ABSTRACT

Title of Thesis: WATERSHED LAND USE AND NUTRIENT DYNAMICS IN MARYLAND COASTAL BAYS, U.S.A.

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Upstream and inshore regions of the Maryland Coastal Bays exhibit degraded water quality. Six streams and three shallow bays were sampled in May and July 2006 and 2007 to compare spatial patterns in relation to land use and nutrient loading. St. Martin River, having a high percentage of crop agriculture and a low percentage of forest and wetlands, experienced the most degraded water quality of the three regions, and stream total nitrogen in its watershed was linked to feeding operations and anthropogenic land use. Despite having a much less developed watershed, Johnson Bay experienced degraded water quality, especially in inshore regions. Sinepuxent Bay had the best water quality of the three bays, but still demonstrated anthropogenic impacts. Nutrient loading from land use is directly related to the observed patterns in St. Martin River, while residence time, groundwater flows, and within-bay cycling has led to water quality degradation in Johnson Bay.

WATERSHED LAND USE AND NUTRIENT DYNAMICS IN MARYLAND COASTAL BAYS, U.S.A.

By

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Chapter I: General Introduction

The Maryland Coastal Bays and Eutrophication

Anthropogenic influences and impacts

The Maryland Coastal Bays are an extensive interconnected estuarine system between the Delmarva Peninsula and its sandy barrier islands (Figure 1.1). Like many other estuaries around the globe over the last 50 years, the watershed of the Coastal Bays has undergone changes with increasing nutrient loads to both its terrestrial and aquatic environments, resulting in water quality degradation (Mackenzie et al. 2002).

Consequently, this region is an excellent system in which to study the effects of land use and estuarine characteristics in terms of nutrient input, water quality, and plankton of individual bays, and potentially a model system for management of these inputs. The Chesapeake Bay on the other side of the Delmarva Peninsula has been the subject of many research and restoration efforts, few of which have proven especially successful to date (Ernst 2003). There have been fewer studies of the Maryland Coastal Bays, though this watershed is facing many of the same ecological and environmental challenges, which may also impact the socioeconomic sector. Employment in Worcester County, the Maryland county in which most of the Coastal Bays are located, is dominated in retail and services (63%), reflective of the importance of the tourism industry (Worcester County 2007). In addition, the catch of summer flounder, a very popular target for recreational fishermen in the Coastal Bays, usually ranges between 40,000 to 135,000 fish per year, but has experienced a decreasing trend since 1980 (Casey et al.

2002). Sustaining developed land and other community activities while maintaining water quality is very important for our society as a whole and for the tourism-based economy of the region.

Increased nutrient concentrations, especially nitrogen and phosphorus, have become an important issue for water quality management in the mid-Atlantic region of the United States over the last few decades (Wazniak et al. 2007). Eutrophication and degraded water quality in estuarine regions, especially coastal bays, can be the result of increased anthropogenic activities in the watershed. These include point-source pollution such as wastewater treatment plants in applicable regions (Costanzo 2001), non-point source pollution from fertilizers and septic systems (Zimmerman et al. 2002, Fielding 2003), changes in land use, clearing of forest and riparian zones, and increases in impervious surfaces (Jordan et al. 1997a). The overload of organic nutrients can lead to high abundances of phytoplankton downstream, which, upon decaying and sinking, can result in hypoxia, demise of submerged aquatic vegetation and the subsequent destruction of fisheries habitat (Boynton et al. 1982, Fisher et al. 1992). Increased nutrient cycling, carbon degradation, and respiration by bacteria may also result indirectly from nutrient over-enrichment and may be an important indicator of whole-ecosystem impacts. These effects could be disastrous to any region that depends upon its ecological resources for its economy, tourism, and scenic beauty.

The physical structure of these shallow (less than 3 m deep) coastal bays makes water chemistry and ecology extremely sensitive to land-derived inputs (Wazniak et al 2004). Tidal exchange is limited to only two inlets, and a long residence time of water derived from both ground and terrestrial sources permits nutrient accumulation and

subsequent ecological impacts (Figure 1.1, Jones et al. 2004a, Fertig et al. 2006). Residence times have been estimated to range from an average of 63 days in Chincoteague Bay, to 12 days in St. Martin River, to less than 10 days in Sinepuxent Bay (Lung 1994). Patterns in brown tide distribution and water quality may be directly linked to residence time patterns, as indicated by modeling studies (Wang 2008). Bays with high land area-to-water area ratios, such as St. Martin River, may further concentrate watershed nutrient loads, in comparison to regions with lower ratios, such as Sinepuxent and Chincoteague Bays. This can be especially important in determining whether or not nutrients from the terrestrial landscape impact the estuarine environment.

Anthropogenic alteration of natural landscape buffers such as forest and wetlands can severely decrease the retention of nutrients by the land, causing them to leak into rivers and estuaries (Norton and Fisher 2000). Even though predominant land cover in the Coastal Bays watersheds is forest and wetlands, crop agriculture (e.g. corn, soybeans) is also widespread. Agriculture is an especially important source of nutrient inputs because the application of fertilizer and animal manure can exceed the uptake requirements of plants within a watershed (Carpenter et al. 1998). Past studies have indicated agriculture, including poultry houses, to be the source of over 50% of nutrient inputs to the bays (Bohlen et al. 1997). Total diffuse agricultural inputs of organic nitrogen and reactive phosphorus may exceed those inputs of equally-sized urban areas (Costa et al 2006, Merseburger et al. 2005). Although the total land area occupied by poultry feeding operations, residential development, and agriculture may be a smaller percent of total land use than natural land cover, concentrated areas of development may also impact adjacent aquatic nutrient concentrations; various studies have indicated spatial proximity

to nutrient loading land uses may be the critical determinant of observed water quality (Houlahan et al. 1992, Osbourne and Wiley 1988, Norton and Fisher 2000).

As the popularity of coastal regions increases, more of the Coastal Bays watershed is being converted to impervious surfaces and low-intensity residential land use. These urban areas may be an especially important source of nutrients in the summer months, when over 250,000 additional people populate this watershed every week, in addition to the 40,000 year-round Worcester county residents. Due to its recreational and natural resources, the Coastal Bays watershed is projected to reach a year-round population of 60,000 by 2020 (EPA 1999). Although the land area is small (453 km^2) relative to the water area (282 km^2), land use still may influence the water quality and biota of individual bays (EPA 1999, EPA 2007).

The response of this ecosystem to land use change may be reflected in both stream and estuarine water quality. Elevated concentrations of total nutrients (TN and TP), as well as certain nutrient species (NO_3^-, NH_4^+, urea, PO_4^{-3}), can help to indicate effects of land use loading as well as dominant sources of nutrient inputs (Beaulac and Reckhow 1982, Cooper 1995). Specific forms of nutrients may be more abundant in watersheds with specific dominant land covers (Jordan et al 1997b). Most nutrients enter the Maryland Coastal Bays from nonpoint sources such as surface runoff, groundwater, and erosion (Boynton et al. 1993, Wells et al. 2004, Glibert et al. 2007). Even when nutrient concentrations are similar in watersheds of varied land use compositions, land cover still may be responsible for the sources of the loading; for example, elevated nitrate levels, though measured in both urban (> 24% impervious surface) and pastoral (> 25% grazed) watersheds, occur as a result of surface water or

groundwater transport, respectively (Schoonover and Lockaby 2006). Although the Maryland Coastal Bays display extremely low concentrations of dissolved inorganic nutrients (< 5µM) in comparison to neighboring Mid-Atlantic estuaries, their predominantly organic N and P loads may still have links to land use and subsequent in-bay cycling patterns (Glibert et al. 2007).

$\delta^{15}N$ as an indicator

In addition to total nutrient concentrations, stable isotope ratios of nitrogen ($\delta^{15}N$) may be helpful in tracking sources of nutrient pollution to the Coastal Bays. This isotope ratio can be used to trace discharged nitrogen from point and diffuse sources, including sewage effluent (Rau *et al.*, 1981; Heaton, 1986; Wada., 1980; Van Dover *et al.*, 1992; Macko & Ostrom, 1994; Cifuentes *et al.*, 1996; McClelland & Valiela, 1998). There are two naturally stable forms of nitrogen, ^{15}N and ^{14}N, with the predominant form being ^{14}N (99.6%). The various sources of nitrogen often have distinguishable ^{15}N to ^{14}N ratios, thereby making it possible to identify the source of the nutrients (Heaton, 1986). Isotopic fractionation occurring during ammonia volatilization, nitrification, and denitrification produce an elevated $\delta^{15}N$ signature, given that the natural abundance of $\delta^{15}N$ is 0.36% (McClelland & Valiela, 1998). Because $\delta^{15}N$ is a "heavy" isotope of N, it accumulates over time and increases in concentration in areas where more nitrogen is processed (Fourqurean et al 1997, Ahad et al. 2006). In 2004 and again in 2006, $\delta^{15}N$ values were found to be unusually high in two of the Maryland Coastal Bays that were not geographically close to one another (Jones et al. 2004b, Fertig et al. 2006). One of these areas was Johnson Bay, which has little urban development but is dominated by

agriculture within its watershed. Another area, the highly developed St. Martin watershed, experienced both high total nitrogen as well as $\delta^{15}N$ concentrations. When comparing these two regions of historically elevated $\delta^{15}N$, it is uncertain if land-based inputs, within-system recycling, or a combination of the two is the main source of elevated $\delta^{15}N$.

Biotic indicators

In the Coastal Bays, phytoplankton and bacteria have the potential to be excellent indicators of nutrient sources, processing, and anthropogenic impacts because they are very responsive to changes in their environment. Micro-algal abundance and turbidity have shown interpretable patterns at low to moderate nutrient loadings (Scanes et al 2007). Phytoplankton blooms can be associated with nutrient enrichment, land use change, nutrient cycling, and changing seasonal conditions- all things which are common in the Maryland Coastal Bays (Boynton et al 1982). In estuaries dominated by freshwater flows such as the Neuse in North Carolina, hydrologic forcing may loosen coupling between nutrient inputs and algae upstream, but advective transport to downstream reaches and circulation patterns may trap nutrients and lead to phytoplankton biomass accumulation in the mid/lower estuary (Arhonditsis et al. 2007, Lessin et al. 2007). Such patterns in chlorophyll *a* have been observed in Newport Bay of the Maryland Coastal Bays, where downriver transport of nutrients from St. Martin River results in phytoplankton blooms (Glibert et al. 2007).

Bacteria and viruses are an important part of nutrient recycling and carbon degradation in estuarine and freshwater systems and can serve as valuable indicators of

eutrophication (Hewson et al 2001, Cochlan et al 1993, Azam et al 1983). The role of these organisms has received little study in the Maryland Coastal Bays.

Bacterial concentrations in coastal areas normally range from 10^5 to 10^7 cells ml^{-1} and may be negatively correlated with salinity through dilution and other factors (Azam et al 1983). Although conditions of salinity, temperature, and nutrients may influence bacterial populations, the most important driver of their abundance is organic matter availability. Organic matter input, usually resulting from watershed land cover and water column phytoplankton, induces a positive bacterial response as part of the microbial loop (Apple et al. 2006, Blankenship 2000). Phytoplankton degradation by microbes also transforms and releases nutrients into the water (Rooney-Varga et al. 2005). Dissolved organic forms of nitrogen, phosphorus, and carbon (DON, DOP, and DOC) show high biological availability to bacteria, leading to higher system respiration but less efficient transfer of carbon to higher trophic levels (Suttle 2005). Bacterial populations found in estuaries and streams of agricultural watersheds have shown positive responses to fertilizer applications, drainage basin size, and manure production, all of which provides useable carbon and may be especially applicable to the Coastal Bays (Apple et al. 2004).

Furthermore, virus-like particles (VLPs), which depend mainly on prokaryotic bacteria as hosts, tend to increase along an eutrophication gradient (Danovaro et al. 2003, Hewson et al. 2001). Recent studies have shown that other physical parameters may have a significant effect on VLP abundance and also the ratio of VLPs to bacteria. Although viruses may be the most abundant biological component in both freshwater and saltwater ecosystems, they are controlled by the abundance of their hosts, the bacteria (Wommack and Colwell 2000). A study in the Brisbane River/Moreton Bay estuary in Southeast

Queensland, Australia, revealed that the ratio of VLPs to bacteria increases as overall abundances increase (Hewson et al. 2001). In studies of the ocean, viral abundance has varied with depth, but this correlation is less apparent with estuarine and freshwater systems where systems are shallow and mixed at least annually (Cochlan et al. 1993). Viruses may also be another useful indicator to address anthropogenic impacts in the Maryland Coastal Bays.

Bay comparisons

Comparisons between individual bays may aid in the understanding of how land use, nutrient inputs, and internal cycling relate to water quality. By quantifying the nutrient loading and land use composition of watersheds within the Coastal Bays system, one may be able to characterize the effects of land use on the estuary. A complete analysis of spatial patterns both among and within individual bays with varied watershed land use compositions would be helpful to identify differences in the way these bays respond to inputs at different times of the year. Relationships between biological, chemical, and physical parameters may differ between different bays, months, and years, indicative of regional and seasonal changes in nutrient cycling as well as precipitation.

Study Site Description

The Coastal Bays system

The Maryland Coastal Bays are coastal lagoons situated on the eastern side of the Delmarva Peninsula, a part of the Mid-Atlantic coastal plain. The watershed surrounding

these coastal lagoons has been divided into six regions by their position and physical characteristics. The ratio of watershed area (452 km^2) to water surface area (282 km^2) is less than 2:1, a low ratio when compared to that of the Chesapeake Bay (14:1). Non-point sources (groundwater, runoff, erosion) are the major contributors to pollution and nutrient inputs to the estuary (Boynton et al., 1996). In this study, the three individual sub-watersheds of St. Martin River in the north, Johnson Bay in the south, and Sinepuxent Bay in the east, were assessed for their spatial patterns in water quality parameters and watershed land use. The first two regions exhibit signs of degraded water quality, despite their different watershed land uses (developed vs. agriculture, respectively), freshwater flows (surface vs. groundwater), and flushing times (river vs. lagoon) (Wazniak et al. 2004, Fertig et al. 2006). The third, Sinepuxent Bay, was given the best ranking out of all the Coastal Baysin the 2004 State of the Maryland Coastal Bays report, due to its high values for all water quality, habitat, and biological resource indicators. Because of its rapid water exchange through the ocean at the Ocean City inlet, Sinepuxent served as a reference site by which to compare the other two bays, which had slower flushing rates and hypothesized larger nutrient inputs.

St. Martin River

St. Martin River, the northernmost sampling region, has a high percentage of developed land and freshwater inputs. It is comprised of two branches- Bishopville Prong and Shingle Landing Prong (Figure 1.2). The north-south Bishopville Prong is then made up of Carey Branch and Bunting Branch, which is bounded in the north by a dam at Bishopville that also serves as the end of tidal influence (Figure 1.2 photo A). This dam

was built in the 1870's to power mill operations, but has since lost its original purpose. It was upgraded in 1959 to become a tumbling dam structure, and it has created a 2 ha shallow (~1 m) pond (Jesien 2006). Five streams flow into Bunting Branch, all of which have headwaters in the Great Delmarva Cypress Swamp, and two of which combine in Delaware before crossing the Maryland border. The town of Selbyville, DE, (population 1700) is included in its watershed area (Selbyville 2008).

In the tidal-fresh portion of the River, the Shell Mill Boat launch 2 km downstream of the dam marks the uppermost limit of boat traffic. The southeastern part of the estuarine watershed is comprised of urban and suburban development surrounded by farmland. Ocean Pines, a year-round canal community founded in 1968, borders the river all the way to the east (Figure 1.2 photo C). Golf courses, condominiums, town-homes, and recreational facilities dominate the surrounding landscape, in addition to a marina and two wastewater facilities that feed into the River. The northern border of the river is composed of mostly agricultural and forested land with some urban development. Draining of the Cypress Swamp for agricultural purposes in the 1930's lowered the water table and made ditching necessary in order to drain the hydric soils of the region.

The study area of St. Martin River contained 25 sampling locations within the tidal-fresh river and adjoining bay which were sampled for water quality parameters (Secchi depth, dissolved oxygen, total and dissolved inorganic nitrogen and phosphorus, chlorophyll, and phaeophytin) in both May and July 2007, and two additional sites in the tidal portion of the Bishopville Prong in July 2007. The total area of water comprised by sampling locations is 8.3 km^2 (Fertig et al., 2006). At six of these sites, nutrients and

chlorophyll were measured in triplicate, and additional parameters, including total suspended solids, bacteria, and viruses, were also sampled.

Johnson Bay

Johnson Bay, south of St. Martin River, is a sub-bay of Chincoteague Bay (Figure 1.3). It is made up of two lagoons on the western side of Chincoteague Bay. The tidal Boxiron Creek drains through extensive marshland into Brockanorton Bay, the northernmost lagoon. The tidal Scarboro Creek and Pikes Creek drain through marshes into the lower Johnson Bay, which is also bounded to the west by the E.A. Vaughn Wildlife Management Area. Girdletree, a small town with a population of 117, is the only concentrated center of development; row crop agriculture and poultry farming dominate are the dominant land use. Mills Island is the major island in southernmost Johnson Bay, isolating a portion of the bay between it and the mainland (Figure 1.3 photo A).

Groundwater is most likely a significant source of freshwater to the system, due to the watershed's low elevation and sandy soil composition (Manheim et al. 2004). Septic systems dominate disposal methods for human waste of the small population spread through the watershed. However, despite a lack of significant point-sources and surface flows, the bay has exhibited high levels of processed, isotopically-heavy $\delta^{15}N$ (Fertig et al. 2006). The current study includes a total of 22 total sites within Johnson Bay, five of which were chosen for intensive analysis of nutrients, phytoplankton, and bacteria in May and July 2007. The total water area of the bay is 50 km^2 (Fertig et al., 2006).

Sinepuxent Bay

Sinepuxent Bay lies in the middle of the Maryland Coastal Bays, between Chincoteague Bay and the inlet of Ocean City (Figure 1.4). Because of this, the residence time of Sinepuxent Bay is much shorter than that of St. Martin River and Johnson Bay (Wang and Wang, 2008). Except for Ocean City to the north, development in its watershed is scattered, and there are few freshwater streams entering this system. Forest and salt marsh dominate the land cover, and water quality has remained relatively pristine in this environment (Figure 1.4 photo B). Sinepuxent served as a relative control and reference location by which to compare the water quality of the other two bays. Three sites extending through the bay were sampled intensively in both May and July 2007 for all parameters.

Hypotheses and Study Objectives

This study focused on the regions of St. Martin River, Johnson Bay, and Sinepuxent Bay in the Maryland Coastal Bays, chosen for their relative differences in land cover and water chemistry, as indicated by previous studies. The following hypotheses were tested in order to understand how land use influences Coastal Bay water quality:

1. Water quality and nutrient loading of St. Martin River, Johnson Bay, and Sinepuxent Bay, is directly related to the land use composition of each basin, and stream nutrient concentrations and export in the St. Martin River watershed reflect the dominant land use of each stream's watershed.

2. St. Martin River has the most degraded water quality, followed by Johnson Bay and then Sinepuxent Bay, the reference site.
3. Upstream and inshore regions of the bays experience more water quality degradation than downstream and offshore regions, especially during wet years.

This thesis addressed these hypotheses through three separate research components:

1. Characterization and comparison of watershed land use composition in relation to stream nutrient concentrations and loading of three Maryland Coastal Bays watersheds.
2. Analysis of estuarine spatial patterns, summertime trends, and correlations among and within these three Coastal Bays by integrating physical parameters (temperature, salinity, Secchi depth, and dissolved oxygen), water chemistry (total N, total P, inorganic and organic N and P, $\delta^{15}N$), and biological measurements (chlorophyll *a*, phytoplankton, bacteria, viruses).
3. Comparison of shifts in spatial patterns of physical parameters, total nutrients, and phytoplankton between wet and dry years to determine unique inter- and intra-bay characteristics that may be responsible for these patterns.

Chapter 2 will address the effects of land use composition and nutrient loading in stream watersheds of the Maryland Coastal Bays and then apply nutrient export coefficient modeling to whole-bay watersheds. Chapter 3 will focus on the bays themselves, looking at patterns in water quality that may be explained by land use or system characteristics. In conclusion, Chapter 4 will be a synthesis of the results achieved in this study and will

explain the links observed between patterns in land use and water quality degradation of the Maryland Coastal Bays.

Figures

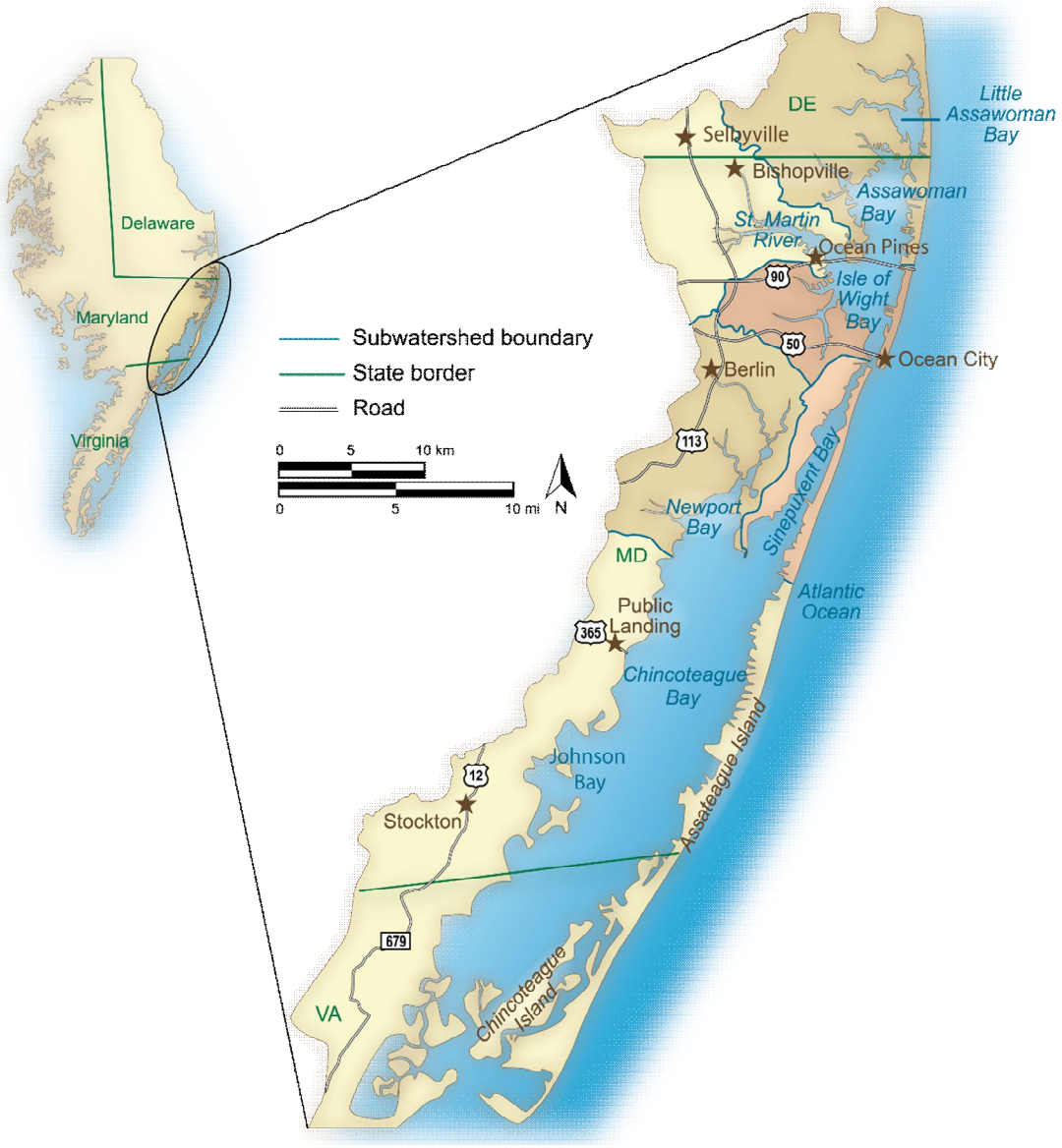


Figure 1.1: The Coastal Bays are located between the Delmarva (Delaware, Maryland, and Virginia) peninsula and its sandy barrier islands. This study focuses on the sub-watersheds of St. Martin River in the north, Sinepuxent Bay, which is close to the inlet at Ocean City, and Johnson Bay in southern Chincoteague Bay. (map courtesy of the Integration and Application Network (ian.umces.edu/symbols/), University of Maryland Center for Environmental Science)

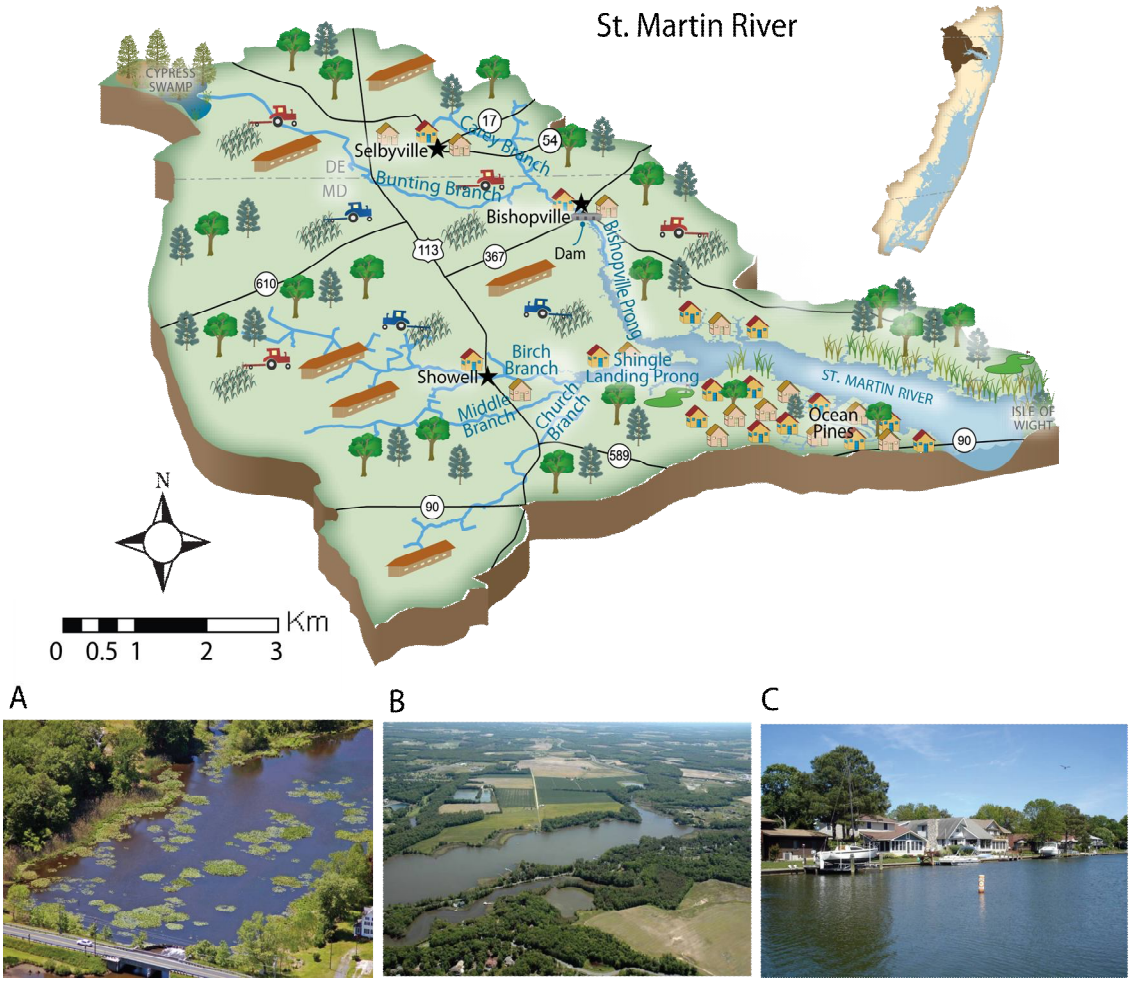


Figure 1.2: St. Martin River is in the northern Coastal Bays, and its watershed extends into Delaware. Bishopville (A) and Shingle Landing (B) are the two upstream prongs of the river that drain most of the land area. The dam on the Bishopville Prong (A) marks the upstream boundary of salt intrusion. The Ocean Pines canal community lies towards the tidal mouth of the river (C). *(photos and map base courtesy of Jane Thomas, University of Maryland Center for Environmental Science Integration and Application Network (IAN))*

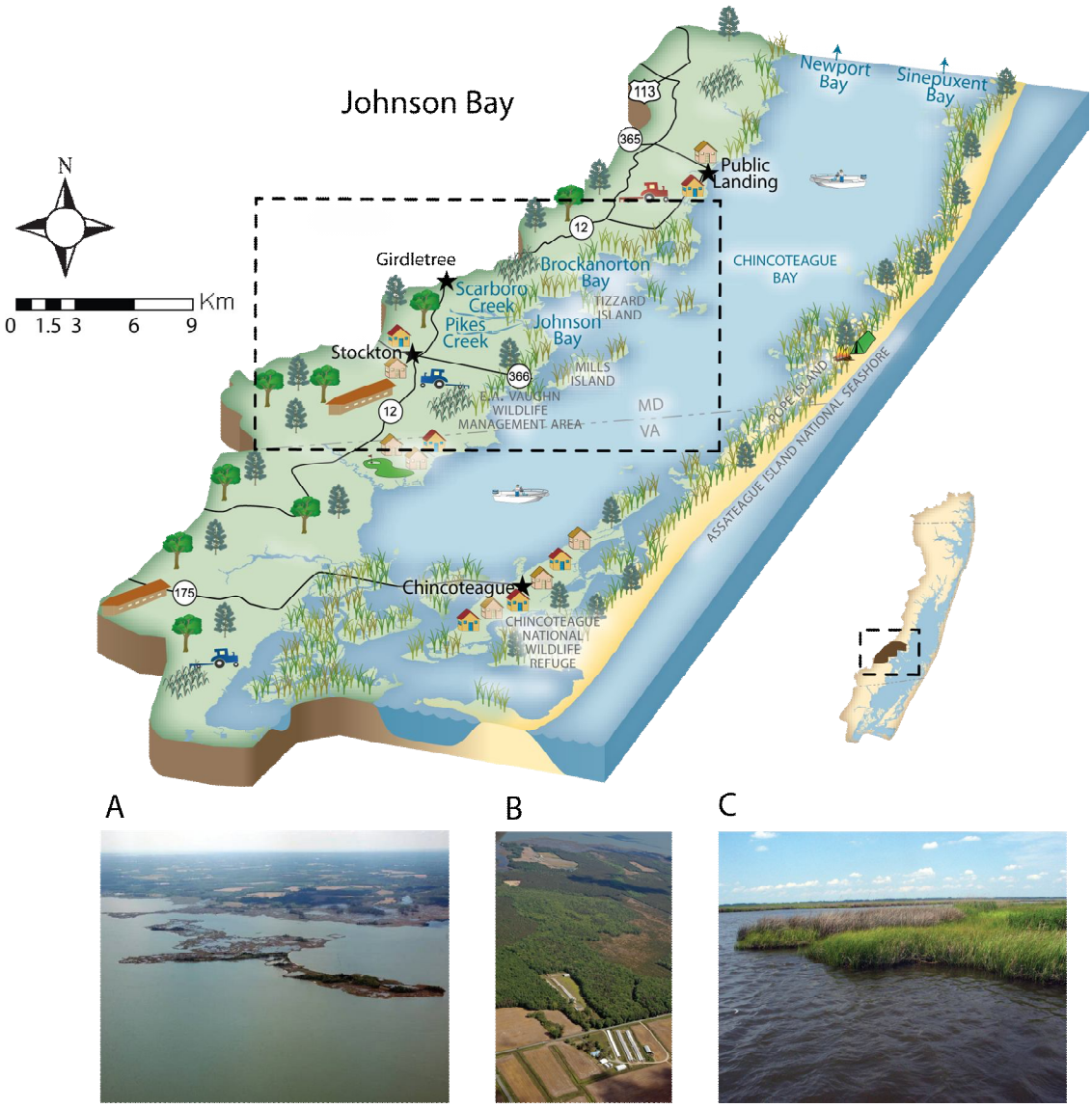


Figure 1.3: Johnson Bay is comprised of two shallow lagoons on the western side of Chincoteague Bay. There are several small islands in it, including Mills Island (A) in the south. Agricultural land use and poultry feeding operations (B) are distributed throughout the bay, but forest and wetlands (C) dominate the landscape. *(photos and map base courtesy of Jane Thomas, University of Maryland Center for Environmental Science Integration and Application Network (IAN))*

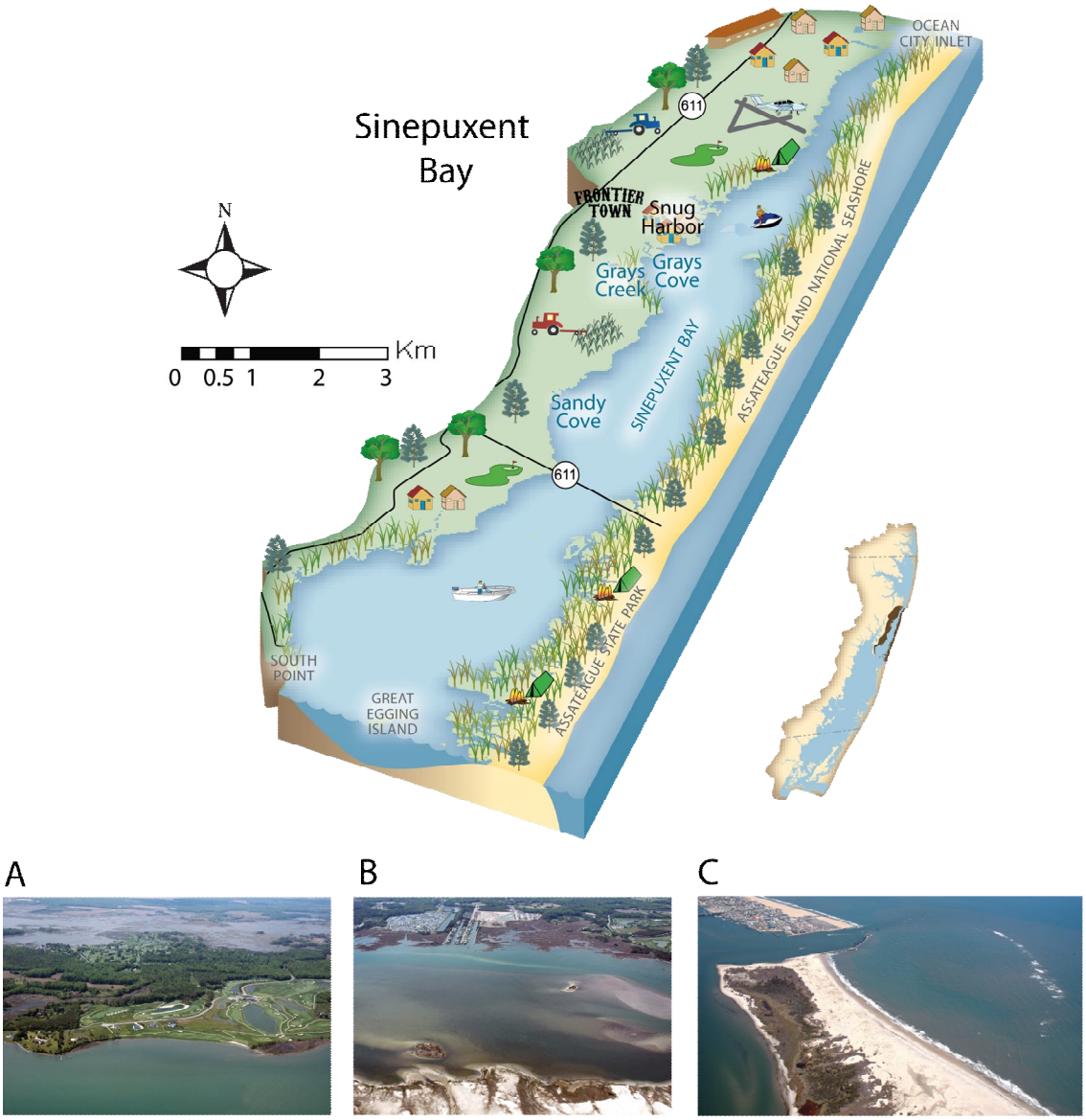


Figure 1.4: Sinepuxent Bay is in the middle of the Coastal Bays. Urban, residential, and recreational development (A) are distributed throughout the watershed, but forest and wetlands are the dominant land use, especially on Assateague Island. This bay is characterized by more abundant seagrasses (B) than the other bays, as well as a shorter water residence time due to the flushing from the Ocean City Inlet (C). *(photos and map base courtesy of Jane Thomas, University of Maryland Center for Environmental Science Integration and Application Network (IAN))*

Chapter II: Characterization and comparison of stream nutrients, land use, and loading patterns in Maryland Coastal Bay watersheds

Abstract

Land use and its relation to nutrient concentrations and loading via streams is an important issue in the Maryland Coastal Bays, USA. Mean monthly concentrations of total nitrogen (TN), ammonium (NH_4^+), nitrate (NO_3^-), and total phosphorus (TP) were measured in six streams in the St. Martin River watershed from July 2006-January 2008 and revealed nutrient increases correlated to watershed development. Watershed land area of feeding operations demonstrated a significant positive relationship with December - March baseflow TN concentrations, as did anthropogenic land area (cropland + urban + feeding operations). TP showed a relationship of increasing concentration with natural land cover (forest + wetlands). The empirical stream data, along with N and P export coefficients from the literature, were used to estimate annual stream watershed export, as well as to derive regionally applicable export coefficients for feeding operations, which could be applied to whole Coastal Bay watersheds. The watershed with the most crop agriculture had the highest N export coefficient, while the highest P export coefficient was highest in a watershed with a historical point-source input and modified channel. This suggests that erosion and land use history may also be important in determining nutrient loading. The N and P loading in the St. Martin watershed, which was the highest of the three bays, was dominated by crop agriculture and feeding operations, respectively.

However, atmospheric deposition contributes to the majority of loads in both Johnson Bay and Sinepuxent Bay. This study suggests that calculation of nutrient loading by export coefficients, using regionally-derived coefficients, may be helpful to compare land use pressures on the individual bays.

Introduction

Like other Atlantic estuaries, the Coastal Bays of Maryland have undergone extreme changes in land use and nutrient loading over the past 100 years. In these regions, forest and wetlands, which were converted to agricultural crop land, have more recently been converted into animal feeding operations and urban development, due to pressures from increasing human population and changes in the local economy (Lee et al. 2000). The population of the Coastal Bays watershed doubled between 1980 and 2000 and is expected to double once again by 2020 (Hager 1996). As development increases along the coast of Maryland, knowledge of the processes of nutrient sources, delivery, and influence upon coastal bays in particular can aid in the preservation of these systems.

Increases in nutrient loading to coastal waters may occur as a result of urban development (Peierls et al. 1991), crop agriculture (Lee et al. 2001) and the concentration of loads by a large ratio of watershed area to water area (Caddy 1993). Enhanced N and P inputs and subsequent water quality degradation can be seen as effects of the last 300 years of anthropogenic watershed disturbance in the United States, including fertilization, atmospheric deposition, and human sewage (Beaulac and Reckhow 1982, Fisher and Oppenheimer 1991, Peierls et al. 1990) However, the greatest land use impact in the sub-watersheds of the Maryland Coastal Bays results from agriculture, comprising one-half to two-thirds of total nutrient inputs (Bohlen et al. 1997). Spatially explicit assessments of land use and loading patterns of sub-watersheds within the region can help to address the cause of water quality patterns and potential system-wide changes.

Streams may be significantly impacted by agricultural and urban development, displaying positive linear relationships between nitrogen (N) and phosphorus (P) concentrations and percent of watershed development (Pionke et al. 2000, Beaulac and Reckhow 1982).

Ranges of export coefficients, derived by dividing watershed export by total area, may also be indicative of anthropogenic impact. In a study of Chesapeake watersheds, stream N discharge was shown to be directly correlated to % cropland and inversely to % forest cover, but there has been less evidence of correlation with P (Jordan et al. 1997). Excess manure and fertilizer from agricultural areas allows surplus N to move readily through soil and P to accumulate in soils and be released into surface waters under heavy precipitation (Carpenter et al. 1998). However, even in agricultural landscapes, riparian forests can serve as effective means of nutrient removal through their trapping, uptake, and denitrification abilities (US Dept. Ag, Peterjohn and Correll 1984). Therefore, the distribution, as well as composition of watershed land use, may affect the impact of nutrient loading on aquatic systems, especially estuaries. Characterizing and quantifying nutrient export from various types of land use is therefore a useful means by which to compare the degree of anthropogenic forcing on different watersheds.

In addition to total N and P export, measurements of stream nutrients within a region can indicate direct or indirect land use contributions. Low-order streams may be especially important indicators of nutrient inputs and effects of watershed land use (Lefebvre et al. 2007). In 1999 and 2001, a synoptic survey of streams in the Isle of Wight and St. Martin River watersheds of the Maryland Coastal Bays revealed several streams having extremely high PO_4^{-3} and $NO_2^- + NO_3^-$ (hereafter represented as NO_3^-, since $NO_2^- < 5\% NO_3^-$ (Novotny and Olem 1994)) concentrations, loads, and total

nutrient yields to the estuary (Primrose 2001). A 2003 study of the Newport/Sinepuxent Bay watershed also revealed excessive NO_3^- yields in ten sub-watersheds and excessive PO_4^{-3} yields in two sub-watersheds (Primrose 2003). Elevated N and P levels in both regions were believed to be associated with row crop agriculture and chicken processing, respectively, though no direct assessments of land use loadings were made. The 2004 State of the Maryland Coastal Bays report indicated high stream nutrient concentrations and poor benthic indices throughout the Coastal Bays watersheds, with especially high NO_3^- concentrations (> 357µM) in the upper tributaries of the St. Martin River (Wazniak et al. 2004). Nutrient enrichment from anthropogenic activities was also found in streams of the Chincoteague Bay watershed, though to a lesser extent. Extensive ditching of tributaries and streams in the region may allow for rapid, direct entrance of groundwater, instead of slow filtration through buffering wetlands. Stream nutrient concentrations in different regions of the Coastal Bays may be indicative of individual hydrological routing mechanisms and the net influence of land use in each particular bay sub-watershed.

The present work focused on three questions that examined the relationship between land use and nutrient export from the Coastal Bays watersheds, with particular emphasis on the St. Martin River:

1. Is the increasing percentage of anthropogenic land use (urban + agriculture) and feeding operations in the St. Martin River watershed related to increased N and P concentrations and export?
2. Does the use of local land use export coefficients in the calculation of total annual N and P loads help to compare land use pressures among these three Coastal Bays?

3. Does overall land use composition of St. Martin River, Johnson Bay, and Sinepuxent Bay vary as a function of distance from each bay's shoreline?

Methods

Study locations

The Maryland Coastal Bays consist of a series of shallow (< 3m) lagoons between the east side of the Delmarva Peninsula and its barrier islands (Figure 1.1). This study focused on streams draining into St. Martin River, as well as using the drainages of Johnson Bay and Sinepuxent Bay as comparison watersheds to estimate nutrient loading (Figure 2.2). All three watersheds are characterized by low topographic relief, poor drainage, high water tables, and hydric soils (MDE 2001). St. Martin River is the northernmost watershed, extending from Maryland into Delaware and encompassing the population centers of Selbyville, DE, and Ocean Pines, MD (Figure 1.1). The River consists of two branches, known as Prongs, one of which is the Bishopville Prong that has a dam 1.3 km below the Delaware State line. According to the State of Delaware (1998), the Delaware portion of the watershed is dominated by agriculture (43%), wetlands (34%), residential (14%), and forest (9%), but no complete watershed-wide assessment of land use has been conducted.

The St. Martin River watershed is also the location of the six stream sites (discussed below), which are used to examine local land use-nutrient relationships and determine applicable nutrient export coefficients for regional feeding operations (Figure 2.1). These sites were numbered according to the percent of their watershed comprised of feeding operations, where site 1 had the lowest (0.14%) and site 6 had the highest (1.6%).

Five of the six sites (2-6) were located above the dam and drain into the Bishopville Prong, while the remaining site (1) drains into the southern branch, the Shingle Landing Prong.

Johnson Bay, the middle portion of Chincoteague Bay in the south, has a relatively undeveloped watershed (4,911 ha) that is dominated by crop agriculture, wetlands and forest. It is thought that groundwater contributes a significant amount of freshwater to this system, as opposed to the surface flow of St. Martin River (Dillow and Greene 1999).

Sinepuxent Bay, characterized by its high flushing rates (due to its location close to the Ocean City inlet) and small watershed area (3,058 ha) has a watershed that is mostly dominated by forest and wetlands on Assateague Island to the east, but there is a significant amount of development on the western shore of the bay. These two bays served as comparison watersheds for using the export coefficient model to determine nutrient loading.

Land use composition and GIS analysis

This study focused on comparing the land use of three sub-watersheds in the Maryland Coastal Bays. These regions include St. Martin River, Johnson Bay, and Sinepuxent Bay, each differing in land use composition, flushing rate, soils, and physical structure. In addition, smaller watersheds within the St. Martin River basin were assessed for their land use and patterns in nutrient export.

GPS coordinates for six stream sites from the Maryland Coastal Bays Program's St. Martin River stream assessment were plotted using ArcMap GIS. USGS 7.5 minute

maps provided topography of the region to manually delineate boundaries of the watershed draining to each sampling location. The small range of topographic relief on the Delmarva Peninsula, as well as the presence of constructed canals, made watershed delineation difficult, but estimates of drainage area for each stream were calculated using topography and original stream patterns. Land Area (m^2) per meter of stream was calculated by taking the watershed area and dividing it by the total length of all streams within the watershed, which would eventually drain to the sampling site. This estimate provides means of comparing land influences on the streams in the watershed.

2002 Land cover data in the ESRI ArcMap v9.2 GIS environment was provided by Worcester County Department of Planning and the State of Delaware Department of Natural Resources. These GIS files were vector data that was derived from visually-interpreted, geo-referenced aerial photography. The minimum mapping resolution of land use data was 10 acres (0.40 ha), which was augmented by tax assessment data that resulted in some urban areas of < 10 acres (0.40 ha). Over 30 different types of digitized land cover (i.e. row crop, high-intensity development, etc) were delineated in the files. However, each state had different categories and names for the same basic land covers. In order to provide information about the entire watershed, land cover was then simplified to 5 broader categories (urban, forest, crop agriculture, wetland, and feeding operations), and compiled to one GIS shapefile. Population data in block format was also obtained from the 2000 Census Bureau for information on regional populations in the UTM NAD 1983 projected coordinate system. Data layers of stream hydrology, shorelines, population, and land cover were clipped to the size of the watersheds of interest using the watershed boundaries described above.

The 2002 Land use/land cover file was further modified for a more exact estimation of total land cover. 2005 aerial photography was obtained from the Maryland Department of Natural Resources and compared with the GIS land use shapefile. Original land use polygons for feeding operations were re-drawn closer to the imagery, which was especially important for poultry houses, the primary feeding operation of the region. In addition, new polygons were drawn for some forested areas that were not delineated by the original shapefile.

In order to examine the relation of land use patterns to shoreline proximity, the Buffer function in ArcMap GIS was used to draw buffers at distances of 100, 200, 500, 1000, and 2000 m from the shoreline of each bay. The watershed land use file was clipped to these buffer boundaries, and land use percentages were extracted for each buffer. The resulting data showed how land use changes as a function of distance from the shoreline.

Stream analysis

The Maryland Coastal Bays Program (Jesien 2008, pers. comm.) provided stream nutrient data from July 2006 to January 2008 for six sites in the St. Martin River watershed, 1-6 (Figure 2.2). Bi-weekly grab samples of whole water (500mL) had been collected mid-stream just below the surface of the water and filtered using 0.45µm Gelman GF/C filters. In addition, an unfiltered sample was taken for TN and TP analysis. Samples were frozen on ice and taken to the Horn Point Laboratory Analytical Services for determination of total and dissolved nutrients. Monthly TN, NO_3^-, NH_4^+, TP, and PO_4^{-3} concentrations and standard errors were computed by taking the mean of all

samples collected for each month during this two-year period. Because the period of sampling did not extend over a full two year period, the only measurements for the months February through June occurred in 2007. Therefore, mean concentrations for these months was calculated using monthly concentration data for one year's samples instead of two.

Average monthly discharge data was obtained for the gauge in Figure 2.1 from the U.S. Geological Survey for the period July 2006- September 2007. The nearby continuous monitoring site and gauging station (USGS 0148471320) Birch Branch at Showell, has a drainage area of 6.38 square miles. Mean discharge ($m^3\ s^{-1}$) was calculated for each month, which was used to determine a total monthly water discharge ($m^3\ month^{-1}$) and water yield ($m\ month^{-1}$). The regional monthly water yield (WY, $m\ month^{-1}$) was computed as:

$$WY = Q * d * 86{,}400\ s\ day^{-1} * A^{-1} \quad \text{Eq. 1}$$

where Q= discharge ($m^3\ s^{-1}$), d= number of days in each month, and A= area of watershed (m^2). The water yield for the Birch Branch USGS site was assumed to apply regionally and was multiplied by the watershed areas of each of the six Coastal Bays Program sites to obtain monthly volumes of stream water ($L\ month^{-1}$). Monthly mean nutrient concentrations in µM were converted to $kg\ L^{-1}$ for N and P and then multiplied by their corresponding monthly water volume. An estimate of annual TN and TP export for each catchment, in kg, was calculated by the summing the months. A mean export coefficient for each watershed, using the USGS gauge monthly water yields, was then estimated by dividing this total load by the watershed area.

The period December- March was used to compute mean high-flow period nutrient concentrations (TN, NO_3^-, NH_4^+, TP, and PO_4^{-3}) for each stream. This time period showed less month-to-month variability, while the discharge in the period April - November showed more variability and decreased dramatically during the period May - October. All reported mean values were computed using data from the high flow season only.

Statistics

Simple linear least-squares regressions were used to examine land use effects on water quality parameters of the stream watersheds. Forest, wetland, urban, feeding operations, and crop agriculture percentages were used as independent variables. In addition, a new category called "anthropogenic" was formed by adding urban, feeding operations, and crop agriculture, while forest and wetland were added to represent "natural" land cover. High flow period mean nutrient measurements were used as dependent variables. Statistical significance was defined as $p < 0.05$, and r^2 values were used to indicate the amount of variance explained by each land use category.

Land use loading

Initially, land use area yield coefficients for crop agriculture, urban, and forest land covers, that had been determined in a synthesis of literature values of nutrient yields from small watersheds (Beaulac and Reckhow 1982), were used to calculate nutrient loading to St. Martin River, Johnson Bay, and Sinepuxent Bay of the Maryland Coastal Bays. However, these export coefficients represented generalized, nationwide values that might not be especially applicable to the region of interest. A new set of land use export coefficients was

then derived from literature that focused on the Delmarva Peninsula and Coastal Bays region, as well as the empirical stream data of this study.

Total mass loading (M, kg y^{-1}) was calculated as:

$$M = (E_{for} * A_{for}) + (E_{crop} * A_{crop}) + (E_{urb} * A_{u}) + (E_{feed} * A_{feed}) + (E_{atm} * A_{wat}) + PS \quad \text{Eq. 2}$$

where A = area (ha), E = export coefficient (kg N or P ha^{-1} y^{-1}), for = forest, crop = crop agriculture, urb = urban and residential , feed = animal feeding operations, atm = atmospheric deposition, wat = water, and PS= point-source annual load. All crop agriculture was simplified to row-crop since corn and soybeans dominate agricultural crops in Worcester County (US Dept. Ag 2004). However, wetlands were not included in the coefficient estimation study, and wetland land cover was assigned a loading coefficient of 0, because many studies have indicated that wetlands may even be a sink for nutrients (Jordan et al. 1983). The loading coefficient for atmospheric input was multiplied only by water area because the coefficients for land uses already included that factor in their calculations.

Crop agriculture was assigned export coefficients of 10 kg N and 0.6 kg P ha^{-1} y^{-1} based on a review of yield coefficient literature for coastal plain watersheds with varying degrees of forest cover (Fisher et al 1998). Forest in the Delmarva coastal plain exports an estimated 0.35 kg N and 0.10 kg P ha^{-1} y^{-1}, as determined by Lee et al. (2001), but a study by Fisher et al. (2007) at the Marshy Hope forested site in the Choptank River Basin estimated these export coefficients to be in the range of 1 kg N and 0.08 kg P ha^{-1} y^{-1}. In the current study, 1 kg N and .09 kg P ha^{-1} y^{-1} were used as estimates of coefficients for forest cover, compiled from Fisher et al (2007) for N and the mean of both Lee et al. (2001) and Fisher et al. (2007) for P. The N export coefficient for urban land determined by Beaulac and Reckhow (1982) was used for residential and urban land

in the region, due to a lack of published data for development in this area. A baseflow P loading coefficient was used from Reckhow et al. (1980).

Direct atmospheric N and P deposition (dry + wet) was calculated as water area multiplied by coefficients determined by Volk et al. (2006) and Volk et al. (in prep), respectively, for the nearby Rehoboth Bay, Delaware. Monthly point-source loading data was obtained from the Ocean Pines Wastewater Treatment Plant and the Assateague Visitor's Center, the two known point-source discharges to the St. Martin River. 2007 nutrient discharge data for the Ocean Pines Wastewater Treatment Facility, located on the mouth of the river, was obtained from J. Ross (pers. comm.).

Stream nutrient loads obtained from the empirical stream data were used as a means to calculate loading coefficients for feeding operations that could be applicable to the whole St. Martin River watershed. For each stream catchment, the abovementioned loading equation was solved for E_{feed}, using total N and P loads as M:

$$E_{feed} = (M - (E_{for} * A_{for}) - (E_{crop} * A_{crop}) - (E_{urb} * A_{u})) * A_{feed}^{-1} \quad \text{Eq. 3}$$

where A = area (ha), E = export coefficient (kg N or P ha^{-1} y^{-1}), for = forest, crop = crop agriculture, urb = urban and residential , and feed = animal feeding operations. There were no known point- source inputs within the stream watersheds, and atmospheric deposition was already included as a part of the reported land use export coefficients.

The six values of E_{feed} determined by the stream loads were averaged to find a regionally-applicable mean value of E_{feed} to be applied to the whole St. Martin River, Johnson Bay, and Sinepuxent watersheds. This feeding operations coefficient, along with the coefficients for crop agriculture, urban, and forest land covers, was used to calculate

total N and P loads for the bay watersheds. Watershed nutrient export was also normalized by catchment area in order to compare normalized nutrient export.

Results

Land use of stream watersheds

The stream watersheds were largely dominated by forest, wetlands, and crop agriculture, with small percentages of feeding operations (Figures 2.2, 2.3). The ratio of land area (m^2) to total stream length (m) ranged between 164 (site 6) and 325 m^2 m^{-1} (site 1) (Table 2.1). This suggested that a large area of watershed is contributing to direct stream flow in this region. Site 1, Church Branch, has a watershed area of 1,284 ha and has the greatest proportion of forest of all the basins (47%). 40% of the area is crop agriculture, 13% is urban land, 0.14% is feedlot operations, and there are no wetlands (Figure 2.2, Table 2.1). Site 2, Slab Bridge, has the smallest watershed, with an area of 131 ha. Forty-nine percent of the Slab Bridge is cropland, 16% is urban, 0.46% is feeding operations, and 34% is forest (Figure 2.2, Table 2.1). Site 3, Carey Branch, is nested within watershed 4 and drains an area of 1,593 ha. 54% of the basin is crop agriculture, 15% is urban, 0.58% is feeding operations, 19% is forest, and is 12% wetlands (Table 2.1). The watershed of site 4, the Dam, is the largest and drains a total land area of 3,056 ha. The basin is 51% crop agriculture, 18% urban, 0.82% feeding operations, 18% forest and 12% wetlands, which are located mainly in the headwaters (Figure 2.3, Table 2.1). Site 5, Buntings Branch, has a mid-sized watershed of 907 ha that is also nested within watershed 4 and has the highest percentage of urban land (22%) of the six watersheds (Figure 2.3). It also contains 46% cropland, 1.3% feeding operations, 14% forest, and

16.7% wetlands (Table 2.1). Site 6, Cemetery Branch, has another small watershed of 133 ha. This basin has the highest percentage of cropland and feeding operations, 64% and 1.58%, respectively. Urban land comprises 16%, forest is 13%, and wetlands are 5% of the land area.

Bay comparisons

The three Maryland coastal bays of St. Martin River, Johnson Bay, and Sinepuxent that were compared in this study differ in their total land area, enclosed water area, and land use composition (Figure 2.1, Table 2.2). St. Martin is the largest watershed, comprised of 10,491 ha, but has the smallest water area (830 ha). Johnson Bay has the second largest land area (4,911 ha) and largest water area (5,023 ha) while Sinepuxent has a land area of 3,058 ha and water area of 2,480 ha. Therefore, St. Martin River's land:water ratio (12.6) is an order of magnitude higher than the other two bays (2.0 and 1.2 for Johnson Bay and Sinepuxent, respectively). The residence time, defined as the average time for new water to stay in a water body, differs immensely between the bays. Johnson Bay has the longest water residence time of about 60 days, while St. Martin River is 20-30 days and the residence time of Sinepuxent is less than 10 days, due to its location close to the Ocean City Inlet (Figure 1.1, Lung 1994, Wang et al. 2008). The year-round populations of the three bay watersheds remain low, according to Census 2000 data. St. Martin has a population density of 0.86 people ha^{-1}, Johnson Bay has 0.10 people ha^{-1}, and Sinepuxent has 0.41 people ha^{-1}. However, these population data do not include seasonal visitors to the region.

Land use of bay watersheds

The three coastal bays differ in their watershed land use compositions (Table 2.2). St. Martin River displays the highest percent of crop agriculture (47.4%) and lowest amount of forest and wetland cover (27.3% and 5.5%) of the three bays. Urban development comprises 17.2% of the watershed, and feeding operations are only 0.5%. The majority of the watershed of Johnson Bay is either forest (37.4%) or wetlands (29.1%), though 31.1% of the land is crop agriculture. Only 2.2% of the Johnson Bay watershed is urban development and 0.1% is comprised of feeding operations. In contrast, Sinepuxent is 22.3% urban land, less than 0.02% feeding operations, 43.2% forest, and 23.3% wetlands. Crop agriculture covers only 11.2% of its watershed.

Land use also displayed different patterns at different distances from the shoreline of each bay (Figure 2.4). In all three watersheds, natural land cover (forest and wetlands) was most abundant close to the shoreline and decreased moving to the watershed interior. However, in the St. Martin River watershed, urban land comprised the largest percentage of land cover (46%) in the first 100 m from the shoreline. Between 100 and 1000 m, crop agriculture went from less than 10% to 55% of the watershed, becoming the dominant land use, and wetlands decreased from 24% to less than 5% of the landscape. In addition, 27% of total watershed feeding operations were within 2000 m of the shoreline. Johnson Bay was almost entirely (94%) wetlands within the first 100 m, but crop agriculture steadily increased from 12% to 48% between 100 m and 2000 m. Urban land was at its highest percent composition between 1000 m and 2000 m, but this was still only 3% of the land area. Despite its small land area, all feeding operations (4.5ha) were found between 1000 m and 2000 m from the coastline. Sinepuxent displayed a pattern of

increasing urban and cropland land use from coast to interior. Cropland reached a maximum of 20% between 1000 m and 2000 m, while forest increased to 59% by 2000 m.

Seasonal trends

Flow conditions at the USGS continuous monitoring site, Birch Branch at Showell, were below the 8-year average (Figure 2.5). Discharge rates ranged from a low of 19.3 L s^{-1} in August to a peak of 707.9 L s^{-1} in November, which were both lower than average for the stream. The water yield for the study period was 38 cm y^{-1}, while the 8-year average was 43 cm y^{-1}. Discharge increased over the months October and November, which was inconsistent with low-flow trends usually observed in streams during these months. However, the high-flow months (December- March) showed less variability.

Mean monthly baseflow concentrations of N and P also showed distinct seasonal trends of peaks in the period November - March and lows in June - October (Figure 2.6). However, sites 1 and 3 demonstrated fewer extreme fluctuations than the other sites, especially TN. During the high-flow months of December-March, NO_3^- was the dominant form of N in the streams and, at times, comprised more than half of TN. NH_4^+ remained low throughout the year in almost all six streams, consistently having concentrations less than 20 µM. Sites 2 and 6 experienced spikes in NH_4^+ during the spring and fall that were coincident with depletion of NO_3^-. Of the six sites, site 1 showed the least amount of intra-annual variability in TN and NO_3^-. TN experienced a maximum in July, 237 ± 1 µM, and a minimum of 137 ± 32 µM in September. Sites 3, 4, and 5

demonstrated trends of increased TN and NO_3^- in the wintertime and decreasing concentrations towards the summer, while 2 had the greatest inter-annual variability in TN. Site 6 displayed the highest monthly TN and NO_3^- concentrations of all the sites, with peaks of 625 ± 114 µM TN and 530 ± 85 µM NO_3^- in January (Figure 2.6). However, concentrations decreased to minimums in June and in July at this site.

TP and PO_4^{-3} concentrations of the stream sites did not display the same seasonal patterns as TN and NO_3^-. PO_4^{-3} concentrations closely mirrored those of TP, comprising a significant percentage of the TP pool throughout the year and peaking in early spring (March-April) or fall (October-November) (Figure 2.6). Similar peaks were observed at site 4, which had the highest observed TP concentration, and at site 2, where both PO_4^{-3} and TP peaked in March and again in October. Concentrations of TP at site 3 showed seasonal patterns similar to those of 2, though PO_4^{-3} remained above 1µM for most of the year. Similar to 2, 3, and 4, site 5 displayed dual summer and fall peaks in August and October for both TP and PO_4^{-3}, while TP concentrations in sites 1 and 6 remained above 3 µM during the entire summer season, though they slightly increased in the fall.

Stream TN and TP export

Total export of TN and TP for the six streams was the greatest in the largest watersheds, but export coefficients did not show the same patterns (Table 2.3). Site 4 experiences the highest total N and P export, due to its large watershed area, but its export coefficient was not the highest of the six watersheds. Site 6, the site with the highest percentage of agriculture and feeding operations and the second-lowest total export of all the watersheds, had the highest N export coefficient, 20.35 kg N ha^{-1} y^{-1} and

the lowest P export coefficient, 0.36 kg P ha^{-1} y^{-1}. Contrary to site 6, site 1 had the highest P export coefficient, 0.47 kg P ha^{-1} y^{-1} and the lowest N export coefficient, 9.33 kg N ha^{-1} y^{-1}, though its N and P export was an order of magnitude higher than those of site 6.

Regression analysis

High flow period (December- March) concentrations were used to assess relationships between land use and downstream water quality, as this is the period of greatest potential nutrient inputs via streamflow.

When analyzed individually, the land use categories of crop agriculture, urban, forest, and wetlands did not have significant relationships with nutrient concentrations. To further explore land use effects, the original categories were grouped into generic categories, "anthropogenic" (crop agriculture + urban + feeding operations) and "natural" (forest + wetlands). TN was the only nutrient concentration that displayed significant relationships at $p < 0.05$ with these generic land uses, mainly because of the narrow ranges of values (Figure 2.7). While not significant at $p < 0.05$, NO_3^- was marginally significant at $p < 0.08$ ($r^2 = 0.58$). As anthropogenic land cover increased, TN increased ($r^2 = 0.67$, $p = 0.04$), and TN also decreased with increasing natural land cover ($r^2 = 0.67$, $p = 0.04$). Although there were no significant relationships demonstrated between TP or PO_4^{-3} and any land use or combination of land uses, both concentrations tended to decrease with increasing anthropogenic land use (Figure 2.7, B). Conversely, there was an increasing, though not significant (PO_4 r^2=0.31, TP r^2=0.22) correlation with natural land cover (Figure 2.7, D). Feeding operations was the only individual, non-generic land use to have a strong positive relationship with TN ($r^2 = 0.71$, $p = 0.03$), despite being less

than 2% of any stream watershed's area (Figure 2.8). Although it was not significant at $p < 0.05$, NO_3^- was marginally significant at $p < 0.07$ ($r^2 = 0.60$).

Discussion

Coastal Bays streams

The increasing percentage of anthropogenic land use (urban + agriculture) and feeding operations in the St. Martin River watershed is related to increased N and P concentrations and export, which is reflected by seasonal variations between watersheds. Stream nutrient concentrations in the St. Martin River watershed were consistent with the eutrophication observed by previous studies of non-tidal streams in the region (Wazniak et al. 2004, Primrose 2001). High flow period mean NO_3^- concentrations were all above 70 µM (1 mg N L^{-1}), indicative of high anthropogenic inputs (Roth et al. 2003). The stream sites also displayed distinct seasonal patterns in nitrogen concentrations and annual nutrient export, supporting the idea that land use, in conjunction with the physical characteristics of an individual watershed, results in a characteristic nutrient-signature (Fisher et al. 2006). Overall, TN was high (~300µM) during the high-flow period of December - March, and decreased in April. 1 was the only site that did not experience a large decrease in NO_3^- concentrations in the summer. Greater infiltration in this stream's watershed, which is in a different region of the watershed than the others, may result in an increase in NO_3^- transport from groundwater discharge instead of surface run-off (Jordan et al. 1997).

Variability in groundwater recharge and discharge rates between watersheds may also contribute to the unpredictability of patterns in TN and NO_3^- (Dillow and Greene

1999). Rates of groundwater recharge in nearby watersheds are in the range of 20.3 - 40.6 cm y^{-1} (Andreassen and Smith 1997, Johnston 1973, Johnston 1977). The high ratio of watershed area per meter of stream length in these watersheds provides further indications of groundwater discharge (Table 2.1). In addition, extensive ditching of tributaries and creeks in the St. Martin River watershed may alter runoff and infiltration patterns, increasing or decreasing nutrient concentrations by increasing connectivity along the flow path or enhancing biological uptake and denitrification, respectively (Abit 2005). Ditching may be responsible for a decrease in direct discharge under both high-flow and low-flow conditions.

NH_4^+ was not a significant component of TN, suggesting little direct discharge of human or animal wastes (Schoonover and Lockaby 2006). A summertime NH_4^+ peak >10 µM was observed at sites 2 and 6, but there was no such peak at any of the other sites. Sites 2 and 6 had the smallest watersheds, which were an order of magnitude smaller than the rest. Extremely low flows in the streams, especially those draining small areas, during the dry summer period could cause water to be stagnant or pond at times in the streams, leading to higher rates of nutrient cycling and subsequently higher NH_4^+ concentrations.

Like nitrogen, phosphorus concentrations also indicate significant anthropogenic inputs, and their speciation revealed differing annual patterns among the streams (Figure 2.6). Three of the streams, sites 2, 3, and 4, demonstrated dual TP peaks (5-6 µM) in the spring (March-April) and fall (October-November) as well as a decrease in PO_4^{-3} to approximately 1 µM or lower in the summer months. These observations of high P are concurrent with high-flow conditions and potential leaching of manure to streams, which could be a significant source of P loads in these agricultural watersheds (Foy and Withers

1995). The remaining streams at sites 1, 5, and 6 also displayed a peak between September and November, but they did not experience a summer PO_4^{-3} depression. In fact, TP and PO_4^{-3} increased between May and August at sites 5 and 6, and site 1 had its overall TP peak in June. These variations in P peaks in the summer and depressions in the winter may result from seasonal variations in subsurface flow and, most importantly, storm flow, due to its affinity for soil particles and sediment accumulation (Scheffer et al. 1992, Gächter et al. 2004). The similarities between TP and PO_4^{-3} concentrations observed in at site 1 on the Church Branch and that of site 4 on the Bishopville Prong were consistent with the pattern observed in the 2001 Synoptic Survey conducted by the Maryland Department of Natural Resources (Primrose 2001). Phosphorus accumulation in soils often results from the excess manure and fertilizers applied in areas in which agriculture and feeding operations comprise a large percentage of the watershed, as exhibited in both of these sub-watersheds (Carpenter et al. 1998).

Land use, especially poultry feeding operations in the region, is linked to N and P export. The differences in N and P export coefficients between watersheds, in addition to average high-flow (December - March) concentrations, demonstrated patterns among the stream watersheds that were consistent with their land use compositions. Sites 3 and 4, which had the largest watersheds, were expected to have the highest N and P export, but when these loads were normalized by land area, they fit in the middle of the range for export coefficients of the six watersheds (Table 2.3). All but the two watersheds with the highest percentage of natural land cover displayed area yields between 10 and 20 kg ha^{-1} y^{-1}, typical of mixed land use watersheds (Fisher et al. 1998). The watershed of site 6, displaying the highest percentage of cropland, the highest amount of feeding operations,

and the lowest natural land cover, had the highest high-flow TN concentration and N export coefficient, but it had the lowest TP concentration and P export coefficient.

This connection between cropland and nutrient loading in Delmarva was previously reported by a study of Delaware and Maryland watersheds that revealed that large percentages of cropland may be the dominant source of nitrogen in streams and rivers in the region (Ritter and Harris 1984, Jordan et. al. 1997). Conversely, the watershed of site 1, with the highest amount of natural land cover (47%) and lowest cropland and feeding operations (40% and 0.14%, respectively) had the highest TP export per hectare per year, suggesting an additional P source in the watershed, such as septic systems, may be leaching into the water (Fielding 2003). However, the estimated populations of watersheds 1 and 6 (33 and 12 people, by 2000 U.S. Census block data) are both low. Historically, the Perdue Hatchery at Showell, MD, was an additional point-source discharge to the site 1 on Church Branch, which was characterized by highly incised channels that were indicative of high flows (MDE 2001, Jesien 2008), but this plant was closed in 2006. In this case, channel erosion, often the most significant source of sediment to rivers and streams (Trimble 1997), may also be a dominant source of P, as a result of years of accumulation from both point-source and non-point discharge to the stream (Noe and Hupp 2005). Historical agricultural land use may result in considerable storage of phosphorus in the landscape, regardless of current land cover (Bennett et al. 1999, 2001). The reversal of overall highest and lowest TN and TP loading rates between sites 1 and 6 may be indicative of their difference in sources of the respective nutrients.

The strong relationships between TN and anthropogenic land use, natural land cover, and poultry feeding operations were found in St. Martin River (Figure 2.7 A and C, Figure 2.8 A). This represents the three main sources of N inputs to stream watersheds (Carpenter et al 1998, Jordan et al. 1997). Even though less than 2% of total land area, feeding operations are a significant source of TN in the St. Martin River watershed. Feeding operations in both Worcester County, MD and Sussex County, DE, are primarily broiler and other meat-type chickens, and these counties ranked 23 and 1, respectively, in the nation for their production levels in 2002 (USDA 2002). Because there were no significant relationships between TN, NO_3^-, or NH_4^+ with individual cropland or urban land percentages, it is possible that only the cumulative effect of land cover modification can be seen in these watersheds. A negative relationship with their converse, natural land cover, suggests that forest and wetlands reduce TN through their runoff filtering capacity or lack of sources (Wahl et al. 1997).

Forested and wetland-dominated watersheds also display an episodic pattern of sediment loading, which may also explain the lack of significant relationships between TP and land use (Ellison and Brett 2006). Although there are no such significant relationships with PO_4^{-3} or TP, regressions suggest negative relationships with all land uses except natural land cover, which exhibits a positive slope. It is possible that forests adjacent to streams are a P source, and poorly-drained, hydric soils enhance the leaching of P in this region (USDA 2008). Forests, especially in the riparian zone, may act as a source of both dissolved organic and inorganic P, especially under low redox conditions, where P that was once adsorbed to soil particles is released (Peterjohn and Correll 1984, Whigham et al. 1988). These findings also concur with a study by Ritter (1986) that

showed a strong relationship between stream nutrient export and watershed hydrologic characteristics on the eastern Delmarva Peninsula. The investigation of a correlation between hydric soils and stream P concentrations in the Coastal Bays may help to support this hypothesis.

Due to a limited sample size and short (<2 year) time frame, further conclusions about specific effects of land use are unclear. Hill (1986) found that a dataset of less than 6 years may provide inaccurate estimates of annual loading due to considerable year-to-year variations, resulting in calculation errors of 20-53%. Because export calculations were made using baseflow discharge from a neighboring watershed, actual export of nitrogen may be lower, and phosphorus, higher, if stormflow was also included (Gächter et al. 2004). Phosphorus transport is highly dependent upon stormflows, especially in agricultural catchments where fertilizers account for the majority of P in topsoil, and subsequently, in runoff (Stutter et al. 2008). Stream variability in monthly mean flows can also be seen in the within-site variability in nutrient concentrations. To further clarify these relationships, sampling over a longer time series and/or including more watersheds would be beneficial.

Watershed loading application

The stream watersheds and export coefficients discussed in the above sections can be used to estimate total nutrient inputs for the Coastal Bays region. The application of local empirical data and land use change on nutrient export to large-scale watersheds may help to compare possible effects of land use and loading between bays. This data has

been used to estimate the nutrient loading to the Coastal Bays from both terrestrial and atmospheric sources.

Stream watersheds were highly variable in their estimates of an export coefficient for feeding operations, ranging from 364 to 2,323 kg N ha^{-1} y^{-1} and 9 to 210 kg P ha^{-1} y^{-1} (Table 2.3). However, these coefficients were within an acceptable range of regional export (Fisher, pers. comm.). The means of these empirically-derived N and P coefficients, 922 kg N ha^{-1} y^{-1} and 55.7 kg P ha^{-1} y^{-1}, were then used to calculate land use loads for the whole-bay watersheds (Table 2.4).

St. Martin River displayed the highest N (99,464 kg N y^{-1}) and P (5,183 kg P y^{-1}) loads, while Johnson Bay displayed loads of 75,795 kg N y^{-1} and 1,218 kg P y^{-1} and Sinepuxent Bay had loads of 39,520 kg N y^{-1} and 673 kg P y^{-1} (Table 2.5). In St. Martin River, crop agriculture was the dominant source of N (50%), while feeding operations contributed the highest percentage of P (56%). Point source inputs into the River were only 4.0% of N inputs and 2.8% of P. In both Johnson Bay and Sinepuxent, atmospheric deposition was still the main contributor of both N and P (74% and 34% of Johnson Bay and 70% and 30% of Sinepuxent's loads), but urban land was the major source of P in Sinepuxent, supplying 35% of the P load in this watershed (Figure 2.9) . Crop agriculture was the second major land use contributor in Johnson Bay, supplying 20% of N and 29% of P.

The use of local land use export coefficients in the calculation of total annual N and P loads revealed differences in land use pressures among the three Coastal Bays. The land use composition and estimated nutrient loading in St. Martin River, Johnson Bay, and Sinepuxent revealed potentially large effects of anthropogenic land cover alteration.

Land use, especially urban and agricultural land, has been linked to increased fluxes of sediment, N, and P in estuaries and coastal environments (Nixon 1995). In the Maryland Coastal Bays, it is believed that terrestrial nutrient loading from these sources is the leading cause of water quality degradation in the region (Wazniak et al 2004, Fertig et al. 2006). Nutrient loads calculated from export coefficients support the hypothesis that diffuse sources dominate the N and P loads of the Coastal Bays, but their contributions may vary by region; crop agriculture and feeding operations contribute most N and P to the St. Martin River, atmospheric deposition and crop agriculture in Johnson Bay, and atmospheric deposition and urban development in Sinepuxent Bay.

However, widespread application of the export coefficient model approach should be cautioned, especially in the determination of an actual loading number, due to coefficient uncertainty, inconsistent local conditions, topography, soils, and other variables that affect nutrient loading (Jordan et al. 1997, Norton and Fisher 2000). Calibration of these models by periodic measurements of concentration and discharge in regional sub-watersheds can be used as an effective alternative, which allows for a more local-based approach (Marchetti and Verna 1992). However, even model calibration through the use of yearly empirical data must be undertaken with caution because aquatic nutrient fluxes are influenced by climate variability, allowing for a wide range of concentrations from year to year (Curran and Robertson 1991, Bachman and Phillips 1996). Annual loads of N and P that were calculated for St. Martin River using this method were close to those determined by previous numerical model used in 2001 by the Maryland Department of the Environment (MDE 2001).

Employing coefficients applicable to the hydrological regime and soil composition of the region (Lee et al. 2001, Fisher et al. 1998, Fisher 2007), as well as empirically-derived poultry feeding operations coefficients, may provide a more accurate assessment of annual N and P loads and relative contributions of each land use to these loads. However, the variability of coefficient estimates for feeding operations among stream watersheds suggests that there are fine-scale differences between watersheds that may include physical characteristics (Lee et al. 2001), manure management practices (Sharpley et al. 1997), and position in relation to natural filters such as vegetation (Lowrance et al. 1984). In addition, the compounding of errors within the feedlot calculations adds uncertainty to these results.

The spatial distribution of land use within a watershed, particularly forest and wetlands, may also have significant effects on nutrient dynamics and the percentage of overall loading that is retained in a watershed (Whigham et al. 1988, Haycock et al. 1993). The overall land use composition of St. Martin River, Johnson Bay, and Sinepuxent Bay varied as a function of distance from each bay's shoreline. St. Martin River, when compared with Johnson Bay and Sinepuxent, displays a large percentage of urban land within the first 500 m of the coastline, while the latter two are primarily wetland and forest (Figure 2.4). The effects of crop agriculture, one of the dominant land uses in the Coastal Bays, may be mitigated by the position of vegetation adjacent to the waterway; other studies on the Atlantic Coastal Plain have determined that the presence of riparian forests and wetlands may reduce 68% of N and 30% of P (Lowrance et al. 1984) and reduce sediment loads up to 90% (Peterjohn and Correll 1984). The proximity of feeding operations to the coastline, particularly in regions dominated by well-drained,

sandy soils like Johnson Bay, may also maximize the transport of their nutrient loads (McGechan et al. 2005, Mueller et al. 1995). Position of these land uses, in combination with other hydrological factors, may help draw a better overall picture of the watershed and identify individual areas of concern that can be used for management purposes.

Implications

Results of the present study support the need for further examination of land use patterns and their subsequent impacts on nutrient loading and water quality of the Maryland Coastal Bays. In order to understand the cumulative effect of anthropogenic inputs on a watershed, sources of nutrients, their spatial positioning, physical characteristics of the land (soils, hydrology), and land use history must be considered. These parameters are important both within and among the Coastal Bays sub-watersheds, where water flows and the effect of land use may vary at fine spatial scales, leading to very different results. Feeding operations, though a small percentage of watershed area, may be especially important in contributing to high nitrogen and phosphorus concentrations and loads. Use of local export coefficients to determine nutrient loading for a watershed is helpful to address relative nutrient contributions of different land uses and compare the land use pressures among watersheds. The ability of management efforts to improve water quality in the Coastal Bays lies in addressing the key sources in each watershed.

Tables

Table 2.1: Stream site location, watershed area, and land use composition for six streams in the St. Martin River watershed of the Maryland Coastal Bays

Site	Stream Name	Latitude (dd)	Longitude (dd)	Area (ha)	Land Area (m^2) per m of Stream	% Cropland	% Urban	% Feeding Operations	% Forest	% Wetlands
1	Church Branch	38.3964	-75.2056	1,284	325	40	13	0.14	47	0
2	Slab Bridge	38.4419	-75.1985	131	228	49	16	0.46	34	0
3	Carey Branch	38.4460	-75.2113	1,593	206	54	15	0.58	19	12
4	Dam	38.4424	-75.1945	3,056	221	51	18	0.82	18	12
5	Buntings Branch	38.4556	-75.2093	907	251	46	22	1.3	14	17
6	Cemetery Branch	38.4494	-75.1986	133	164	64	16	1.6	13	5
USGS Gauge	Birch Branch	38.4093	-75.2124	1,652	--	--	--	--	--	--

Table 2.2: Physical descriptions of three watersheds in the Maryland Coastal Bays

Bay	Land area (ha)	% Cropland	% Urban	% Feeding Operations	% Forest	% Wetlands	Soil type (coast --> interior)	Pop. density (No. ha^{-1})	Water area (ha)	Land:water ratio	Residence time (days)	Average depth (m)
St. Martin River	10,491	47	17	0.50	29	6	well-drained to hydric	0.86	830	12.6	20-30	1.2
Johnson Bay	4,911	31	2	0.09	37	29	hydric to well-drained	0.10	5,023	2.0	60	1.1
Sinepuxent	3,058	11	22	0.02	43	23	well-drained to hydric	0.41	2,480	1.2	10-20	1.6

Table 2.3: Mean winter (December-March) baseflow N and P species concentrations, annual loading, and estimates of N and P feeding operations (Est. Feedlot N/P loading coeff.) loading coefficients for six streams in the St. Martin River watershed. Loading coefficients were calculated by using estimated stream loads, land use composition, and adjusted loading coefficients for other land uses (cropland, urban, forest) and then solving for a feeding operations coefficient for each watershed.

Site	NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	TN export (kg N y^{-1})	TP export (kg P y^{-1})	TN yield coeff. (kg N ha^{-1} y^{-1})	TP yield coeff. (kg P ha^{-1} y^{-1})	Est. Feedlot N yield coeff. (kg N ha^{-1} y^{-1})	Est. Feedlot P yield coeff. (kg P ha^{-1} y^{-1})
1	5.3	93.4	185.6	1.10	2.82	11980	608	9.33	0.47	2323	210
2	8.2	161.9	263.2	0.85	2.59	1505	49	11.52	0.37	1290	38
3	8.6	94.9	191.4	0.96	2.82	15143	621	9.51	0.39	364	34
4	12.0	105.0	241.4	1.09	3.48	32026	1371	10.48	0.45	375	31
5	9.9	157.2	275.6	0.69	2.14	11931	327	13.15	0.36	451	13
6	5.3	328.5	430.6	0.78	1.84	2712	48	20.35	0.36	730	9

Table 2.4: Literature sources, locations, and export coefficients of different types of land use, applicable to the Maryland Coastal Bays region. Empirical stream export results obtained in this study were used to compute export coefficients for feeding operations (poultry) in this region.

Land use	*kg N ha^{-1} y^{-1}*	*Reference*	*kg P ha^{-1} y^{-1}*	*Reference*	*Location*
Crop agriculture	10	Fisher et al. 1998	0.23	Lee et al., 2001	Choptank River (Delmarva)
Urban	10	Beaulac and Reckhow, 1982	0.35	Reckhow et al., 1980	N = nationwide P = Higgins Lake (MI)
Feeding Operations	292	this study	55.7	this study	Coastal Bays (MD)
Forest	1	Lee et al., 2001, Fisher et al. 2007 (unpub.)	0.09	Lee et al., 2001, Fisher et al. 2007 (unpub.)	Choptank River (Delmarva)
Atmosphere	11.2	Volk et al. 2006	0.082	Volk et al. (in prep)	Rehoboth Bay (DE)

Table 2.5: Land use annual N and P loading and percent contribution from various land uses for three Maryland Coastal Bays watersheds, using export coefficients obtained from locally-applicable literature and empirical data (see Table 2.4).

St. Martin River	Load (kg y^{-1})	Yield coeff. (kg ha^{-1} y^{-1})	%Cropland	% Urban	% Feeding Operations	% Forest	% Atmos. Dep.	% Point Source
N	99,464	9	50	18	15	3.1	9.3	4.0
P	5,183	0.49	22	12	56	5.3	1.3	2.8

Johnson Bay	Load (kg y^{-1})	Yield coeff. (kg ha^{-1} y^{-1})	%Cropland	% Urban	% Feeding Operations	% Forest	% Atmos. Dep.	% Point Source
N	75,795	15	20	1.4	1.7	2.4	74	0
P	1,218	0.25	29	3.2	21	13.6	34	0

Sinepuxent	Load (kg y^{-1})	Yield coeff. (kg ha^{-1} y^{-1})	%Cropland	% Urban	% Feeding Operations	% Forest	% Atmos. Dep.	% Point Source
N	39,520	13	9	17	0.4	3.3	70	0.13
P	673	0.22	11.7	35	4.1	18	30	0.74

Figures

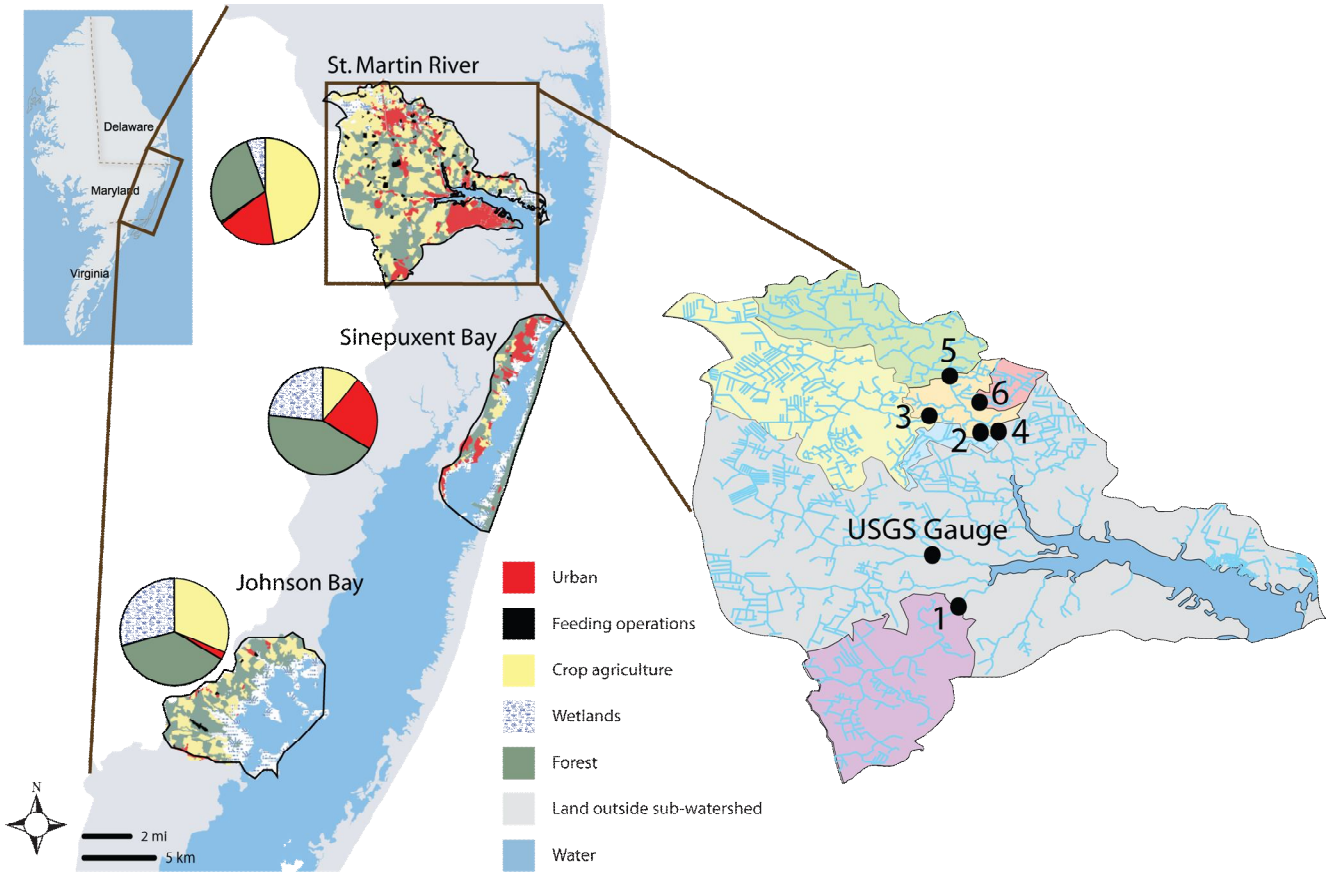


Figure 2.1: Study watersheds and land use composition of St. Martin River, Johnson Bay, and Sinepuxent Bay in the Maryland Coastal Bays. Land use data was obtained from the Maryland Department of Planning (2002) and 2005 aerial photography from the Maryland Department of Natural Resources. Six sites (1, 2, 3, 4, 5, and 6) were monitored monthly in the St. Martin River watershed from July 2006- January 2008 for nutrient concentrations. Discharge data for July 2006-September 2007 was obtained from the USGS Birch Branch continuous flow site and normalized by area to calculate monthly discharge from each watershed in the region.

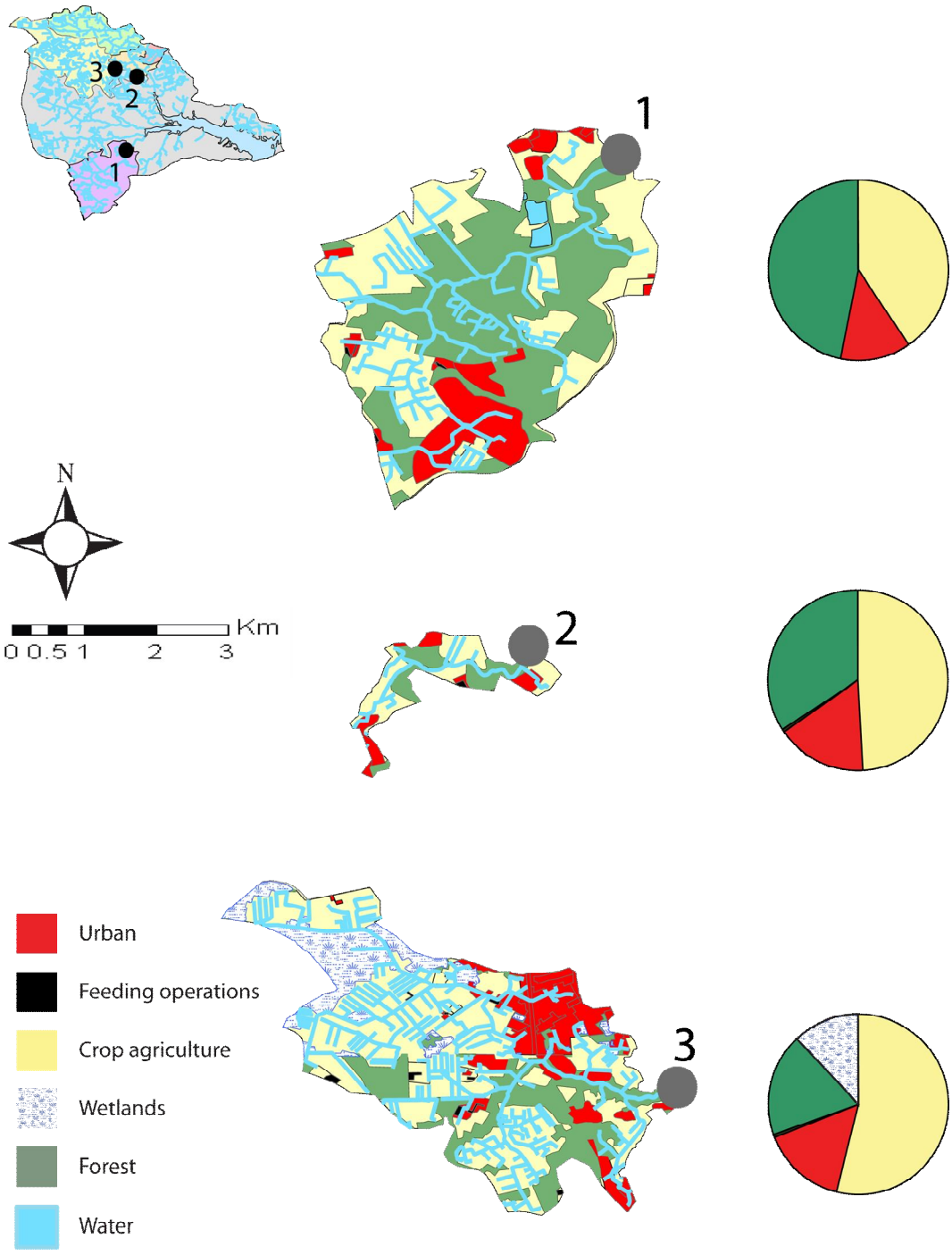


Figure 2.2: Location and watershed land use composition of stream sites 1, 2 and 3 in the St. Martin River region.

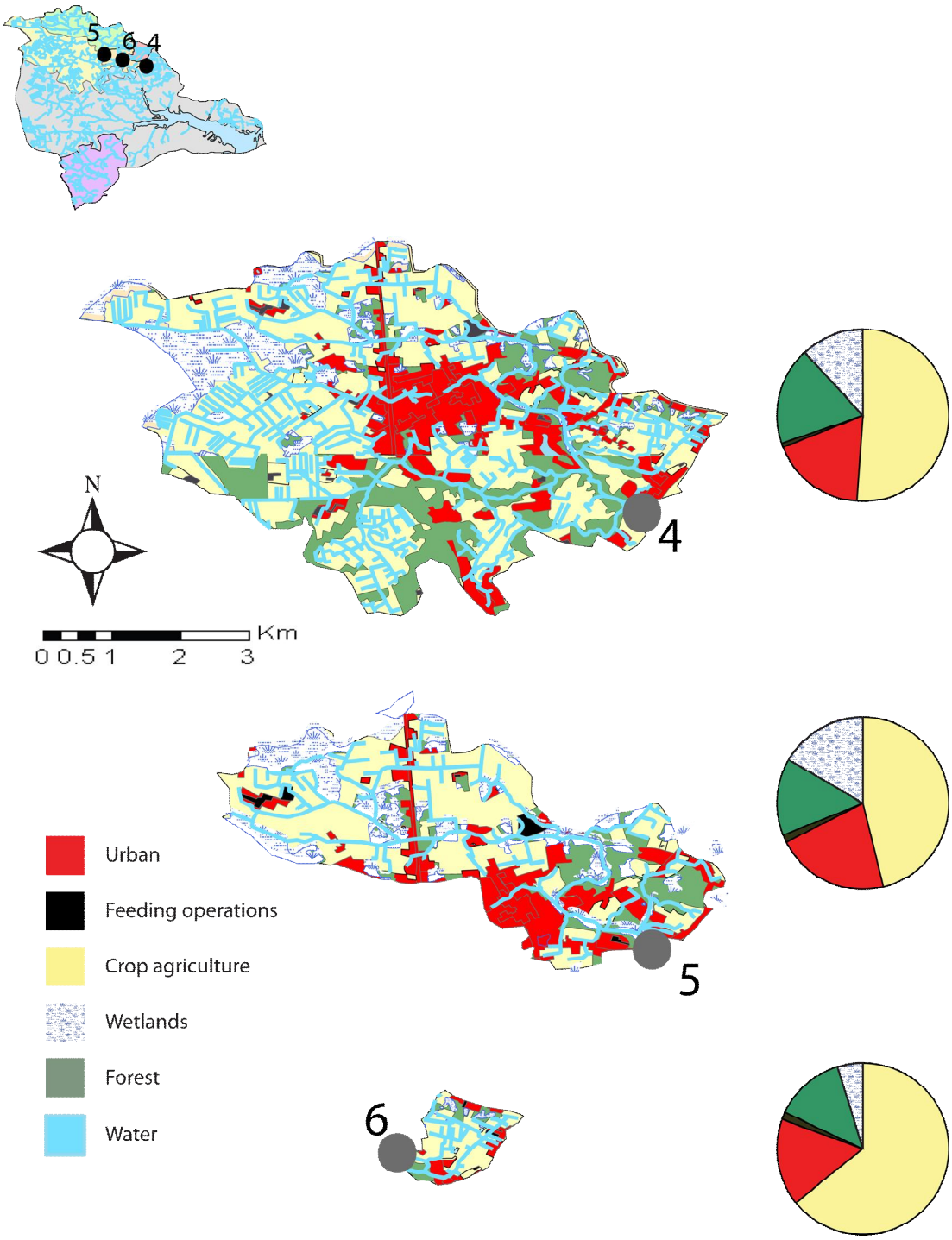


Figure 2.3: Location and watershed land use composition of stream sites 4, 5 and 6 in the St. Martin River region.

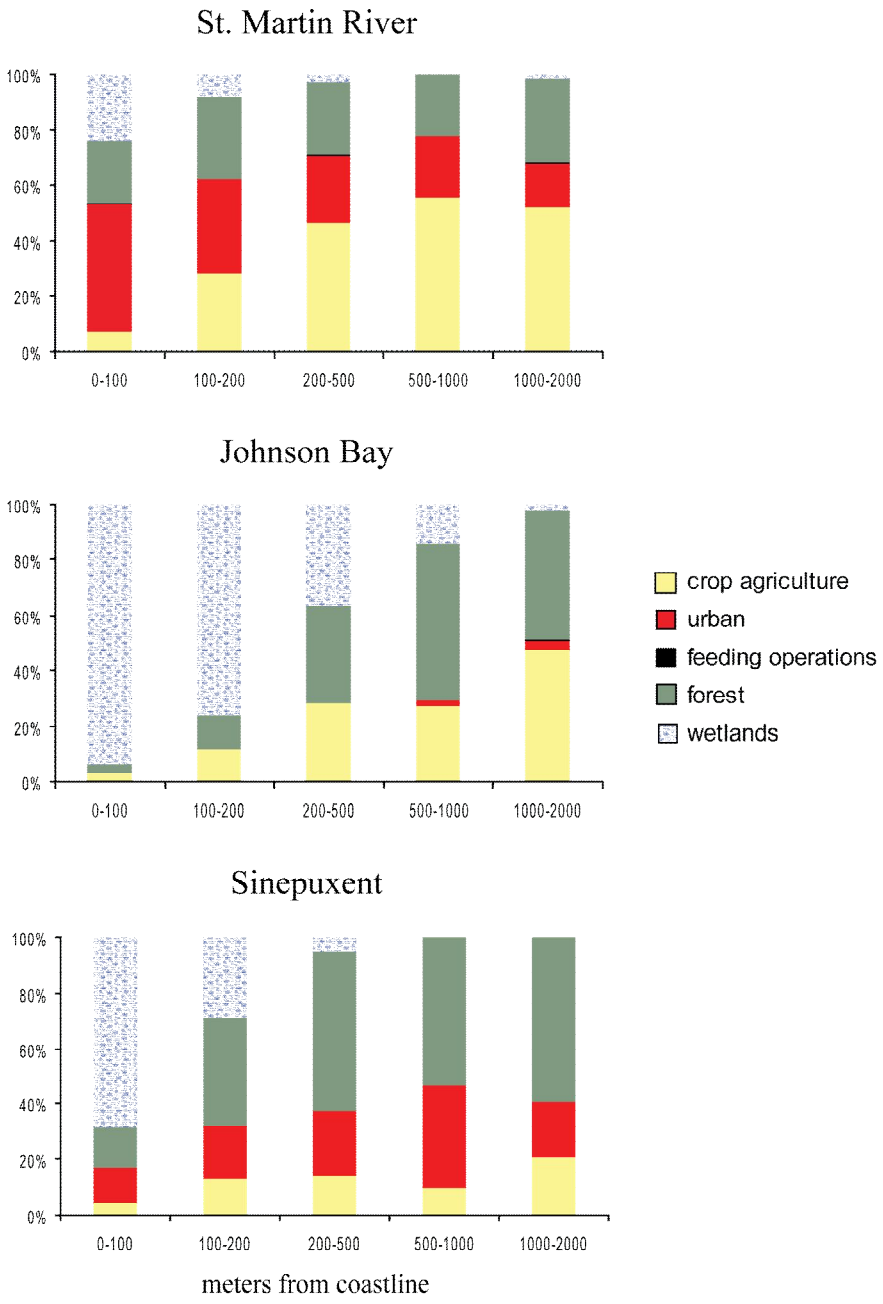


Figure 2.4: Land use composition as a function of distance from the coastline of three Maryland Coastal Bays. 2002 land use/land cover data was provided by the Maryland Department of Planning and the Delaware Department of Natural Resources. Using the "buffer" function in the ArcMap GIS environment, land use files were clipped and analyzed at different distances, and composition of land cover was computed by dividing individual land use area by total area between the shoreline distances.

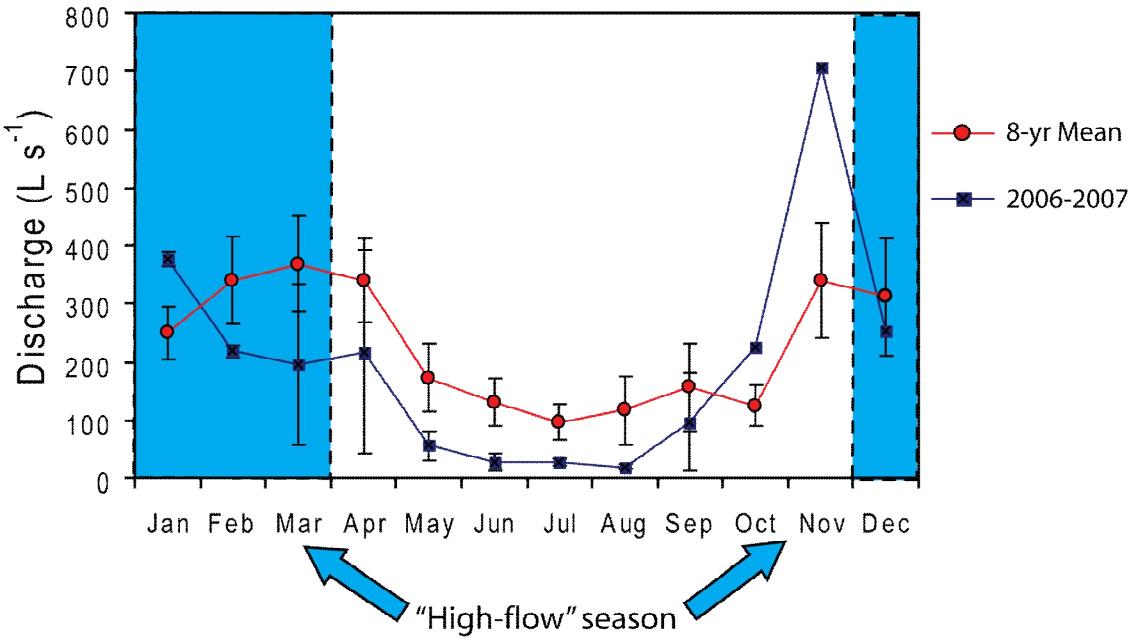


Figure 2.5: Average monthly discharge at the USGS continuous monitoring gauge on Birch Branch for 8 years and for the study period (2006-2007). This gauging site is located within the St. Martin River (see Figure 2.2) and representative of flow conditions experienced by different sites. Mean monthly flows were calculated from data made available by the US Geological Survey for the 8-year period Dec. 1999-Sept 2007. Study period means were calculated from July 2006-September 2007. The mean October, November, and December discharges included available 2006 data only. Blue areas represent the "high-flow" season used for nutrient vs. land use regression analyses.

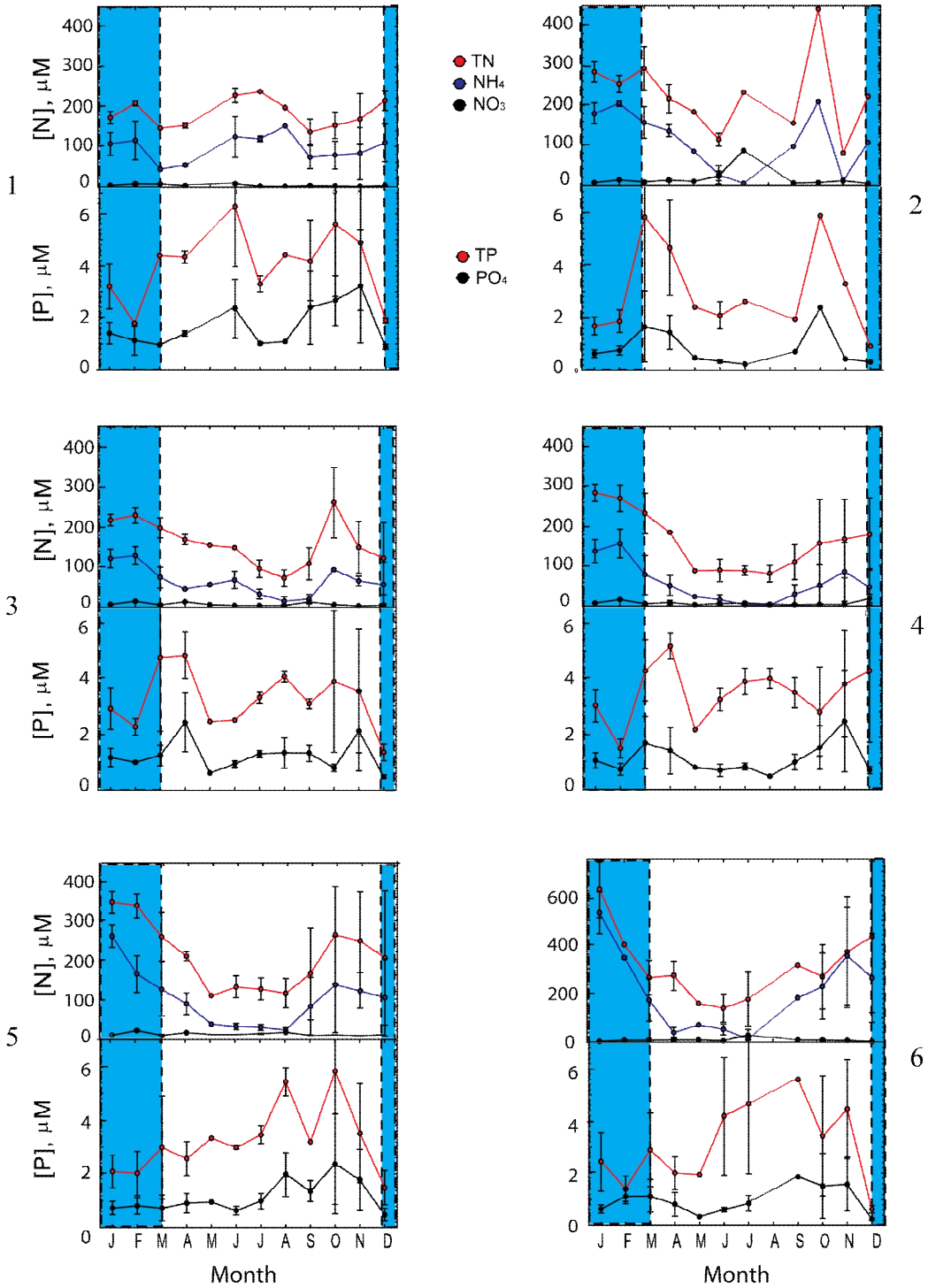


Figure 2.6: Sites 1-6 monthly mean baseflow concentrations of nitrogen and phosphorus species. Data was collected by monthly grab samples July 2006-January 2008. Error bars represent the standard error of each month over this time period. Blue areas represent the "high-flow" season concentrations used for N and P vs. land use regression analyses. March was the only month with a single measurement, and thus, no standard error could be computed.

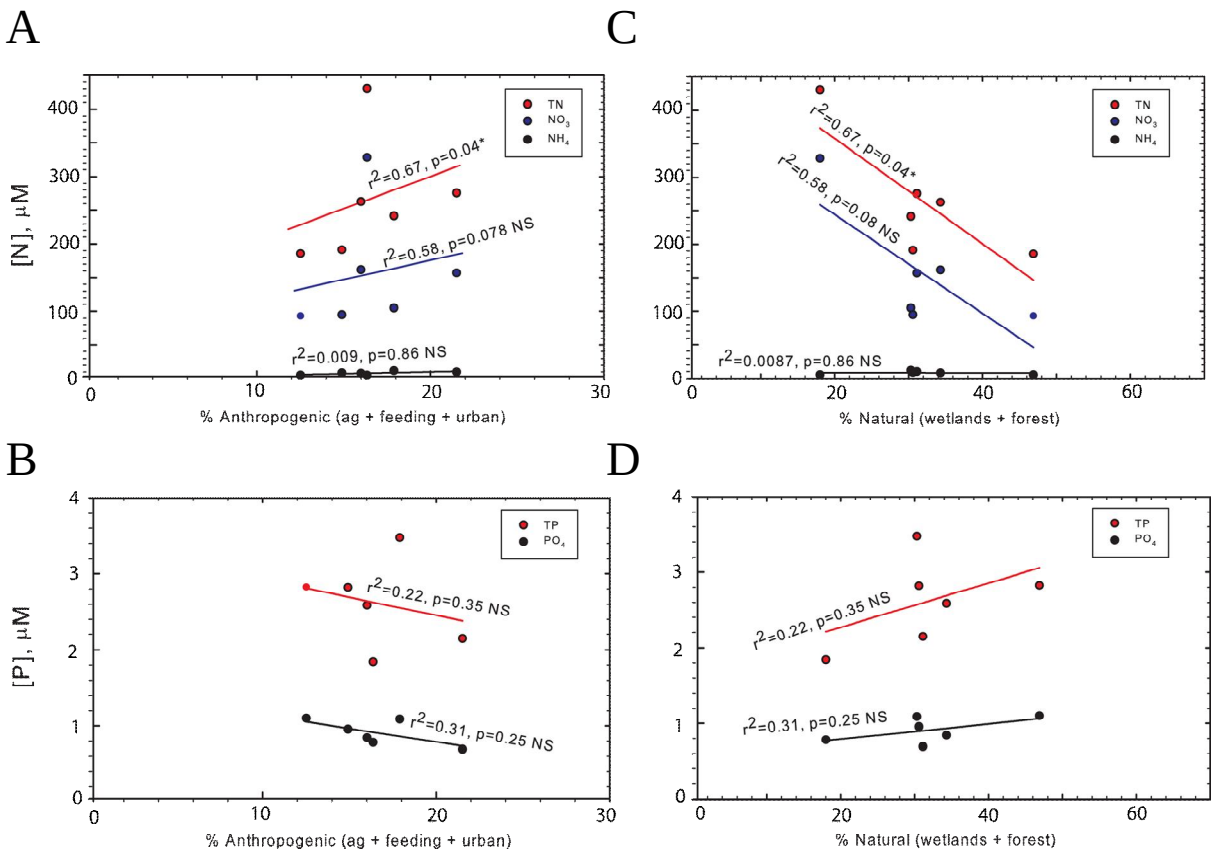


Figure 2.7: Regression analysis results of mean winter nitrogen and phosphorus species vs. % of stream watershed consisting of anthropogenic (agricultural, feeding operations, and urban) (A and B) and natural (forest and wetlands) (C and D) land use. Mean concentrations of nutrient species were calculated for the high-flow period December-March using data from December 2006-January 2008 for six stream sites. Watershed land use data was obtained from Maryland Department of Planning 2002 and Delaware Department of Natural Resources land use/land cover files. Statistically significant ($p < 0.05$) results are denoted by *, and non-significant results are denoted by "NS."

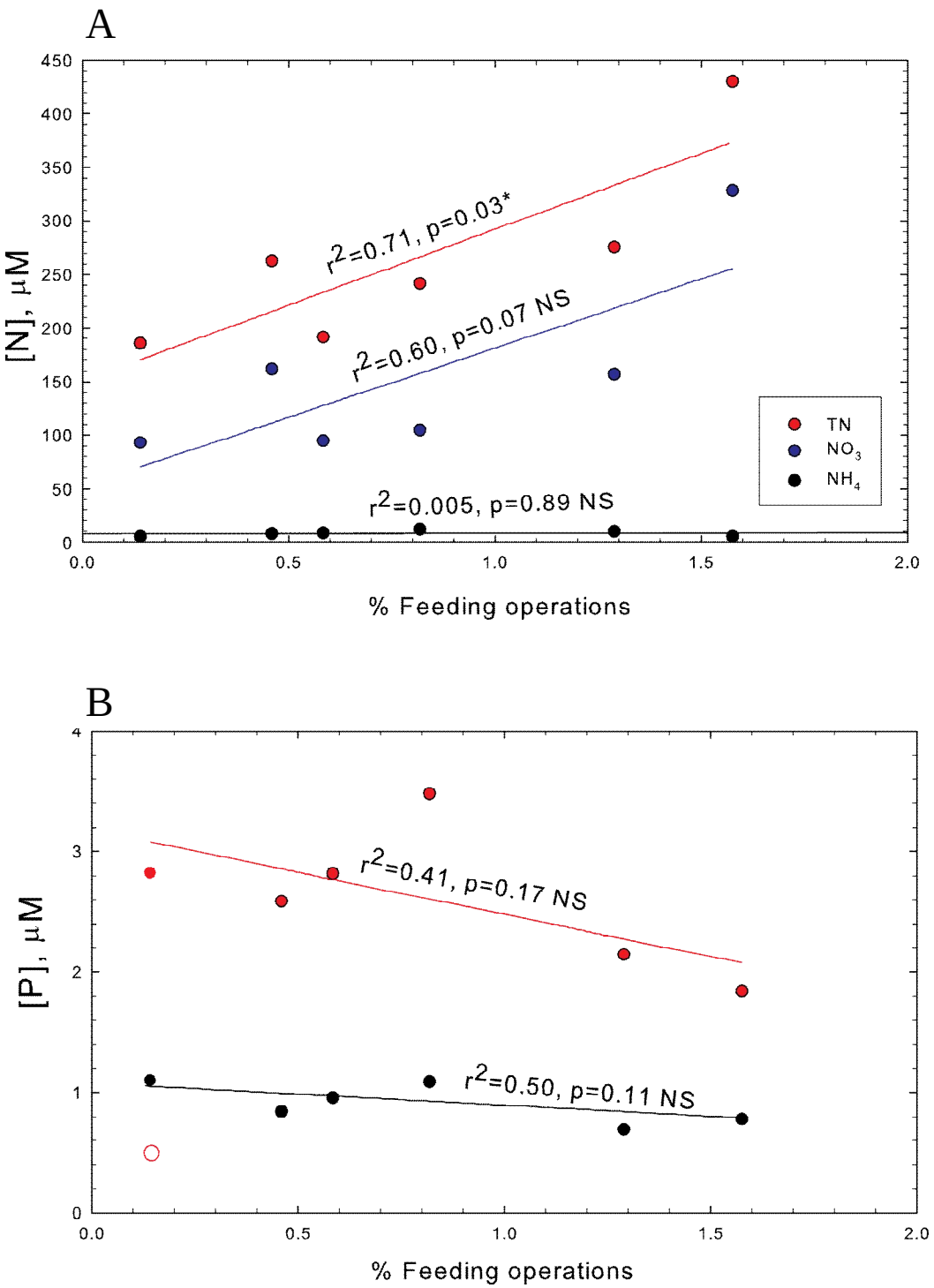


Figure 2.8: Regression analysis results of mean winter nitrogen (A) and phosphorus (B) species vs. % of stream watershed area consisting of feeding operations. Mean concentrations of nutrient species were calculated for the high-flow period December-March using data from December 2006-January 2008 for six stream sites. Watershed land use data was obtained from Maryland Department of Planning 2002 and Delaware Department of Natural Resources land use/land cover files, which were then edited using 2005 aerial photography provided by the Maryland Department of Natural Resources. Statistically significant ($p < 0.05$) results are denoted by *, and non-significant results are denoted by "NS."

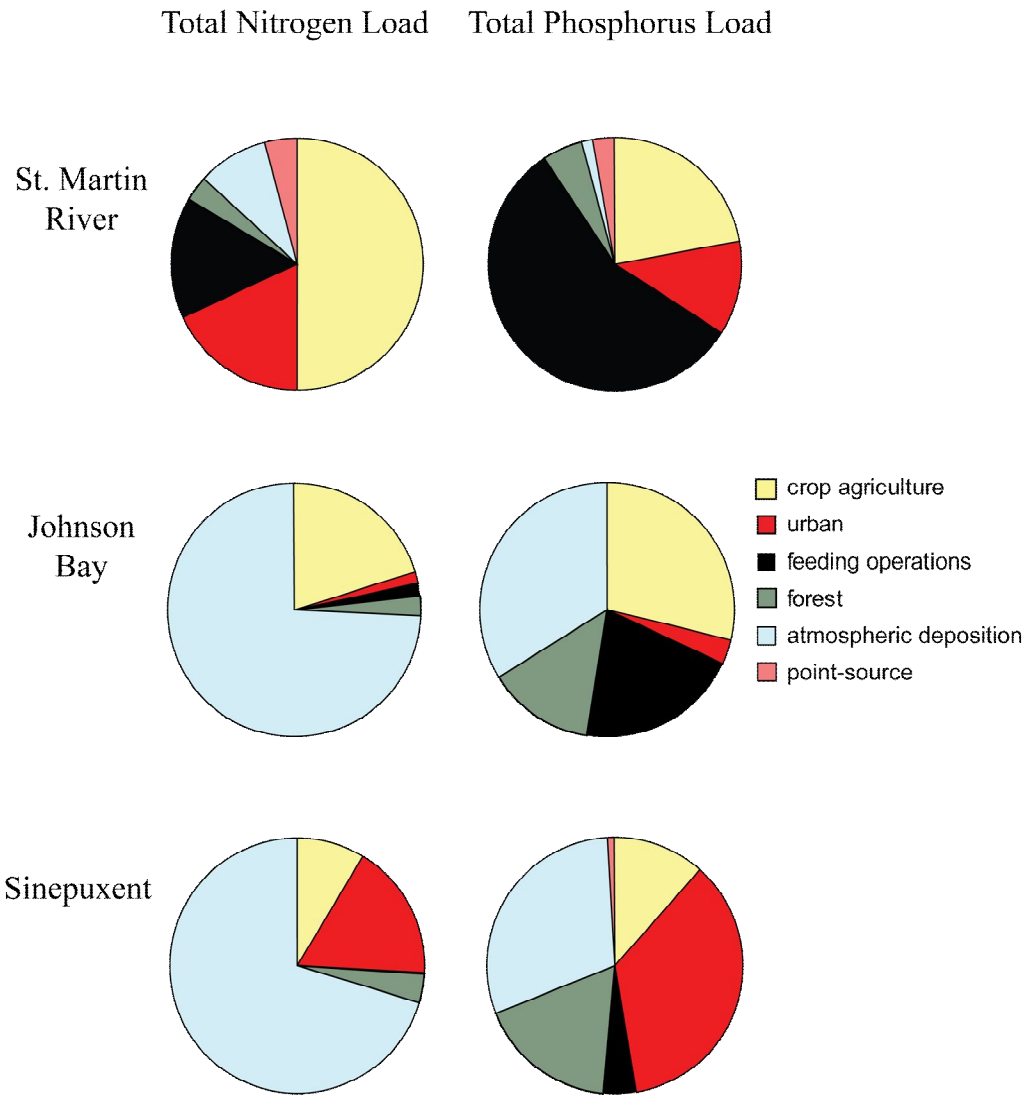


Figure 2.9**:** Calculations of yearly nitrogen and phosphorus loading contributed by each land use for three of the Maryland Coastal Bays, using export loading coefficients provided by Fisher et al (1998), Beaulac and Reckhow (1982), Lee et al (2001), Fisher et al. (2007), and Reckhow et al. (1980). Feeding operations coefficients were calculated using stream loads obtained from empirical stream data collected July 2006-January 2007. Stream watershed land use composition, along with the adjusted land use loading coefficients were used to solve for a feeding operations coefficient for each watershed and a mean coefficient value to be applied to the larger Coastal Bay watersheds. Atmospheric deposition was calculated from coefficients provided by Volk et al. (2006, and in prep.). Point source data was obtained from the Ocean Pines Wastewater Treatment Plant and the Assateague National Seashore Visitor's Center for 2007 N and P loads.

Chapter III: Analysis of spatial patterns in water quality in three Maryland Coastal Bays, U.S.A.

Abstract

The Coastal Bays of Maryland display different spatial patterns in water quality that can be attributed to their different basin characteristics. Two of these shallow bays were sampled in the late spring and summertime months of May and July 2006 and three in 2007 to compare their nutrient patterns in relation to physical attributes, monthly variation, and precipitation. Results demonstrated that the tidal St. Martin River, with a highly agricultural and developed watershed, exhibited high upstream total nitrogen (TN) and total phosphorus (TP) concentrations, mostly in organic form. Low dissolved oxygen (DO) and high bacterial abundance indicates a net heterotrophic state in St. Martin River. Erosion and nutrient release from sediments influenced water quality in Johnson Bay, which has a long water residence time (~60 days), little freshwater input, and is dominated by natural land cover (forest and wetlands). Precipitation influenced all areas of this bay, with increasing TP and chlorophyll *a* concentrations in July. Sinepuxent Bay was used as a reference endpoint site in 2007 because of a high flushing rate due to its location close to the Ocean City Inlet, but this bay also displayed evidence of degraded water quality and increased nutrient cycling. This study demonstrates that the water quality of the Maryland Coastal Bays is influenced by external nutrient inputs and increased within-bay nutrient cycling, reflecting increasing anthropogenic pressures and an inability of the system to maintain net export of nutrients out of the region.

Introduction

Like other estuarine systems in the United States, the Maryland Coastal Bays are currently experiencing water quality and habitat degradation due to anthropogenic nutrient loading and land use change. Located between the Delmarva Peninsula and its sandy barrier islands, the Coastal Bays are comprised of a series of lagoons with watersheds of various sizes and land use compositions.

Because these bays are shallow (< 3 m), exhibit restricted tidal exchange, and have limited freshwater inflow, they are especially susceptible to eutrophication (Bricker et al. 1999). Non-point source pollution (mainly row crop agriculture such as corn and soybeans and commercial poultry operations) contributes an estimated 95% of the total nutrient load to the Coastal Bays, due to an absence of industrial and wastewater treatment plants and predominant reliance mainly on septic systems in the surrounding watersheds (Boynton et al. 1993).

A broad-scale survey conducted in 2004 assessed regional patterns in water quality and indicated high concentrations of total nitrogen, total phosphorus and elevated $\delta^{15}N$, which is a sensitive indicator of processed nitrogen and potential wastewater input (Costanzo et al. 2001, Jones et al. 2004, Wazniak et al. 2004). In the Maryland Coastal Bays, organic forms of both nitrogen (N) and phosphorus (P) are more abundant than inorganic species of N and P, which tend to remain lower than 5µM and 1µM, respectively. Dissolved organic nitrogen (DON) may range between 10 and 30µM and total nitrogen (TN) may be greater than 30µM (Glibert et al. 2007). The four regions studied previously: St. Martin River, Public Landing, Johnson Bay, and Southern Chincoteague Bay, demonstrated degradation in water quality parameters in 2004 and

once again in 2006, resulting in conditions below threshold values for seagrasses, fisheries, and other aquatic life that had been established by the Maryland Coastal Bays Program and the Maryland Department of Natural Resources (Wazniak et al. 2004, Fertig et al. 2006). High turbidity and bottom oxygen concentrations lower than a threshold value of 3 mg L^{-1} were consistent in the upstream reaches of St. Martin River and also in Johnson Bay (Jones et al. 2004, Fertig et al. 2006). The state of the water quality in Johnson Bay was of particular concern because, unlike St. Martin River and Public Landing, it is relatively undeveloped, has intact marshes, and had exhibited acceptable nutrient levels in previous years (Jones et al. 2004). Studies have indicated that nutrients have increased in most of the Coastal Bays since 1991, after a period when concentrations were decreasing (Wazniak et al. 2007).

In addition to increased nutrient levels, the Maryland Coastal Bays also have experienced dramatic shifts in their macrobiotic communities, including decreases in seagrass cover (Wazniak et al 2004), more intense phytoplankton blooms of the brown tide organism *Aureococcus anophagefferens* (Trice et al. 2004) and other harmful algae species (Tango et al. 2005), and chlorophyll concentrations above the established Maryland Coastal Bays Program threshold of 15 μgL^{-1} (Wazniak et al. 2007). Increased turbidity from nutrient enrichment may be a leading source of stress to seagrass-dominated coastal lagoons, which have very high light requirements (Orth et al. 2006, Dennison et al. 1993). Declines in seagrass beds can have significant consequences for organisms that rely on them for habitat and feeding, such as brant geese and bay scallops (Milne and Milne 1951). In addition, forage finfish, which also depend on seagrass habitat in the Coastal Bays, have experienced a downward trend in population since the

mid-1980's, as indicated by both trawl and seine surveys (Casey et al. 2002). Therefore, increases in nutrient concentrations can have cascading effects on populations of upper level organisms as well as fisheries production.

A shift to a eutrophic state in the Coastal Bays may also have an effect on nutrient cycling and release from sediments, bacterial communities, and virus abundance. Bacteria function as sources and recyclers of dissolved organic carbon (DOC), as well as regenerators of dissolved organic nutrients from inorganic forms (Azam et al. 1983). High levels of dissolved organic nutrients may be conducive to the growth of bacterial populations in the Maryland Coastal Bays, enhancing respiration and resulting in less efficient transfer of carbon to higher trophic levels (Suttle 2005). Virus abundance is also indirectly promoted by eutrophication because nutrients increase the abundance of the bacteria, the main host of viruses (Danovaro et al. 2003). Therefore, in situations where viruses have been correlated to chlorophyll *a* concentrations, there is usually an even stronger correlation with bacteria (Paul et al. 2003). Gradients in eutrophication have been linked to gradients in bacteria and viral abundance, as exhibited in the waters of Brisbane River/Moreton Bay in Australia (Hewson et al. 2001). However, no such studies of these possible correlations had been conducted previously in the Maryland Coastal Bays.

Assessment of fine-scale spatial patterns in physical parameters, nutrient enrichment, and biological indicators may aid in the understanding and identification of regions of concern both within and among the Coastal Bays. The varied susceptibility of estuarine systems occurs as a response to many different conditions, including relative flushing, tidal currents, physiographic setting, and even biotic factors (National Research

Council 2000). Current detailed physical and water quality monitoring data has not been sufficient in determining the variability nor predicting future conditions associated with these variables, as demonstrated by a mapping study of environmental gradients in Chincoteague Bay (Allen et al. 2007). An analysis of both spatial and temporal changes, including differences between wet and dry years, is important in revealing patterns at multiple scales, especially in such a diverse environment as the Maryland Coastal Bays. Three regions, St. Martin River, Johnson Bay, and Sinepuxent, were chosen for fine-scale water quality assessment (Figure 3.1).

It was hypothesized that water quality degradation in the Maryland Coastal Bays is caused by land-derived nutrient inputs. This study posed the following four questions in order to examine this hypothesis:

1. How do physical, chemical, and biological parameters differ between the bays of St. Martin River, Johnson Bay, and Sinepuxent Bay and between the months of May and July?
2. Is the water quality in upstream and inshore sections of St. Martin River and Johnson Bay, respectively, more degraded than downstream and offshore sections?
3. How does water quality in the bays and sections of the bays differ between wet and dry years?
4. Do correlations reveal relationships between nutrients, chlorophyll *a*, bacteria, and dissolved oxygen?

Methods

Study locations

St. Martin River, which has a watershed of 10,531 ha, extending into Delaware, is the largest estuary in the Coastal Bays. Its watershed is 46% crop agriculture and 16% urban development, with only 35.5% covered by forest or wetlands (Table 3.1). Johnson Bay, a sub-basin of Chincoteague Bay to the south, has a watershed of 9,935 ha and is 66.5% forest and wetland cover. The third bay, Sinepuxent, located towards the Ocean City Inlet, was used for relative comparison to the other two bays along a gradient of land use, geographical position, and flushing time. Sinepuxent has a small watershed of 3,058 ha that is 66.5% forest and wetlands, and it has the shortest water residence time of the three bays. In the State of the Maryland Coastal Bays Report (2004) water quality was characterized as being good, with low N, P, and chlorophyll *a* concentrations, making it a reference location by which to evaluate the other two bays.

St. Martin was divided on the basis of physical position and preliminary bathymetric maps into four sections: 1) the Bishopville Prong (Bishop), 2) the Shingle Landing Prong (Shingle), 3) Middle, and 4) Mouth sections (Figure 3.1). There were 21 total sampling locations in 2006 and 25 sampling locations in 2007 within the tidal-fresh river and adjoining estuary (Table 3.2). The sampling sites were chosen to get a broad spatial perspective in the respective bays, based on the statistical procedures used in previous studies (Pantus and Dennison 2005, Jones et al 2004). Two additional sites towards the river's source were added in July 2007. In 2007, six of these sites were focus sites, where all nutrients, chlorophyll *a*, and phaeophytin were measured in triplicate, and

additional samples were also collected for total suspended solids (TSS), volatile suspended solids (VSS), bacteria, and viruses (Appendix Tables G and H).

In Johnson Bay, a total of 28 sites were sampled in 2006 and 22 sites were sampled in 2007, five of which were chosen as focus sites in 2007 (Table 3.2). Sites in this bay were also grouped into four sections based on position within the bay and in relation to land forms. Johnson Bay was divided into: 1) Brockanorton Bay (Brock), 2) Johnson Bay (Johns), 3) Mid, and 4) Mills Island (Mills) sections (Figure 3.1).

Sinepuxent Bay was used as a reference site for the inter-bay analysis. Three sites were sampled for all parameters in 2007 (Figure 3.1, Table 3.2). This region had not been sampled in 2006.

Field sampling

Data from the summer of 2006 were used to compare inter-annual trends between wet (2006) and dry (2007) years. All sites had been sampled for physical parameters (Secchi depth, salinity, temperature, and dissolved oxygen (DO)), nutrients, (total nitrogen (TN) and total phosphorus (TP)) and biological parameters (chlorophyll *a* and phaeophytin) during field trips May 22-26 and July 13-17, 2006. Dissolved inorganic nutrients, bacteria, and viruses were not measured in 2006, and only single samples were taken at each site. However, all methods in the field and laboratory were identical to those of 2007.

In May and July 2007, all bay sites were sampled by boat for total (TN, TP) and dissolved inorganic N and P (NH_4^+, NO_3^-, PO_4^{-3}), chlorophyll *a*, particulate $\delta^{15}N$, bacteria, and virus abundance. $NO_2^- + NO_3^-$ will hereafter be reported as NO_3^- because the

concentration of NO_2^- is usually < 5% of NO_3^- (Novotny and Olem 1994). Sampling in May took place on May 30 and 31st from 0900 to 1900 each day, with St. Martin sampling occurring on the first day and Johnson Bay and Sinepuxent on the following day. July sampling took place on July 17th for Johnson Bay, July 18th for St. Martin River, and July 19th for Sinepuxent. Weather was hot and sunny for all study periods, and there were no precipitation events between sampling days. Drought conditions and lack of rain preceded May sampling and continued throughout the summer.

Salinity, temperature, dissolved oxygen, percent dissolved oxygen, and conductivity were measured both at the surface and at the bottom (depth recorded in Appendix Tables B-F) of each site location using a pre-calibrated YSI water quality probe. In order to determine Secchi depth and subsequent turbidity, a 20 cm diameter Secchi disk was lowered until the difference between the black and white quadrants could not be seen, and that depth was then recorded.

Water samples were collected from the surface using 30 and 60 ml acid-washed syringes and filtered through combusted Whatman GF/F filters onboard the vessel for dissolved nutrient concentrations. Sixty mL of seawater was filtered through a single filter for chlorophyll-*a* at each site, wrapped in a combusted aluminum foil packet using forceps, and stored in the dark on ice until returned to the lab for analysis. Total suspended particulate organic matter (SPOM) and particulate $\delta^{15}N$ was also collected by filtering 60 mL of seawater through a combusted filter and stored just as the chlorophyll *a* filter.

During the filtering process mentioned previously, 20 mL of the resultant filtrate was collected directly in 20 mL acid-washed polycarbonate scintillation vials. All

samples were then stored in the dark in a cooler containing ice until taken to the lab, where they were frozen at -20°C (Clesceri et al 1989). A total of four vials were taken at each site, to be analyzed for dissolved inorganic phosphorus (PO_4^{-3}), dissolved inorganic nitrogen (NO_3^-), urea, and dissolved organic carbon (DOC) at each site. In addition, 20 mL of unfiltered surface water was collected by syringe and stored in a 30mL acid-washed polycarbonate bottle for whole-water TN and total phosphorus TP analysis. At the focus sites in each bay, 50 mL duplicate whole-water samples were preserved using 1% Formalin in 60mL acid-washed Nalgene bottles for bacterial counts. Samples were placed in the dark and stored on ice. Ten liters of water was collected in three acid-washed, site-water rinsed, cubitainers from surface waters at each intensive site. This was analyzed for total suspended solids (TSS) and volatile suspended solids (VSS), the organic component of VSS. Cubitainers were covered by a tarp until they could be brought back to the lab in order to protect them from having their contents degraded or processed by sunlight.

Laboratory analysis

All nutrient samples were analyzed by Analytical Services at the University of Maryland Center for Environmental Science (UMCES) Horn Point Laboratory in Cambridge, MD. Nutrient samples were frozen and then analyzed within 72 hours for TN and TP using persulfate digestion (Valderrama,1981), DIN ($NH_4^+$and NO_3^- for all sites) (Parsons et al., 1984, Valderrama, 1981), DIP (PO_4^{-3}) (Sola'rano and Sharp, 1980) and DOC (Sharp et al., 1995). Urea samples were frozen and later analyzed by the direct method of Revilla et al (2005), modified by using microplate analysis with a

spectrophotometer equipped with a low volume plate reader. Aluminum foil packets containing filters for $\delta^{15}N$ analysis were dried in a drying oven at 60°C for 72 hours. Filters were rolled carefully using forceps, pressed into tin pellets using a pellet press, inserted into a numbered well plate, and analyzed for $\delta^{15}N$ at the UC-Davis Stable Isotope Laboratory.

Samples for chlorophyll *a* analysis were placed into polyethylene centrifuge tubes, to which 7 mL of 90% acetone was added (Arar 1997). The samples were capped and vortexed for 30 seconds and placed in the freezer, which was set at -25°C in the dark. They were removed 24 hours later and transported by cooler to the dark fluorometry room, where they were vortexed for 15 seconds and then centrifuged for 10 minutes at maximum speed. Sample supernatant (5 mL) was removed using a glass Pasteur pipette and placed in a disposable borosilicate culture tube. The tube was wiped with a Kimwipe to remove fingerprints and placed in the fluorometer. The reading (Fo) was recorded, and 150 µL of 0.1 N HCl was added to the sample using an autopipette. After 90 seconds, the reading (Fa) was recorded. Spectral extinction coefficients were determined by absorbance readings, which were read for resultant chlorophyll and phaeophytin concentrations.

Bacteria were enumerated using the SYBR Green I method of Patel et al. (2007). Two mL samples were taken from each 60 mL sample bottle and diluted by 10 mL seawater (salinity 29) that had been filtered through 0.022 µm pore filters. Dilution was necessary due to the high abundance of bacteria in the samples, which causes overlap and difficulty in enumeration in undiluted samples. Samples were stored in sterile containers, gently agitated, and stored at 4° C until they were ready to be mounted on glass slides.

Two mL of each 5:1 diluted solution was filtered through a 0.02 Whatman Anodisc AL2O3 filter and backed by a moist 0.8 µm pore size microdisc filter. The 0.02 µm filter was blotted with a Kimwipe, dried in a dark drawer for 45 minutes, and then placed onto a 100 µL droplet of dilution 1:400 SYBR Green solution in a sterile petri dish. The filter was placed in the dark for 18 minutes and then mounted on a slide with a 10 µL droplet of dilution 1:1 phosphate-buffered saline solution (PBS)/Glycerol: 10% p-phenylenediamine. 20 µL of 1:1 of this solution was placed on the coverslip before it was placed on top of the filter. Bacteria and viruses were enumerated using a Nikon Eclipse E800 microscope with a TE-FM epifluorescence attachment. Filters were placed under blue light excitation at 100x oil immersion magnification. A grid divided the slide into fields, and ten were chosen randomly per slide. Up to 120 VLPs and bacteria were counted in each field, and the equation Count*100*RSF*5/2= Total bacterial or VLP abundance was used, in which Count = number counted per field, RSF= recticle scaling factor: 13529.710, determined by the equation: filterable area of 0.02 µm pore size Anodisc filter (3.46x108µm2)/ area of the 10x10 eyepiece reticle (determined by stage micrometer, 25600 μm^2).

Total suspended solids (TSS) were measured in the laboratory by filtering the collected seawater through a pre-weighed 0.7 µm pore size Whatman GF/F filter. Cubitainers of seawater were thoroughly mixed, and up to 500 mL was poured to fill the flask. When the vacuum was applied, total volume of the filtrate was recorded. The filters were then allowed to dry in a drying oven at 60°C for 24 hours, after which they were re-weighed. The TSS (mg L^{-1}) was determined by the following equation:

$$(W_{final} - W_{initial})/ V_{filt} \qquad \text{Eq. 4}$$

Where W_{final} = final weight of both filter and solids on filter, $W_{initial}$ = the initial filter's weight without solids, and V_{filt} = volume of seawater filtered. VSS, the organic component of TSS, was also measured by combusting filters overnight in a muffle furnace at 450°C. This procedure removes the organic component contained on the filter, which can be calculated by subtracting the resultant weight from the TSS weight. The concentration of carbon in the VSS was calculated as the VSS/2 (fraction of organic matter that is carbon) (Parsons and Takahashi 1973). Carbon contributions from phytoplankton and bacteria were calculated by multiplying the mean chlorophyll concentrations for each bay during each month in 2007 by a C:chl *a* ratio of 30:1 (Parsons and Takahashi 1973) and the bacteria cell abundance by 3.02×10^{-11} (Fukuda et al. 1998). These estimates were then used to calculate the fractionation of chlorophyll *a* and bacterial carbon as a percent of VSS carbon.

Statistical analysis

The statistical analysis software program SAS v. 9.1 (SAS Institute, Cary, NC) was used to assess nutrient and biological parameters. All measurements are reported as means ± standard error. Analyses were conducted separately for the 2007 TSS, VSS, bacteria, and viruses with the focus site data since these parameters were measured only at these sites. During all statistical analyses, significance was measured at an alpha level of .05, using the Tukey-Kramer adjusted r-square value. Because sampling was conducted in the same locations months apart and also in two different years, a factorial design of the ANOVA procedure using PROC MIXED was performed to compare parameters and address significant differences between the bays and regions within the

bays for both 2006 and 2007. Tukey's adjusted r-square probability of differences, a more conservative measure of significance, was used to identify differences among groups. Comparisons were made between overall bays, regions of each bay, months, and years, and complete results can be found in Tables I-M of the Appendix.

Correlations were run separately on the data of St. Martin River and Johnson Bay for each bay and then each month in 2007, since this was the most complete dataset. Sinepuxent was excluded from individual site statistical analyses because its complete dataset had too few observations. Because some of the variables were not normally distributed, correlations were conducted on the data using the nonparametric Spearman Rank correlation procedure, in which variable values are assigned numbers in order from greatest to least, and the correlations are drawn using those numbers. Correlation coefficients were deemed statistically significant at the 0.05 level. Separate correlations were conducted for these sites to address differences in the additional variables that were measured for each month. Complete results can be found in Tables 3.5 and 3.6.

Results

Rainfall

In 2006, rainfall was low before the May sampling period, especially in the month prior. There was a total of only 16.2 cm of rain from January 1st, 2006 to May 22nd. However, several large rain events between late May and mid July produced an additional 22.8cm of rainfall between the May and July 2006 sampling dates (Figure 3.2). From January 1 to May 30, 2007, there was 27.7cm of rainfall, but only 6.7cm fell

between the May and July sampling events. Average precipitation for this region from January through May is 48.59 cm, and June through July is 16.43 cm. Therefore, rainfall before June 2006 was below normal, while the period from June to July was above average. In 2007, rainfall before June was lower than normal but above that of 2006, but the period between June and July endured drought conditions. Therefore, precipitation patterns in 2006 were opposite that of 2007, and rainfall between May and July sampling periods in 2006 was almost four times the rainfall during the same time in 2007 (Figure 3.2). Weather in both years was sunny and warm, with air temperatures in the range of 25-30°C.

Secchi depth

In 2007, overall Secchi depth was overall significantly shallower in July than in May, which ranged from 0.2 to 0.4 m in Johnson Bay, 0.3 to 1.1m in St. Martin River, and 0.25 to 1.5 m in Sinepuxent (Figure 3.3 A). Sinepuxent had the deepest mean Secchi depth (0.75 ± 0.07 m), and St. Martin Secchi depth was shallower than Sinepuxent. In the St. Martin River, the Mouth had a significantly deeper Secchi depth than the other three sections (Figure 3.4 A). There were significant differences between sections in Johnson Bay, where Brock (0.34 ± 0.014 m) and Johns (0.34 ± 0.015 m) both had overall shallower Secchi depths than the Mid section (0.41 ± 0.015 m) (Figure 3.5 A). Johnson Bay was the only bay that had a significantly deeper mean May Secchi depth in 2006 (0.43 ± 0.02 m) than 2007 (0.29 ± 0.01 m) (Table 3.3). However, there were no differences between years in any of the bays in July. In St. Martin River, the Mouth was

the only section which had significantly shallower Secchi depths in May 2006 (0.60 ± 0.03 m) than in May 2007 (0.84 ± 0.05 m) (Table 3.4).

Dissolved oxygen

Since there were few differences between dissolved oxygen (DO) measured at the surface and at the bottom, bottom values were used for ANOVA analysis (Appendix Tables B-F). Overall DO values in 2007 were extremely low and below saturation (6-7 mg L^{-1}) in all of the bays, especially in May (Figure 3.3 B). Maximum levels increased in July, with Johnson Bay ranging 2.46-5.70 mgL^{-1}, St. Martin 1.02-7.19 mgL^{-1}, and Sinepuxent 4.25-5.23 mgL^{-1}, but there were no significant differences between bays. In St. Martin River, there were significant differences in DO concentrations between sections during different months ($p = 0.0002$ and $p = 0.0003$) (Figure 3.4 B). The Mouth (5.53 ± 0.33 mgL^{-1}) had significantly higher DO than the Bishopville (3.17 ± 0.45 mgL^{-1}) and Shingle Landing (2.75 ± 0.55 mgL^{-1}) Prongs in July, but this was not apparent in May. Johnson Bay showed a similar pattern, with the inshore Johns section (3.54 ± 0.18 mgL^{-1}) having significantly greater DO concentration than the Mills section (4.27 ± 0.19 mgL^{-1}) (Figure 3.5 B).

There were no measures of dissolved oxygen (DO) in May of 2006, so only July samples could be compared to those of 2007 (Table 3.3). St. Martin was the only bay that had significantly lower DO in July 2007 than in July 2006. Sections of St. Martin River also showed different patterns in different years, with the Bishopville Prong, Shingle Landing Prong, and Middle all having significantly lower concentrations in 2007

than in 2006. However, there was a lack of significant sectional or yearly differences for either month in Johnson Bay.

Salinity

Because of the different structure of each bay, there were significant differences in surface salinities. In May, Johnson Bay ranged from 25.8 - 26.9, while St. Martin exhibited a range from freshwater to mesohaline, 0 - 25.5, and Sinepuxent ranged from 27.1 - 27.4 (Figure 3.3 C). Salinities increased in July, when Johnson Bay ranged from 30.9 - 32.6, St. Martin 0.1 - 30.4, and Sinepuxent 30.9 - 31.3. In St. Martin River, there were significant differences in salinity based on month and section, with both Prongs of the river having lower salinities than those downstream. A salinity gradient was observed as distance increased from the dam on the Bishopville Prong (start of freshwater intrusion into the tidal portion of the river) to the Mouth (Figure 3.6). However, there were few differences among sections in Johnson Bay (Figures 3.4 C and 3.5 C).
Salinity in 2006 was significantly higher than in 2007 for the bays, and in both May and July, Johnson Bay had overall higher salinity than St. Martin. Patterns between sections were similar between the years (Tables 3.3, 3.4, and 3.5).

Temperature

Because the Coastal Bays are shallow and well-mixed, there were few discrepancies between surface and bottom temperatures (Appendix Tables B-F). Since nutrients were collected from surface water, surface temperature values were used for

overall analysis. Temperatures increased over the summer, ranging from 22.6-26.0°C in Johnson Bay, 23.6-31.2°C in St. Martin River, and 25.0-25.1°C in Sinepuxent in May, to 22.6-29.2°C, 28.9-33.4°C, and 26.5-28.6°C for each of the bays in July (Figure 3.3 D). Overall, St. Martin had overall significantly higher temperatures than Johnson Bay, and May was the only month when the Bishopville Prong (28.30 ± 0.62°C) was significantly warmer than the Middle (24.34 ± 0.48°C) and Mouth (24.39 ± 0.32°C) (Figure 3.4 D). Johnson Bay showed fewer significant differences between sections, with only the inshore Brock section (28.44 ± 0.37°C) was significantly warmer than Mills (26.50 ± 0.40°C) in July (Figure 3.5 D).

Total suspended solids

In 2007, total suspended solids had the greatest range in May in Johnson Bay, 20.12 to 100.60 mg L^{-1}, while St. Martin ranged from 10.11 to 50.25 mg L^{-1} and Sinepuxent ranged from 20.18 to 50.35 mg L^{-1}, and all three bays increased in July (Figure 3.3 E). Although there were no significant differences in TSS between bays in 2007, the VSS in St. Martin River (22.44 ± 1.43 mg L^{-1}) was significantly greater than both Johnson Bay (15.18 ± 1.56 mg L^{-1}) and Sinepuxent (13.94 ± 2.02 mg L^{-1}) in July. Within the St. Martin River, the VSS of the Shingle Landing Prong (14.75 ± 0.93 mg L^{-1}) was overall significantly greater than the Middle (9.96 ± 1.04 mg L^{-1}), but there were no differences between sections in Johnson Bay (Figure 3.4 E).

Nitrogen

TN concentrations of the three bays in 2007 increased from May to July and was dominated by organic N (Figures 3.7 and 3.8). There were no significant differences or interaction effects between bays for NH_4^+, NO_3^-, or urea, but the NH_4^+ increased from May to July and was especially apparent in Johnson Bay and Sinepuxent (Figure 3.8A). TN in May ranged from 45.25 to79.13 μM in Johnson Bay, from 29.70 to 125.00 μM in St. Martin, and from 49.10 to 52.53 μM in Sinepuxent (Figure 3.7). July samples of TN were between 33.40-77.87 μM in Johnson Bay, 59.00-140.00 μM in St. Martin, and 51.97-75.30 μM in Sinepuxent. The overall TN concentration in St. Martin River (72.52 ± 2.78 μM) was higher than Johnson Bay (57.03 ± 2.62μM), which was especially apparent in July. Both Prongs of St. Martin River had higher TN than the Middle and Mouth sections, but there were no significant differences between the two prongs or in any nutrient species (Figures 3.9 and 3.10). In Johnson Bay, Mills was significantly lower than the other sections, and Brock and Johns had the highest concentrations of TN (Figure 3.11). NH_4^+ concentrations only showed significant differences in July, when Johns (3.47 ± 0.34 μM) was significantly greater than Brock (1.64 ± 0.32 μM) and Mills 1.06 ± 0.37μM) (Figure 3.12 A) .

TN in all the bays was significantly higher in both May and July 2007 than in 2006 (Table 3.3). There were more significant differences in sectional patterns in May for St. Martin River, while Johnson Bay had more differences between sections in July concentrations. In May 2006, the Bishopville Prong's TN was not significantly different from any other sections, but its TN was the highest of all the sections in 2007 (Table 3.4). TN was higher in July 2007 than in July 2006, but there were no significant differences in

sectional patterns. In contrast, Johnson Bay had more sectional differences between years in July than May, and Brock was the only section that had a significantly higher concentration in July 2007 than in July 2006 (63.44 ± 2.78 vs. 52.10 ± 2.73 μM) (Table 3.5). In July 2007, Brock was significantly greater than both Mid and Mills. However. this did not occur in 2006.

Phosphorus

Phosphorus concentrations were also dominated by organic components in the bays and were significantly greater in July than in May (Figure 3.7). PO_4^{-3} was only a minor component of TP in the bays, but was also significantly higher in July than in May, especially in Johnson Bay and Sinepuxent (Figure 3.8). TP in May ranged from 2.88 to 4.12 μM in Johnson Bay, from 1.21 to 6.43 μM in St. Martin River, and from 3.01 to 3.06 μM in Sinepuxent, while in July, TP ranged from 1.54 to 4.04 μM in Johnson Bay, from 2.01 to 10.80 μM in St. Martin, and from 2.33-3.80 μM in Sinepuxent. However, the only significant difference between TP concentrations of the bays was in July when St. Martin (4.34 ± 0.28 μM) was significantly higher than Johnson Bay (2.84 ± 0.26 μM). In St. Martin River, TP was significantly higher in the Bishopville Prong (4.17 ± 0.53 μM and 8.49 ± 0.43 μM) than the Mouth (1.38 ± 0.32 μM and 2.44 ± 0.32 μM) in both months, respectively, but it was only higher than the Shingle Landing Prong (5.89 ± 0.53 μM) and Middle (3.66 ± 0.47 μM) in July (Figure 3.9). There were no significant interactive effects between section and month for PO_4^{-3}; the Bishopville Prong had significantly greater PO_4^{-3} concentrations than the other three sections. In Johnson Bay,

Brock was the only section that was not significantly different in TP from May to July (Figure 3.11).

Between 2006 and 2007, TP samples showed significant effects of the interaction between bay and year, suggesting that the bays had different responses to the same yearly conditions. Johnson Bay TP was significantly higher for May in both years, as well as July 2006, but TP in July 2007 was significantly higher in St. Martin River than in Johnson Bay (3.45 ± 0.29 μM vs. 2.84 ± 0.11 μM, respectively). In St. Martin River, the Bishopville Prong (3.09 ± 0.21 μM) was only significantly different from the Mouth section (2.17 ± 0.09 μM) in May 2006, but in May 2007 it was significantly higher than both the Middle and Mouth sections. July values lacked significant interactive effects.

Dissolved organic carbon

DOC concentrations were highest in July and also in upstream or inshore sections (Figures 3.7 E, 3.9 E, and 3.11 E). In 2007, May values for dissolved organic carbon (DOC) ranged from 4.75 to 6.93 mg L^{-1} in Johnson Bay, from 2.02 to 13.58 mg L^{-1} in St. Martin River, and from 4.74 to 5.31 mg L^{-1} in Sinepuxent (Figure 5C). Johnson Bay had a higher concentration of DOC than St. Martin River in May, but there was no difference in July. In St. Martin River, July concentrations (5.60 ± 0.25 mgL^{-1}) were significantly higher than May (4.42 ± 0.27 mg L^{-1}), and overall the Bishopville Prong (6.11 ± 0.39 mg L^{-1}) was significantly higher than the Mouth (3.89 ± 0.26 mg L^{-1}) (Figure 3.11 C). The inshore sections of Johnson Bay, Brock (5.74 ± 0.21mg L^{-1}) and Johns (5.73 ± 0.22 mg L^{-1}) were significantly greater than Mid (4.62 ± 0.22mg L^{-1}) and Mills (4.26 ± 0.24 mg L^{-1}).

$\delta^{15}N$

July $\delta^{15}N$ samples ranged from 8.71 to 21.08‰ in Johnson Bay, from 9.01 to 27.24‰ in St. Martin, and from 11.56 to 16.42‰ in Sinepuxent (Figure 3.7 F). The bays showed overall significant differences in $\delta^{15}N$. Johnson Bay (14.54 ± 0.69‰) had a higher $\delta^{15}N$ than St. Martin River (11.87 ± 0.70‰) ($p = 0.0325$). Data from the May sampling is not available due to loss during isotope analysis. Although there were no significant differences between sections of St. Martin River, July samples in Johnson Bay showed that Brock (17.8 ± 1.0‰) was significantly greater than Johns (13.5 ± 1.1‰) and Mills (12.0 ± 1.2‰) (Figure 3.11 F).

Chlorophyll a

Chlorophyll *a* was higher overall in July than in May, but its ranges in 2007 varied little from month to month in the bays (Figure 3.13 A). In both months, St. Martin chlorophyll *a* (12.98 ± 1.86 μg L^{-1} and 34.02 ± 1.78 μg L^{-1}) was significantly greater than Johnson Bay (27.82 ± 1.65 μgL^{-1} and 17.66 ± 1.71 μgL^{-1}). In St. Martin River, the Shingle Landing Prong was the only section that was overall greater than the Mouth (Figure 3.14 A). There were no differences between sections in Johnson Bay (Figure 3.15 A).

May chlorophyll *a* concentrations in Johnson Bay were overall significantly greater in 2007 than in 2006, but concentrations in July 2006 were higher than in July 2007 (Table 3.3). For the month of May, there were no significant differences between sections in 2006, but in 2007, the Bishopville and Shingle Landing Prongs were

significantly higher in chlorophyll *a* concentrations than the Mouth. Patterns in Johnson Bay lacked significant differences between years in either month.

Phaeophytin

In 2007, only the month showed significant effects for phaeophytin, in which July concentrations were significantly greater overall than May (Figure 3.13 B). In St. Martin River in May, the Bishopville and Shingle Landing sections were significantly greater than the Mouth, (Figure 3.14 B), but Shingle Landing's phaeophytin concentration (14.80 ± 1.67 μg L^{-1}) was only significantly greater than the Bishopville Prong (5.64 ± 1.36 μg L^{-1}) in July. Johnson Bay lacked significant differences between sections.

May phaeophytin concentrations were significantly greater in 2006 than in 2007, but in July, there were no significant differences between bays, years, or their interaction ($p > 0.05$). In addition, there were no sectional differences between sections in either May or July 2006.

Bacteria

In 2007, free-living bacteria abundances were higher in St. Martin (4.45×10^7 cells mL^{-1}) than both Johnson Bay (1.08×10^7 cells mL^{-1}) and Sinepuxent (1.03×10^7 cells mL^{-1}) ($p < 0.0001$) (Figure 3.13 C). In St. Martin River, both Bishopville and Shingle Landing Prongs overall had greater bacterial abundances than the Mouth (Figure 3.14 C). Bacterial abundance also differed between sections in Johnson Bay, where Brock was significantly greater than both Mid and Mills (Figure 3.15 C).

Viruses

Viral abundance also increased from May to July 2007. In May, abundances ranged from 9.64 x 10^7 to 2.20 x 10^8 viruses mL^{-1} in Johnson Bay, from 1.57 x 10^8 to 2.29 x 10^8 viruses mL^{-1} in St. Martin, and from 1.01 x 10^8 to 1.29 x 10^8 viruses mL^{-1} in Sinepuxent, while in July, abundances ranged from 1.14 x 10^8 to 1.92 x 10^8 viruses mL^{-1} in Johnson Bay, from 1.42 x 10^8 to 2.49 x 10^8 viruses mL^{-1} in St. Martin, and from 9.17 x 10^7 to 1.07 x 10^8 viruses mL^{-1} in Sinepuxent (Figure 3.13 D). Overall, St. Martin had higher abundances than both Johnson Bay and Sinepuxent, and Johnson Bay was also significantly higher than Sinepuxent. In St. Martin River, all three upstream sections were significantly greater than the Mouth (Figure 3.14 D). In Johnson Bay, viral abundance was greater in Brock than in Mills, but there was a lack of interactive effects between sections and months.

Carbon composition of suspended solids

In both May and July, chlorophyll *a* from phytoplankton comprised less than 30% of VSS carbon, and bacteria was less than .02% of VSS carbon in all three bays (Figure 3.16). In May, 25% and 24% of the VSS carbon was comprised of phytoplankton in Johnson Bay and Sinepuxent, respectively, while in St. Martin River, it was only 10%. These percent contributions of total chlorophyll *a* decreased dramatically in July for Johnson Bay (7%) and Sinepuxent (11%). In St. Martin River, May carbon content that was estimated to be chlorophyll *a* contributed less than 20% of VSS in all four sections (Figure 3.17). The percent contribution of chlorophyll carbon was highest in the two Prongs (Bishopville and Shingle Landing) and lowest at the Mouth (9%). In July, the

Middle section's chlorophyll *a* percentage increased to 15% of carbon, while the Prongs decreased slightly. In Johnson Bay, only three of the sections could be analyzed for % carbon contribution of chlorophyll *a*, due to site data availability. In all three regions, chlorophyll carbon contributed less than 30% of VSS, but this decreased to less than 10% in July (Figure 3.18). The Mid section experienced the largest decrease, from 28% to less than 6%.

Correlation analysis

Correlation analyses conducted separately on data from May and July 2007 displayed distinct seasonal patterns. The three highest Spearman correlation coefficients for each analysis are listed in Table 3.6 for months (A) and bays (B). In May, the highest correlation coefficient of chlorophyll *a* was with NO_3^- ($r^2 = 0.54$). However, in July, both TN and TP concentrations explained the most variation in chlorophyll *a* ($r^2 = 0.82$ and 0.78), but none of the inorganic nutrients displayed significant correlations. Both bacteria and virus abundance displayed few correlations with nutrients or chlorophyll in May, and almost all significant correlations were with the physical parameters of temperature, salinity, and dissolved oxygen. However, nutrients, DOC, chlorophyll, bacteria, and viruses all became increasingly correlated with each other in July (Table 3.7 B). Dissolved oxygen showed separate correlation patterns through the summer, having more significant negative correlations in July than in May, especially with TN, TP, and chlorophyll *a*, which is possibly due to higher respiration ($r^2 = 0.74, 0.74, 0.43$) In May, TN, TP, NH_4^+, and NO_3^- were also significantly correlated with salinity, while only TN and TP correlated with salinity in July (Table 3.7 A and B).

Correlation analyses conducted separately on the 2007 data from St. Martin River and Johnson Bay also demonstrate differences between the bays (Table 3.6). One of the most striking differences in correlation results is the lack of correlations in St. Martin River between DO and physical parameters, nutrients, or biological parameters and the abundance of significant correlations for the DO of Johnson Bay (Table 3.8 A and B). Chlorophyll *a* in St. Martin River displayed a strong significant correlation with TP (r^2 = 0.83), while in Johnson Bay, chlorophyll *a* is most strongly correlated with Secchi depth (r^2 = 0.78) and less strongly with TP (r^2 = 0.45). Urea also displayed a significant correlation in Johnson Bay with chlorophyll *a* (r^2 = 0.63) which was not apparent in St. Martin. St. Martin River displayed several strong correlations between bacteria and TN, TP, DOC, chlorophyll *a*, and VSS (r^2 = 0.74, 0.78, 0.83, 0.90, 0.85), while in Johnson Bay, bacteria was only correlated with DOC, viruses, depth, salinity, Secchi depth, and DO (r^2= 0.52, 0.69, 0.48, 0.49, 0.50, and 0.51). In addition, salinity was correlated with most nutrients in Johnson Bay but not in St. Martin River.

Discussion

Bay trends and patterns

Physical, chemical, and biological parameters differed between the bays of St. Martin River, Johnson Bay, and Sinepuxent Bay and between the months of May and July. The spatial pattern of water quality in the Maryland Coastal Bays was also highly variable among the bays studied (St. Martin River, Johnson Bay, and Sinepuxent) and sections within each bay, due to local differences in watershed inputs and basin flushing

characteristics. St. Martin River exhibited the highest nutrient and chlorophyll *a* concentrations and lowest DO and water clarity, especially in upstream areas, but Johnson Bay and Sinepuxent also demonstrated anthropogenic influence and tendency towards a net heterotrophic environment, especially as the summer progressed. This hypothesis also can be supported by the continuous monitoring data from Johnson Bay, which revealed DO concentrations between 5 and 8 mg L^{-1} during the 2006 sampling periods (Figure 3.19). Mean DO concentrations in 2007 were even lower. Although respiration was not directly measured, high bacterial abundance in these bays may be contributing to these low DO concentrations. Overall, biological and physical factors displayed more variation between months (May and July) and years (2006 and 2007) than water chemistry.

Phytoplankton concentrations, based on chlorophyll *a* concentrations, do not comprise a major percentage of suspended organic matter in the Coastal Bays. Phaeophytin concentrations also indicated potentially more grazing activity in July than in May. Allochthonous organic matter inputs may be dominant sources of carbon and organic nutrients in the estuarine environment (Thottathil et al. 2008, Smith and Hollibaugh 1993).

Elevated $\delta^{15}N$, especially in Johnson Bay, may be more indicative of within-system nutrient processing of biotic material than direct inputs of human or animal waste (Ahad et al. 2006). The elevated $\delta^{15}N$ signature is a result of isotopic fractionation during ammonia volatilization, nitrification and denitrification (McClelland & Valiela, 1998). $\delta^{15}N$ in the range of those found in the Coastal Bays during this study may be related to the longer residence time of the water, which allows for more bacterial respiration and

subsequent cycling events. Inshore and inland areas where water remains for longer periods of time may also have higher $\delta^{15}N$ than offshore areas that experience quicker flushing rates (Mutchler et al. 2007).

Bacterial and viral abundances in the three Coastal Bays are similar to those of other eutrophic systems such as Moreton Bay and the Noosa River in Australia, where bacteria and viruses range 0.05 to 2.4 x 10^7 mL^{-1} and 0.5 x 10^7 to 3.0 x 10^8 mL^{-1}, respectively (Hewson et al. 2001). High concentrations of organic nutrients and DOC, most likely resulting from non-point source waste products (Fertig et al. 2006) are available to the bacteria, leading to increased respiration of the system and decreased efficiency of carbon transfer between tropic levels (Suttle 2005). Similar to other studies (Paul 2003, Boehme et al. 1993), a significant correlation between bacteria and viruses was evident in July, reflecting the increase in bacteria as hosts for viruses as the summer progresses. Viruses may be indirectly linked to increasing nutrients due to stimulation of their bacterial hosts (Danovaro et al. 2003).

Correlation results revealed that parameters may be tightly or loosely coupled, depending on bay or month. Previous studies of coastal areas have demonstrated a link between bacterial and viral abundances with salinity, which co-varies with nutrients, temperature, and chlorophyll *a* (Hewson et al. 2001, Cochlan 1993, Paul et al. 1993). Correlations within each bay differed by location, indicating substantial differences in cycling patterns, inputs, and biological responses; St. Martin River's correlations revealed strong relationships between both total and inorganic nutrients and biological parameters (chlorophyll *a*, bacteria, viruses), while Johnson Bay nutrients were strongly correlated to physical parameters. July correlations displayed more relationships among

variables, indicating a tighter coupling between them during the progression of the summer.

St. Martin River

As a freshwater-driven estuary, St. Martin River displays spatial patterns in physical, chemical, and biological parameters consistent with upstream inputs and downstream dilution, as depicted in the conceptual diagram, Figure 3.20. Results of this study indicate that the degraded water quality of this system is driven by land-derived nutrient inputs, as opposed to internal cycling. Both Bishopville and Shingle Landing Prongs had the highest TN and TP concentrations of the four sections of the river, though physical characteristics such as Secchi depth, DO, and temperature did not show many significant differences. High N and P loadings, especially in the watershed of the Bishopville Prong, most likely are linked to crop agriculture and feeding operations (Primrose 2001, Wazniak et al. 2004, Chapter I). A low percentage of dissolved inorganic N and P throughout all regions of St. Martin River suggests that nutrients, phytoplankton, and bacteria are tightly coupled and the river is also functioning as a NO_3^- sink. The observed patterns in water quality are especially important in this region because of plans to modify the Bishopville dam and restore streams, as part of a cooperative effort among state, federal, and local agencies (Jesien 2006). This process, consisting of restoration of a seepage forested wetland close to the major drainage pool and opening of the stream to fish passage, will cause the largest effects in water quality immediately below the dam on the Bishopville Prong, which has been shielded from direct upstream influences. It is possible that the release of nutrients from the sediment trapped behind the dam may also

lead to a sudden flux of nutrients downstream. However, it is expected that in the future, the pool and surrounding wetlands will help to buffer run-off before it enters directly into the waterway.

A pattern of decreasing nutrients along the downstream gradient was demonstrated in both months and in both wet and dry regimes. The higher amounts of N, P, and TSS that were observed in July 2007 versus May 2007 were most likely the result of a lack of dilution of these inputs, especially since there was a lack of rain between sampling events. In addition, the lack of a decrease in riverine nutrients during low rainfall periods may be an indication that groundwater is also potentially a substantial source of nutrients to St. Martin River, especially during periods of baseflow (Dillow and Greene 1999). TP was significantly higher and TN was significantly lower in 2006 than in 2007, but the lack of differences between sections reveals that the effects of precipitation and run-off are equivalent throughout the river.

Chlorophyll *a* concentrations increased dramatically between May and July and also under wet conditions (July 2006), when spatial patterns between sections were most apparent. River flow conditions dominate up-estuary processes and the flushing of nutrients by storm events may result in increased phytoplankton uptake and bloom formation, especially in nutrient-rich upstream areas (Arhonditsis et al. 2007). A strong significant correlation between TP and chlorophyll *a* indicates the importance of phytoplankton in this bay, as opposed to Johnson Bay, which showed no such relationship. This may explain the enhanced concentrations of phytoplankton in July 2006, when TP also increased. Seasonal changes in nutrient dynamics and physical conditions contribute to the formation of mid-summer blooms in the St. Martin River, as

seen in other estuarine systems (Boynton et al. 1982). However, the dominance of organic, rather than inorganic N and P may suggest that this fraction of the nutrient pool is indeed a useable source of nutrients for phytoplankton (Dafner et al. 2007, Glibert et al 2007). Although chlorophyll *a* is commonly used as evidence of eutrophication and the concentrations in St. Martin River are the highest of the three Coastal Bays in this study, this measure must be regarded as only an estimate of phytoplankton abundance (Cochlan 1993). The Maryland Coastal Bays have also been characterized by blooms of brown tide microalgae, including a bloom that occurred and declined before this study's May 2007 sampling (Wazniak et al. 2007, Trice et al. 2004), which may have added to the high DOC and low DO at this time.

The observed unsaturated low dissolved oxygen (DO) concentrations and high proportion of organic nutrients in St. Martin River is consistent with high biological oxygen demand (BOD) and heterotrophy, especially since this system is not stratified by temperature or salinity (Wazniak et al. 2007, Fertig et al. 2006, this study). This is also reflected in the lack of correlations between DO and other physical parameters. The resulting net heterotrophic environment, (e.g. when respiration exceeds production) may be directly linked to increased nutrient loading by increasing the net ecosystem metabolism of the river (Caffrey 2004). High upstream inputs of TN and TP, significant correlations between bacteria, chlorophyll *a*, and DOC, and an overall downstream gradient in water quality, supports the hypothesis that land-derived nutrient inputs are driving these effects. Terrestrial organic matter and subsequent bacterial processing have been shown to influence carbon cycling and subsequent heterotrophic activity in similar riverine and estuarine systems such as the York River in Virginia, the Satilla River in

Georgia, and the Neuse estuary in North Carolina (Raymond et al. 2000, Cai et al. 1999, Christian et al. 1991).

The abundance of bacteria and viruses were the highest of the three bays in St. Martin River. However, virus abundance of all three bays was greater than that of the Chesapeake Bay by an order of magnitude, perhaps due to the highly organic composition of the Coastal Bays (Wommack et al. 2000). The Maryland Coastal Bays also have higher virus abundances than other systems such as Moreton Bay, Australia, and Key Largo, Florida, which range between 0.05 to 3.0 x 10^8 VLP mL^{-1} and 0.015 to 0.12 VLP mL^{-1} (Hewson et al. 2001, Paul et al. 1993). These systems are, however, much less eutrophic and more highly flushed. The increase in bacterial abundance from May to July may be due to the significant relationship between bacteria and an increase in organic matter from phytoplankton, as well as DOC. In addition, significant correlations between bacteria and total nutrients (which were mainly organic), DOC, VSS, and chlorophyll *a* reveal the importance and tight coupling of components of the microbial loop in St. Martin River, further supporting the idea of a heterotrophic environment (Azam et al. 1983). Although other bays such as Johnson Bay in the Maryland Coastal Bays (this study), Key Largo in Florida (Paul et al. 1993), and the Gulf of Mexico (Boehme et al. 1993), have demonstrated strong significant correlations between bacterial and viral abundances, in this study, St. Martin River lacked significant correlations between the two. It is possible that a longer time frame is necessary to determine this possible link.

Johnson Bay

Results indicated that conditions within the bay, as well as subsequent biological cycling, are responsible for water quality degradation in Johnson Bay, as opposed to strictly land-derived inputs. Nutrients in Johnson Bay displayed small differences from section to section in 2007, suggesting that the physical characteristics and long residence time of the bay influence overall water quality, though inshore regions may display impacts from agricultural land (Figure 3.21). Although the watershed is composed of over 60% forest and wetlands, Johnson Bay still exhibited the water quality problems of shallow Secchi depth, low DO, and high concentrations of TSS, DOC, and organic nutrients in the same range as that of St. Martin River. Significant differences in TP between dry and wet years, especially in the two near-shore sections of Johns and Brock, reveal that storm events may flush nutrients from cropland into the bay, resulting in greater turbidity and higher chlorophyll *a* concentrations, as opposed to periods of drought. Poultry operations concentrated near Scarboro Creek in the southern part of the Johnson Bay watershed, as well as crop agriculture throughout, may be linked to higher inshore nutrient concentrations. However, other factors in Johnson Bay such as residence time-dependent cycling, release of nutrients (possibly due to erosion and sediment characteristics), and groundwater may also affect water quality. Studies in other aquatic ecosystems have indicated that land use may be only one of many factors linked to high nutrient concentrations, turbidity, and chlorophyll *a* concentrations, and its effects may not be directly observable (Caccia and Boyer 2005, Christian et al. 1991, Withers and Lord 2002).

The erosion of silty clay sediment in Johnson Bay may be a significant source of water column nutrients when erosion occurs (Bartberger 1976). The annual rate of erosion in the Maryland part of Chincoteague Bay, which contains Johnson Bay, is -0.043 ha km^{-1} y^{-1} (-0.17 acres mi^{-1} y^{-1}) (Hennessee, 2002). Shoreline erosion contributes up to eight times the amount of sediment delivered by streams in this region (Bartberger 1976). This high rate may account for the high concentrations of TSS which are comparable to that of St. Martin River and Sinepuxent, as well as the release of N and P buried in the sediment. A study of the northern Coastal Bays estimated that 8.5% of the TP and TN loads between 1850 and 1989 have come from erosion, and this percentage may be greater in the southern bays where rates are even higher (Wells et al. 2002).

The observed concentrations of PO_4^{-3} in July further maintains the importance of sediments in the cycling and water column release of nutrients in Johnson Bay, especially inshore areas. In July 2007, PO_4^{-3} concentrations in Johnson Bay were the highest of the three bays, and there was a decreasing trend from the inshore Brock and Johns sections to Mid and Mills. Estuarine sediment which may have been serving as a phosphorus sink, especially in the shallow areas receiving high amounts of organic matter, may release inorganic P during the assimilation of organic P by bacteria (Clavero et al. 1999) and the desorption of adsorbed Fe(III)-bound PO_4^{-3} under anoxic conditions (Froelich 1988, Andrieux and Aminot 1997). In some estuaries, inherent sediment stores of PO_4^{-3} may surpass terrestrial inputs by a factor of 2-4 (Schlungbaum and Nausch 1990). In addition, a massive seagrass die-off a year before this study may have added additional organic matter to the system (Koch 2008, pers. comm.) The shallow depth, low DO, high organic

content, and high bacterial abundance of Johnson Bay fit the conditions necessary for summertime PO_4^{-3} release.

Correlations in Johnson Bay reveal strong relationships between salinity and nutrients. Although TN and TP concentrations were slightly greater in the inshore areas of Brock and Johns than around Mills Island, DOC was significantly greater in these areas, especially in July 2007. In addition, the strong correlation between bacteria and viruses and a lack of correlation between bacteria and chlorophyll *a* supports the idea that viruses may be controlling the abundances of their bacterial hosts (Paul 2003).

Although parameters varied between wet and dry years, similar to the variations observed in St. Martin River, there were few differences between sections. These results are consistent with the physical structure of Johnson Bay, which lacks significant surface-water inputs. Other studies of both estuarine and freshwater systems have revealed a link between increased rainfall and nutrient delivery (Benson et al. 2008, Costa et al. 2006). One of the few marked differences between sections in the wet and dry years was the high concentrations of phaeophytin in May 2006 which plummeted in July, especially in the inshore areas of Brock and Johns. TP increased dramatically in response to the rain between samplings, which was not apparent in the dry year of 2007. The apparent phytoplankton bloom most likely resulted from a flush of nutrients after the June storm and may have overcome high grazing rates that were evident in phaeophytin concentrations before the storm.

Sinepuxent

Sinepuxent Bay, which was used as an endpoint site in terms of its faster flushing rate and lower percentage of developed land, also exhibited effects of water quality degradation (Figure 3.22). It was hypothesized that Sinepuxent's short residence time (< 10 days), as compared with St. Martin River (20-30 days) and Johnson Bay (60 days) would display different patterns in water quality due to increased tidal dilution and flushing (Lung 1994, Wang et al. 2008). However, Sinepuxent's water quality showed signs of anthropogenic degradation, especially when compared to previous data (Wazniak et al. 2004), which was an unexpected result.

Similar to processes in Johnson Bay, erosion may be a key factor in increasing nutrient concentrations in the Sinepuxent system as well, due to the bay's sediment make-up and the observed wearing-down of portions of its shores (Wells et al. 2003). Wells et al. (2002) indicated that between 1850 and 1989, up to 14% of TN and 30% of TP loading in Sinepuxent was derived from sediment. The observed July PO_4^{-3} concentrations are consistent with this hypothesis. Sinepuxent's high organic nutrient content and $\delta^{15}N$ also indicate the possibility for increased nutrient cycling.

Although Sinepuxent's watershed is small when compared to that of St. Martin River and Johnson Bay, its large percentage of development may proportionally contribute to higher concentrations of nutrients. Nutrient transport has been shown to be directly linked to land development rates (Interlandi and Crockett 2003), percentage of impervious surfaces (Schoonover and Lockaby 2006), and wastewater (Whitall et al. 2004), which are all components of urban development. However, it is possible that a fraction of nutrients discharged off the other side of the barrier island from the Ocean

City Wastewater Treatment Facility may be transported back through the inlet and into the bay, due to circulation patterns near the barrier island. Therefore, urban development both within and outside the watershed may result in water quality degradation, despite a shorter water residence time.

Summary and implications

Land use, shallow depth, and the long residence time of the Maryland Coastal Bays have made these systems highly susceptible to water quality degradation. St. Martin River appears to be highly influenced by its freshwater inputs and surrounding land use drainage, while Johnson Bay appears to exhibit water quality degradation as a result of a lack of flushing and subsequent internal nutrient cycling. Physical, chemical, and biological parameters in the three areas studied indicate that the worst water quality conditions are found in St. Martin River, followed by Johnson Bay, and Sinepuxent Bay. Water quality in July samplings were more degraded than those in May. Upstream and inshore sections of St. Martin River and Johnson Bay, respectively, experience more degraded conditions than downstream and offshore sections. There were few significant differences between wet and dry years, though the upstream and inshore sections experienced more negative changes during wet years. Correlation analyses in both St. Martin River and Johnson Bay indicated that N and P concentrations have a strong relationship with physical and biological parameters, especially in St. Martin River. There is also a stronger relationship among water quality parameters in July than in May.

These results indicate that the probable net heterotrophic nature, high organic content, and seasonal changes measured in these bays are consistent known responses to

eutrophication, which may be amplified by sediment release and biological cycling. In the time period 2004-2007, the water quality in these regions has not improved, with wet years showing the effects of land-derived surface runoff more than dry years. Further study over a longer time period could identify finer scale changes and seasonal patterns that would be useful in determining the direct and indirect factors and sources leading to water quality degradation that are specific to each bay and each unique watershed.

Tables

Table 3.1: Physical description of watersheds and bay areas of the St. Martin River, Johnson Bay, and Sinepuxent.

Bay	Land area (ha)	% Cropland	% Urban	% Feeding Operations	% Forest	% Wetlands	Soil type (coast --> interior)	Population	Water area (ha)	Land:water ratio	Residence time (days)	Average depth (m)
St. Martin River	10,491	47	17	0.50	29	6	well-drained to hydric	9,080	830	12.6	20-30	1.2
Johnson Bay	4,911	31	2	0.09	37	29	hydric to well-drained	469	5,023	2.0	60	1.1
Sinepuxent	3,058	11	22	0.02	43	23	well-drained to hydric	1,247	2,480	1.2	10-20	1.6

Table 3.2: Description of measurements and samples taken in 2006 and 2007, including number of samples, physical parameters, chemical parameters, and biological parameters. Sinepuxent Bay was only sampled in 2007. "NA" = Not Applicable

Bay	Year	Site Type	No. sites	Physical parameters	Chemical parameters	Biological parameters
St. Martin River	2007	Total sites	(May) 25 (July) 27	Depth, Secchi depth, temperature, salinity, DO	NH_4^+, NO_3^-, Urea, TN, PO_4^{-3}, TP, DOC, $\delta^{15}N$ (July)	Chl *a*, Phaeophytin
		High replicate	6	same, plus TSS, VSS	same	same, plus bacteria, virus abundance
	2006	Total sites	21	Secchi depth, temperature, DO, salinity	TN, TP	Chl *a*, Phaeophytin
Johnson Bay	2007	Total sites	22	Depth, Secchi depth, temperature, salinity, DO	NH_4^+, NO_3^-, Urea, TN, PO_4^{-3}, TP, DOC, $\delta^{15}N$ (July)	Chl *a*, Phaeophytin
		High replicate	5	same, plus TSS, VSS	same	same, plus bacteria, virus abundance
	2006	Total sites	28	Secchi depth, temperature, DO, salinity	TN, TP	Chl *a*, Phaeophytin
Sinepuxent Bay	2007	All high replicate	3	Depth, Secchi depth, temperature, salinity, DO, TSS, VSS	NH_4^+, NO_3^-, Urea, TN, PO_4^{-3}, TP, DOC, $\delta^{15}N$ (July)	Chl *a*, Phaeophytin, bacteria, virus abundance
	2006	NA	NA	NA	NA	NA

Table 3.3: Whole-bay comparison between 2006 (wet year) and 2007 (dry year) physical, chemical, and biological parameters in St. Martin River and Johnson Bay. Results are given in the form mean (std. err, n). ND means that the parameter was not determined for the time.

Month	Bay	Year	Secchi Depth (m)	Temperature (°C)	Salinity	DO (mgL^{-1})	TN (µM)	TP (µM)	Chlorophyll *a* (μgL^{-1})	Phaeophytin (μgL^{-1})
May	St. Martin River	2006	0.61 (0.02, 21)	22.54 (0.24, 21)	26.94 (0.34, 21)	ND	54.60 (1.15, 21)	2.38 (0.07, 21)	8.26 (0.87, 21)	30.45 (2.81, 21)
		2007	0.70 (0.04, 21)	24.82 (0.30, 21)	22.69 (0.52, 21)	2.32 (0.14, 21)	48.14 (3.59, 21)	2.06 (0.21, 21)	13.08 (1.09, 21)	4.81 (0.94, 21)
	Johnson Bay	2006	0.43 (0.02, 28)	20.29 (0.20, 28)	31.63 (0.06, 28)	ND	51.45 (1.42, 28)	3.27 (0.10, 28)	5.06 (1.86, 28)	36.43 (3.12, 28)
		2007	0.29 (0.01, 28)	23.89 (0.20, 28)	26.38 (0.06, 28)	2.94 (0.09, 28)	60.39 (1.39, 28)	3.53 (0.06, 28)	27.82 (1.21, 28)	5.43 (1.80, 28)
July	St. Martin River	2006	0.33 (0.02, 21)	31.61 (0.33, 21)	25.98 (0.41, 21)	6.64 (0.35, 21)	69.90 (3.41, 21)	4.69 (0.24, 21)	52.95 (6.34, 21)	11.36 (1.43, 21)
		2007	0.39 (0.02, 21)	29.43 (0.07, 21)	28.10 (0.40, 21)	4.78 (0.31, 21)	80.09 (4.58, 21)	3.45 (0.29, 21)	32.90 (2.95, 21)	7.80 (0.94, 21)
	Johnson Bay	2006	0.41 (0.02, 28)	29.25 (0.16, 28)	26.55 (0.18, 28)	5.04 (0.15, 28)	50.71 (1.56, 28)	5.14 (0.17, 28)	34.70 (2.26, 28)	10.71 (1.32, 28)
		2007	0.42 (0.01, 28)	27.73 (0.25, 27)	32.10 (0.06, 27)	4.75 (0.16, 28)	53.67 (2.10, 28)	2.84 (0.11, 28)	17.66 (1.68, 26)	9.09 (2.13, 26)

Table 3.4: Intra-bay comparison between 2006 (wet year) and 2007 (dry year) physical, chemical, and biological parameters in St. Martin River sections. Results are given in the form mean (std. err, n). ND means that the parameter was not determined for the time.

Month	Section	Year	Secchi Depth (m)	Temperature (°C)	Salinity	DO (mgL^{-1})	TN (µM)	TP (µM)	Chlorophyll *a* (μgL^{-1})	Phaeophytin (μgL^{-1})
May	Bishop	2006	0.6 (0.05, 2)	24.6 (0.3, 2)	24.3 (0.6, 2)	ND	63.4 (6.0, 2)	3.1 (0.4, 2)	9.7 (4.6, 2)	53.0 (13.0, 2)
		2007	0.5 (0.1, 2)	26.9 (2.0, 2)	19.6 (2.9, 2)	1.9 (0.3, 2)	76.5 (10.9, 2)	3.7 (0.7, 2)	22.4 (3.9, 2)	10.3 (0.3, 2)
	Shingle	2006	0.6 (0.03, 3)	23.7 (0.2, 3)	25.2 (0.1, 3)	ND	57.6 (0.2, 3)	2.5 (0.0, 3)	5.8 (0.9, 3)	39.2 (10.3, 3)
		2007	0.5 (0.1, 3)	25.8 (1.2, 3)	19.4 (0.4, 3)	3.3 (0.8, 3)	70.5 (6.0, 3)	3.4 (0.4, 3)	18.5 (0.9, 3)	11.6 (2.1, 3)
	Middle	2006	0.7 (0.02, 5)	22.7 (0.3, 5)	26.3 (0.4, 5)	ND	57.0 (0.3, 5)	2.5 (0.0, 5)	8.1 (1.1, 5)	25.2 (3.0, 5)
		2007	0.6 (0.02, 5)	24.3 (0.4, 5)	22.1 (0.5, 5)	2.0 (0.1, 5)	49.2 (3.0, 5)	2.1 (0.2, 5)	13.5 (1.3, 5)	5.5 (1.2, 5)
	Mouth	2006	0.6 (0.03, 11)	21.8 (0.2, 11)	28.2 (0.2, 11)	ND	51.1 (1.1, 11)	2.2 (0.0, 11)	8.8 (1.4, 11)	26.3 (2.3, 11)
		2007	0.8 (0.05, 11)	24.4 (0.1, 11)	24.4 (0.2, 11)	2.3 (0.1, 11)	36.4 (1.2, 11)	1.4 (0.0, 11)	9.7 (0.6, 11)	1.7 (0.3, 11)
July	Bishop	2006	0.2 (0.0, 2)	33.4 (0.1, 2)	23.9 (0.4, 2)	8.0 (0.5, 2)	88.9 (2.0, 2)	6.2 (0.2, 2)	103.6 (8.6, 2)	16.8 (3.3, 2)
		2007	0.3 (0.1, 2)	29.9 (0.2, 2)	25.4 (0.3, 2)	3.2 (1.3, 2)	102.0 (24.6, 2)	5.8 (0.7, 2)	54.3 (0.8, 2)	7.3 (2.6, 2)
	Shingle	2006	0.3 (0.03, 3)	33.6 (0.1, 3)	23.0 (0.6, 3)	7.1 (1.3, 3)	94.1 (2.8, 3)	6.2 (0.1, 3)	70.5 (25.6, 3)	12.7 (4.2, 3)
		2007	0.3 (0.03, 3)	29.2 (0.2, 3)	25.4 (0.4, 3)	3.3 (0.7, 3)	112.8 (1.8, 3)	5.2 (0.2, 3)	48.5 (4.9, 3)	13.6 (1.5, 3)
	Middle	2006	0.3 (0.02, 5)	32.4 (0.5, 5)	25.4 (0.4, 5)	7.9 (0.2, 5)	75.1 (3.7, 5)	5.0 (0.3, 5)	52.5 (9.4, 5)	9.6 (3.4, 5)
		2007	0.4 (0.1, 5)	29.5 (0.2, 5)	27.7 (0.4, 5)	4.6 (0.5, 5)	84.0 (6.0, 5)	3.7 (0.4, 5)	35.5 (6.2, 5)	9.6 (2.8, 5)
	Mouth	2006	0.4 (0.01, 11)	30.4 (0.2, 11)	27.4 (0.2, 11)	5.7 (0.4, 11)	57.5 (1.5, 11)	3.8 (0.1, 11)	39.2 (5.1, 11)	10.8 (1.9, 11)
		2007	0.4 (0.02, 11)	29.4 (0.1, 11)	29.5 (0.2, 11)	5.5 (0.3, 11)	65.4 (1.4, 11)	2.4 (0.1, 11)	23.6 (0.9, 11)	5.5 (0.4, 11)

Table 3.5: Intra-bay comparison between 2006 (wet year) and 2007 (dry year) physical, chemical, and biological parameters in Johnson Bay sections. Results are given in the form mean (std. err, no. of samples). ND means that the parameter was not determined for the time.

Month	Section	Year	Secchi Depth (m)	Temperature (°C)	Salinity	DO (mgL^{-1})	TN (µM)	TP (µM)	Chlorophyll *a* (μgL^{-1})	Phaeophytin (μgL^{-1})
May	Brock	2006	0.4 (0.04, 8)	21.0 (0.6, 8)	31.2 (0.1, 8)	ND	57.2 (1.0, 8)	3.6 (0.1, 8)	9.0 (0.6, 8)	42.8 (1.9, 8)
		2007	0.3 (0.02, 8)	24.6 (0.4, 8)	26.1 (0.1, 8)	3.0 (0.1, 8)	62.5 (2.6, 8)	3.3 (0.1, 8)	25.4 (3.0, 8)	9.8 (6.2, 8)
	Johns	2006	0.4 (0.02, 7)	20.4 (0.3, 7)	31.6 (0.1, 7)	ND	57.4 (1.1, 7)	3.7 (0.1, 7)	0.4 (7.3, 7)	46.1 (9.1, 7)
		2007	0.3 (0.02, 7)	23.1 (0.3, 7)	26.4 (0.1, 7)	2.4 (0.1, 7)	65.0 (1.5, 7)	3.8 (0.1, 7)	29.3 (1.6, 7)	3.0 (0.4, 7)
	Middle	2006	0.4 (0.03, 7)	19.9 (0.0, 7)	31.9 (0.0, 7)	ND	48.3 (1.4, 7)	3.0 (0.1, 7)	6.8 (1.0, 7)	36.5 (2.0, 7)
		2007	0.3 (0.02, 7)	23.2 (0.1, 7)	26.4 (0.1, 7)	2.8 (0.1, 7)	58.8 (1.8, 7)	3.6 (0.1, 7)	28.5 (2.5, 7)	3.1 (0.8, 7)
	Mills	2006	0.5 (0.03, 6)	19.6 (0.1, 6)	31.9 (0.1, 6)	ND	40.6 (1.2, 6)	2.6 (0.2, 6)	3.2 (0.2, 6)	16.6 (2.5, 6)
		2007	0.3 (0.01, 6)	24.7 (0.1, 6)	26.8 (0.0, 6)	3.6 (0.1, 6)	54.0 (3.6, 6)	3.5 (0.2, 6)	28.5 (2.3, 6)	5.2 (0.7, 6)
July	Brock	2006	0.4 (0.04, 8)	29.6 (0.2, 8)	26.1 (0.3, 8)	5.1 (0.2, 8)	52.1 (2.7, 8)	4.9 (0.4, 8)	29.7 (4.4, 8)	8.2 (2.0, 8)
		2007	0.4 (0.00, 8)	28.4 (0.3, 8)	32.1 (0.2, 8)	4.8 (0.3, 8)	63.4 (2.8, 8)	3.2 (0.2, 8)	19.5 (1.4, 8)	8.3 (1.0, 8)
	Johns	2006	0.4 (0.04, 7)	29.7 (0.5, 7)	25.6 (0.1, 7)	5.8 (0.4, 7)	58.7 (2.4, 7)	6.0 (0.2, 7)	40.6 (5.6, 7)	15.3 (1.7, 7)
		2007	0.4 (0.04, 7)	28.1 (0.4, 7)	32.3 (0.1, 7)	4.7 (0.1, 7)	57.2 (3.9, 7)	3.0 (0.2, 7)	20.5 (1.7, 7)	9.3 (1.8, 7)
	Middle	2006	0.4 (0.02, 7)	28.9 (0.1, 7)	27.2 (0.2, 7)	4.5 (0.2, 7)	47.5 (1.1, 7)	5.0 (0.2, 7)	31.8 (1.9, 7)	8.0 (3.8, 7)
		2007	0.5 (0.01, 7)	27.8 (0.2, 7)	32.1 (0.0, 7)	4.5 (0.5, 7)	50.6 (1.6, 7)	2.8 (0.2, 7)	15.0 (2.7, 7)	6.4 (1.3, 7)
	Mills	2006	0.4 (0.05, 6)	28.7 (0.1, 6)	27.5 (0.3, 6)	4.7 (0.1, 6)	43.3 (3.0, 6)	4.5 (0.3, 6)	37.9 (4.9, 6)	11.9 (1.9, 6)
		2007	0.4 (0.02, 6)	26.5 (0.8, 6)	32.0 (0.1, 6)	5.0 (0.2, 6)	40.1 (1.9, 6)	2.2 (0.2, 6)	15.6 (6.3, 6)	12.8 (9.3, 6)

Table 3.6: Summary of Spearman correlations for months (A) and bays (B) in 2007. The top three correlation coefficients are recorded for correlations with chlorophyll a, bacteria, and DO. Statistical significance of correlations is denoted by *** = $p < 0.0001$, ** = $p < 0.01$, and * = $p < 0.05$.

A)

	May			**July**		
Parameter	Correlation	Spearman Corr.	+/-	Correlation	Spearman Corr.	+/-
Chl *a*	NO_3^-	**0.54	-	TN	***0.82	+
	Salinity	*0.36	+	Salinity	***0.81	-
	Temp	*0.35	-	TP, Bacteria, Secchi	***0.78	+, -, -
Bacteria	Viruses	***0.85	+	Salinity	***0.95	-
	Salinity	***0.81	-	TN	***0.80	+
	Depth	*0.55	-	Chl *a*	***0.78	+
DO	Salinity	**0.57	+	TN, TP	***0.74	-
	Viruses	*0.51	-	Depth	***0.72	+
	VSS	*0.46	-	Salinity, Bacteria	***0.71	+, -

B)

	St. Martin River			**Johnson Bay**		
Parameter	Correlation	Spearman Corr.	+/-	Correlation	Spearman Corr.	+/-
Chl *a*	Bacteria	***0.90	+	Secchi	***0.78	-
	Secchi	***0.87	-	Salinity	***0.68	-
	TP	***0.83	+	DOC	**0.57	+
Bacteria	Secchi	***0.91	-	Viruses	**0.69	+
	Chl *a*	***0.90	+	DOC	*0.52	+
	DOC	***0.83	+	DO	*0.51	-
DO	PO_4^{-3}	**0.47	-	TN	***0.77	-
	Temp	**0.34	-	TP	***0.69	-
	Secchi	**0.29	+	Viruses	**0.68	-

Table 3.7: Monthly correlation results for all focus site parameters in St. Martin River, Johnson Bay, and Sinepuxent, May (A) and July (B) 2007. Spearman correlation coefficients are recorded for each variable. Bold variables indicate overall significance at the $p < 0.05$ level, * denotes significance at $p < 0.05$, ** denotes significance at $p < 0.01$, and *** denotes $p < 0.0001$.

A)

	NO_3^-	urea	TN	PO_4^{-3}	TP	DOC	Chl *a*	Phaeo	TSS	VSS	Bacteria	Viruses	Depth	Temp	Salinity	Secchi	DO
NH_4^+	***0.61	*0.31	**0.49	**0.48	*0.37	*0.34	-0.13	0.15	0.27	0.08	0.13	-0.06	**-0.53	0.22	**-0.40	-0.15	*-0.33
NO_3^-		0.21	0.25	0.23	0.18	-0.10	**-0.54	0.28	0.09	0.12	0.12	-0.08	-0.21	**0.43	***-0.57	0.07	-0.25
urea			0.12	0.12	0.04	0.09	-0.08	-0.04	0.00	0.02	0.03	0.11	-0.16	0.04	-0.24	0.05	-0.23
TN				0.51	***0.80	*0.38	0.20	***0.59	-0.05	*0.39	*0.52	0.32	***-0.90	**0.44	**-0.57	*-0.32	-0.19
PO_4^{-3}					***0.57	**0.45	0.11	0.26	-0.06	0.06	-0.20	-0.25	**-0.52	-0.09	-0.23	-0.17	-0.20
TP						0.23	0.31	**0.52	-0.18	*0.34	0.39	0.19	***-0.81	0.12	**-0.41	**-0.47	0.05
DOC							0.21	0.30	-0.04	0.07	0.08	0.07	*-0.35	-0.13	-0.03	**-0.40	-0.04
Chl *a*								0.12	0.13	0.23	-0.18	-0.10	-0.19	*-0.35	*0.36	-0.23	0.16
Phaeo									-0.13	0.31	0.41	0.19	**-0.53	**0.50	**-0.56	-0.24	-0.07
TSS										0.15	-0.11	-0.08	-0.07	0.05	0.01	0.14	-0.22
VSS											0.04	0.06	-0.29	*0.38	-0.25	0.07	0.20
Bacteria												***0.85	*-0.55	**0.64	***-0.81	-0.18	*-0.46
Viruses													-0.36	*0.49	**-0.65	-0.06	*-0.51
Depth														*-0.33	***0.63	0.24	0.28
Temp															***-0.76	0.17	**-0.42
Salinity																-0.03	**0.57
Secchi																	-0.20
DO																	

B)

	NO_3^-	urea	TN	PO_4^{-3}	TP	DOC	Chl *a*	Phaeo	TSS	VSS	$\delta^{15}N$	Bacteria	Viruses	Depth	Temp	Salinity	Secchi	DO
NH_4^+	**0.41	0.30	0.02	0.30	0.12	0.30	-0.21	0.19	*0.34	0.04	-0.01	-0.21	*-0.47	-0.18	-0.11	0.10	-0.06	-0.11
NO_3^-		0.23	-0.03	-0.11	-0.04	0.17	0.06	0.05	0.17	0.05	-0.09	0.01	-0.34	0.03	0.21	-0.06	-0.11	0.17
urea			*0.35	-0.12	*0.31	*0.37	0.19	0.06	-0.07	0.16	-0.01	0.29	0.12	-0.17	*0.34	-0.30	*-0.33	*-0.33
TN				0.03	***0.95	***0.78	***0.82	0.21	-0.19	**0.39	*-0.33	***0.80	**0.69	***-0.79	***0.68	***-0.86	***-0.82	***-0.74
PO_4^{-3}					0.18	0.10	-0.20	0.27	0.16	-0.10	*0.33	-0.23	-0.14	**-0.40	-0.24	0.23	0.03	-0.14
TP						***0.79	***0.78	0.26	-0.01	***0.45	-0.28	***0.73	**0.62	***-0.88	***0.64	***-0.79	***-0.82	***-0.74
DOC							***0.66	0.23	0.05	*0.38	-0.13	**0.65	0.32	***-0.69	**0.51	***-0.70	***-0.69	**-0.55
Chl *a*								0.02	-0.18	**0.44	*-0.37	***0.78	**0.57	***-0.65	***0.75	***-0.81	***-0.78	**-0.43
Phaeo									-0.22	-0.12	-0.14	0.23	0.34	-0.19	-0.21	-0.14	-0.02	-0.04
TSS										***0.58	0.08	-0.17	**-0.60	-0.15	0.10	0.18	-0.17	0.12
VSS											-0.21	0.37	-0.06	**-0.42	**0.52	**-0.48	**-0.50	**-0.42
$\delta^{15}N$												-0.37	-0.35	*0.32	**-0.47	*0.39	0.28	*0.32
Bacteria													**0.67	**-0.63	***0.76	***-0.95	***-0.77	**-0.71
Viruses														-0.40	*0.42	**-0.62	*-0.46	**-0.53
Depth															***-0.57	***0.64	***0.75	***0.72
Temp																***-0.73	***-0.75	**-0.51
Salinity																	***0.78	***0.71
Secchi																		***0.57
DO																		

Table 3.8: Correlation results for all focus site parameters in (A) St. Martin River and (B) Johnson Bay, 2007. Spearman correlation coefficients are recorded for each variable. Bold variables indicate overall significance at the $p < 0.05$ level, * denotes significance at $p < 0.05$, ** denotes significance at $p < 0.01$, and *** denotes $p < 0.0001$.

A)

	NO_3^-	urea	TN	PO_4^{-3}	TP	DOC	Chl *a*	Phaeo	TSS	VSS	Bacteria	Viruses	Depth	Temp	Salinity	Secchi	DO
NH_4^+	***0.79	*0.34	0.28	**0.44	0.21	**0.60	0.20	0.11	**0.55	**0.49	*0.47	-0.27	*-0.35	**0.57	-0.17	*-0.40	-0.14
NO_3^-		0.17	0.20	*0.41	0.11	**0.44	0.14	0.10	**0.49	*0.35	0.36	-0.08	*-0.34	**0.46	-0.24	-0.30	-0.15
urea			0.19	0.10	0.10	0.26	0.07	-0.10	0.23	0.23	0.36	0.09	-0.03	*0.39	0.09	-0.27	-0.05
TN				***0.71	***0.88	*0.43	***0.68	*0.39	0.05	*0.39	**0.74	*0.47	**-0.60	***0.67	-0.33	***-0.63	-0.22
PO_4^{-3}					***0.66	***0.63	*0.46	*0.41	0.20	*0.40	**0.75	0.09	***-0.71	**0.61	**-0.48	**-0.57	**-0.47
TP						*0.35	***0.83	0.31	0.17	**0.57	***0.78	0.40	***-0.64	***0.71	-0.25	***-0.83	-0.32
DOC							0.36	0.29	0.27	**0.57	***0.83	0.02	*-0.41	**0.52	-0.29	**-0.45	-0.21
Chl *a*								-0.04	0.23	***0.78	***0.90	*0.53	-0.19	**0.63	0.35	***-0.87	-0.06
Phaeo									-0.16	0.07	0.41	0.38	**-0.54	0.22	**-0.51	-0.13	0.05
TSS										**0.56	0.45	-0.28	-0.19	0.28	-0.01	-0.30	-0.33
VSS											***0.85	0.09	-0.20	**0.68	0.15	***-0.73	-0.09
Bacteria												0.29	**-0.68	**0.72	-0.25	***-0.91	-0.27
Viruses													0.14	-0.01	0.26	-0.25	0.30
Depth														***-0.62	***0.81	**0.50	0.46
Temp															-0.30	***-0.75	**-0.34
Salinity																0.05	0.49
Secchi																	**0.29
DO																	

B)

	NO_3^-	urea	TN	PO_4^{-3}	TP	DOC	Chl *a*	Phaeo	TSS	VSS	Bacteria	Viruses	Depth	Temp	Salinity	Secchi	DO
NH_4^+	**0.50	0.30	0.12	***0.77	-0.11	-0.34	**-0.54	*0.39	**0.58	**0.64	-0.09	-0.10	0.12	**0.64	***0.71	***0.66	-0.03
NO_3^-		0.16	-0.36	0.29	*-0.42	**-0.51	**-0.52	0.03	**0.50	0.34	-0.27	*-0.47	0.33	*0.44	**0.52	**0.48	**0.49
urea			0.24	0.18	0.21	0.13	0.06	0.06	-0.11	0.04	-0.23	-0.02	-0.08	-0.07	0.06	**0.02**	-0.20
TN				0.10	***0.74	***0.76	0.35	**0.51	-0.18	-0.17	0.44	**0.65	***-0.77	-0.19	*-0.40	*-0.40	***-0.77
PO_4^{-3}					0.06	-0.34	**-0.58	*0.38	0.29	**0.57	-0.35	-0.15	0.12	*0.45	***0.74	***0.76	-0.03
TP						***0.76	*0.45	0.33	**-0.60	*-0.45	0.37	*0.50	***-0.78	**-0.59	**-0.55	**-0.47	***-0.69
DOC							**0.57	0.10	**-0.51	**-0.58	*0.52	**0.72	***-0.78	**-0.57	***-0.77	***-0.72	***-0.66
Chl *a*								0.01	*-0.42	**-0.56	0.27	0.25	*-0.43	*-0.46	***-0.68	***-0.78	-0.25
Phaeo									0.15	0.27	0.39	0.15	-0.24	0.32	0.18	0.08	*-0.39
TSS										***0.74	-0.12	-0.36	*0.43	***0.82	**0.61	*0.42	*0.37
VSS											-0.30	-0.36	**0.49	***0.75	***0.77	**0.63	0.18
Bacteria												**0.69	*-0.48	-0.09	*-0.49	*-0.50	*-0.51
Viruses													*-0.56	-0.29	-0.44	-0.46	**-0.68
Depth														*0.43	**0.63	*0.44	**0.61
Temp															***0.79	**0.58	**0.44
Salinity																***0.88	*0.44
Secchi																	*0.29
DO																	

Figures

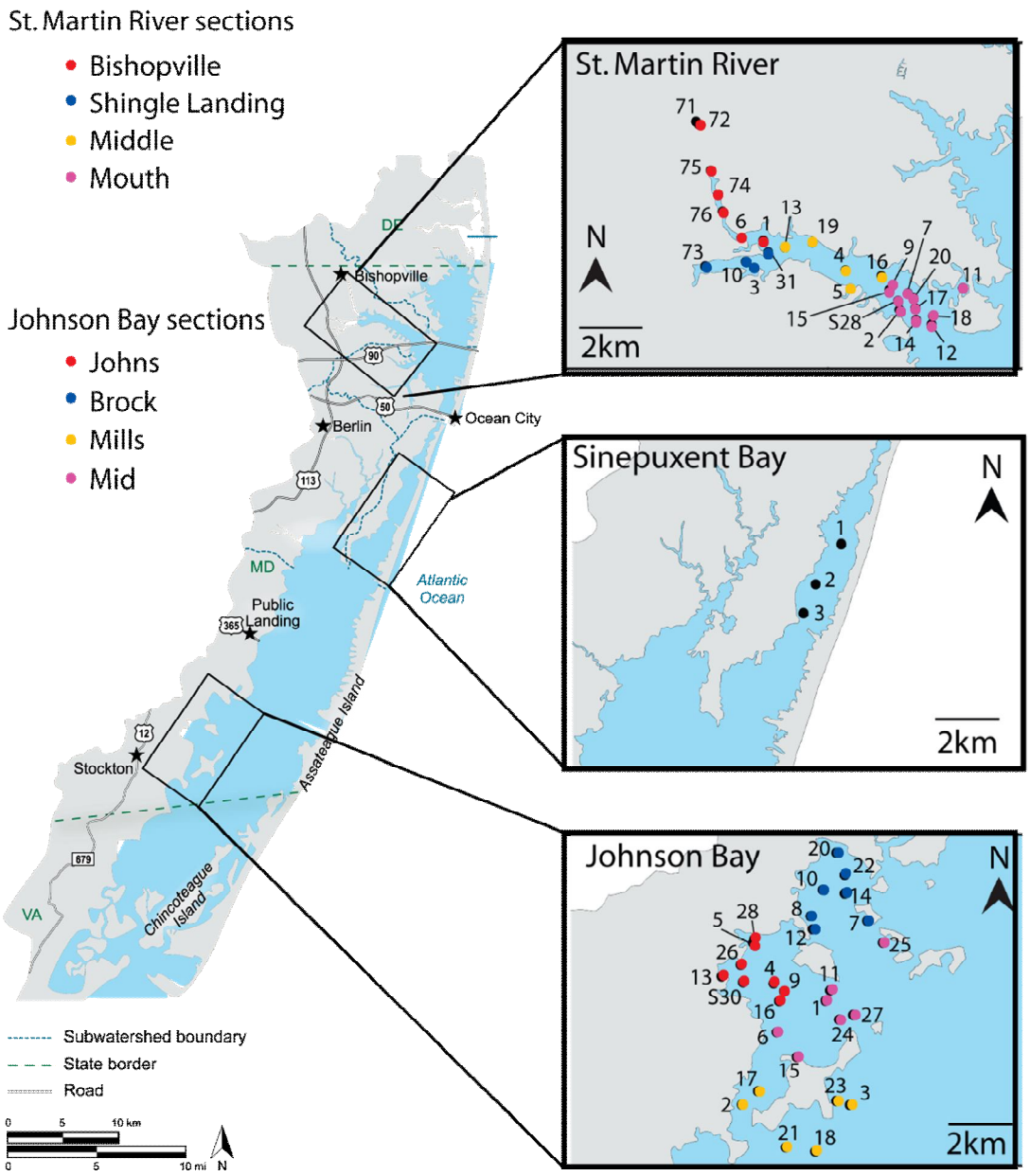


Figure 3.1: Sampling sites in the Maryland Coastal Bays in May and July 2006 and 2007. St. Martin River and Johnson Bay were sampled in both years and divided into sections (denoted by colors) for additional fine-scale analysis. Sinepuxent was added in 2007 as an additional bay-wide comparison.

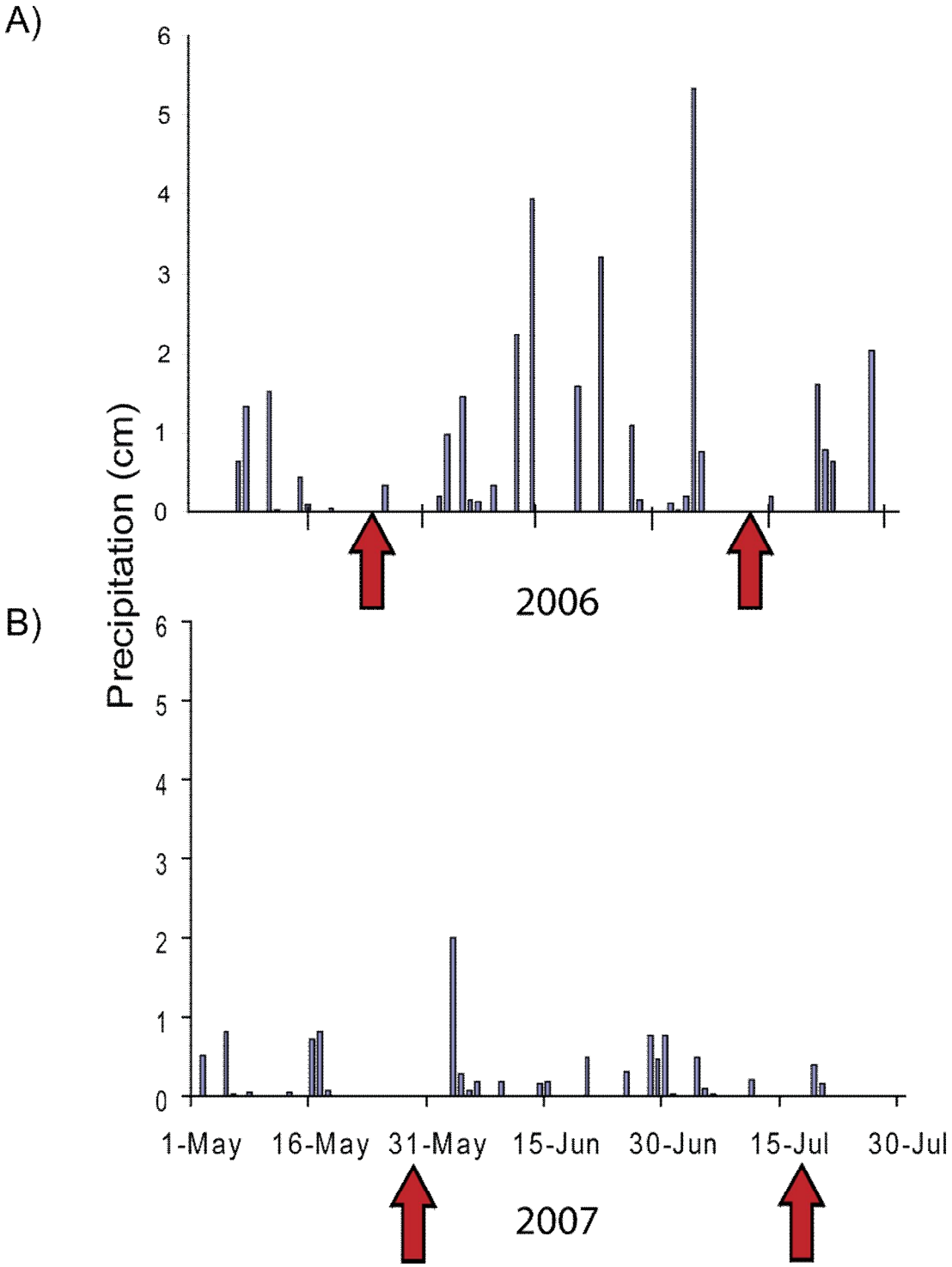


Figure 3.2: Precipitation patterns preceding and during the summer 2006 (A) and 2007 (B) samplings, depicted by arrow locations. The time period between May and July 2006 received an order of magnitude more rainfall than the same period in 2007.

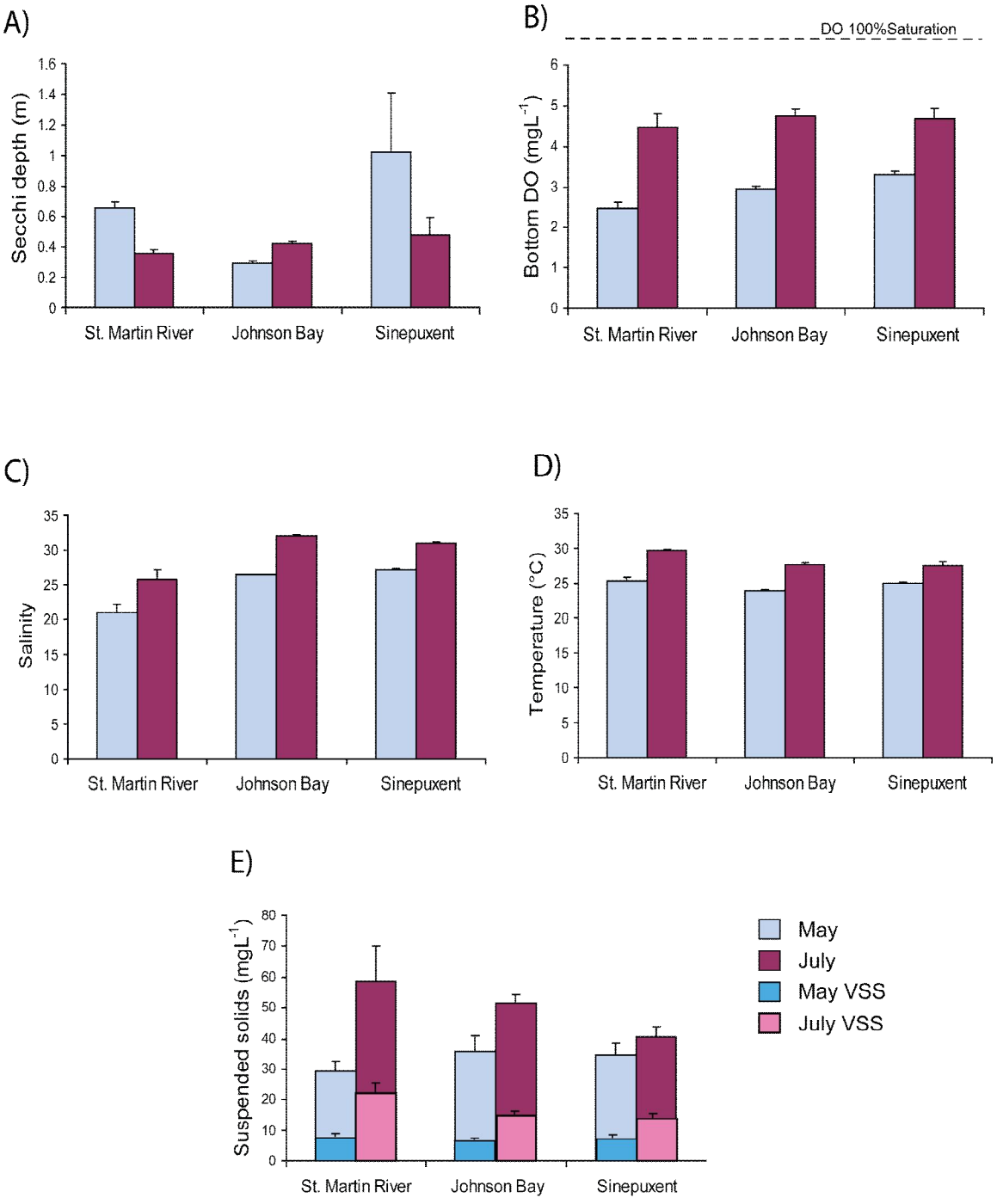


Figure 3.3: Physical parameters measured in St. Martin River, Johnson Bay, and Sinepuxent for May and July 2007. Error bars represent standard error of the mean for each month in each variable (A-E). In graph E, the bottom stacks of the bars are the fraction of total suspended solids that was composed of volatile suspended solids (VSS).

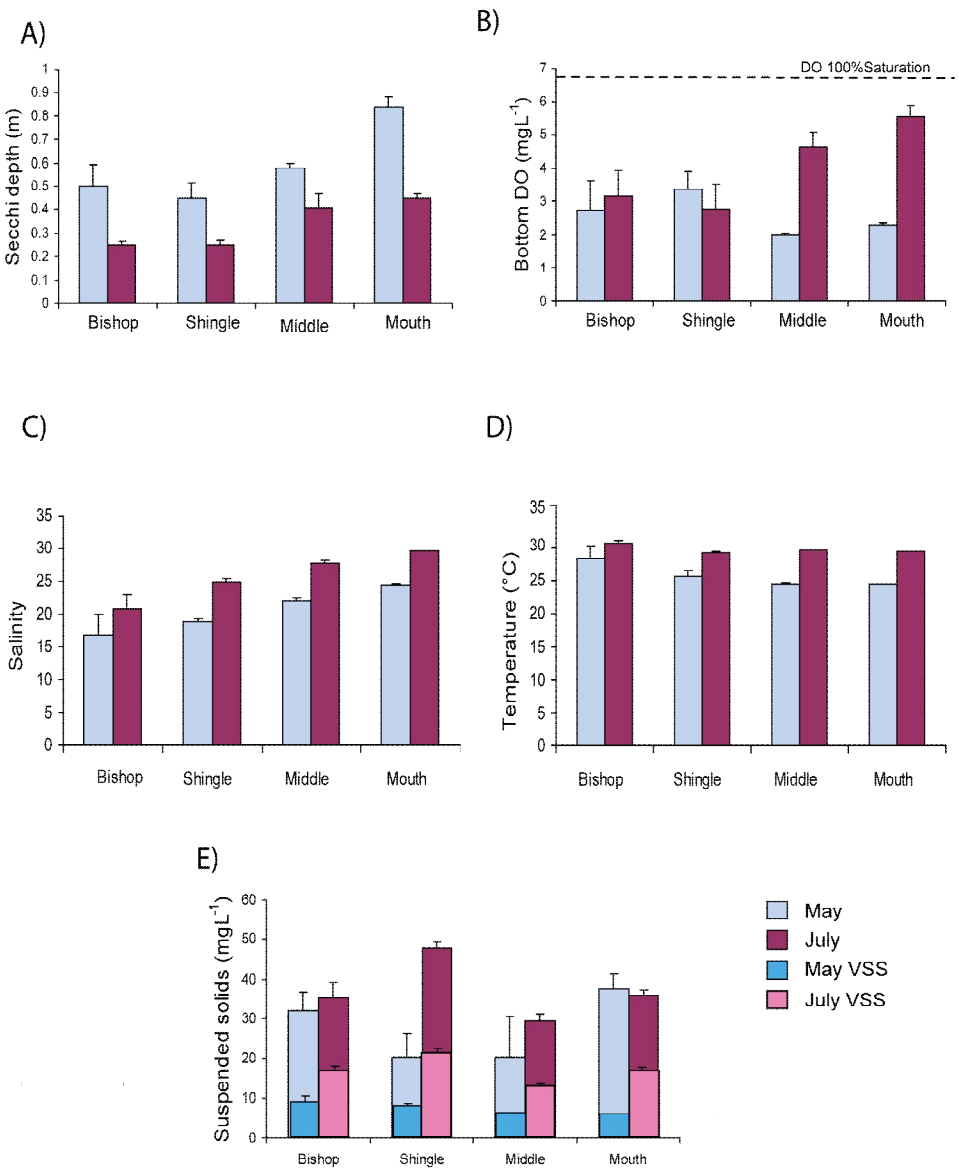


Figure 3.4: Physical parameter results for sections of St. Martin River in May and July 2007. The river was divided into the four sections of Bishop and Shingle (upstream prongs), Middle, and the Mouth (see Figure 1). Error bars represent standard errors of each section's mean for each parameter (A-E). In graph E, volatile suspended solids (VSS) are represented as the bottom stacked bars, as a fraction of total suspended solids for each section.

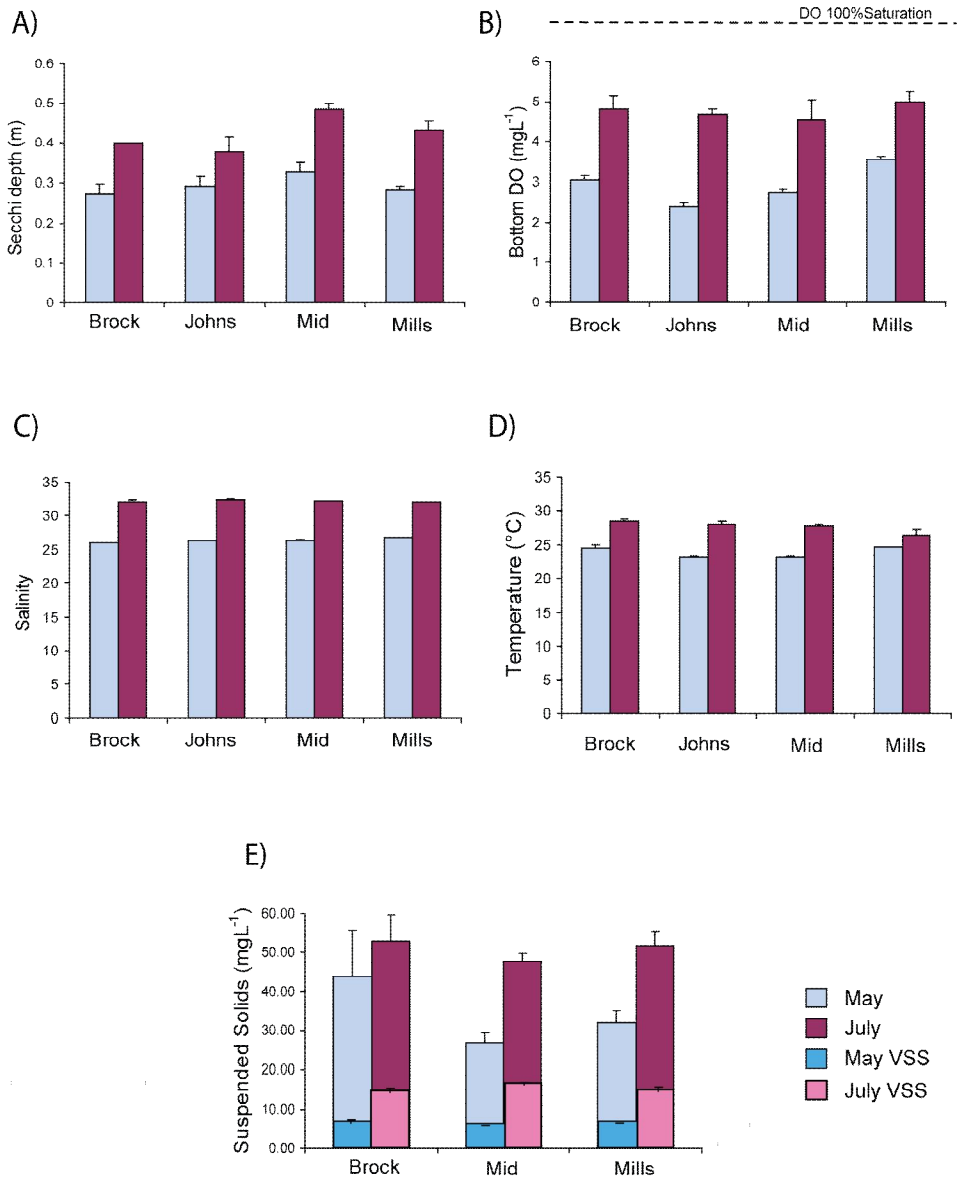


Figure 3.5: Means of physical parameters (A-E) in sections of Johnson Bay for May and July 2007. Error bars represent standard error about the mean for each section. In graph E, volatile suspended solids (VSS, bottom bars) are shown as a fraction of total suspended solids (TSS) in May and July. TSS samples were only collected in Brock, Mid and Mills sections.

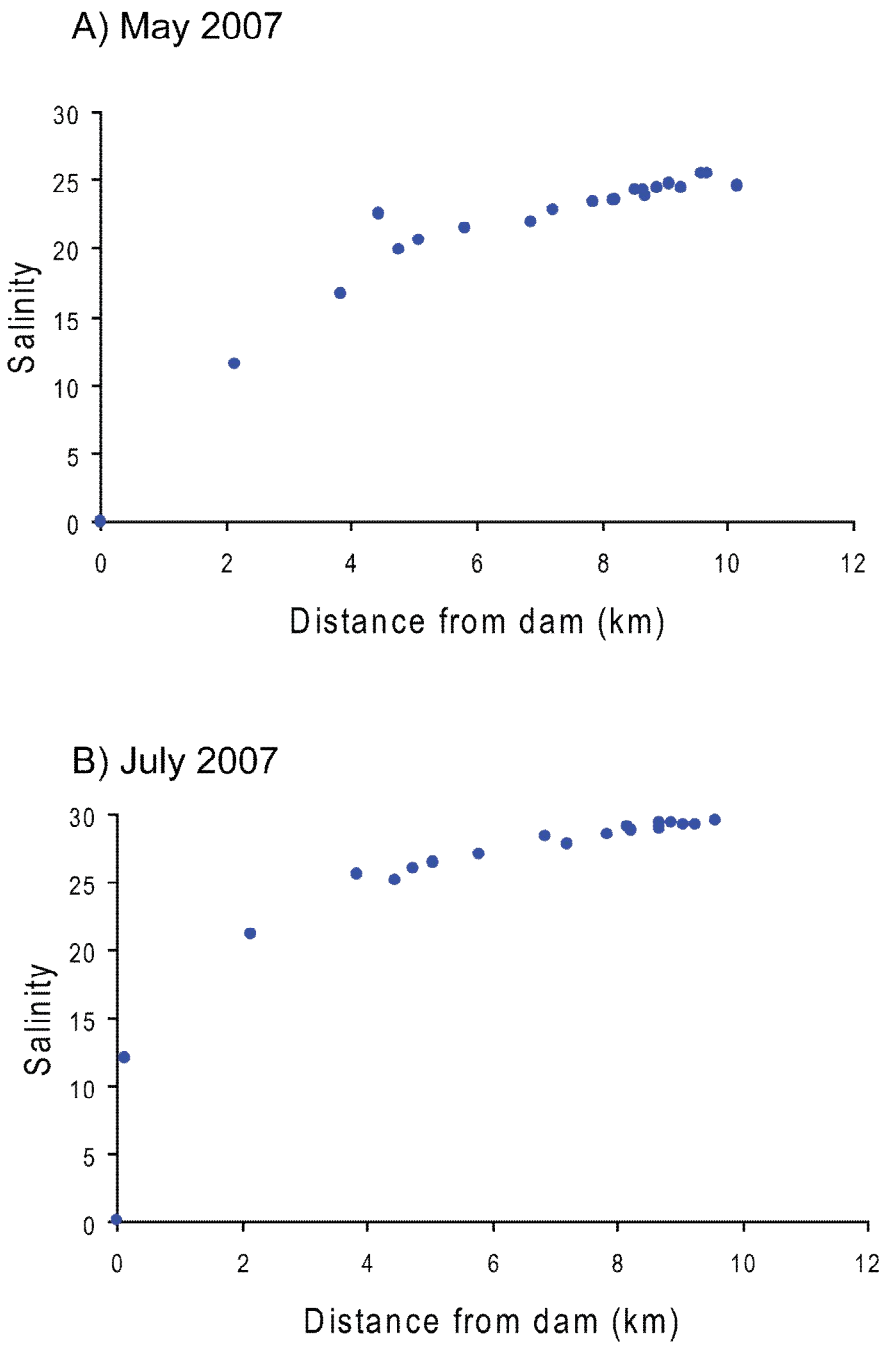


Figure 3.6: St. Martin River salinity, as a function of distance from the dam on the Bishopville Prong (upstream freshwater boundary) to the mouth of the river for samples in May (A) and July (B) 2007. Due to YSI meter dysfunction, all sites were not measured in July.

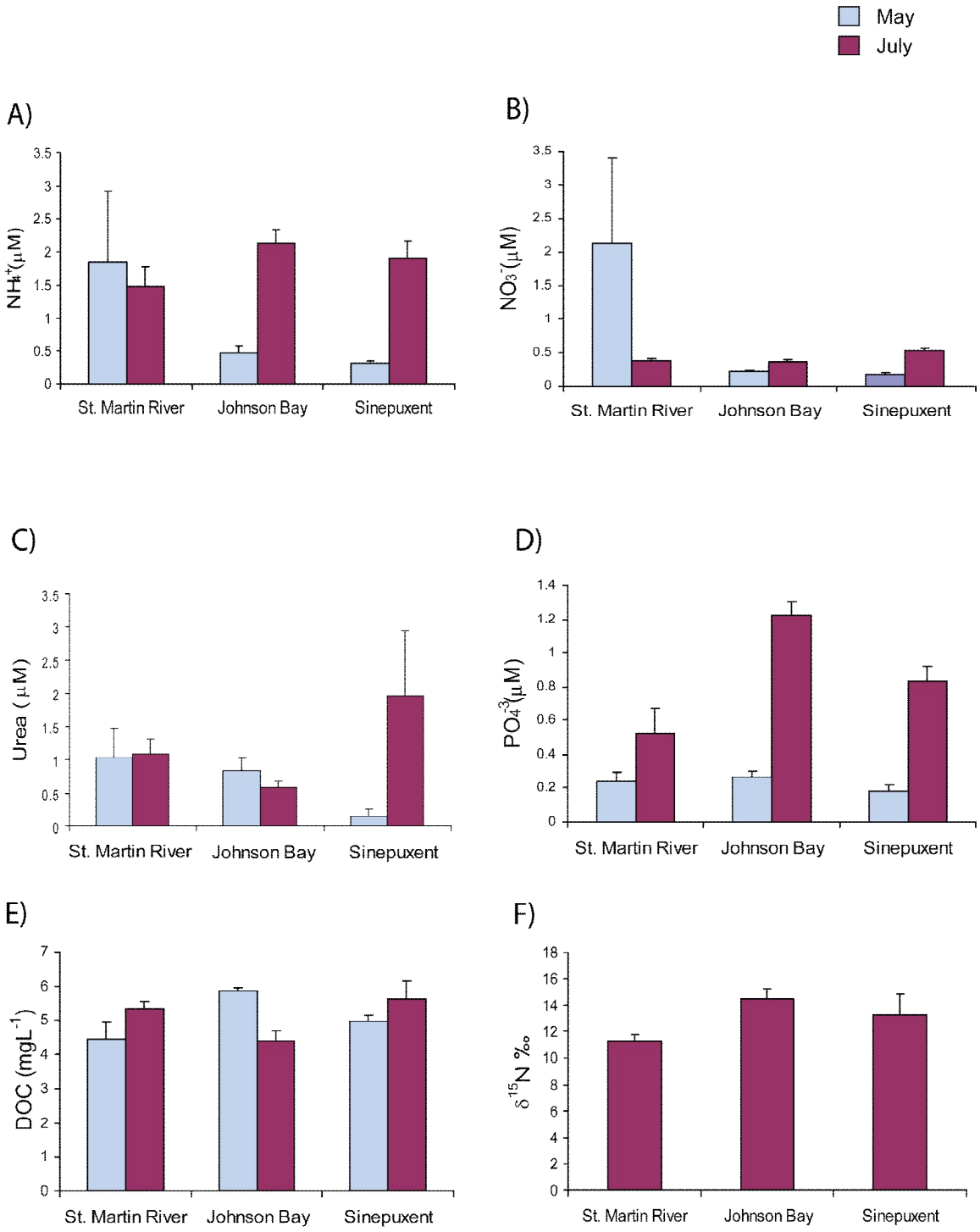


Figure 3.7: May and July 2007 nutrient concentrations for the three Maryland Coastal Bays in this study. Error bars represent standard error about the mean. $\delta^{15}N$ is the ratio of the natural isotope ^{15}N to ^{14}N, indicative of wastewater inputs and/or increased nutrient cycling within the system.

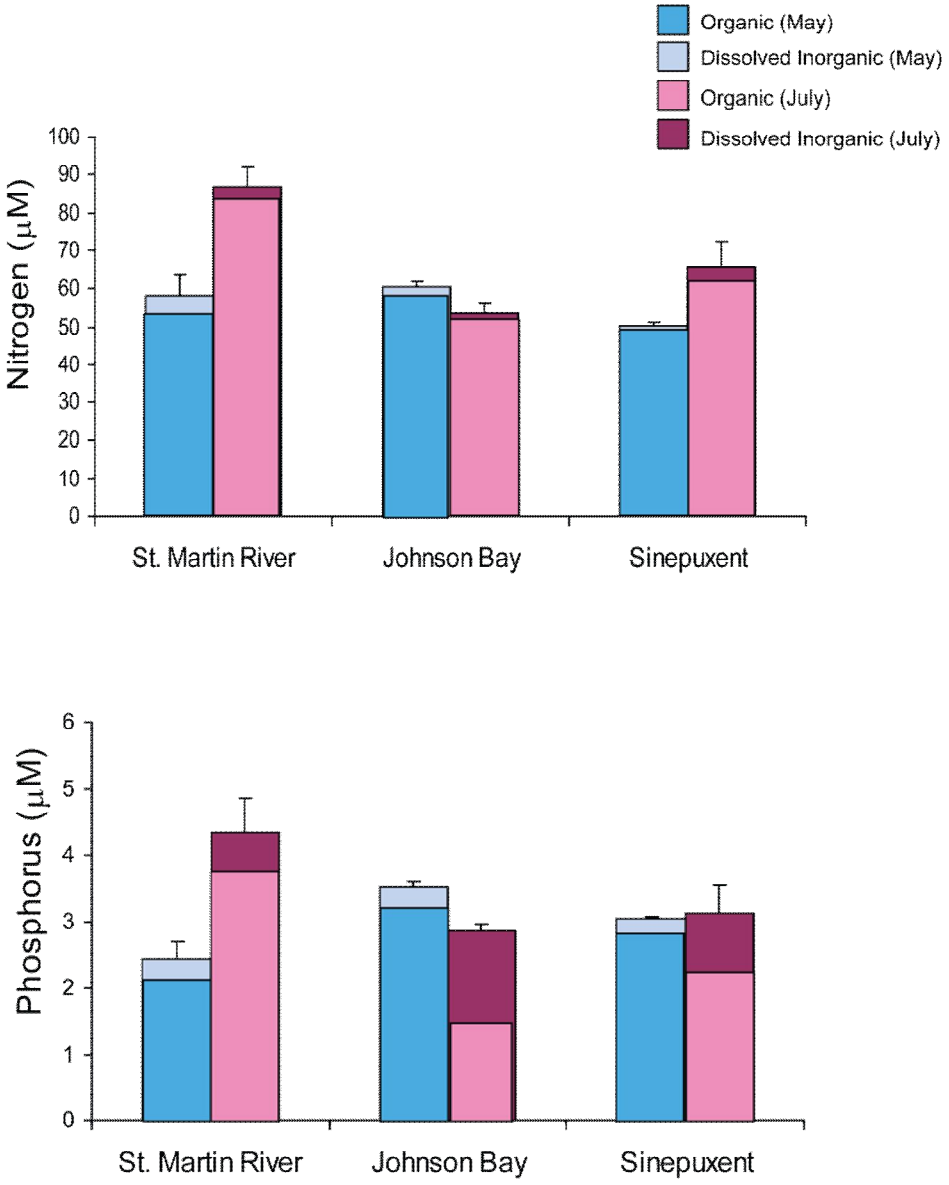


Figure 3.8: Organic and dissolved inorganic fractionation of total nitrogen and total phosphorus pools in May (blues) and July (pinks) 2007. Error bars represent standard errors about the mean. Dissolved inorganic fractions (NH_4^+ + NO_3^- and PO_4^{-3}) are the upper portions of each bar graph, and organic fractions (dissolved and particulate) are the bottom portions.

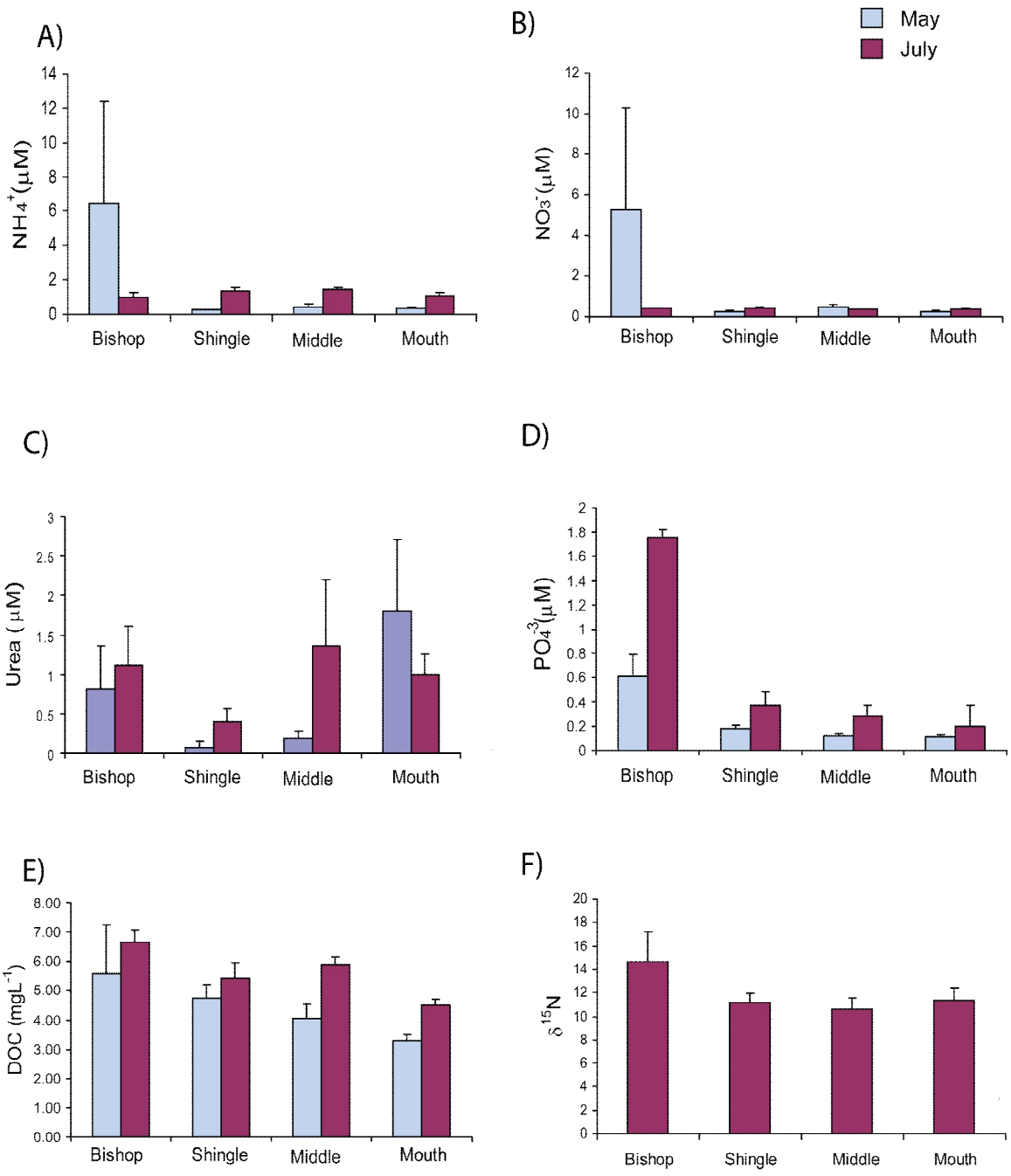


Figure 3.9: Mean nutrient concentrations of sections in the St. Martin River, May and July 2007. Error bars represent standard error about the mean (bars). $\delta^{15}N$ is the ratio of the natural isotope ^{15}N to ^{14}N, indicative of wastewater inputs and/or increased nutrient cycling within the system.

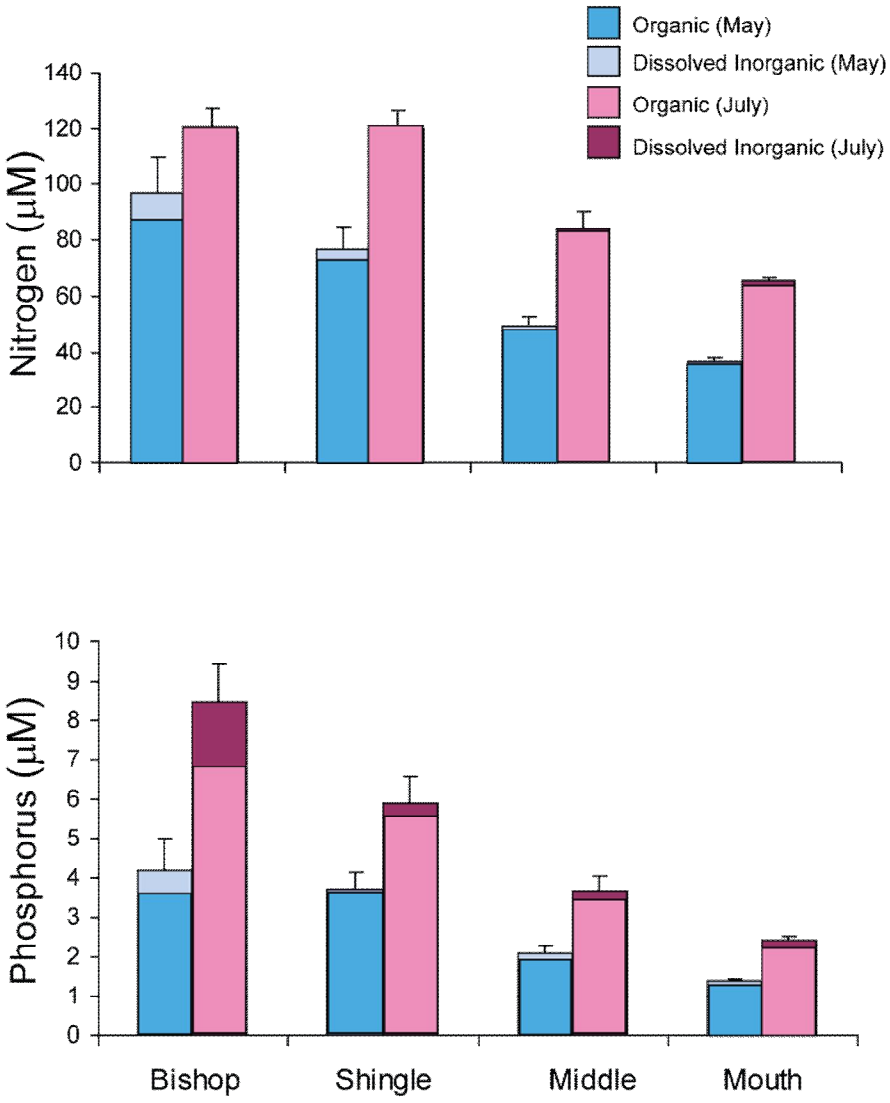


Figure 3.10: Organic and dissolved inorganic composition of nitrogen and phosphorus concentrations in the different sections of St. Martin River, May and July 2007. Error bars represent the standard error about the mean (bars). Dissolved inorganic fractions (NH_4^+ + NO_3^- and PO_4^{-3}) are the upper portions of each bar graph, and organic fractions (dissolved and particulate) are the bottom portions.

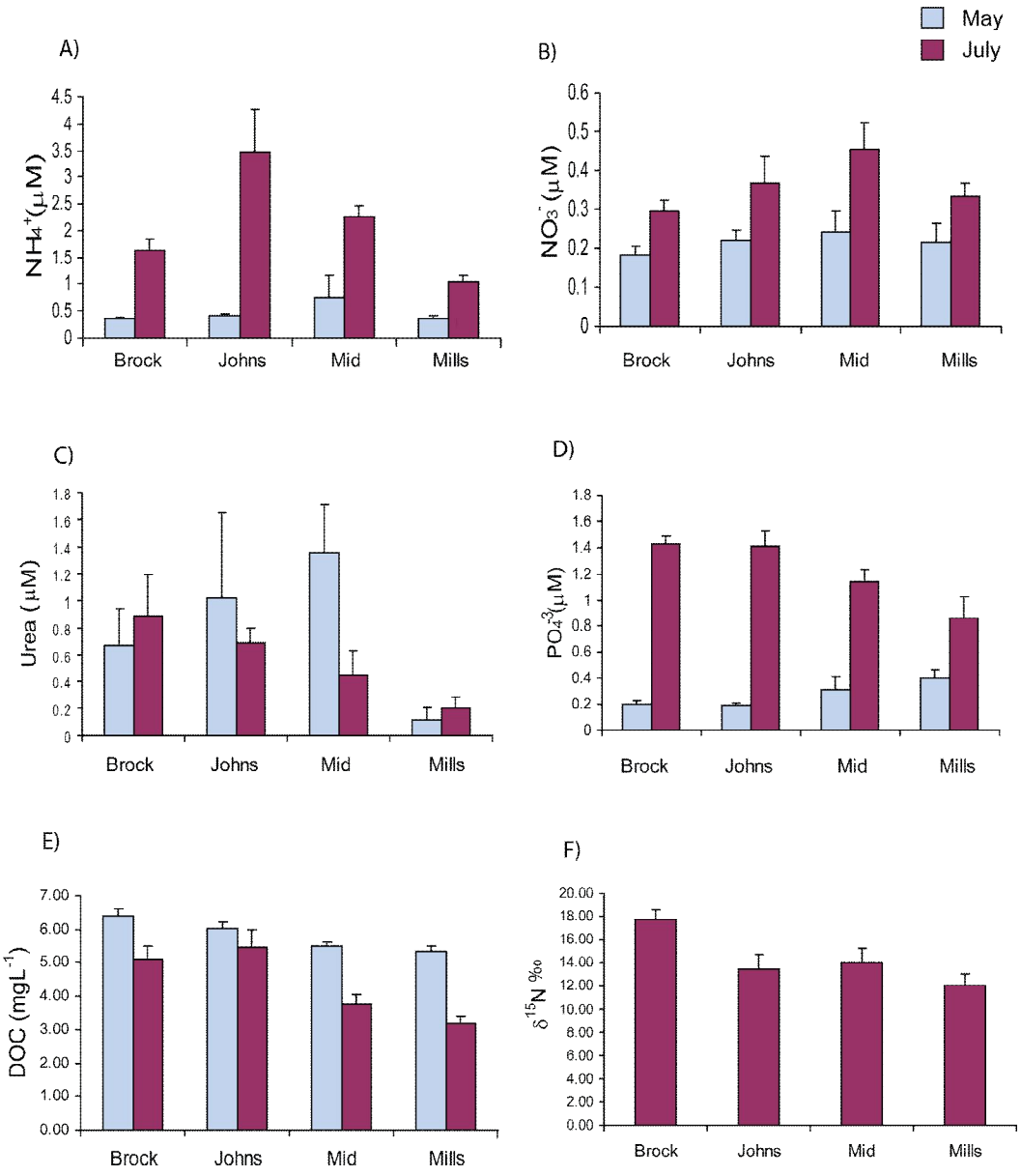


Figure 3.11: Mean nutrient concentrations of sections in Johnson Bay, May and July 2007. Error bars represent standard error about the mean.

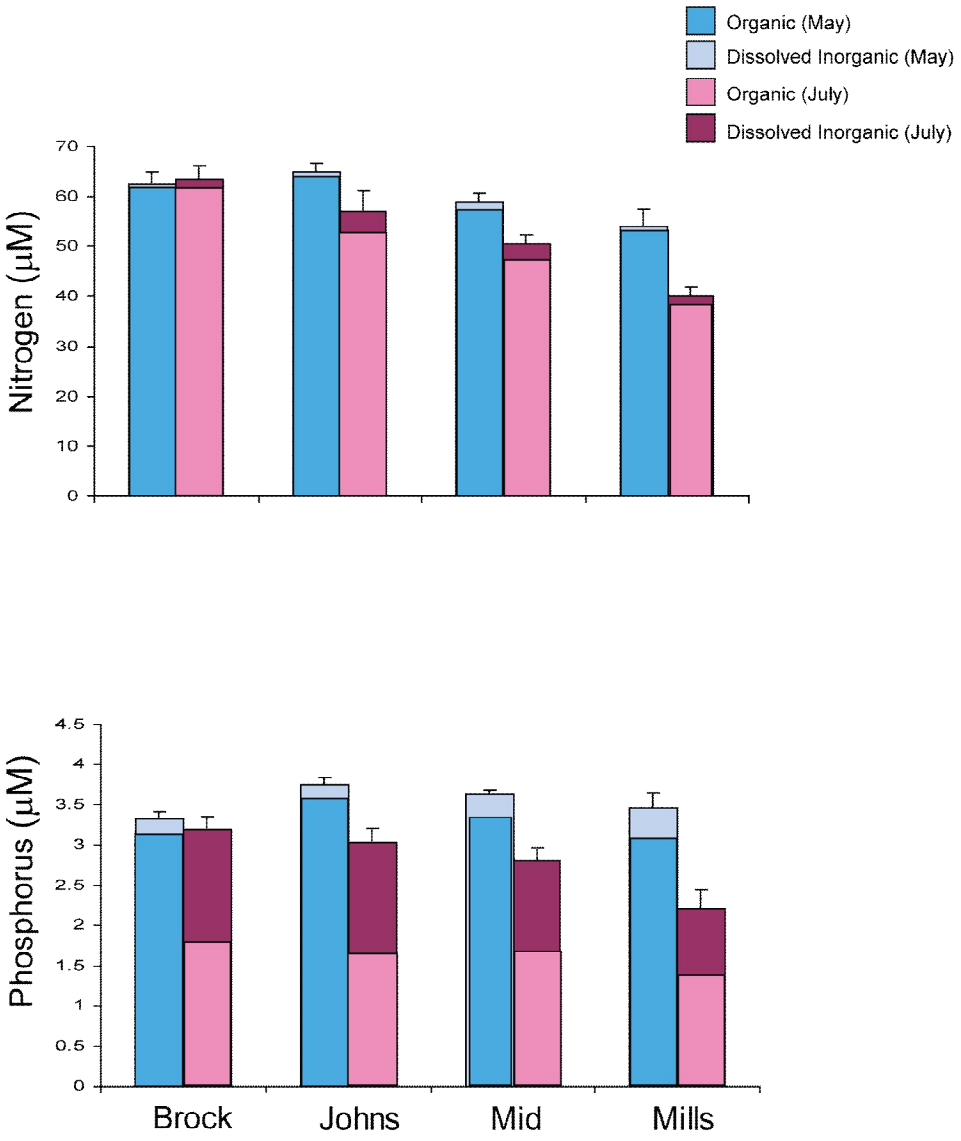


Figure 3.12: Dissolved inorganic (NH_4^+ + NO_3^- and PO_4^{-3}) and organic fractionation of nitrogen and phosphorus in the sections of Johnson Bay May and July 2007. Error bars represent the standard error about the mean (bars).

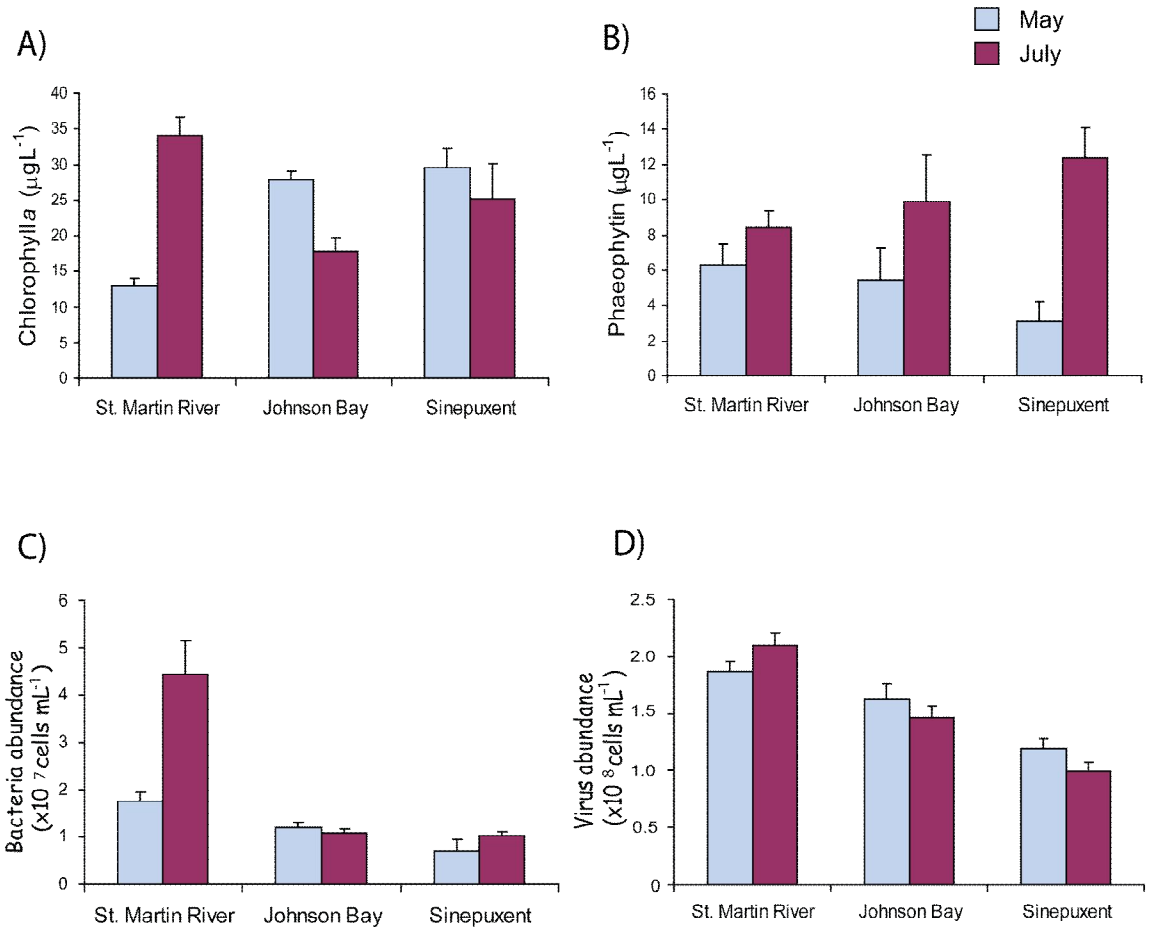


Figure 3.13: Biological parameters measured in the three Maryland Coastal Bays in May and July 2007. Bars represent means for each bay, with standard error denoted by the error bars.

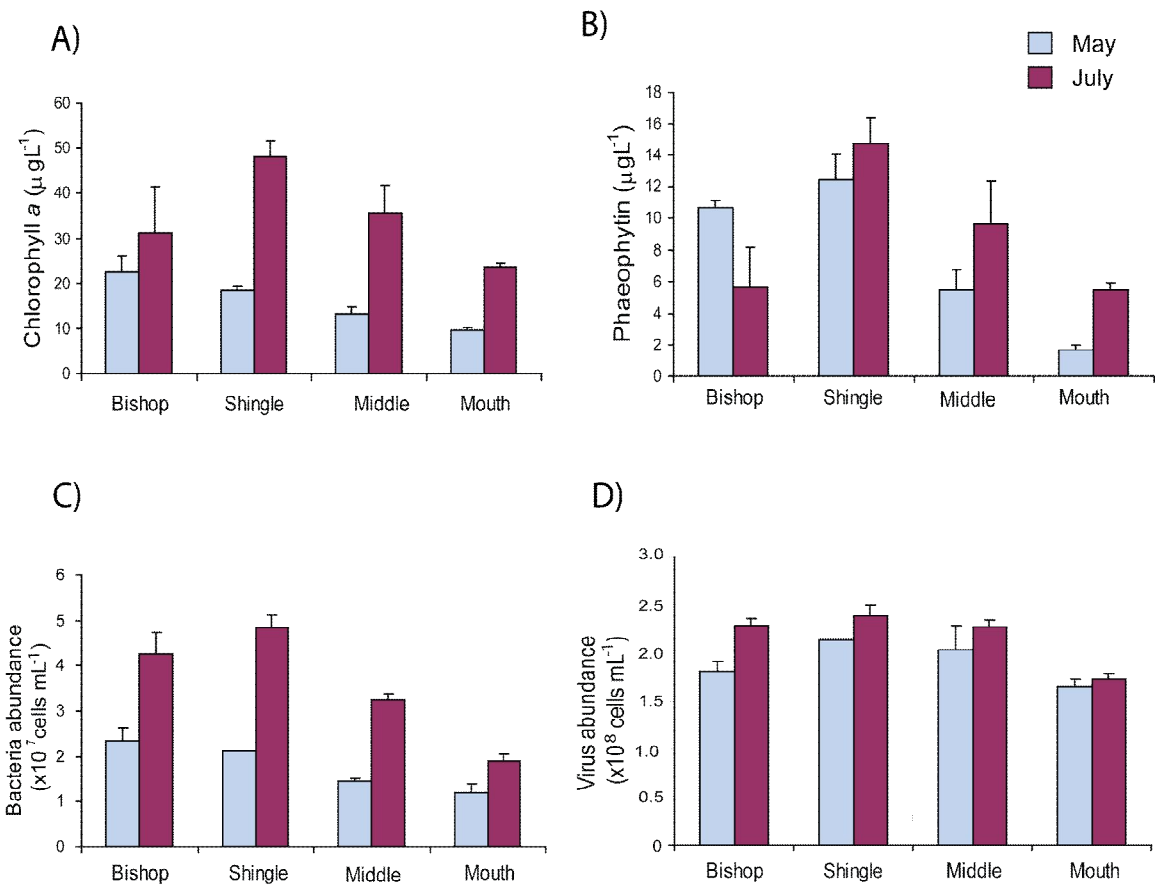


Figure 3.14: Means of biological parameters for the sections of St. Martin River in May and July 2007. Error bars represent the standard error about the mean for each month.

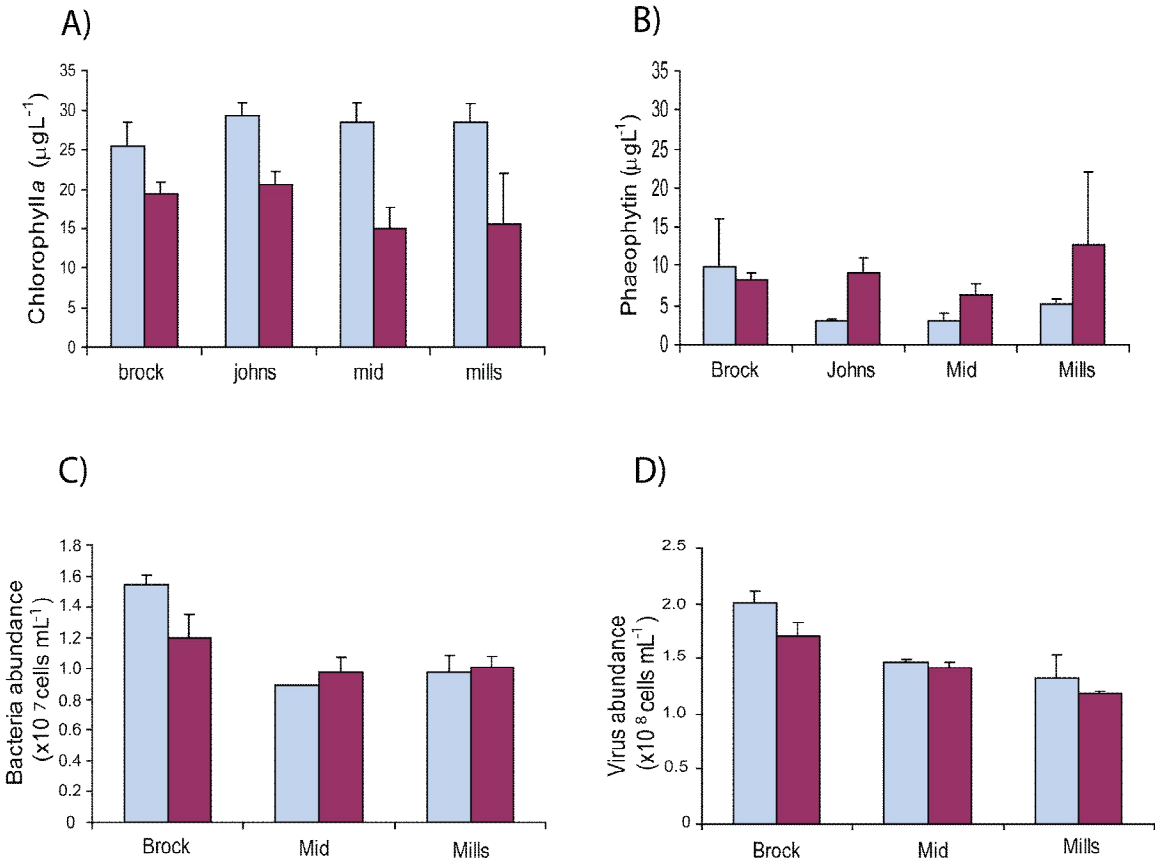


Figure 3.15: Means of biological parameters for the sections of Johnson Bay in May and July 2007. Error bars represent the standard error about the mean for each month.

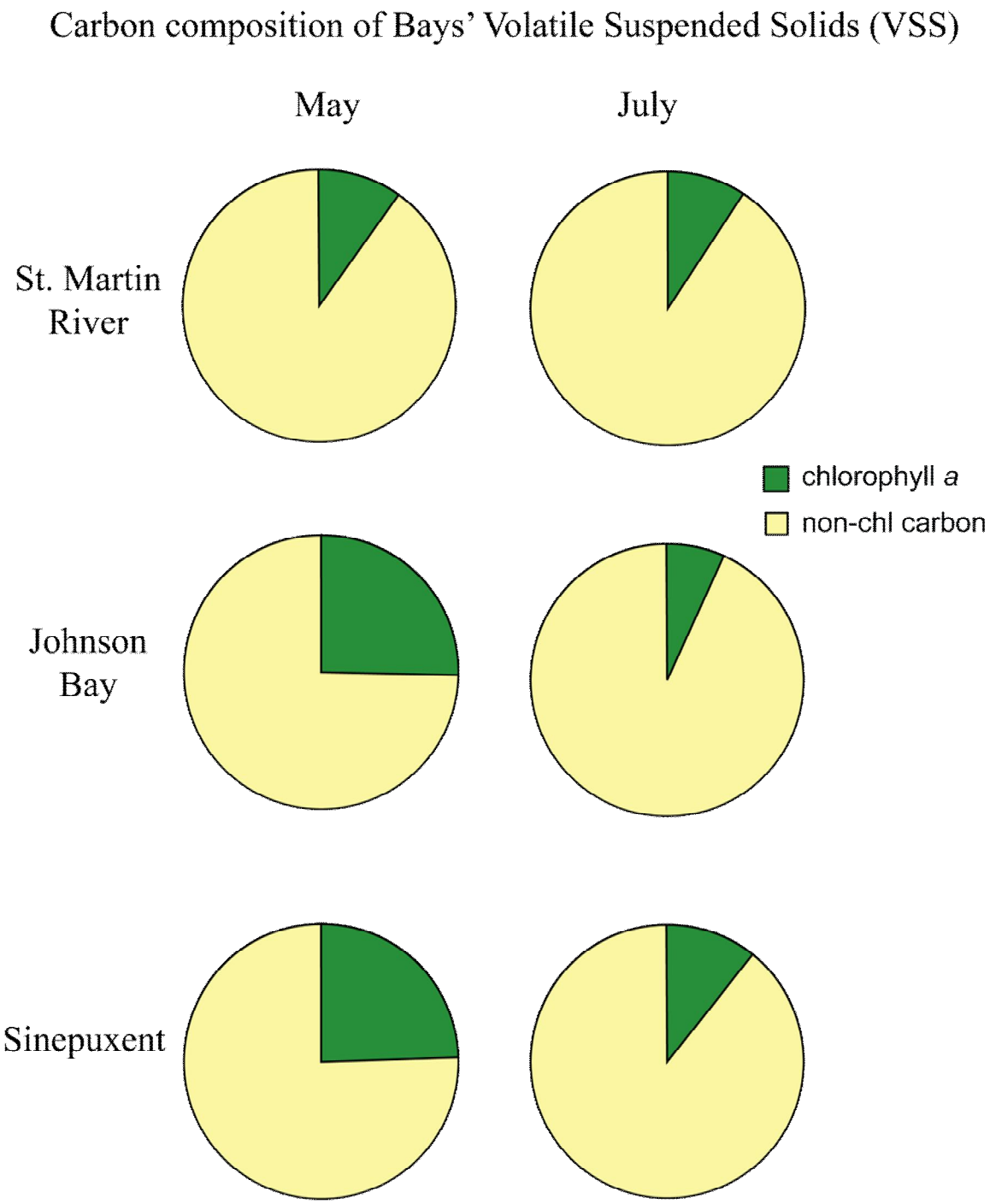


Figure 3.16: Fractionation of Volatile Suspended Solids (VSS) measured in the three Maryland Coastal Bays in May and July 2007. Carbon content of total VSS was calculated for the mean of each bay by dividing by a factor of 2, and mean chlorophyll *a* concentration was converted to carbon content by multiplying by a C:Chl ratio of 30:1.

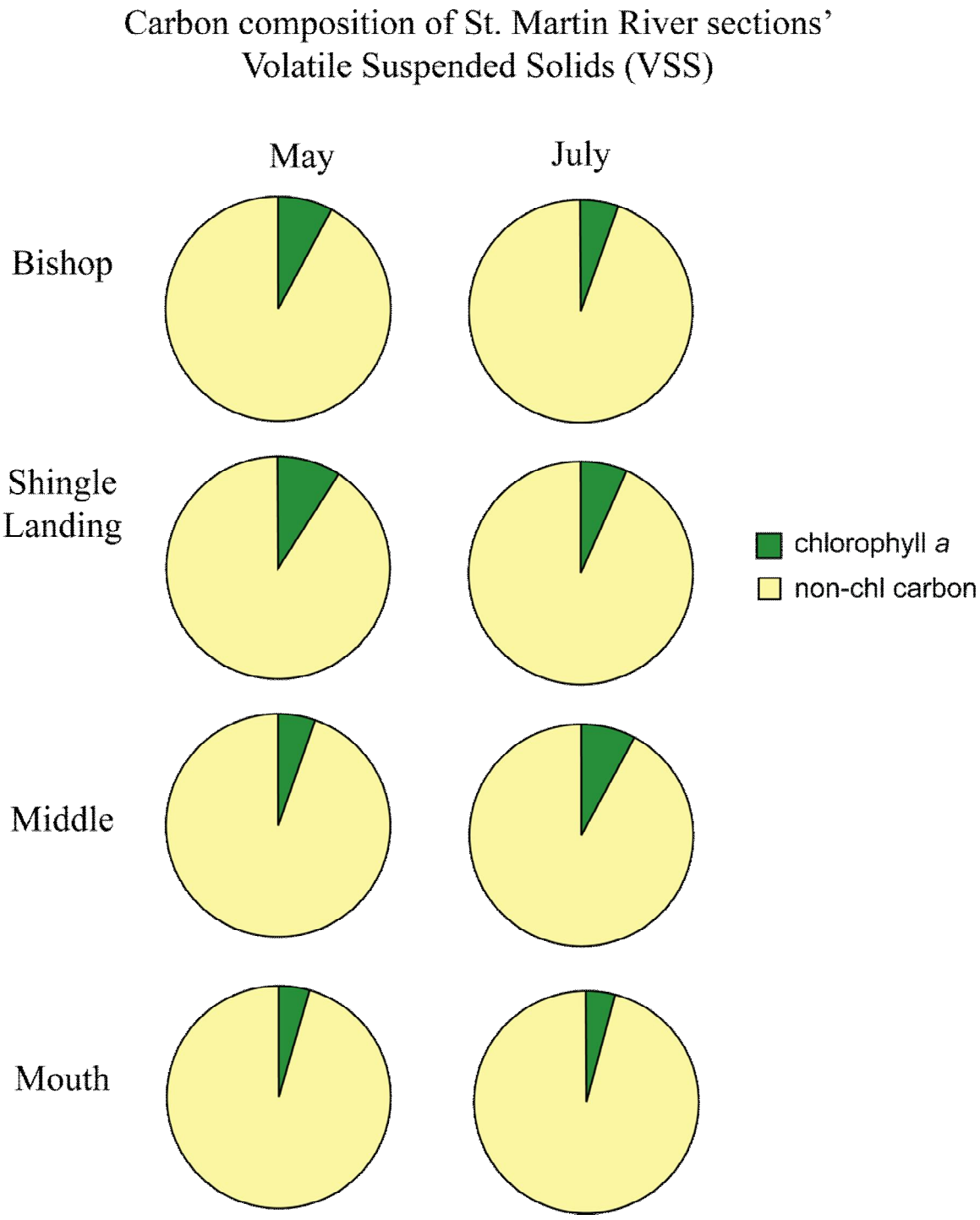


Figure 3.17: Sectional analysis of volatile suspended solid (VSS) fractionation in St. Martin River May and July 2007. Carbon content of total VSS was calculated for the mean of each section by dividing by a factor of 2, and mean chlorophyll *a* concentration was converted to carbon content by multiplying by a C:Chl ratio of 30:1.

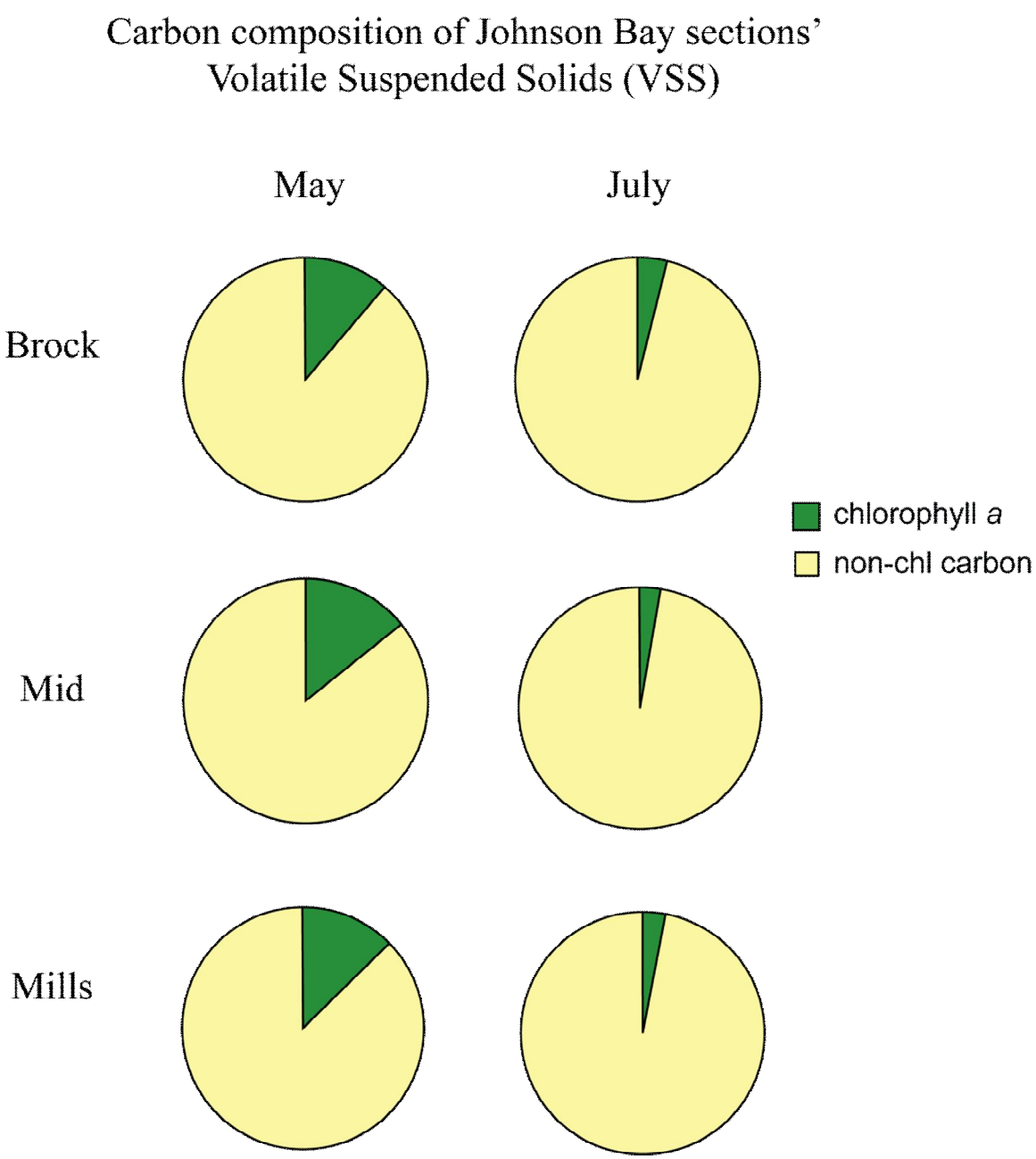


Figure 3.18: Sectional analysis of volatile suspended solid (VSS) fractionation in Johnson Bay, May and July 2007. Carbon content of total VSS was calculated for the mean of each section by dividing by a factor of 2, and mean chlorophyll *a* concentration was converted to carbon content by multiplying by a C:Chl ratio of 30:1.

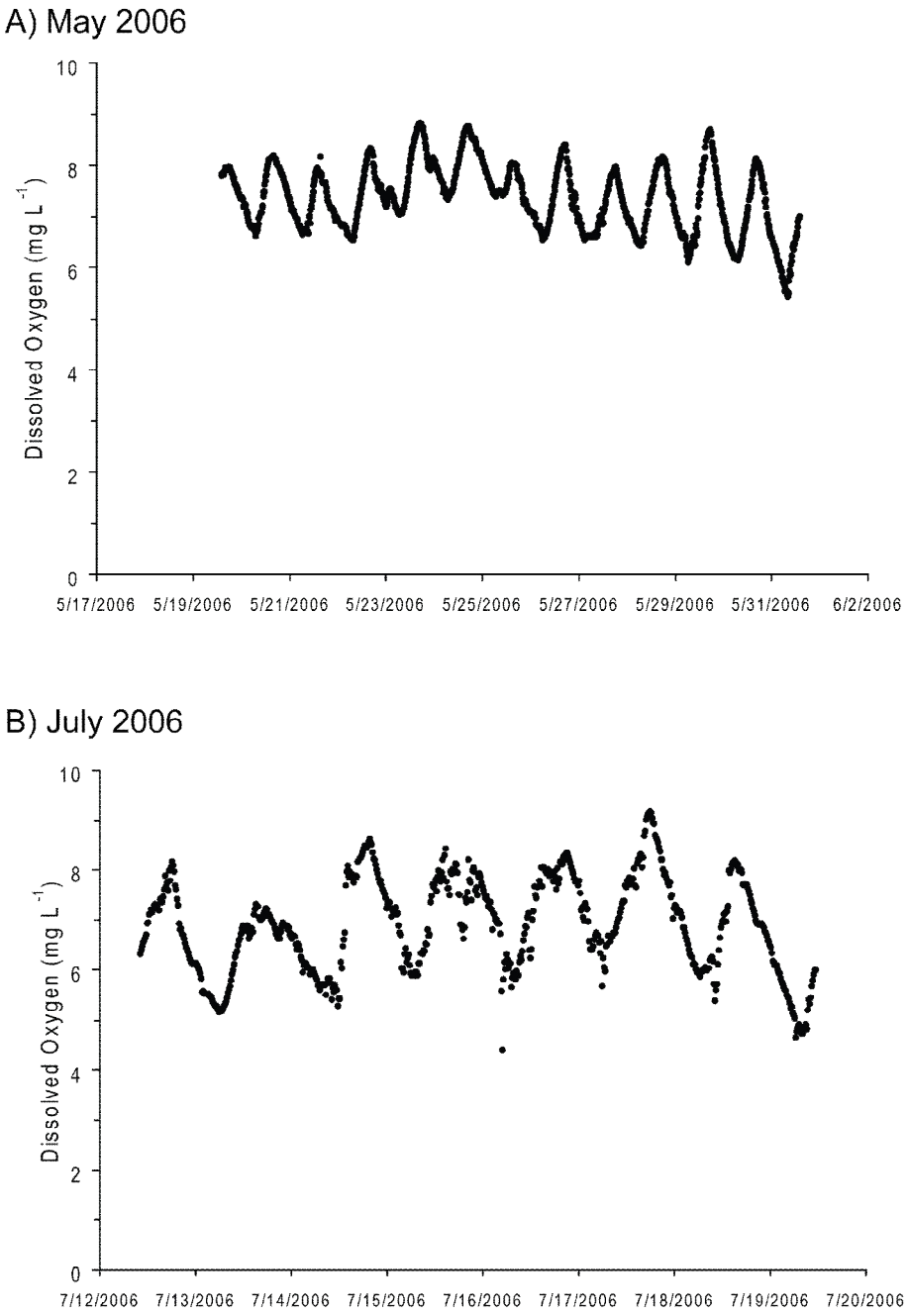


Figure 3.19: Continuous monitoring data from Johnson Bay for the sampling periods of May and July 2006. Dissolved oxygen ranged between 6 and 8 mg L^{-1}, with daily fluctuations of ~ 3 mg L^{-1} in July. DO was highest at mid-day. DO in Johnson Bay was mainly unsaturated.

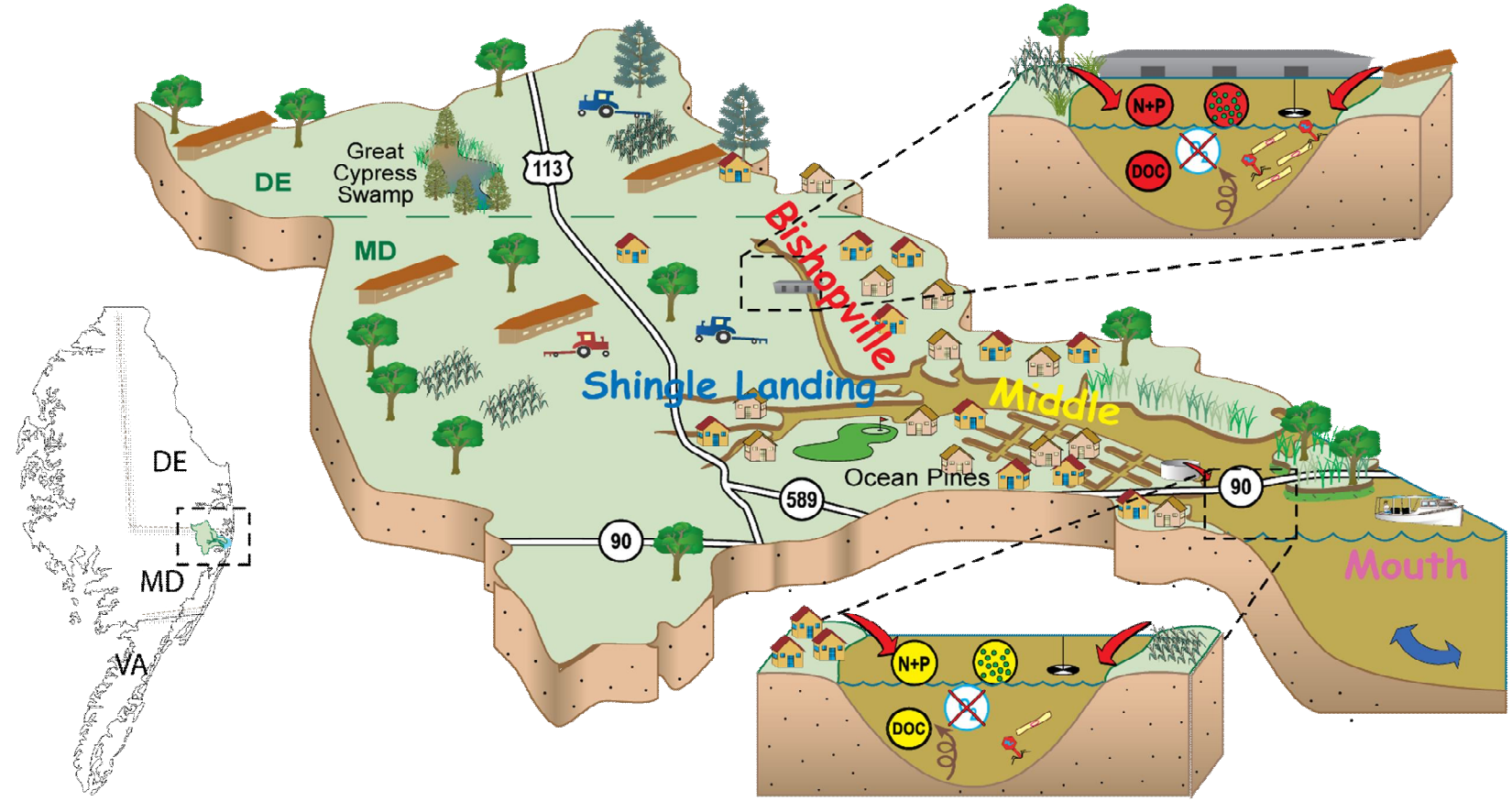
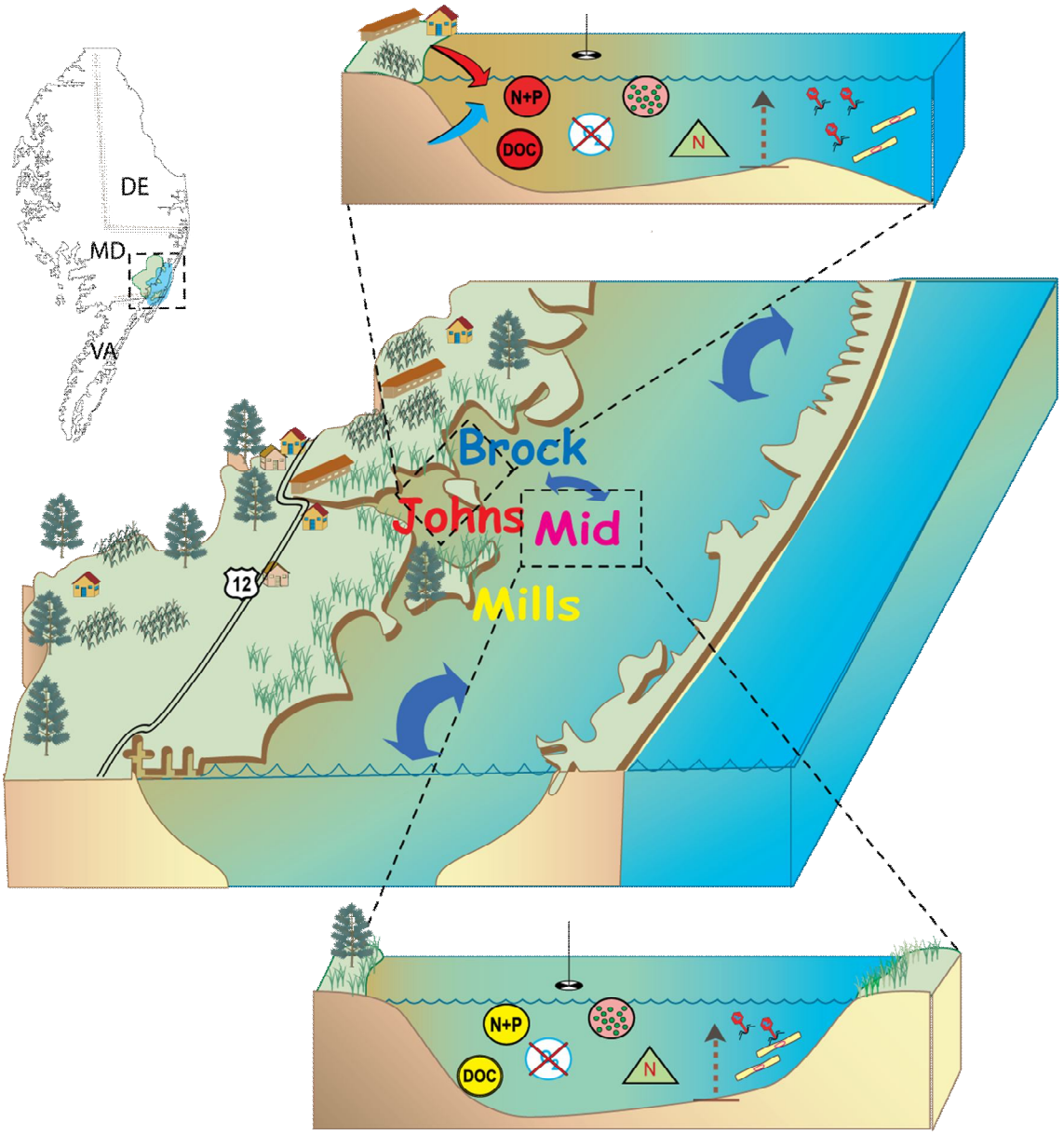
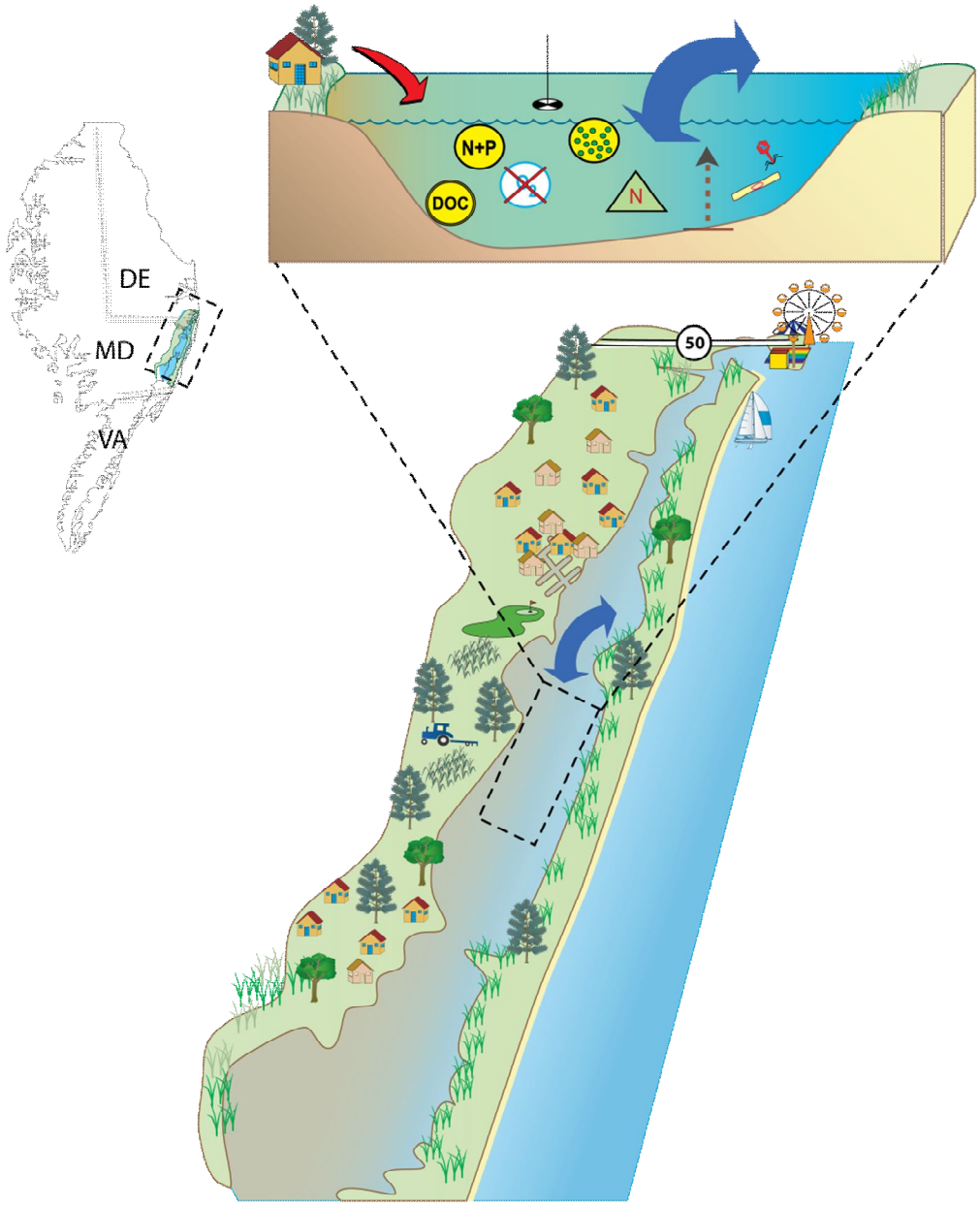


Figure 3.20: Conceptual diagram of St. Martin River



Johnson Bay can be divided into the lagoons of Brock and Johns closest to the land, the offshore Mid, and the region around Mills Island. Surface run-off and groundwater are sources of freshwater to the system, which experiences slow tidal flushing . High ceoncentrations of nitrogen and phosphorus (N+P), dissolved organic carbon (DOC), chlorophyll a, low dissolved oxygen, and high $\delta^{15}N$ (N) contribute to degraded water quality, especially closer to the land. High bacterial and viral abundances and fluxes from sediment lead to nutrient cycling and regeration

Figure 3.21: Conceptual diagram of Johnson Bay



Sinepuxent Bay is closest to the Ocean City Inlet and experiences faster tidal flushing than the other two bays. However, inputs from urban development and regeneration from sediment flux contribute to moderate concentrations of nitrogen and phosphorus (N+P), dissolved organic carbon (DOC), and chlorophyll a. Sinepuxent also has high $\delta^{15}N$ (N) as well as low summertime dissolved oxygen. The abundances of bacteria and viruses are lower than the other two bays but still in the range of eutrophic systems.

Figure 3.22: Conceptual diagram of Sinepuxent

Chapter IV: Synthesis

The Maryland Coastal Bays of St. Martin River, Johnson Bay, and Sinepuxent Bay show evidence of both watershed land use and physical structure impacts. Because the Coastal Bays have such shallow depths and are positioned between the Delmarva Peninsula and its barrier islands, they display different patterns in water quality than their neighbor, the much-studied Chesapeake Bay. The proportion of influence that both watershed and within-bay characteristics has on water quality varies by geographic location. Poultry feeding operations, as well as other anthropogenic watershed land use, have a dominant impact on water quality of St. Martin River, while sediment type, tidal exchange, water residence time, and erosion rate are most likely the key elements that determine the extent of water quality degradation in Johnson Bay.

Export coefficient modeling as a means of estimating watershed nutrient loads in the Coastal Bays is also a helpful means by which to compare the bays. However, this method should be implemented carefully and calibrated with field measurements to ensure accuracy on a local scale. The results of the stream study in the watershed of St. Martin River revealed that the nutrient export calculated from small stream watersheds may provide more information about local watershed processes than more generalized coefficient modeling. The results of this study, especially the feeding operations export coefficients that were derived from empirical data, are applicable to nearby regions, but the calculation of exact loads must be cautioned, given the variability and error present in export coefficients. Variations in export coefficients for feeding operations in different geographical regions depend upon methods of waste management, leading to the possibility of a wide range of loading coefficients for the same type of animal husbandry.

In the Coastal Bays, watershed export coefficients derived from normalizing nutrient export by area may also provide useful information by which to compare watersheds of different land use composition. Export coefficient modeling, when applied at the whole-watershed scale, is helpful to compare the bays and the effects of land use pressures on their N and P loads.

Studying the Coastal Bays and their watersheds revealed relationships between land use, nutrient concentrations, and individual bay characteristics. High total nitrogen and phosphorus concentrations, mostly organic, are evident in all three study sites of St. Martin River, Johnson Bay, and Sinepuxent, despite their variations in watershed land use and circulation patterns. In St. Martin River, nutrients were high in tributaries of both the Shingle Landing and Bishopville Prongs. Regression analysis results indicate that poultry feeding operations, which have increased in the Coastal Bays watershed over the last 50 years, may be directly linked to stream nitrogen concentrations and loading to the estuary. Natural land cover demonstrates the opposite trend (increasing natural cover decreases TN concentrations), stressing the importance of wetlands and forest as buffers in the region. Residential development and agricultural land located close to the coastline, as well as a lack of wetlands (less than 10% of the St. Martin watershed area) may be linked to more direct nutrient inputs to the river. In both Sinepuxent Bay and Johnson Bay, land use is dominated by forest and wetlands. The presence of this natural land cover, especially close to the coastline may be responsible for the lower concentrations observed in these locations, as opposed to St. Martin River where crop agriculture is the dominant land use.

Soil, sediment, and erosion, which are most often overlooked when assessing causes of water quality degradation, may become increasingly important factors in the Maryland Coastal Bays and their watersheds. In the St. Martin River, channel incision and erosion, especially in areas that had been affected by historical processing plants (e.g. former chicken hatcheries) may be releasing stores of P from trapped sediment. This would most likely explain high P loading in certain sub-watersheds. In addition, hydric soils may assist in P release even from forested areas, particularly after periods of precipitation. The resulting high TP concentrations observed in the bays themselves during a wet year versus a dry year reflects the affinity of P for soil particles and the ability to be discharged into the water column by intense rain. A lack of difference between sections of the bays under these conditions, even in a linear system such as St. Martin River, reveals that these effects are felt throughout the estuary and not only in areas closest to the land.

Nutrient species composition varied between the streams and estuarine region of St. Martin River but is relatively constant between sections of the bays. In most of the St. Martin streams included in this study, NO_3^- comprised about half of TN in all but the summer season, but the two polyhaline prongs exhibited low dissolved inorganic concentrations of both N and P. These observations support the idea that the Coastal Bays, like most estuaries, are NO_3^- sinks and bioreactors, where high rates of processing are occurring at the interface between saltwater and freshwater. Extremely low bay-wide inorganic nutrient concentrations despite increased concentrations of TN, TP, and PO_4^{-3} in July reveals the importance of biological cycling and flux from sediment in contributing to the observed water quality trends. July $\delta^{15}N$ was also indicative of

increased cycling in all three bays (>10‰), including Sinepuxent where water residence time is less than a sixth of Johnson Bay and half of that of St. Martin River. High natural bacteria abundances and summertime phytoplankton blooms (including brown tide, not addressed in this study) may aid in the recycling and flux of organic nutrients, linking eutrophication to the bays' state of degraded water quality.

Low dissolved oxygen continues to be a problem in the Coastal Bays, decreasing the viability of ecological and economic resources including seagrass, macro- and microalgae communities, benthic animals, and fisheries. Shallow water, high temperatures, slow tidal flushing, and phytoplankton blooms resulting from high nutrient concentrations each may contribute to the oxygen problem in various degrees between bays. Spatial analysis reveals that eutrophication is having widespread indirect, as well as direct, effects on the bays' water quality and environmental conditions.

Integrating the results of land, stream, and bay analyses draws a picture of the heterotrophic environment that has developed in the Maryland Coastal Bays. High organic nutrient concentrations, summertime fluxes, phytoplankton, and bacterial populations provide evidence of the tight coupling between physical, chemical, and biological components no matter the specific watershed land use composition, flushing time, or location among these Bays as a whole. A lack of water column stratification and undersaturation of dissolved oxygen leads to the hypothesis that biological oxygen demand is affecting water quality at all spatial scales, especially those closest to nutrient sources. Land use pressures may be a primary source of nutrients in the St. Martin River, but long residence times, erosion from sediment, and subsequent microbial processing

may also lead to the observed high nutrient concentrations in bays such as Johnson Bay, which also can be very susceptible to slight increases in nutrient loading.

Linking land-derived sources of N and P to patterns in estuarine water quality increases the awareness of direct and indirect effects of anthropogenic nutrient loading. Low percentages of development or faster flushing times may not preclude a bay from being degraded, and unique features of each bay may be responsible for a continuing downward trend, despite load reductions or attenuation. This study helped to bring together spatial, physical, chemical, and biological interfaces in order to explain the problems continuing to face the Maryland Coastal Bays as the region undergoes system-wide changes.

APPENDIX

Table A: Monthly nutrient species concentrations (calculated from the period July 2006-January 2008) for six streams in the St. Martin River watershed. Values are given in the format Mean (standard error, n). Standard errors were not reported for measurements with n=1. Months without any recorded measurements are listed as not determined, "ND." Concentrations in bold print represent the high flow season, which was used for regression analysis.

Site 1

	NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)
J	**3.70 (0.73, 5)**	**106.44 (29.10, 5)**	**172.90 (15.53, 5)**	**1.41 (0.42, 5)**	**3.20 (0.86, 5)**
F	**7.34 (3.21, 2)**	**115.23 (48.78, 2)**	**208.00 (6.00, 2)**	**1.13 (0.57, 2)**	**1.80 (0.01, 2)**
M	**7.02 (0.00, 1)**	**42.80 (0.00, 1)**	**147.00 (0.00, 1)**	**0.97 (0.00, 1)**	**4.40 (0.00, 1)**
A	3.35 (0.60, 2)	52.90 (4.30, 2)	153.50 (6.50, 2)	1.40 (0.10, 2)	4.35 (0.23, 2)
M	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)
J	7.52 (2.02, 2)	124.15 (51.85, 2)	227.75 (18.25, 2)	2.36 (1.13, 2)	6.29 (2.32, 2)
J	2.09 (0.84, 2)	119.00 (7.00, 2)	237.00 (1.00, 2)	1.02 (0.06, 2)	3.30 (0.30, 2)
A	1.65 (0.00, 1)	152.00 (0.00, 1)	198.00 (0.00, 1)	1.09 (0.00, 1)	4.43 (0.00, 1)
S	3.40 (1.11, 5)	72.90 (29.11, 5)	137.42 (31.96, 5)	2.40 (1.42, 5)	4.19 (1.54, 5)
O	2.28 (0.30, 2)	78.10 (34.90, 2)	153.50 (33.50, 2)	2.66 (0.95, 2)	5.59 (2.78, 2)
N	1.70 (0.13, 2)	83.00 (65.00, 2)	169.50 (62.50, 2)	3.22 (2.18, 2)	4.88 (2.59, 2)
D	**3.26 (0.16, 2)**	**109.25 (47.75, 2)**	**214.50 (23.50, 2)**	**0.89 (0.11, 2)**	**1.90 (0.09, 2)**

Site 2

NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)
6.76 (1.48, 5)	**180.00 (25.61, 5)**	**283.80 (26.11, 5)**	**0.63 (0.14, 5)**	**1.71 (0.34, 5)**
13.28 (1.22, 3)	**204.50 (6.83, 3)**	**253.33 (21.62, 3)**	**0.76 (0.18, 3)**	**1.88 (0.42, 3)**
8.26 (3.54, 2)	**157.00 (40.00, 2)**	**293.50 (55.50, 2)**	**1.67 (1.35, 2)**	**5.83 (4.17, 2)**
12.84 (3.56, 2)	136.50 (15.50, 2)	216.50 (35.50, 2)	1.46 (0.67, 2)	4.67 (1.82, 2)
9.85 (0.00, 1)	84.40 (0.00, 1)	184.00 (0.00, 1)	0.48 (0.00, 1)	2.41 (0.00, 1)
22.80 (11.50, 2)	25.87 (22.43, 2)	114.05 (16.95, 2)	0.34 (0.06, 2)	2.10 (0.51, 2)
85.80 (0.00, 1)	5.05 (0.00, 1)	232.00 (0.00, 1)	0.23 (0.00, 1)	2.61 (0.00, 1)
0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)
5.78 (0.00, 1)	96.10 (0.00, 1)	156.00 (0.00, 1)	0.71 (0.00, 1)	1.96 (0.00, 1)
6.47 (0.00, 1)	209.00 (0.00, 1)	442.00 (0.00, 1)	2.39 (0.00, 1)	5.89 (0.00, 1)
11.20 (0.00, 1)	10.30 (0.00, 1)	80.10 (0.00, 1)	0.43 (0.00, 1)	3.30 (0.00, 1)
4.39 (0.00, 1)	**106.00 (0.00, 1)**	**222.00 (0.00, 1)**	**0.32 (0.00, 1)**	**0.93 (0.00, 1)**

Site 3

	NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)
J	**7.34 (1.13, 5)**	**120.96 (23.45, 5)**	**217.30 (13.65, 5)**	**1.15 (0.32, 5)**	**2.91 (0.74, 5)**
F	**15.13 (1.45, 3)**	**128.07 (22.66, 3)**	**228.67 (18.67, 3)**	**0.98 (0.04, 3)**	**2.27 (0.30, 3)**
M	**6.41 (2.59, 3)**	**73.80 (25.56, 3)**	**198.17 (24.60, 3)**	**1.24 (0.38, 3)**	**4.75 (2.64, 3)**
A	13.80 (1.50, 2)	45.83 (0.72, 2)	169.00 (13.00, 2)	2.43 (1.06, 2)	4.82 (0.83, 2)
M	6.81 (0.00, 1)	56.75 (0.00, 1)	154.00 (0.00, 1)	0.59 (0.00, 1)	2.46 (0.00, 1)
J	5.14 (0.75, 2)	68.05 (20.95, 2)	148.00 (0.00, 2)	0.93 (0.12, 2)	2.51 (0.00, 2)
J	5.01 (0.71, 5)	33.07 (11.94, 5)	95.39 (22.02, 5)	1.29 (0.11, 5)	3.31 (0.21, 5)
A	4.95 (2.06, 2)	15.55 (10.86, 2)	72.25 (20.05, 2)	1.33 (0.55, 2)	4.07 (0.20, 2)
S	13.52 (4.70, 4)	21.07 (11.31, 4)	108.03 (40.02, 4)	1.31 (0.30, 4)	3.08 (0.17, 4)
O	7.00 (0.02, 2)	92.75 (3.25, 2)	260.50 (87.50, 2)	0.78 (0.13, 2)	3.88 (2.54, 2)
N	4.07 (0.46, 2)	65.30 (11.20, 2)	149.10 (64.90, 2)	2.12 (1.45, 2)	3.53 (2.21, 2)
D	**5.65 (3.48, 2)**	**56.80 (55.21, 2)**	**121.45 (89.55, 2)**	**0.46 (0.07, 2)**	**1.35 (0.31, 2)**

Site 4

NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)
7.58 (1.91, 5)	**137.42 (29.79, 5)**	**283.80 (21.58, 5)**	**1.09 (0.30, 5)**	**3.22 (0.61, 5)**
16.03 (1.80, 3)	**156.90 (36.76, 3)**	**269.67 (33.79, 3)**	**0.75 (0.23, 3)**	**1.56 (0.37, 3)**
5.69 (2.72, 3)	**77.60 (48.83, 3)**	**232.00 (50.51, 3)**	**1.79 (1.02, 3)**	**4.57 (1.18, 3)**
8.86 (5.35, 2)	51.40 (24.10, 2)	185.50 (0.50, 2)	1.48 (0.91, 2)	5.53 (0.48, 2)
3.47 (0.00, 1)	23.60 (0.00, 1)	87.55 (0.00, 1)	0.83 (0.00, 1)	2.30 (0.00, 1)
6.31 (1.27, 2)	16.08 (12.52, 2)	89.15 (27.85, 2)	0.71 (0.23, 2)	3.46 (0.43, 2)
7.64 (1.03, 6)	3.46 (2.90, 6)	87.62 (11.98, 6)	0.86 (0.13, 6)	4.16 (0.52, 6)
4.42 (2.95, 2)	1.92 (1.19, 2)	80.53 (20.48, 2)	0.49 (0.01, 2)	4.28 (0.39, 2)
3.45 (1.24, 4)	29.97 (24.00, 4)	109.94 (43.99, 4)	1.03 (0.31, 4)	3.72 (0.59, 4)
4.42 (1.94, 2)	51.76 (50.24, 2)	157.75 (109.25, 2)	1.60 (0.85, 2)	2.99 (1.72, 2)
4.14 (0.23, 2)	85.30 (73.70, 2)	168.55 (98.45, 2)	2.63 (1.98, 2)	4.06 (2.05, 2)
18.82 (10.38, 2)	**48.00 (44.90, 2)**	**179.95 (91.05, 2)**	**0.72 (0.14, 2)**	**4.57 (2.76, 2)**

Table A: (Continued)

	Site 5					Site 6				
	NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	NH_4^+ (µM)	NO_3^- (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)
J	**7.06 (0.49, 5)**	**250.40 (27.94, 5)**	**332.80 (26.74, 5)**	**0.73 (0.25, 5)**	**2.09 (0.60, 5)**	**3.61 (0.74, 5)**	**529.60 (85.25, 5)**	**624.80 (113.76, 5)**	**0.63 (0.16, 5)**	**2.45 (1.12, 5)**
F	**18.23 (2.45, 3)**	**157.37 (44.35, 3)**	**324.67 (28.67, 3)**	**0.82 (0.31, 3)**	**2.02 (0.81, 3)**	**7.88 (2.22, 3)**	**346.33 (4.81, 3)**	**400.00 (0.00, 3)**	**1.12 (0.28, 3)**	**1.40 (0.48, 3)**
M	**6.52 (2.97, 3)**	**120.73 (66.18, 3)**	**248.67 (59.18, 3)**	**0.73 (0.49, 3)**	**2.98 (1.91, 3)**	**7.58 (6.16, 3)**	**174.33 (87.39, 3)**	**265.00 (70.54, 3)**	**1.13 (0.62, 3)**	**2.89 (1.40, 3)**
A	13.05 (1.55, 2)	85.05 (26.95, 2)	201.00 (11.00, 2)	0.92 (0.37, 2)	2.57 (0.64, 2)	8.63 (3.78, 2)	39.40 (20.90, 2)	273.00 (59.00, 2)	0.82 (0.46, 2)	2.00 (0.62, 2)
M	9.00 (0.00, 1)	34.70 (0.00, 1)	105.00 (0.00, 1)	0.96 (0.00, 1)	3.34 (0.00, 1)	8.73 (0.00, 1)	71.10 (0.00, 1)	160.50 (0.00, 1)	0.34 (0.00, 1)	1.94 (0.00, 1)
J	8.88 (0.40, 2)	28.40 (8.10, 2)	126.50 (26.50, 2)	0.64 (0.16, 2)	2.99 (0.05, 2)	5.34 (0.71, 2)	52.30 (22.40, 2)	140.70 (58.30, 2)	0.61 (0.09, 2)	4.19 (2.28, 2)
J	10.58 (1.37, 5)	26.22 (7.48, 5)	121.26 (26.81, 5)	1.00 (0.29, 5)	3.47 (0.33, 5)	29.95 (22.33, 3)	14.25 (5.45, 3)	177.60 (111.24, 3)	0.85 (0.31, 3)	4.65 (2.68, 3)
A	14.00 (2.80, 2)	19.55 (5.95, 2)	110.68 (35.33, 2)	1.98 (0.81, 2)	5.44 (0.53, 2)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)	0.00 (0.00, 0)
S	6.75 (0.17, 2)	78.23 (70.78, 2)	158.23 (112.78, 2)	1.37 (0.39, 2)	3.20 (0.00, 2)	8.70 (0.00, 1)	183.00 (0.00, 1)	314.00 (0.00, 1)	1.85 (0.00, 1)	5.60 (0.00, 1)
O	7.66 (3.75, 2)	131.75 (118.25, 2)	253.50 (118.50, 2)	2.37 (1.85, 2)	5.84 (4.97, 2)	7.88 (5.52, 2)	229.70 (135.30, 2)	268.50 (131.50, 2)	1.52 (1.25, 2)	3.43 (2.30, 2)
N	6.10 (1.92, 2)	116.95 (43.05, 2)	238.75 (119.75, 2)	1.77 (1.14, 2)	3.52 (1.85, 2)	6.65 (4.37, 3)	353.00 (199.23, 3)	369.47 (226.49, 3)	1.58 (1.03, 3)	4.45 (1.91, 3)
D	**7.92 (3.69, 2)**	**100.16 (94.85, 2)**	**196.40 (164.60, 2)**	**0.48 (0.24, 2)**	**1.49 (0.63, 2)**	**2.28 (0.31, 2)**	**263.60 (181.40, 2)**	**432.50 (309.50, 2)**	**0.24 (0.06, 2)**	**0.62 (0.15, 2)**

Table B: May 2007 St. Martin River site sampling data

Site	Latitude (decimal degrees)	Longitude (decimal degrees)	Section	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Salinity	DO (mgL^{-1})	% DO	Bottom Temp (°C)	Salinity	DO (mgL^{-1})	% DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})
SM1	38.4124	-75.1739	Bishop	1.1	0.6	24.8	22.5	2.68	34.5	25.5	14.1	2.26	29.5	0.24	0.26	0	65.60	0.28	2.99	2.72	18.56	9.98
SM2	38.3945	-75.1314	Mouth	1.6	0.9	25.0	24.3	2.54	32.3	24.7	14.0	2.23	28.8	0.24	0.26	0.62	35.85	0.16	1.31	3.20	9.59	0.98
SM3	38.4057	-75.1770	Shingle	0.9	0.5	24.9	19.6	3.45	43.4	25.3	20.3	2.68	38.9	0.3	0.25	0	68.10	0.26	3.27	5.32	17.13	10.19
SM4	38.4047	-75.1481	Mid	1.3	0.6	23.8	21.9	2.64	32.6	25.1	24.0	1.92	24.3	0.735	1.015	0	50.00	0.13	2.11	5.63	11.54	5.83
SM5	38.4000	-75.1467	Mid	2.1	0.6	25.7	22.9	2.23	30.8	25.0	24.3	1.82	24.2	0.247	0.270	0.40	43.73	0.14	1.76	3.64	12.54	3.73
SM6	38.4131	-75.1807	Bishop	0.5	0.4	28.9	16.7	8.16	113.1	28.3	19.2	1.56	27.7	0.530	0.303	0	87.45	0.93	4.34	5.01	26.30	10.53
SM7	38.3986	-75.1286	Mouth	1.6	0.7	23.9	23.9	2.82	34.8	23.9	24.4	2.34	30.3	0.2	0.23	0.48	37.10	0.18	1.45	3.20	10.97	2.89
SM9	38.4009	-75.1333	Mouth	1.6	0.7	24.0	23.5	2.73	33.8	24.3	24.9	1.84	26.3	0.28	0.26	0.05	41.10	0.12	1.54	2.27	13.26	-0.29
SM10	38.4073	-75.1796	Shingle	0.8	0.4	28.3	18.6	4.55	61.0	27.5	19.4	4.88	64.4	0.2525	0.3	0	81.85	0.14	4.09	4.57	20.28	15.67
SM11	38.3996	-75.1112	Mouth	0.6	0.6	24.2	24.6	2.56	31.7	24.2	24.6	2.58	31.9	0.22	0.26	0	42.50	0.11	1.42	3.44	9.61	2.01
SM12	38.3908	-75.1213	Mouth	1.8	1	24.6	25.5	2.28	28.3	24.0	25.8	2.15	27.2	0.21	0.27	1.23	34.00	0.08	1.29	3.65	7.44	2.00
SM13	38.4105	-75.1670	Mid	1.8	0.6	24.5	20.6	2.61	32.3	25.5	16.8	2.04	25.8	0.72	0.47	0	56.80	0.13	2.51	4.60	18.13	8.98
SM14	38.3919	-75.1262	Mouth	1.5	0.9	25.3	24.4	2.72	35.0	25.2	24.5	2.73	34.6	1.027	0.313	6.12	34.17	0.11	1.29	3.45	7.39	1.58
SM15	38.3996	-75.1344	Mouth	1.7	0.7	24.1	23.6	2.81	34.7	24.5	25.1	2.21	27.0	0.21	0.21	9.19	40.70	0.06	1.51	4.26	11.97	3.28
SM16	38.4031	-75.1369	Mid	1.6	0.6	24.1	23.4	2.59	32.4	24.4	14.0	2.12	29.3	0.17	0.2	0.37	41.00	0.08	1.61	3.45	10.91	1.97
SM17	38.3948	-75.1263	Mouth	1.3	1.1	24.3	24.7	2.63	32.2	24.2	25.3	2.29	28.7	0.23	0.21	0	32.70	0.15	1.21	3.90	8.53	0.92
SM18	38.3928	-75.1208	Mouth	1.8	1	24.4	25.5	2.39	30.4	24.1	25.5	2.09	26.2	0.28	0.28	0.18	29.70	0.10	1.52	2.02	6.63	1.48
SM19	38.4116	-75.1584	Mid	1.2	0.5	23.6	21.5	2.64	32.9	25.4	22.9	2.10	26.9	0.25	0.32	0.20	54.60	0.14	2.54	3.03	14.26	7.04
SM20	38.3975	-75.1270	Mouth	1.6	0.9	24.0	24.5	2.63	32.6	24.1	25.0	2.26	28.3	0.31	0.24	1.90	35.60	0.09	1.34	3.02	10.55	1.66
SMS28	38.3967	-75.1317	Mouth	1.8	0.7	24.5	24.3	2.89	36.1	24.6	25.2	2.18	34.8	0.19	0.23	0	36.80	0.10	1.34	3.89	11.04	1.81
SM31	38.4094	-75.1724	Shingle	1	0.6	24.3	19.9	2.77	35.8	25.5	20.9	2.34	29.3	0.24	0.25	0	61.60	0.17	2.84	3.58	18.13	8.80
SM71	38.4423	-75.1944	ND	0.7	0.5	29.8	0.0	5.54	77.2	21.7	0.0	2.53	32.3	13.633	26.100	1.61	117.33	0.96	3.25	13.58	10.82	22.54
SM72	38.4417	-75.1935	Bishop	0.7	0.7	ND	ND	ND	ND	26.3	11.6	4.41	60.9	24.3	20.2	0.99	109.00	0.92	2.92	10.42	ND	11.47
SM73	38.4064	-75.1924	Shingle	0.4	0.3	25.4	17.7	3.48	44.2	25.3	17.8	3.50	44.6	0.29	0.23	0.29	96.70	0.17	4.73	5.53	ND	14.99
SM74	38.4242	-75.1878	Bishop	0.5	0.3	31.2	11.6	0.12	2.5	ND	ND	ND	ND	0.663	0.293	2.30	125.00	0.32	6.43	4.09	ND	ND

Table C: July 2007 St. Martin River site sampling data

Site	Latitude (decimal degrees)	Longitude (decimal degrees)	Section	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Surface Salinity	Surface DO (mgL^{-1})	Surface % DO	Bottom Temp (°C)	Bottom Salinity	Bottom DO (mgL^{-1})	Bottom % DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})	$\delta^{15}N$ (‰)
SM1	38.4124	-75.1739	Bishop	1.4	0.3	29.7	25.1	4.54	69.0	29.7	25.6	4.54	67.1	1.72	0.36	0.00	77.40	0.82	5.12	5.41	55.09	9.90	13.15
SM2	38.3945	-75.1314	Mouth	1.8	0.5	29.7	29.0	6.83	116.7	28.9	29.4	5.32	81.3	1.91	0.60	1.68	73.80	0.23	2.64	2.62	26.30	6.38	19.04
SM3	38.4057	-75.1770	Shingle	0.9	0.3	29.2	25.3	4.09	62.9	28.5	25.1	2.29	32.8	2.13	0.38	0.00	111.00	0.35	4.94	5.62	45.35	12.01	13.33
SM4	38.4047	-75.1481	Mid	1.7	0.5	29.3	28.4	5.86	93.1	29.2	28.3	5.94	87.0	1.60	0.25	0.00	75.50	0.22	2.93	5.85	33.03	5.59	10.26
SM5	38.4000	-75.1467	Mid	1.5	0.3	29.4	27.8	5.48	93.1	28.2	28.1	3.14	47.9	1.16	0.33	2.00	78.63	0.25	3.31	5.54	27.54	5.43	9.22
SM6	38.4131	-75.1807	Bishop	0.9	0.2	30.1	25.6	4.67	87.2	29.9	24.8	1.94	31.5	1.51	0.37	2.79	126.67	0.42	6.44	6.17	53.47	4.67	10.17
SM7	38.3986	-75.1286	Mouth	0.8	0.4	29.2	29.4	6.31	98.9	28.6	29.3	4.34	66.2	1.75	0.55	1.79	63.40	0.18	2.21	4.99	20.85	6.09	9.72
SM9	38.4009	-75.1333	Mouth	0.9	0.4	29.4	28.8	6.46	106.5	29.0	29.1	5.63	86.1	0.68	0.26	0.24	71.60	0.15	2.81	4.58	27.73	3.68	9.02
SM10	38.4073	-75.1796	Shingle	1.1	0.3	28.9	24.9	3.85	60.1	28.4	25.0	2.97	43.4	0.90	0.30	0.65	116.33	0.40	5.62	6.20	42.15	12.17	11.05
SM11	38.3996	-75.1112	Mouth	0.5	0.5	30.0	30.4	7.06	111.8	30.4	30.6	7.09	103.3	1.45	0.37	0.76	61.60	0.13	2.01	4.79	18.85	5.49	11.82
SM12	38.3908	-75.1213	Mouth	1.9	0.5	29.1	30.4	6.84	109.3	28.6	29.7	6.30	85.3	1.28	0.33	0.00	68.60	0.23	2.41	4.74	18.85	6.20	10.10
SM13	38.4105	-75.1670	Mid	1.3	0.3	29.7	26.5	6.17	103.1	29.4	26.6	4.97	83.7	1.86	0.35	4.37	97.00	0.22	4.52	6.77	51.65	18.93	9.24
SM14	38.3919	-75.1262	Mouth	1.8	0.5	29.5	29.3	6.35	95.7	28.5	29.6	3.93	57.7	0.78	0.35	1.09	65.67	0.21	2.86	4.79	26.54	4.45	9.11
SM15	38.3996	-75.1344	Mouth	1.8	0.5	29.3	29.1	6.52	107.1	28.9	29.2	5.63	81.3	1.24	0.32	0.31	67.00	0.18	2.53	4.51	22.72	5.11	9.64
SM16	38.4031	-75.1369	Mid	1.8	0.6	29.2	28.6	6.34	101.1	28.7	28.9	4.30	79.3	1.51	0.34	0.04	69.30	0.25	2.95	5.88	17.99	5.08	13.98
SM17	38.3948	-75.1263	Mouth	2.0	0.5	29.1	29.3	6.77	90.0	28.6	29.3	4.17	48.4	1.44	0.53	1.46	59.00	0.28	2.38	3.44	24.58	5.91	9.83
SM18	38.3928	-75.1208	Mouth	1.4	0.3	29.2	29.5	7.44	117.3	28.6	29.7	7.19	86.2	0.82	0.28	0.01	64.50	0.23	2.38	4.85	24.29	3.46	10.69
SM19	38.4116	-75.1584	Mid	1.1	0.4	30.1	27.0	6.22	99.1	29.3	27.1	4.80	75.6	0.98	0.37	0.36	99.60	0.49	4.57	5.26	47.40	12.97	10.53
SM20	38.3975	-75.1270	Mouth	1.8	0.5	29.1	29.4	6.35	94.1	28.8	29.4	4.81	59.0	0.38	0.26	0.88	59.70	0.17	2.23	4.71	22.57	6.20	16.69
SMS28	38.3967	-75.1317	Mouth	1.8	0.4	29.3	30.1	6.87	107.2	29.0	29.3	6.39	84.4	0.90	0.27	2.76	64.60	0.23	2.37	5.31	25.87	7.51	9.43
SM31	38.4094	-75.1724	Shingle	0.6	0.2	29.6	26.1	5.46	84.0	29.6	26.1	4.73	73.1	1.28	0.41	0.16	111.00	0.23	5.16	5.09	58.14	16.49	10.47
SM71	38.4423	-75.1944	ND	0.3	0.0	31.4	0.1	0.82	12.2	31.6	0.1	1.40	20.0	7.82	0.66	1.60	87.10	0.93	6.97	9.22	ND	ND	9.51
SM72	38.4417	-75.1935	Bishop	0.2	0.2	33.4	12.1	6.77	105.6	33.4	12.4	6.32	62.1	0.55	0.36	2.36	123.00	3.81	10.80	5.62	32.60	3.87	12.59
SM73	38.4064	-75.1924	Shingle	0.5	0.3	29.0	23.1	2.77	42.5	29.7	22.6	1.02	11.7	0.90	0.60	0.75	140.00	0.51	7.85	4.77	46.93	18.54	9.88
SM74	38.4242	-75.1878	Bishop	0.7	0.2	29.9	21.2	2.77	40.9	29.1	23.8	2.32	35.3	0.59	0.31	1.21	135.00	1.91	10.47	6.42	46.07	15.41	12.89
SM75	38.4300	-75.1900	Bishop	0.3	0.2	30.1	18.7	3.42	52.0	30.0	20.5	2.01	28.0	1.26	0.57	0.13	127.00	3.04	10.00	8.17	0.08	0.00	27.24
SM76	38.4200	-75.1900	Bishop	1.2	0.3	30.3	22.7	4.18	74.0	29.2	23.6	1.90	36.9	0.47	0.30	0.19	123.00	0.57	8.11	8.13	0.10	0.00	11.93

Table D: May 2007 Johnson Bay site sampling data

Site	Latitude (decimald egrees)	Longitude (decimal degrees)	Section	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Salinity	DO (mgL^{-1})	% DO	Bottom Temp (°C)	Salinity	DO (mgL^{-1})	% DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})
JB1	38.0670	-75.3323	Mid	1.4	0.3	23.1	26.4	2.68	32.6	23.0	26.5	2.66	7.8	0.24	0.10	2.78	55.00	0.15	3.65	5.70	27.59	4.59
JB2	38.0421	-75.3585	Mills	0.4	0.3	24.8	26.8	3.55	44.7	24.8	26.8	3.58	45.2	0.54	0.37	ND	62.10	0.22	4.12	5.93	32.89	7.57
JB3	38.0415	-75.3254	Mills	1.5	0.3	24.7	26.7	3.72	47.2	24.6	26.7	3.74	47.0	0.28	0.12	0	49.10	0.49	3.26	4.75	21.00	3.58
JB4	38.0715	-75.3482	Johns	1.1	0.3	23.0	26.3	2.59	31.5	23.0	26.3	2.59	37.5	0.42	0.25	1.21	64.80	0.17	4.00	5.92	34.75	4.45
JB5	38.0813	-75.3542	Johns	0.7	0.3	22.8	26.5	ND	ND	22.8	26.4	ND	ND	0.29	0.11	0.49	63.10	0.15	3.62	6.10	29.88	1.77
JB6	38.0595	-75.3474	Mid	1.2	0.3	23.1	26.3	2.72	33.2	23.0	26.3	2.67	32.6	0.23	0.10	2.05	69.30	0.12	4.00	5.13	37.47	4.42
JB7	38.0862	-75.3190	Brock	0.8	0.3	22.8	26.2	2.86	34.6	22.8	26.2	2.89	34.9	0.25	0.11	0.77	55.70	0.18	3.35	5.55	30.31	1.18
JB8	38.0876	-75.3364	Brock	1.0	0.3	23.7	26.1	2.78	34.1	23.3	26.1	2.80	34.2	0.45	0.23	0.52	58.80	0.13	3.04	5.75	24.86	2.49
JB9	38.0695	-75.3449	Johns	1.1	0.3	23.0	26.6	2.66	32.5	23.0	26.6	2.64	32.1	0.60	0.30	0.58	61.90	0.15	3.41	5.33	23.43	3.59
JB10	38.0938	-75.3325	Brock	1.0	0.3	25.5	26.0	3.04	38.5	25.4	26.0	2.99	38.1	0.40	0.19	0.11	63.17	0.22	3.19	6.94	27.40	3.20
JB11	38.0695	-75.3308	Mid	1.2	0.3	22.9	26.4	2.65	32.2	22.8	26.4	2.62	31.8	0.29	0.18	0.96	59.40	0.18	3.55	5.68	24.29	4.35
JB12	38.0844	-75.3359	Brock	0.5	0.4	23.0	26.2	2.82	34.2	23.0	26.2	2.80	34.0	0.32	0.13	0.35	57.60	0.15	3.16	6.03	24.00	2.79
JB13	38.0733	-75.3641	Brock	0.5	0.2	24.8	25.9	2.85	35.5	24.7	25.9	2.84	35.6	0.52	0.16	2.36	79.13	0.29	3.93	6.89	34.13	6.86
JB14	38.0928	-75.3258	Brock	0.8	0.3	25.5	26.2	3.59	45.7	25.5	26.2	3.60	45.8	0.31	0.23	0.23	59.40	0.18	3.36	6.45	26.58	4.03
JB15	38.0535	-75.3414	Mid	0.9	0.4	23.8	26.8	3.20	39.0	23.7	26.8	3.18	39.1	0.56	0.29	0.63	58.15	0.89	3.44	5.83	16.46	1.61
JB16	38.0671	-75.3465	Johns	1.1	0.3	23.1	26.5	2.63	32.1	23.1	26.5	2.56	31.5	0.37	0.13	4.68	59.80	0.15	3.50	6.17	31.02	3.03
JB17	38.0453	-75.3535	Mills	0.5	0.3	24.8	26.7	3.13	46.7	24.7	26.7	3.69	46.2	0.27	0.13	0	68.00	0.21	3.92	5.47	36.04	6.40
JB18	38.0305	-75.3363	Mills	1.8	0.3	24.4	26.8	3.67	46.8	24.2	26.8	3.64	45.2	0.27	0.12	0	45.25	0.43	2.88	5.49	24.00	5.11
JB20	38.1028	-75.3281	Brock	0.6	0.2	26.0	25.8	3.17	41.0	26.0	25.8	3.16	40.5	0.33	0.12	1.02	65.20	0.30	3.18	6.88	6.14	53.06
JB21	38.0316	-75.3453	Mills	1.5	0.3	24.5	26.9	3.22	40.3	24.4	26.9	3.19	39.8	0.58	0.34	0.50	49.50	0.58	3.30	5.23	28.92	2.56
JB22	38.0973	-75.3257	Brock	1.3	0.3	25.3	26.0	3.41	43.2	25.3	26.0	3.29	41.6	0.33	0.28	0	61.20	0.18	3.34	6.73	29.88	4.62
JB23	38.0426	-75.3295	Mills	1.4	0.3	24.9	26.8	3.49	44.1	24.7	26.8	3.46	43.7	0.30	0.21	0.08	50.13	0.50	3.26	5.13	28.30	5.68
JB24	38.0623	-75.3282	Mid	1.4	0.4	23.2	26.5	2.74	33.4	23.1	26.5	2.64	32.1	3.27	0.51	1.88	56.50	0.32	3.68	5.17	31.74	3.46
JB25	38.0808	-75.3143	Mid	0.9	0.3	22.9	26.3	2.82	34.2	22.9	26.3	2.81	34.0	0.37	0.29	1.19	55.60	0.23	3.46	5.33	32.17	-0.87
JB26	38.0760	-75.3581	Johns	0.9	0.4	22.6	26.1	2.41	29.3	22.7	26.4	2.00	23.7	0.37	0.27	0	68.10	0.20	3.92	6.18	27.87	3.48
JB27	38.0634	-75.3239	Mid	1.5	0.4	23.2	26.4	2.70	33.1	23.2	26.4	2.70	32.8	0.30	0.22	0	57.60	0.27	3.57	5.57	29.59	4.30
JB28	38.0822	-75.3539	Johns	0.8	0.3	22.8	26.4	2.31	28.1	22.8	26.4	2.11	26.2	0.36	0.19	0	65.75	0.16	3.91	5.66	33.75	3.00
JBS30	38.0718	-75.3576	Johns	1.5	0.2	24.6	26.1	2.81	24.8	23.6	26.3	2.46	30.2	0.49	0.27	0.19	71.70	0.34	3.89	6.79	24.58	1.82

Table E: July 2007 Johnson Bay site sampling data

Site	Latitude (decimal degrees)	Longitude (decimal degrees)	Section	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Salinity	DO (mgL^{-1})	% DO	Bottom Temp (°C)	Salinity	DO (mgL^{-1})	% DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})	$\delta^{15}N$ (‰)
JB1	38.0670	-75.3323	Mid	1.6	0.5	28.1	32.1	6.41	87.9	28.0	32.1	5.70	89.2	1.45	0.32	0.90	55.50	0.98	3.26	0.08	0.00	12.75	12.75
JB2	38.0421	-75.3585	Mills	0.8	0.4	27.0	31.8	5.21	74.2	27.0	31.8	3.97	71.9	1.29	0.33	0.59	46.50	1.31	3.15	21.14	9.79	15.25	15.25
JB3	38.0415	-75.3254	Mills	2.0	0.5	27.4	32.2	5.61	84.7	27.4	32.1	5.54	84.0	1.25	0.43	0.00	33.40	0.53	1.93	25.58	1.32	10.97	10.97
JB4	38.0715	-75.3482	Johns	1.3	0.4	27.0	32.1	4.16	62.0	27.0	32.1	4.18	62.6	7.35	0.33	0.19	50.80	1.30	2.98	13.26	6.65	14.03	14.03
JB5	38.0813	-75.3542	Johns	0.9	0.3	29.0	32.4	5.33	81.4	29.5	32.4	5.03	73.8	4.14	0.19	1.00	50.30	1.54	3.85	20.42	13.63	20.52	20.52
JB6	38.0595	-75.3474	Mid	1.4	0.5	27.1	31.9	4.65	69.7	27.1	31.9	2.64	54.5	2.43	0.51	0.75	54.60	0.92	3.39	20.71	7.54	12.57	12.57
JB7	38.0862	-75.3190	Brock	1.0	0.4	28.7	32.4	5.28	80.5	28.8	ND	5.24	80.4	2.41	0.21	0.63	51.80	1.20	3.12	ND	ND	15.74	15.74
JB8	38.0876	-75.3364	Brock	1.4	0.4	28.8	32.2	5.70	90.7	28.9	32.1	5.38	84.5	1.04	0.21	0.30	61.10	1.47	3.28	ND	ND	18.92	18.92
JB9	38.0695	-75.3449	Johns	1.4	0.5	26.7	32.2	4.89	69.4	26.8	32.1	4.28	73.2	2.20	0.22	ND	51.80	1.08	2.98	19.28	1.51	10.72	10.72
JB10	38.0938	-75.3325	Brock	1.4	0.4	28.7	32.1	5.12	80.5	28.6	32.0	4.95	73.8	2.17	0.38	0.96	63.77	1.44	3.25	19.99	6.69	21.08	21.08
JB11	38.0695	-75.3308	Mid	1.5	0.5	28.1	32.1	5.27	81.1	28.1	32.1	5.40	77.8	2.64	0.44	0.00	50.70	1.13	3.03	14.55	7.53	15.30	15.30
JB12	38.0844	-75.3359	Brock	0.9	0.4	29.1	32.2	5.34	81.8	29.2	ND	5.26	82.4	1.27	0.34	0.82	57.50	1.65	3.41	13.83	8.52	19.51	19.51
JB13	38.0733	-75.3641	Brock	0.9	0.4	26.6	30.9	3.42	57.1	26.7	31.9	2.46	47.3	1.95	0.20	0.21	77.87	1.60	4.05	23.48	11.29	18.78	18.78
JB14	38.0928	-75.3258	Brock	0.9	0.4	ND	32.2	6.24	88.0	28.5	32.2	5.14	83.8	2.14	0.38	0.67	60.40	1.28	2.89	22.14	4.48	16.81	16.81
JB15	38.0535	-75.3414	Mid	1.7	0.5	27.1	32.1	4.67	70.0	27.0	32.0	2.85	42.5	1.65	0.26	1.15	53.60	1.12	2.76	13.21	6.00	20.48	20.48
JB16	38.0671	-75.3465	Johns	1.4	0.5	27.1	32.1	4.74	70.6	27.1	32.1	4.56	64.3	0.46	0.22	0.87	44.20	1.17	2.75	17.27	6.25	12.13	12.13
JB17	38.0453	-75.3535	Mills	1.4	0.4	27.2	31.8	4.69	70.5	27.1	31.9	4.66	70.8	0.62	0.21	0.28	38.60	1.37	2.37	24.72	-2.11	12.59	12.59
JB18	38.0305	-75.3363	Mills	1.9	0.4	22.6	32.0	5.73	86.5	27.3	32.1	5.53	82.9	1.27	0.24	0.25	39.80	0.49	1.54	-15.25	58.43	10.20	10.20
JB20	38.1028	-75.3281	Brock	1.0	0.4	28.8	32.2	4.94	82.2	28.8	32.2	4.89	67.8	1.48	0.33	2.92	69.10	1.36	2.44	19.25	9.27	17.73	17.73
JB21	38.0316	-75.3453	Mills	2.0	0.4	27.2	32.0	6.90	84.2	27.2	32.0	5.25	79.6	0.81	0.31	0.06	38.17	0.52	1.97	17.84	4.62	8.71	8.71
JB22	38.0973	-75.3257	Brock	0.9	0.4	28.4	32.2	5.39	84.7	28.4	32.0	5.12	71.0	0.68	0.30	0.63	66.00	1.33	3.06	18.13	9.51	13.54	13.54
JB23	38.0426	-75.3295	Mills	1.4	0.5	27.6	32.1	5.82	83.7	27.4	32.1	5.03	79.7	1.10	0.46	0.03	44.07	0.92	2.32	19.71	4.66	14.51	14.51
JB24	38.0623	-75.3282	Mid	1.8	0.5	28.1	32.0	5.41	88.1	27.9	32.1	4.57	70.1	2.44	0.82	0.29	48.20	1.15	2.48	18.13	6.66	14.42	14.42
JB25	38.0808	-75.3143	Mid	1.0	0.4	28.0	32.2	5.36	83.5	28.1	32.2	5.07	82.3	2.23	0.46	0.04	48.10	1.65	2.37	19.56	11.08	11.33	11.33
JB26	38.0760	-75.3581	Johns	1.3	0.3	28.9	ND	7.01	93.3	28.9	32.4	5.10	78.7	3.61	0.38	0.67	64.20	1.34	3.11	26.28	13.80	13.09	13.09
JB27	38.0634	-75.3239	Mid	1.8	0.5	27.8	32.1	6.68	93.8	27.8	32.1	5.58	88.5	3.00	0.38	0.00	43.70	1.07	2.30	18.70	6.22	11.36	11.36
JB28	38.0822	-75.3539	Johns	0.9	0.4	29.2	32.4	5.40	85.0	29.3	32.1	4.80	34.6	3.81	0.61	0.59	71.80	2.00	2.31	25.69	14.48	12.22	12.22
JBS30	38.0718	-75.3576	Johns	1.0	0.3	28.5	32.6	5.13	78.7	28.8	32.2	4.82	69.9	2.72	0.62	0.80	67.20	1.45	3.25	21.57	8.48	11.76	11.76

Table F: May and July 2007 Sinepuxent site sampling data

May

Site	Latitude (decimald egrees)	Longitude (decimal degrees)	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Salinity	DO (mgL^{-1})	% DO	Bottom Temp (°C)	Salinity	DO (mgL^{-1})	% DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})
SPX1	38.2770	-75.1464	2.5	0.3	25.1	27.4	3.46	43.3	24.9	27.5	3.38	42.4	0.34	0.22	0.15	49.20	0.15	3.06	5.31	24.91	5.33
SPX2	38.2615	-75.1429	1.5	1.5	25.1	27.1	3.38	42.6	24.9	27.1	3.36	42.6	0.34	0.18	0	49.10	0.13	3.01	4.88	30.02	2.40
SPX3	38.2505	-75.1491	1.3	1.3	25.0	27.3	3.16	40.0	24.5	27.3	3.14	39.9	0.29	0.11	0.33	52.53	0.26	3.06	4.74	33.89	1.67

July

Site	Latitude (decimal degrees)	Longitude (decimal degrees)	Depth (m)	Secchi depth (m)	Surface Temp (°C)	Salinity	DO (mgL^{-1})	% DO	Bottom Temp (°C)	Salinity	DO (mgL^{-1})	% DO	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})	$\delta^{15}N$ (‰)
SPX1	38.2770	-75.1464	1.3	0.4	28.6	30.9	5.39	83.9	28.5	30.9	4.49	73.1	1.56	0.50	1.02	75.30	1.01	3.80	6.37	33.46	10.39	11.56
SPX2	38.2615	-75.1429	1.7	0.4	27.5	31.3	7.15	86.3	27.4	31.2	5.23	81.3	2.42	0.50	3.95	69.27	0.76	3.23	5.88	25.87	15.81	11.75
SPX3	38.2505	-75.1491	1.8	0.7	26.5	31.3	5.29	80.4	26.4	31.4	4.25	60.7	1.73	0.60	0.89	51.97	0.73	2.33	4.68	16.22	10.73	16.42

Table G: May 2007 Focus site sampling data (additional parameters)

Site	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})	TSS (mgL^{-1})	VSS (mgL^{-1})	Bacteria ($x10^7$ cells mL^{-1})	Viruses ($x10^8$ cells mL^{-1})
JB10	0.33	0.16	0	59.4	0.19	3.18	6.37	27.87	2.06	40.82	6.75	1.59	2.20
JB10	0.37	0.1	0.33	64.9	0.3	3.24	8.38	27.87	3.66	30.33	3.90	14.34	1.95
JB10	0.49	0.31	0	65.2	0.18	3.14	6.06	26.44	3.87	100.60	9.30	ND	ND
JB13	0.8	0.14	0	79.7	0.24	3.95	6.28	35.61	7.36	30.61	5.50	1.50	1.76
JB13	0.38	0.22	6.51	78.7	0.18	3.93	7.29	33.46	6.24	20.41	6.60	1.68	2.14
JB13	0.365	0.12	0.57	79	0.44	3.92	7.10	33.32	6.97	40.44	8.20	ND	ND
JB15	0.54	0.29	0.10	57.2	0.85	3.37	5.59	8.37	0.98	20.12	5.65	0.88	1.51
JB15	0.52	0.28	1.80	58.9	0.85	3.45	5.84	33.89	2.98	30.15	5.85	0.89	1.43
JB15	0.63	0.3	0	58.4	0.97	3.51	6.05	7.13	0.87	30.46	6.70	ND	ND
JB21	0.25	0.12	0	48.3	0.7	3.33	5.65	26.01	4.11	20.12	7.25	1.17	1.84
JB21	0.235	0.13	0.57	53.6	0.512	3.28	4.98	33.32	1.28	30.06	6.85	7.58	1.47
JB21	1.24	0.78	0.94	46.6	0.52	3.28	5.06	27.44	2.30	40.40	6.50	ND	ND
JB23	0.33	0.35	0.23	50.2	0.5	3.28	4.91	26.73	7.56	30.33	6.55	11.52	1.01
JB23	0.28	0.15	0	50	0.51	3.29	5.85	29.45	4.68	30.46	7.00	0.83	0.96
JB23	0.29	0.13	0	50.2	0.5	3.22	4.63	28.73	4.78	40.61	6.20	ND	ND
SM5	0.31	0.3	1.21	44.5	0.1	1.81	2.28	14.41	3.64	30.46	9.35	1.53	2.29
SM5	0.23	0.25	0	42.9	0.22	1.67	4.33	12.26	3.59	10.11	7.00	1.40	1.79
SM5	0.2	0.26	0	43.8	0.1	1.8	4.30	10.97	3.95	ND	7.05	ND	ND
SM6	0.44	0.26	0	87.8	0.85	4.35	5.57	31.88	13.23	30.46	ND	ND	1.63
SM6	0.62	0.34	0	86.7	1.03	4.31	4.12	13.83	5.32	40.61	5.90	20.54	1.85
SM6	0.53	0.31	0	87.9	0.91	4.35	5.34	33.17	13.04	30.77	5.90	ND	ND
SM10	0.27	0.3	0	81.9	0.12	4.06	3.03	22.86	15.59	10.15	5.55	2.14	2.14
SM10	0.235	0.3	0	81.8	0.15	4.12	4.17	17.13	16.95	20.41	6.20	ND	ND
SM10	ND	ND	0	ND	ND	ND	6.50	20.85	14.46	30.61	6.30	ND	ND
SM14	2.43	0.43	0.06	33.6	0.15	1.28	2.77	9.78	1.56	42.30	6.80	10.17	1.57
SM14	0.44	0.28	16.26	34.4	0.11	1.32	3.22	7.93	2.15	40.20	6.70	1.39	1.73
SM14	0.21	0.23	2.04	34.5	0.08	1.27	4.35	4.45	1.05	30.80	6.50	ND	ND
SM71	13.8	28.4	0.94	117	1.24	3.22	12.92	11.25	24.73	10.11	7.90	ND	ND
SM71	14.6	29.7	2.35	118	0.64	3.31	14.15	12.69	22.04	50.00	8.60	ND	ND
SM71	12.5	20.2	1.54	117	0.99	3.21	13.67	8.53	20.85	ND	ND	ND	ND
SM 74	0.53	0.24	0.70	122	0.29	6.52	6.61	ND	ND	20.30	15.10	2.63	1.98
SM 74	0.82	0.37	0.25	123	0.24	6.26	2.60	ND	ND	50.25	10.05	ND	ND
SM 74	0.64	0.27	5.95	130	0.44	6.51	3.07	ND	ND	20.30	9.45	ND	ND
SPX1	0.31	0.21	0.44	48.6	0.24	3.2	5.10	48.93	10.60	30.06	8.05	0.87	1.29
SPX1	0.4	0.29	0	49.9	0.15	3.01	4.79	-0.22	0.57	20.18	4.65	1.01	1.01
SPX1	0.32	0.15	0	49.1	0.06	2.97	6.05	26.01	4.82	30.06	5.70	ND	ND
SPX2	0.4	0.27	0	48.9	0.13	3.03	4.64	29.59	2.70	50.30	11.20	0.22	1.27
SPX2	0.33	0.14	0	48.9	0.13	2.99	5.33	29.16	3.65	40.82	8.65	ND	ND
SPX2	0.28	0.12	0	49.5	0.13	3.02	4.69	31.31	0.86	20.20	7.30	ND	ND
SPX3	0.28	0.11	0.75	52.1	0.28	3.16	4.64	29.31	2.57	40.24	6.70	ND	ND
SPX3	0.26	0.1	0	52.9	0.21	3.08	4.37	31.31	5.13	30.18	5.85	ND	ND
SPX3	0.315	0.11	0.24	52.6	0.3	2.94	5.23	41.05	-2.68	50.35	7.45	ND	ND

Table H: July 2007 Focus site sampling data (additional parameters)

Site	NH_4^+ (µM)	NO_3^- (µM)	Urea (µM)	TN (µM)	PO_4^{-3} (µM)	TP (µM)	DOC (mgL^{-1})	Chl-*a* (μgL^{-1})	Phaeo (μgL^{-1})	TSS (mgL^{-1})	VSS (mgL^{-1})	Bacteria ($x10^7$ cells mL^{-1})	Viruses ($x10^8$ cells mL^{-1})	$\delta^{15}N$ (‰)
JB10	1.77	0.38	1.94	61.40	1.15	3.26	5.59	17.84	8.13	67.20	14.97	1.08	1.74	11.99
JB10	1.80	0.46	0.82	67.40	1.45	3.15	4.87	18.99	5.47	64.20	16.20	0.82	1.33	12.83
JB10	2.94	0.31	0.11	62.50	1.71	3.33	5.12	23.15	6.48	70.23	13.60	ND	ND	12.95
JB13	1.65	0.17	0	72.90	1.60	4.09	5.50	21.28	12.08	40.47	14.07	1.56	1.81	12.39
JB13	1.51	0.21	0	80.40	1.44	4.24	6.07	23.15	10.92	30.47	11.27	1.32	1.92	10.54
JB13	2.70	0.21	0.61	80.30	1.75	3.81	5.65	26.01	10.87	45.27	18.60	ND	ND	9.23
JB15	2.21	0.21	2.12	58.60	1.04	2.73	4.61	13.98	5.30	43.23	16.97	0.88	1.37	15.28
JB15	1.94	0.33	1.34	48.10	1.07	2.83	4.15	13.40	5.03	52.87	17.93	1.07	1.47	12.22
JB15	0.81	0.23	0	54.10	1.25	2.72	3.47	12.26	7.68	47.17	14.67	ND	ND	11.76
JB21	1.04	0.31	0.18	36.80	0.54	2.05	2.86	16.27	4.62	50.90	13.00	1.13	1.23	14.27
JB21	0.54	0.37	0	36.50	0.46	1.95	2.74	17.84	2.97	67.53	19.63	0.98	1.14	15.06
JB21	0.86	0.26	0.00	41.20	0.57	1.90	2.79	19.42	2.03	55.53	17.30	ND	ND	13.92
JB23	1.06	0.22	0.09	41.50	0.95	2.71	2.88	23.15	0.78	48.13	13.63	0.92	1.18	10.72
JB23	0.91	0.32	0	43.90	0.77	2.08	3.44	18.85	5.85	45.27	12.40	ND	ND	9.61
JB23	1.34	0.83	0	46.80	1.04	2.16	2.85	17.13	7.34	43.73	13.40	ND	ND	10.68
SM5	1.14	0.36	1.23	77.10	0.17	3.32	4.77	27.73	8.49	29.30	14.40	2.99	2.41	7.96
SM5	0.94	0.36	0.74	77.80	0.24	3.21	5.99	37.04	0.92	26.50	13.23	3.26	2.28	9.55
SM5	1.41	0.28	4.03	81.00	0.33	3.40	5.85	17.84	6.88	32.20	13.40	ND	ND	10.16
SM6	1.33	0.32	3.83	131.00	0.36	6.45	7.71	52.08	5.17	37.08	15.68	4.28	2.23	13.74
SM6	1.58	0.32	2.17	129.00	0.49	6.52	4.22	52.51	5.64	40.56	17.08	4.00	2.13	8.32
SM6	1.62	0.48	2.38	120.00	0.42	6.36	6.57	55.81	3.21	48.80	21.44	ND	ND	8.44
SM10	0.58	0.31	0.63	117.00	0.46	5.20	5.57	41.48	16.83	46.24	20.56	4.58	2.49	9.98
SM10	1.02	0.31	1.30	117.00	0.42	5.64	7.37	35.32	-4.88	50.95	23.95	5.13	2.28	14.46
SM10	1.09	0.29	0	115.00	0.32	6.01	5.66	49.65	24.56	46.25	20.60	ND	ND	8.70
SM14	0.64	0.29	0	67.60	0.23	2.98	4.96	26.87	3.81	34.68	17.60	2.04	1.66	8.47
SM14	0.49	0.33	3.16	61.80	0.22	2.72	4.96	24.00	9.02	34.56	16.04	1.80	1.79	9.19
SM14	1.20	0.42	0.10	67.60	0.18	2.88	4.45	28.73	0.51	38.64	18.16	ND	ND	9.67
SM71	6.33	0.47	3.00	83.20	0.99	5.09	8.84	ND	ND	166.55	45.80	5.53	1.71	10.85
SM71	6.82	0.61	1.60	81.00	0.91	5.43	9.62	ND	ND	176.10	51.80	10.93	1.42	8.75
SM71	10.30	0.91	0.20	97.10	0.89	10.40	9.22	ND	ND	156.55	45.50	ND	ND	8.92
SM74	0.42	0.31	0	132.00	1.87	10.60	5.47	33.60	18.50	22.48	13.64	3.30	2.48	10.79
SM74	0.45	0.30	3.34	135.00	2.11	10.40	6.90	50.94	19.21	34.72	19.40	5.51	2.31	12.25
SM74	0.90	0.32	0.28	138.00	1.74	10.40	6.90	53.66	-2.89	29.44	15.60	ND	ND	15.64
SPX1	1.97	0.48	0.22	77.40	1.34	3.75	6.88	36.61	7.57	45.00	15.37	1.10	1.07	12.34
SPX1	1.64	0.64	2.86	73.80	0.96	3.76	5.54	27.30	15.49	55.83	18.67	0.95	0.92	11.56
SPX1	1.08	0.37	0	74.70	0.72	3.90	6.70	36.47	8.12	48.00	16.13	ND	ND	10.77
SPX2	1.91	0.35	0.03	63.70	0.76	3.22	6.25	23.86	19.01	49.77	18.43	ND	ND	13.04
SPX2	2.68	0.49	11.42	68.90	0.68	3.35	5.92	28.16	12.70	37.57	13.27	ND	ND	10.96
SPX2	2.66	0.67	0.41	75.20	0.84	3.13	5.45	25.58	15.74	39.53	12.17	ND	ND	11.23
SPX3	2.36	1.10	0.44	53.90	0.93	2.19	4.85	14.41	10.04	29.13	9.87	ND	ND	12.54
SPX3	1.42	0.37	1.15	53.60	0.69	2.29	5.15	17.27	9.99	31.87	10.07	ND	ND	13.32
SPX3	1.41	0.34	1.08	48.40	0.58	2.50	4.03	16.98	12.17	28.23	11.47	ND	ND	23.40

Table I: ANOVA results for 2007 inter-bay comparisons and 2007 intra-bay St. Martin River sectional comparisons, where n= number of samples; df = comparison-wide degrees of freedom, sample degrees of freedom; F = F-value of analysis; P = probability (significance level)

2007 All Bays

Parameter	Variation	n	df	F	P
Secchi	Bay	112	2,104	23.44	<0.0001
	Month		1,104	22.38	<0.0001
	Bay*Month		2,104	29.21	<0.0001
Bottom DO	Bay	110	2,104	30.25	<0.0001
	Month		1,104	2.03	0.1372
	Bay*Month		2,104	0.29	0.7465
Salinity	Bay	110	2,104	26.53	<0.0001
	Month		1,104	14.82	0.0002
	Bay*Month		2,104	0.24	0.7859
Temperature	Bay	110	2,104	19.88	<0.0001
	Month		1,104	74.46	<0.0001
	Bay*Month		2,104	1.45	0.2398
TSS	Bay	82	2,76	0.36	0.6966
	Month		1,76	7.57	0.0074
	Bay*Month		2,76	1.21	0.3047
VSS	Bay	82	2,76	5.08	0.0085
	Month		1,76	51.56	<0.0001
	Bay*Month		2,76	3.28	0.043
DOC	Bay	112	2,106	0.45	0.6382
	Month		1,106	0.01	0.936
	Bay*Month		2,106	7.74	0.0007
NH_4^+	Bay	111	1,105	1.32	0.2527
	Month		2,105	0.27	0.7645
	Bay*Month		2,105	1.78	0.173
NO_3^-	Bay	112	1,106	0.2	0.6551
	Month		2,106	1.39	0.2541
	Bay*Month		2,106	1.38	0.2561
Urea	Bay	110	2,104	0.97	0.3817
	Month		1,104	1.72	0.1931
	Bay*Month		2,104	1.61	0.2043
TN	Bay	112	1,106	4.3	0.0405
	Month		2,106	8.53	0.0004
	Bay*Month		2,106	10.57	<0.0001
PO_4^{-3}	Bay	111	1,105	22.27	<0.0001
	Month		2,105	9.01	0.0002
	Bay*Month		2,105	7.62	0.0008
TP	Bay	112	1,106	1.06	0.306
	Month		2,106	0.31	0.734
	Bay*Month		2,106	11.49	<0.0001
Chlorophyll *a*	Bay	106	1,100	0.66	0.4181
	Month		2,100	0.78	0.4609
	Bay*Month		2,100	40.28	<0.0001
Phaeophytin	Bay	108	1,102	4.05	0.0468
	Month		2,102	0.08	0.9235
	Bay*Month		2,102	0.29	0.7522
$\delta^{15}N$	Bay	58	2,55	3.65	0.0325
Bacteria	Bay	43	2,37	11.5	0.0001
	Month		1,37	3.77	0.0598
	Bay*Month		2,37	5.3	0.0095
Viruses	Bay	44	2,38	16.97	<0.0001
	Month		1,38	0.12	0.7309
	Bay*Month		2,38	1.88	0.1662

2007 St. Martin River sections

Parameter	Variation	n	df	F	P
Secchi	Section	50	3,42	19.27	<0.0001
	Month		1,42	52.09	<0.0001
	Section*Month		3,42	2.73	0.0556
Bottom DO	Section	49	3,41	2.1	0.1144
	Month		1,41	16.94	0.0002
	Section*Month		3,41	7.69	0.0003
Salinity	Section	49	3,41	28.81	<0.0001
	Month		1,41	52.59	<0.0001
	Section*Month		3,41	0.29	0.8305
Temperature	Section	49	3,41	12.22	<0.0001
	Month		1,41	140.79	<0.0001
	Section*Month		3,41	4.12	0.0121
TSS	Section	29	3,21	1.83	0.1719
	Month		1,21	7.47	0.0125
	Section*Month		3,21	3.33	0.0393
VSS	Section	29	3,21	4.55	0.0131
	Month		1,21	127.85	<0.0001
	Section*Month		3,21	2.9	0.0587
DOC	Section	50	3,42	8.04	0.0002
	Month		1,42	10.29	0.0026
	Section*Month		3,42	0.33	0.8005
NH_4^+	Section	49	3,41	2.12	0.1123
	Month		1,41	0.42	0.5211
	Section*Month		3,41	2.44	0.0783
NO_3^-	Section	50	3,42	2.24	0.0972
	Month		1,42	2.1	0.155
	Section*Month		3,42	2.24	0.098
Urea	Section	50	3,42	0.98	0.4133
	Month		1,42	0.21	0.6494
	Section*Month		3,42	0.81	0.4950
TN	Section	50	3,42	57.98	<0.0001
	Month		1,42	68.52	<0.0001
	Section*Month		3,42	1.08	0.3664
PO_4^{-3}	Section	50	3,42	10.34	<0.0001
	Month		1,42	6.73	0.013
	Section*Month		3,42	2.73	0.0558
TP	Section	50	3,42	44.61	<0.0001
	Month		1,42	49.23	<0.0001
	Section*Month		3,42	5.47	0.0029
Chlorophyll *a*	Section	47	3,39	5.1	0.0045
	Month		1,39	26.99	<0.0001
	Section*Month		3,39	1.47	0.2387
Phaeophytin	Section	49	3,41	18.54	<0.0001
	Month		1,41	1.6	0.2132
	Section*Month		3,41	3.83	0.0165
$\delta^{15}N$	Section	26	3,22	1.31	0.2977
Bacteria	Section	17	3,9	9.42	0.0039
	Month		1,9	34.63	0.0002
	Section*Month		3,9	1.72	0.2316
Viruses	Section	18	3,10	7.94	0.0053
	Month		1,10	9.68	0.011
	Section*Month		3,10	1.09	0.3968

Table J: ANOVA results for 2007 intra-bay Johnson Bay sectional comparisons, where n= number of samples; df = comparison-wide degrees of freedom, sample degrees of freedom; F = F-value of analysis; P = probability (significance level)

2007 Johnson Bay sections

Parameter	Variation	n	df	F	P
Secchi	Section	56	3,48	4.87	0.0049
	Month		1,48	71.48	<0.0001
	Section*Month		3,48	1.1	0.3586
Bottom DO	Section	55	3,47	3.13	0.0342
	Month		1,47	104.09	<0.0001
	Section*Month		3,47	0.88	0.4573
Salinity	Section	55	3,47	5.72	0.002
	Month		1,47	8124.5	<0.0001
	Section*Month		3,47	8.09	0.0002
Temperature	Section	55	3,47	3.54	0.0214
	Month		1,47	205.37	<0.0001
	Section*Month		3,47	6.38	0.001
TSS	Section	30	2,24	1.05	0.3669
	Month		1,24	7.09	0.0136
	Section*Month		2,24	0.42	0.6596
VSS	Section	30	2,24	0.16	0.8532
	Month		1,24	130.88	<0.0001
	Section*Month		2,24	0.8	0.4604
DOC	Section	56	3,48	11.75	<0.0001
	Month		1,48	43.19	<0.0001
	Section*Month		3,48	2.21	0.0988
NH_4^+	Section	56	3,48	4.82	0.0051
	Month		1,48	44.99	<0.0001
	Section*Month		3,48	4.19	0.0103
NO_3^-	Section		3,48	2.04	0.121
	Month	56	1,48	19.76	<0.0001
	Section*Month		3,48	0.52	0.6712
Urea	Section	54	3,46	1.92	0.1399
	Month		1,46	1.01	0.3212
	Section*Month		3,46	1.25	0.3011
TN	Section	56	3,48	14.32	<0.0001
	Month		1,48	15.13	0.0003
	Section*Month		3,48	2.77	0.0515
PO_4^{-3}	Section	55	3,47	1.72	0.1748
	Month		1,47	225.78	<0.0001
	Section*Month		3,47	8.36	0.0001
TP	Section	56	3,48	4.53	0.0071
	Month		1,48	46.45	<0.0001
	Section*Month		3,48	4.7	0.0059
Chlorophyll *a*	Section	54	3,46	0.5	0.6864
	Month		1,46	24.02	<0.0001
	Section*Month		3,46	0.73	0.5396
Phaeophytin	Section	54	3,46	0.55	0.6485
	Month		1,46	1.89	0.1763
	Section*Month		3,46	0.49	0.6892
$\delta^{15}N$	Section	28	3,24	5.28	0.0061
Bacteria	Section	19	2,13	9.38	0.003
	Month		1,13	0.67	0.4269
	Section*Month		2,13	2.42	0.1282
Viruses	Section	19	2,13	10.68	0.0018
	Month		1,13	1.82	0.2005
	Section*Month		2,13	0.41	0.67

Table K: ANOVA results comparing bays (St. Martin River and Johnson Bay) and years (2006 and 2007) in May and July, where n= number of samples; df = comparison-wide degrees of freedom, sample degrees of freedom; F = F-value of analysis; P = probability (significance level)

May 2006-2007 Bays

Parameter	Variation	n	df	F	P
Secchi	bay	98	1,94	156.6	<0.0001
	year		1,94	1.47	0.2277
	bay*year		1,94	22.01	<0.0001
Temperature	bay	98	1,94	47.32	<0.0001
	year		1,94	160.69	<0.0001
	bay*year		1,94	8.12	0.0054
Salinity	bay	98	1,94	233.37	<0.0001
	year		1,94	299.35	<0.0001
	bay*year		1,94	3.28	0.0734
TN	bay	98	1,94	5.21	0.0247
	year		1,94	0.39	0.5353
	bay*year		1,94	14.92	0.0002
TP	bay	98	1,94	102.04	<0.0001
	year		1,94	0.06	0.8003
	bay*year		1,94	6.39	0.0131
Chlorophyll *a*	bay	98	1,94	16.58	<0.0001
	year		1,94	94.64	<0.0001
	bay*year		1,94	39.98	<0.0001
Phaeophytin	bay	98	1,94	1.82	0.1801
	year		1,94	134.24	<0.0001
	bay*year		1,94	1.2	0.276

July 2006-2007 Bays

Parameter	Variation	n	df	F	P
Secchi	bay	98	1,94	10.06	0.002
	year		1,94	3.32	0.0715
	bay*year		1,94	1.76	0.1879
Bottom DO	bay	98	1,94	11.67	0.0009
	year		1,94	20.32	<0.0001
	bay*year		1,94	10.77	0.0014
Temperature	bay	97	1,93	81.59	<0.0001
	year		1,93	67.79	<0.0001
	bay*year		1,93	2.16	0.145
Salinity	bay	97	1,93	71.11	<0.0001
	year		1,93	199.63	<0.0001
	bay*year		1,93	39.91	<0.0001
TN	bay	98	1,94	62.29	<0.0001
	year		1,94	5.17	0.0252
	bay*year		1,94	1.56	0.2143
TP	bay	98	1,94	0.15	0.7025
	year		1,94	77.79	<0.0001
	bay*year		1,94	6.94	0.0098
Chlorophyll *a*	bay	96	1,92	23.22	<0.0001
	year		1,92	28.46	<0.0001
	bay*year		1,92	0.19	0.6655
Phaeophytin	bay	96	1,92	0.04	0.8394
	year		1,92	2.66	0.1063
	bay*year		1,92	0.37	0.5436

Table L: ANOVA results comparing sections of St. Martin River and years (2006 and 2007) in May and July, where n= number of samples; df= comparison-wide degrees of freedom, sample degrees of freedom; F= F-value of analysis; P= probability (significance level)

May- St. Martin River

Parameter	Variation	n	df	F	P
Secchi	section	42	3, 34	5.83	0.0025
	year		1, 34	0.03	0.8720
	section*year		3, 34	7.71	0.0005
Temperature	section	42	3, 34	12.88	<0.0001
	year		1, 34	41.52	<0.0001
	section*year		3, 34	0.63	0.6011
Salinity	section	42	3, 34	41.13	<0.0001
	year		1, 34	150.20	<0.0001
	section*year		3, 34	1.75	0.1749
TN	section	42	3, 34	41.47	<0.0001
	year		1, 34	0.20	0.6610
	section*year		3, 34	15.06	<0.0001
TP	section	42	3, 34	47.62	<0.0001
	year		1, 34	0.37	0.5481
	section*year		3, 34	14.94	<0.0001
Chlorophyll *a*	section	42	3, 34	4.90	0.0062
	year		1, 34	38.17	<0.0001
	section*year		3, 34	6.75	0.0011
Phaeophytin	section	42	3, 34	9.40	0.0001
	year		1, 34	110.97	<0.0001
	section*year		3, 34	2.48	0.0778

July- St. Martin River

Parameter	Variation	n	df	F	P
Secchi	section	42	3, 34	14.20	<0.0001
	year		1,34	3.22	0.0818
	section*year		3, 34	0.76	0.5267
DO	section	42	3, 34	1.00	0.4056
	year		1,34	41.65	<0.0001
	section*year		3, 34	7.49	0.0006
Temperature	section	42	3, 34	20.90	<0.0001
	year		1,34	182.73	<0.0001
	section*year		3, 34	16.54	<0.0001
Salinity	section	42	3, 34	80.25	<0.0001
	year		1,34	61.05	<0.0001
	section*year		3, 34	0.44	0.7240
TN	section	42	3, 34	44.44	<0.0001
	year		1,34	13.02	0.0010
	section*year		3, 34	0.62	0.6072
TP	section	42	3, 34	75.76	<0.0001
	year		1,34	34.38	<0.0001
	section*year		3, 34	1.40	0.2588
Chlorophyll *a*	section	42	3, 34	11.38	<0.0001
	year		1,34	16.71	0.0003
	section*year		3, 34	1.16	0.3405
Phaeophytin	section	42	3, 34	1.69	0.1880
	year		1,34	3.03	0.0906
	section*year		3, 34	1.32	0.2842

Table M: ANOVA results comparing sections of Johnson Bay and years (2006 and 2007) in May and July, where n= number of samples; df= comparison-wide degrees of freedom, sample degrees of freedom; F= F-value of analysis; P= probability (significance level)

May- Johnson Bay

Parameter	Variation	n	df	F	P
Secchi	section	56	3, 48	3.03	0.0381
	year		1, 48	59.38	<0.0001
	section*year		3, 48	2.69	0.0567
Temperature	section	56	3, 48	5.95	0.0016
	year		1, 48	237.51	<0.0001
	section*year		3, 48	4.13	0.0110
Salinity	section	56	3, 48	44.98	<0.0001
	year		1, 48	13462	<0.0001
	section*year		3, 48	2.36	0.0829
TN	section	56	3, 48	20.87	<0.0001
	year		1, 48	45.76	<0.0001
	section*year		3, 48	1.66	0.1873
TP	section	56	3, 48	12.02	<0.0001
	year		1, 48	14.57	0.0004
	section*year		3, 48	10.63	<0.0001
Chlorophyll *a*	section	56	3, 48	0.33	0.8010
	year		1, 48	106.40	<0.0001
	section*year		3, 48	1.54	0.2155
Phaeophytin	section	56	3, 48	4.79	0.0054
	year		1, 48	97.36	<0.0001
	section*year		3, 48	4.33	0.0089

July- Johnson Bay

Parameter	Variation	n	df	F	P
Secchi	section	56	3, 48	3.08	0.0362
	year		1, 48	0.24	0.6237
	section*year		3, 48	0.48	0.6997
DO	section	56	3, 48	1.99	0.1284
	year		1, 48	1.65	0.2057
	section*year		3, 48	2.20	0.0998
Temperature	section	55	3, 47	6.01	0.0015
	year		1, 47	33.86	<0.0001
	section*year		3, 47	0.82	0.4915
Salinity	section	55	3, 47	8.83	<0.0001
	year		1, 47	#####	<0.0001
	section*year		3, 47	14.13	<0.0001
TN	section	56	3, 48	17.11	<0.0001
	year		1, 48	1.74	0.1929
	section*year		3, 48	3.28	0.0288
TP	section	56	3, 48	7.67	0.0003
	year		1, 48	189.42	<0.0001
	section*year		3, 48	2.61	0.0621
Chlorophyll *a*	section	54	3, 46	1.28	0.2917
	year		1, 46	37.23	<0.0001
	section*year		3, 46	0.84	0.4805
Phaeophytin	section	54	3, 46	1.14	0.3412
	year		1, 46	0.43	0.5370
	section*year		3, 46	0.38	0.7685

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