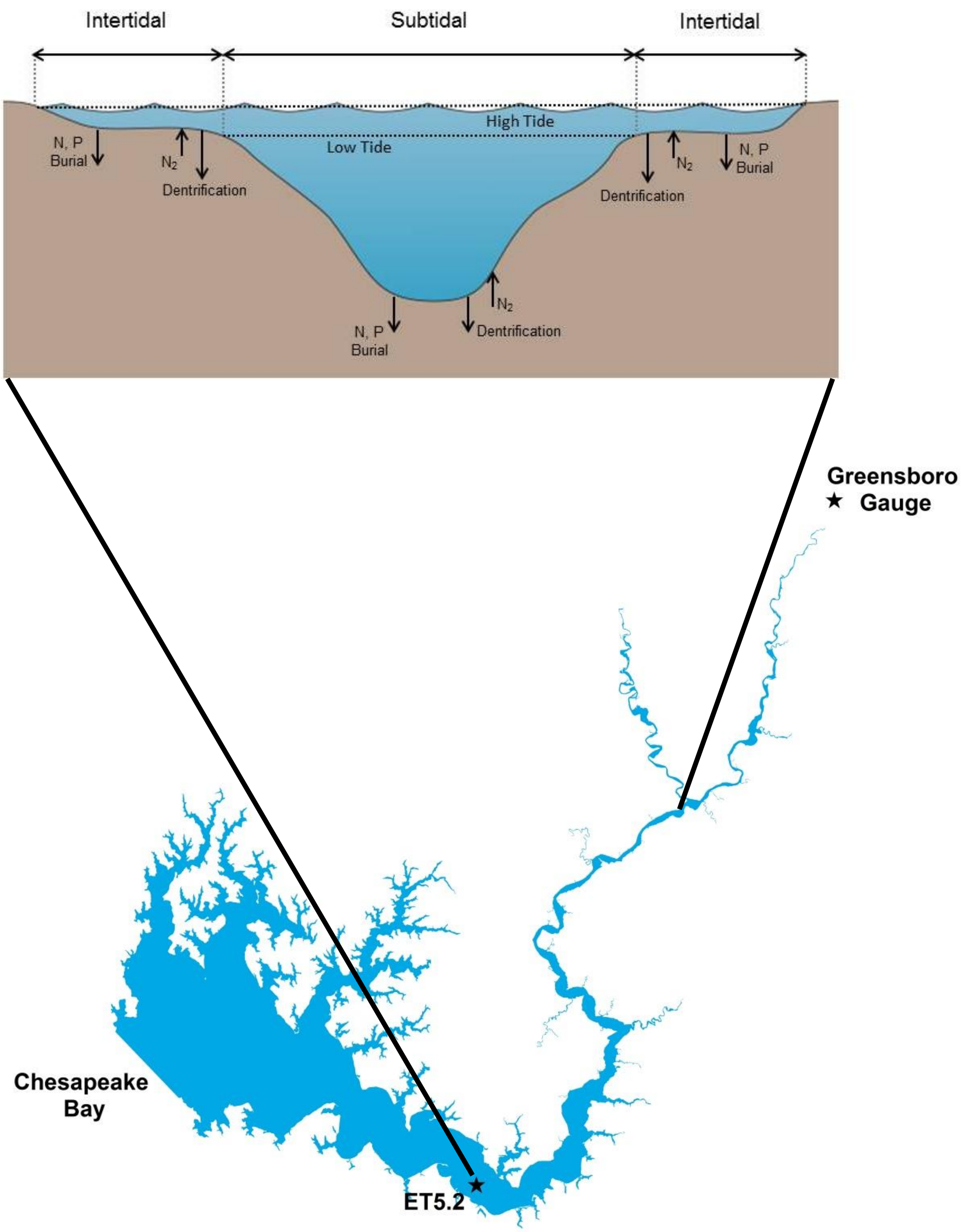
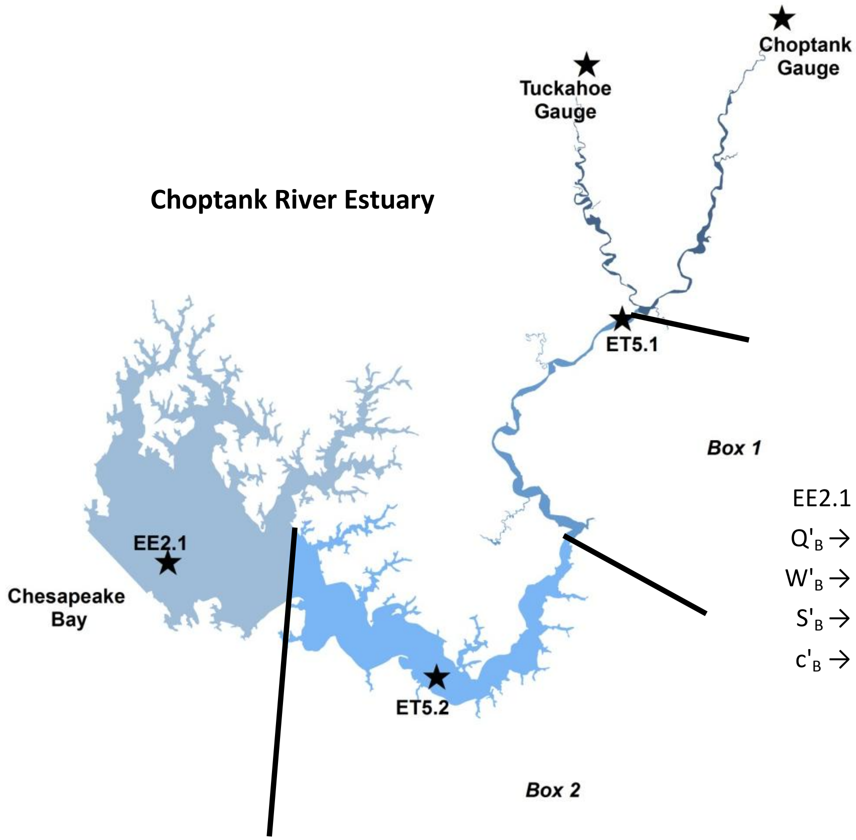


Figure 3-3: Nutrient removal processes in the Choptank River Estuary, which include burial in intertidal and subtidal sediments and wetlands, as well as the reduction of nitrate to N_2 gas through denitrification.



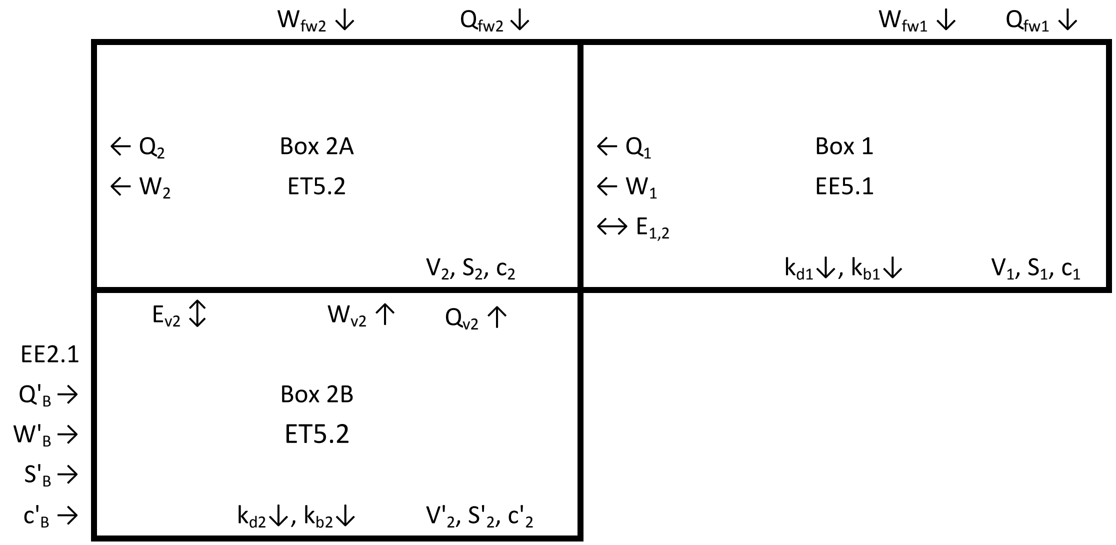


Figure 3-4: Structure of the two-dimensional box model is shown above, where V is the volume, Q is flow, E is non-advective exchange, W is load, S is salinity, c is concentration, and k is removal through denitrification (k_d) and burial (k_b).

The box boundaries are shown in the figure of the Choptank River Estuary to the left. Box 2 is further divided into two-dimensions, above and below the average pycnocline depth of 5 m.

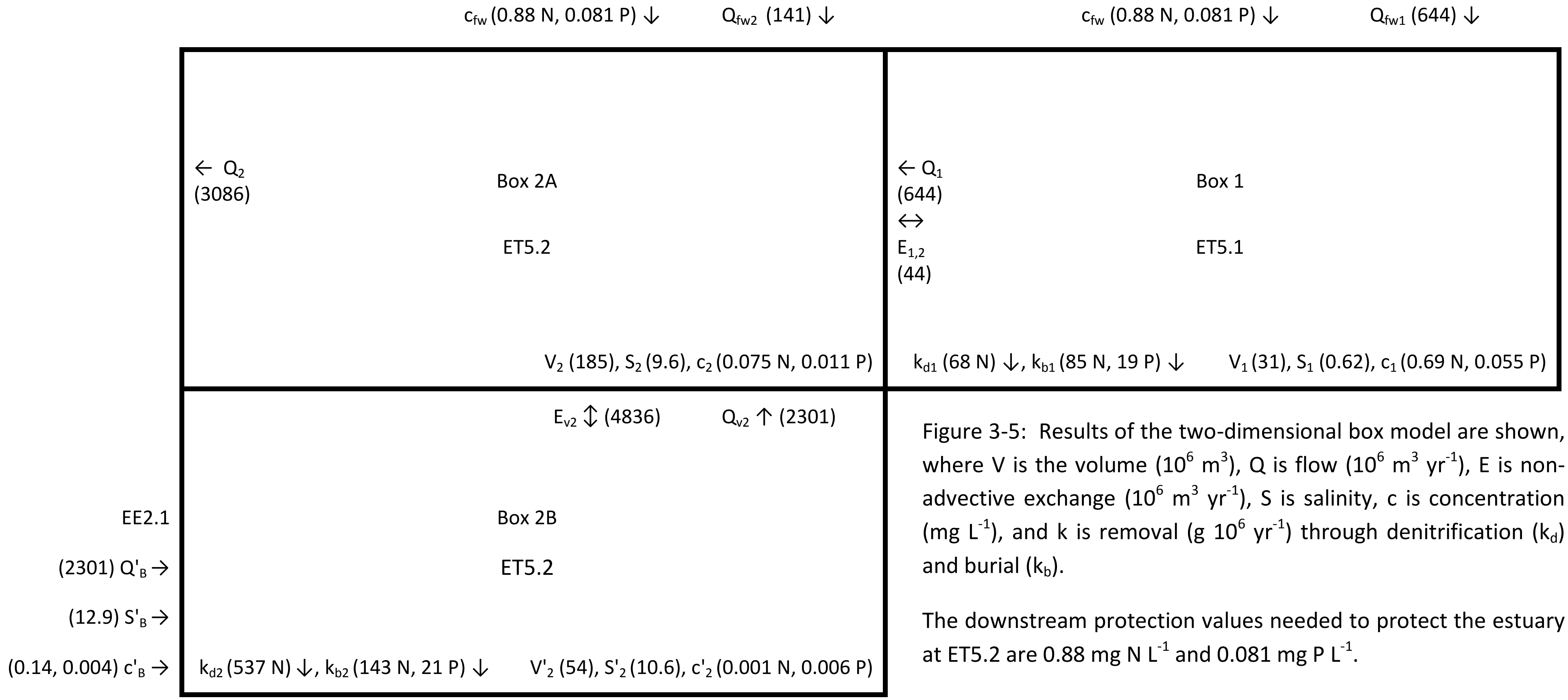


Figure 3-5: Results of the two-dimensional box model are shown, where V is the volume (10^6 m^3), Q is flow (10^6 m^3 yr^{-1}), E is non-advective exchange (10^6 m^3 yr^{-1}), S is salinity, c is concentration (mg L^{-1}), and k is removal (g 10^6 yr^{-1}) through denitrification (k_d) and burial (k_b).

The downstream protection values needed to protect the estuary at ET5.2 are 0.88 mg N L^{-1} and 0.081 mg P L^{-1}.

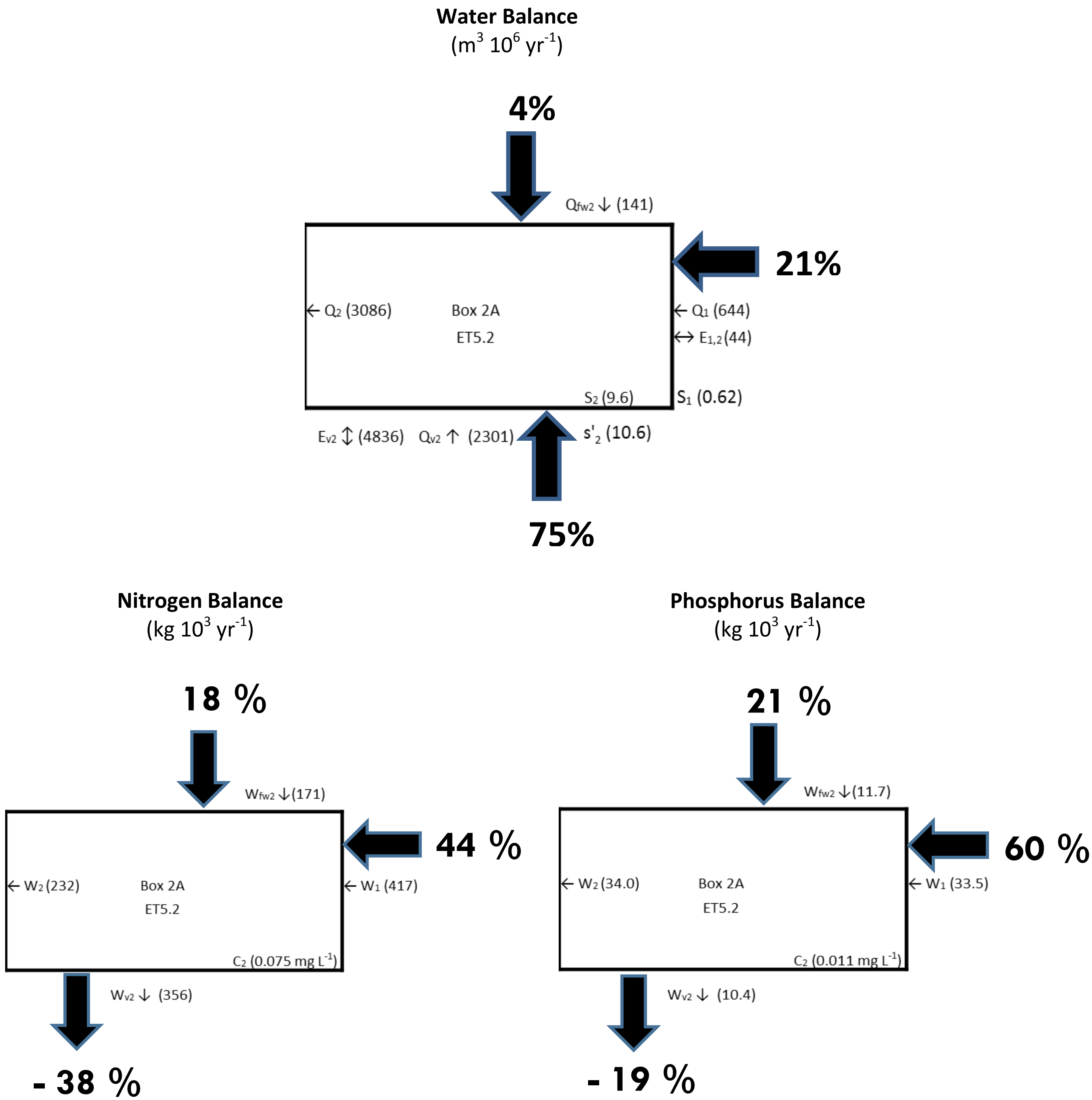


Figure 3-6: Water balance and loading for upper box, 2A, at ET5.2. While the majority of the flow is from Chesapeake Bay water, most nutrients are entering from the surrounding watersheds and upper Choptank River.

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