FINAL REPORT

to

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Nutrient and Ecological Histories in Barnegat Bay, New Jersey

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Executive Summary

There is a debate going on about Barnegat Bay in New Jersey, namely whether nutrient-eutrophication, specifically nitrogen, is causing algal blooms and increased macrophytes, and possibly secondary impacts (e.g., anoxia, loss of submerged aquatic vegetation, increase in jelly fish, decreases in fish and crab populations, etc). The debate revolves around the fact that Barnegat Bay is poorly flushed, and that current eutrophication effects are only part of the natural conditions exacerbated by current nitrogen loading (i.e., with some of the negative effects coming from other stressors such as boat traffic, loss of connected wetlands, loss of freshwater flows and the withdrawal of cooling waters for the Oyster Creek Nuclear Generating Station).

The primary objective of this project was to collect sediment cores from the tidal region of Barnegat Bay and determine the chronology of nutrient changes (i.e., nitrogen and phosphorus) and associated ecosystem level responses. Changes in various biogeochemical proxies (e.g., stable isotopes of carbon and nitrogen, etc.), along with changes in diatom community structure, were used to infer changes in nutrient loading and land use throughout the watershed. An additional objective of this study was to quantify rates of sediment mass accumulation and marsh accretion averaged over the past 100 years or more. With the threat of increased sea level rise over the next 20 to 50 years, this information can provide a much-needed baseline to evaluate the impacts of changes in land form and use throughout coastal areas.

To accomplish these goals, four sites were selected and sediment cores were collected from marsh sites below Mantoloking Bridge (Reedy Creek, BB-1); Mid-Bay (near Wire Pond; Murray Grove, BB-2); Discharge Canal of Oyster Creek Nuclear Facility (BB-3) and downstream near West Creek (BB-4). Cores were sectioned and dated using ²¹⁰Pb and ¹³⁷Cs radiometric methods. All cores provided sufficient temporal coverage (> 50-80 yr) for detailed chemical analyses. Published laboratory clean-techniques were used throughout. Protocols are outlined in standard operating procedures (SOPS) at the Academy of Natural Sciences and University of Delaware.

Sediments were analyzed for the following parameters by the Academy of Natural Sciences (Patrick Center): organic carbon, total nitrogen, total phosphorus, and stable isotopes of carbon and nitrogen. In addition, specific sections were analyzed for diatoms. Sediments for radionuclide measurements (²¹⁰Pb and ¹³⁷Cs) were analyzed at University of Delaware, School of Marine Science and Policy.

Major Findings

Sediment accumulation rates determined from the average of ²¹⁰Pb and ¹³⁷Cs results ranged from 0.048 to 0.081 g/cm²/yr, and corresponding accretion rates ranged from 0.18 to 0.30 cm/yr. These accretion rates are comparable to those measured in other Mid-Atlantic barrier-lagoon marshes, but they fall on the low end of the range for estuarine marshes such as the Delaware Estuary. Accretion rates at the coring sites fall at, to just below, rates of relative sea level rise (uncorrected for land subsidence) recorded by nearby tide gauges. These relatively low rates of accretion render the marsh vulnerable to inundation should the rate of sea level rise accelerate in the future.
Sediment concentrations of carbon, nitrogen and phosphorus are typical for tidal fresh and marine marshes throughout the region, especially marshes within a barrier-lagoon estuary such as Barnegat Bay. Sediment organic carbon concentrations ranged from 3.2% and 33.7% dw, total nitrogen ranged from 0.23 to 1.4% N and total sediment phosphorus ranged from 0.02 to 0.39% P. Sediment nitrogen concentrations increased towards the surface in three cores (BB-1, BB-2 and BB-4), while phosphorus concentrations showed only a small increase towards the surface at three sites, but a larger increase in BB-4, the most downstream location. Sediment organic carbon exhibited highest levels in the surface sections of BB-2 and to some extent BB-4, with lower concentrations at BB-3.

Sediment nitrogen accumulation rates increased twofold at the upbay site (BB-1) starting in the mid-1950s while the other locations exhibited small or no increase with time. Phosphorus accumulation increased only slightly with time. Rates increased between the 1940s and 1950s in cores BB-1 and BB-3, with only a slight increase at the surface, for BB-2. In core BB-4, the downbay-most location, there was an abrupt increase starting in the early 1990s. The remaining wetland areas within the Bay can sequester approximately 79±11% of the nitrogen and 54±34% of the phosphorus estimated to be entering the Bay from upland sources. This illustrates the important ecosystem services that marshes can perform and how important it is to maintain and enhance marshes within Barnegat Bay.

Diatom assemblages first changed in the late 1880s-early 1900s, prior to substantial development in the Barnegat Bay area. This shift may be a signal of indirect impact (atmospheric deposition) or land clearing and agriculture. Diatom metrics indicate major shifts toward more eutrophic or mesotrophic conditions starting in the 1940-1950s (cores BB-1, BB-2 and BB-3). These changes are consistent with an increase in sediment nutrients found in the same cores, and appear to indicate impacts from increasing population and land use in the northern part of Barnegat Bay, an area with urban and sub-urban land use. The southern site, BB-4, is situated in a rural or semi-rural area and was the least impacted. Species composition changed in the early 1900s, but not as much as the major shifts displayed by the northern sites throughout the 20th century. Overall, the irreversible shifts recorded by diatom species in cores BB-1, BB-2 and BB-3 suggest that, despite the fact that the Barnegat Bay wetlands are protected by both federal and state laws, these sites remain impacted by anthropogenic disturbances and did not return to their natural, reference conditions. On the contrary, the most recent changes suggest an increase in habitat deterioration and pollution. Thus, the changes recorded in diatom species convey a strong message to decision makers and managers to identify and limit all sources of nutrients that contribute to the degradation of the estuary and its watershed.

Recommendations for Future Research and Monitoring

- Since many species found in Barnegat Bay sediment samples have not yet been described in the literature, it is necessary to characterize the undescribed species and determine their autecology. We started investigating these diatoms and their ecological significance in collaboration with Dr. Mike Sullivan (Florida State University) and Dr. Sherry Cooper (Bryn Athyn College), both scientists with extensive knowledge of diatoms from coastal wetlands, including Delaware Bay. This work is in progress and would improve our
wetland diatom-based ecological knowledge. This will help directly by improving our ability to interpret water quality changes based on existing diatom stratigraphies.

- Develop a surface-sample diatom calibration dataset for Barnegat Bay and adjacent wetlands and use it to determine the ecological preferences of diatom species from this area. This work will require collection of both surface sediment and water chemistry samples (Atlantic coastal marshes) at several points along the salinity/nutrient gradient (north-south transect), and analysis of relationships between diatoms and measured chemical variables.

- Analyze the existing and new cores for additional indicators of nutrient enrichment, harmful algal blooms, and ecosystem change. While preliminary research was performed on sterols (a form of naturally produced hydrocarbons) that indicate brown tide (*Aureococcus anophagefferens*), a specific project should be undertaken to assess the time course history of blooms in the Bay. This, along with other algal metrics (e.g., dinoflagellate analysis), can help us understand the timing and development of nutrient enrichment.

- Results of this project revealed that Barnegat Bay marshes can bury a substantial portion of the nitrogen entering the Bay. Burial is only one method for nitrogen sequestration that these marshes can perform. To better assess the total removal potential from coastal wetlands, additional cores (n<5) need to be obtained to broaden the data set and strengthen the estimate. In addition, denitrification studies and measurements should be undertaken in marshes across the salinity gradient of the Bay. Denitrification is a microbial process that converts dissolved nitrate, a dominant form of nitrogen, to nitrogen gas. These ecosystem services are an important component of nutrient management and Total Maximum Daily Loads (TMDLs).

The New Jersey Department of Environmental Protection (NJDEP) is evaluating the appropriate indices to be used to measure the ecosystem health of New Jersey's shallow, lagoon-type estuaries — our coastal bays. These include bays such as Great Bay, Great Egg Harbor Bay, Absecon Bay, Ludlam Bay and Barnegat Bay. The federal government (USEPA and NOAA) has already developed a suite of indicators (e.g., EPA’s National Coastal Assessment Report 2005 and NOAA’s National Estuarine Eutrophication Assessment update) and has applied them to New Jersey's coastal bays with mixed results, especially as state level management tools, due to both geographic scale issues and the inability of the USEPA and NOAA metrics to identify proximate sources and causes of impairments. Further information is needed for NJDEP to develop water quality management tools; this study was designed to directly assist NJDEP in the development and/or enhancement of its nutrient criteria.
A) Introduction

Sediment cores from marshes provide an excellent means for documenting long-term (e.g., decadal scales) changes in land use, nutrient and contaminant loadings and related ecological changes. Importantly, sediment chronologies help provide an understanding of whether or not source reduction programs (e.g., wastewater treatment and waste site remediation projects) are successful, and under what time scale a river/estuarine-wide response can be detected. The response time is an important parameter in many water quality models (i.e., TMDL) when source reduction and load allocations will be determined.

In addition, NJDEP is interested in evaluating and developing various indicators for ecosystem health of New Jersey's shallow, lagoon-type estuaries. Factors such as submerged aquatic vegetation (SAV) and specific phytoplankton blooms are two of many indicators being assessed. This project will help in the development of algal indicators via an assessment of current conditions along with a historical perspective. The proposed project also meets goals and objectives as outlined in the Characterization Report and Comprehensive Conservation and Management Plan (BBNEP, 2005).

A1: Background

Nutrients, trace metals and organic contaminants in water are derived from many sources. Natural sources of metals include the weathering products of soils which are then transported in the dissolved or particulate phases. Anthropogenic sources of metals and organic contaminants are introduced to the water via atmospheric deposition, industrial discharges (e.g., mining, metal processing, manufacturing), municipal discharges (waste water treatment), and stormwater runoff of contaminated parcels. Many of these same sources are also noted for discharges of nitrogen and phosphorus, especially waste water treatment facilities and agricultural runoff (via surface runoff and indirectly through groundwater flows). Due to the particle-reactive nature of most trace metals, phosphorus, and organic compounds, sediments are potential repositories for contaminants and, under certain conditions, can be used to provide a historical record of pollution (Simpson et al., 1983; Orson et al., 1990; 1992; Valette-Silver, 1993; Hornberger et al., 1999; Cooper and Brush, 1993; Church et al., 2006; Ridgeway and Shimmield, 2002; Velinsky et al., 2007; Hartzell et al., 2010, and others). With minimal post-depositional diagenetic remobilization, chemical transformations, biological mixing, and hydraulic processes, the
sediment column can record the chronology of nutrient and chemical contaminant loading and burial in estuarine waters.

Coring information can be used for the construction of sediment budgets (Schubel and Hirschberg, 1977; Brush et al., 1982; Officer et al., 1984) and to understand chemical/nutrient accumulation in aquatic environments (Owens and Cornwell, 1995; Cornwell et al., 1996; Latimer and Quinn, 1996; Van Metre and Callender, 1997; Church et al., 2006; Velinsky et al., 2007; 2010a,b,c; Hartzell et al., 2010). Also, dated sediment cores can provide loadings information of contaminants or chemicals over time (e.g., Rippey and Anderson, 1996; Santschi et al., 2001). However, specific chemicals, such as nitrogen and phosphorus can undergo substantial diagenetic re-mobilization depending on the redox conditions (see Burdige, 2006), and as such, accumulation records derived from sediment cores may be limited in certain environments.

Phosphorus is transported to the oceans from rivers and estuaries and up to 90% is in a particulate form (Meybeck, 1982; Froelich et al., 1982; Lebo, 1991; Follmi, 1996; Litke, 1999; Jordan et al., 2008). Once bound phosphorus is buried, it has the potential to be recycled back into the water column depending on many factors (Froelich et al., 1982; Boynton et al., 1995; Jordan et al., 2008; Figure 1). In some sub-tidal environments, only a small portion of the buried phosphorus (e.g., 5 to 30%) is retained, hindering interpretation of anthropogenic sources with time. However, Kahn and Brush (1994), Cornwell et al. (1996), and Church et al. (2006) found no major change in phosphorus with depth in sediment cores, and concentration profiles tracked changes in loadings over time. Controlling factors that would enhance retention of buried phosphorus are the magnitude and rate of phosphorus loadings, sediment accumulation rate, and the magnitude and rate of remobilization of phosphorus in the sediments.

Nitrogen is transported in rivers and estuaries mostly in the dissolved form and its cycling is much more complex (Meybeck, 1982, Van Breemen et al. 2002; Castro et al., 2003; Figure 1). As such, retention of nitrogen in coastal and riverine sediments is potentially more restricted than for phosphorus. As with phosphorus, controlling factors may include the rate of sediment accumulation and the magnitude of nitrogen loading. The stable isotopes of nitrogen ($^{14}$/$^{15}$N) can help determine the source, fate and cycling of nitrogen in a water body and could be reflected in the nitrogen buried in sediments (see Kendall, 1998). For example, Church et al. (2006) showed an increase in $\delta^{15}$N of sediment N with time that is reflective of increases in urbanization in the
Delaware Estuary, similar to other urbanized waters (McClelland et al., 1997; Kendall, 1998; Lake et al., 2001; Ulseth and Hershey, 2005).

Sediment core records for rivers and estuaries can be extremely useful in determining if pollution control actions were/are effective in reducing contaminant loadings, as well as providing a time frame for system response (Owens and Cornwell, 1995; Zhang et al., 1993; Smol, 2008). In addition, biological material, and in some cases chemical information, retained in the sediments can help determine changes in ecosystem processes and health (Smol, 2008; Potapova and Charles, 2007; Bennion et al., 2001; Cooper, 1999; 1995; Cooper and Brush, 1993). Specific diatoms and foraminifera can be used as proxies to determine changes in response to watershed and estuarine changes in nutrient loadings and concentrations. Pollen content of sediments has been very useful in describing past changes in vegetation in relation to land use changes over time (Cooper and Brush, 1993; Brush and Brush, 1994), whereas biogenic silica, a chemically determined proxy, in conjunction with other chemical proxies can be used to determine aquatic productivity (see Conley and Schelske, 2001). Overall, chemical and biological proxies in sediments cores can provide a wealth of information about watershed and aquatic ecosystem change and sediment core data is especially important for modeling programs in which forecasts are developed by extending past trajectories.

A2: Objectives of Study

The objective of this study was to collect sediment cores from the tidal marshes of Barnegat Bay, New Jersey, and determine the chronology of carbon, nitrogen and phosphorus concentrations, their accumulation rates with time, and related ecological responses. To meet this objective we obtained and analyzed the chemical characteristics of sediment cores from marsh depositional areas fringing the barrier island lagoon system. In addition to providing insight into the temporal variability of nitrogen and phosphorus in the estuary, we also sought to understand how the trophic status of the system has changed over decadal time scales.

Lastly, New Jersey Department of Environmental Protection is evaluating and developing various indicators for ecosystem health of New Jersey's shallow, lagoonal estuaries (see EPA's National Coastal Assessment Report (US EPA, 2005) and NOAA’s National Estuarine Eutrophication Assessment (Bricker et al., 1999). Factors such as submerged aquatic vegetation (SAV) and specific phytoplankton blooms are two of many indicators we assessed. This project
starts in the development of algal indicators via an assessment of current conditions along with a historical perspective. A retrospective look at diatoms incorporated into marsh core sediments will help yield information towards this goal. In addition, attempts were made to evaluate other indicators of change in the Barnegat Bay including foraminifera identification and analysis of specific sterols that indicate *Aureococcus anophagefferens* the algae that is responsible for “brown tides” in the Bay.

A3: Study Area

The Barnegat Bay-Little Egg Harbor estuary (BB; Barnegat Bay) is located along the central New Jersey coastline in the Atlantic Coastal Plain province (Figure 2). Barnegat Bay is a back-barrier lagoon-type estuary that extends from Point Pleasant south to Little Egg Inlet. The variety of highly productive shallow water and adjacent upland habitats found in this system include barrier beach and dune, submerged aquatic vegetation (SAV) beds, intertidal sand and mudflats, salt marsh islands, fringing tidal salt marshes, freshwater tidal marsh, and palustrine swamps.

The Barnegat Bay system is composed of three shallow bays (Barnegat Bay, Manahawkin Bay and Little Egg Harbor), is approximately 70 km in length, 2 to 6 km wide, and up to 7 m deep. The Bay watershed covers an area of approximately 1700 km² and has been extensively developed over the past 70 years. The tidal waters cover approximately 280 km² with a ratio of watershed area to water area of 6.1. The current land use (2006) of the watershed is agriculture (~1%), wooded/forest (~28%), tidal and non-tidal wetlands (~18%), urban areas (~20%) and open water (30%; Lathrop and Haag, 2007). Importantly, watershed development (urban area) has increased over time. From 1986 to 2006 the amount of urban land cover increased from 15 to up to 21% of the land area, while forested land cover has decreased (NJ DEP, see [www.state.nj.us/dep/bmw/ReportOcean.htm](http://www.state.nj.us/dep/bmw/ReportOcean.htm); Lathrop, 2004). The population of the watershed has increased substantially from the 1940s (40,000) to over 570,000 year-round resident currently (US Census Reports). During the height of the summer season the population can rise to approximately 1,000,000.
Changes in the Barnegat Bay-Little Egg Harbor Watershed and Nutrient Enrichment

The water quality of the Barnegat Bay is affected by persistent pollution impacts (i.e., high nutrient loads, algal blooms, eutrophication and low dissolved oxygen) from agricultural runoff and stormwater discharges, in addition to having somewhat restricted tidal flushing (BBNEP, 2005; Kennish et al., 2007). Approximately 50-66% of the nutrient load is from surface waters with a substantial amount from atmospheric deposition (22-40%) and lesser amounts from groundwater inflow (~ 10%) (Hunchak-Kariouk and Nicholson, 2001; Bowen et al., 2007; Wieben and Baker, 2009). Wieben and Baker (2009) estimate that greater than 60% of the nitrogen load is from the Toms and Metedeconk rivers in the upper section of the Bay. Kennish et al. (2007), using the NLOAD model framework, estimated the land-derived nitrogen loading to the Bay of 7 X 10^5 kg N/yr and on an aerial basis of 3.9 kg N/ha-yr. Approximately, 15% of the nitrogen load to surface waters (and to groundwaters) is derived from the application of fertilizer in the watershed (Castro et al., 2003; Borgatti, 2008). While development of the watershed has most likely increased loadings over time, a major change in the discharge of nutrients occurred in 1980. Prior to 1980, wastewater discharges and loadings of N and P were direct to the Bay, after which, between 1976 and 1979, the Ocean County Utilities effluent system was redirected to discharge wastewater approximately 2 km offshore of New Jersey. As such, there are few if any, point source discharges of nutrients to the Bay (not including stormwater runoff).

In general, there appears to be a lack of water quality (i.e., nutrient) monitoring data for the tidal Barnegat Bay prior to the early 1990s. Limited data from the 1970s by Durand (1979) for the southern sections of Barnegat Bay and Great Bay show a range in nitrate concentrations between 6 to 70 µg N/L, while dissolve nitrate levels currently range from 5 up to 1000 µg N/L (NJ DEP, see www.state.nj.us/dep/bmw/ReportOcean.htm) throughout the entire Bay. There is a large seasonal change in nitrogen concentrations as well as a spatial gradient with higher concentrations in the northern sections of the Bay, i.e., from Barnegat Inlet to the Metedeconk River. The levels of nutrients result in elevated of chlorophyll a concentrations in the Bay that can range up to 40 to 50 µg/L. Recurring phytoplankton blooms, including harmful algal blooms, have been shown over time, with brown tides (*Aureococcus anaphagefferans*) sporadically occurring since 1995 (Olsen and Mahoney, 2001; Gastrich et al., 2004).
Overall, Barnegat Bay has shown increased development along with low freshwater inflow and flushing (i.e., high residence time of water) and high nutrient levels that result in eutrophic conditions. These conditions hinder the ecological and recreational benefits of Barnegat Bay and as such there are a number of management goals to restore the Bay. While restoration will most likely not bring the Bay back to “pristine” conditions (Duarte and Conley, 2009; Palmer, 2009), information as to how ecosystems will respond, and respond over time, is needed to set reasonable restoration goals in the future.

The goal of this project was to obtain a historical perspective on nutrient inputs and ecological response in Barnegat Bay using dated sediment cores, and to evaluate whether pollution controls have been effective, as well as to help develop restoration targets for the future.

B) Field and Laboratory Methods
B1: Field Sampling

Sediment cores were collected on July 29-30, 2009, by staff from The Academy of Natural Sciences and University of Delaware (UDEL) at four locations in the tidal river and estuary (Figure 2; Table 1). It should be noted that core BB-3 was located in the discharge canal for the Oyster Creek Nuclear Power Plant, in which the water temperature is artificially elevated. Eight cores were obtained, and all provided good sediment chronologies based on $^{210}\text{Pb}$ and $^{137}\text{Cs}$ measurements.

Cores were collected during mid to low tide from interior locations away from any obvious disturbances (e.g., creek banks and ditching). At each site two cores were obtained, one for chemical analysis and the other for stratigraphic descriptions of each site. Push-piston cores of approximately 1 to 1.5 m in length were retrieved by a tripod/pulley system (Figure 3). The cores were taken to the laboratory, extruded vertically, and sectioned in 2-cm intervals. Samples were stored in pre-cleaned jars at -10°C at either Academy or UDEL facilities. Chain-of custody procedures were followed from the time of collection, shipping and until the analyses were completed.
B2: Laboratory Methods

Published laboratory clean-techniques were used throughout (Church et al., 2006; US EPA, 1997; APHA, AWWA and WEF, 1995) using protocols as outlined in standard operating procedures (SOPS) at the Academy of Natural Sciences and University of Delaware (ANSP; June 2009). All materials coming in contact with the samples were either glass or metal and were cleaned of any contaminants prior to use. Sample ID forms were used and each sample was given a unique laboratory number for sample tracking.

Sediments were analyzed for the following parameters at laboratories operated by the Academy of Natural Sciences (Patrick Center): organic carbon, total nitrogen and total phosphorus, and stable isotopes of carbon and nitrogen. In addition, specific sections were analyzed for diatoms via sample digestion, mounting and glass slide light microscopy. Sediments for radioisotope measurements (\(^{210}\)Pb and \(^{137}\)Cs) were analyzed at University of Delaware (School of Marine Science and Policy). Below are brief descriptions of each chemical, biological, or physical method.

B2.1: Radioisotope Measurements and Sedimentation Rates

Sediment bulk density and loss-on-ignition (LOI) measurements were made for each core subsample to aid the interpretation of downcore radionuclide and nutrient data. Dry-bulk density \(\rho_d\) was calculated from porosity \(\phi\) as follows:

\[
\rho_d = (1 - \phi) \rho_s
\]  

(1)

where \(\rho_s\) (g/cm\(^3\)) is the density (specific gravity) of unconsolidated solids. Particle densities of 1.5 g/cm\(^3\) and 2.65 g/cm\(^3\) were assumed for organic and mineral components, respectively, and the relative proportion of these components in a given subsample was determined by LOI analysis as described below. In general, bulk density varies with the particle density and porosity, whereas porosity varies with particle grain size, grain shape, and post-depositional compaction. In a compositionally uniform sediment column, bulk density typically increases with depth (porosity decreases) as porewater is expelled by self-weight compaction. Sediment porosity \(\phi\) was computed gravimetrically from water content \(W_c\) following:

\[
\phi = \left( \frac{W_c \rho_s}{W_c \rho_s + (1-W_c) \rho} \right)
\]  

(2)
where \( W_c = W_{\text{wet}} - W_{\text{dry}} / W_{\text{wet}} \) and \( \rho \) is the density of pore fluid (assumed 1.0 g/cm\(^3\)). Note that porosity and water content are dimensionless. Water content was measured by weighing a portion of wet sediment dissected from the core and then again after drying in a convection oven at 100°C for 24 h. The dried sediment was then ground to a fine powder using a mortar and pestle for later LOI and radionuclide analysis.

LOI measurements were used to determine the amount of organogenic (combustible) and minerogenic (residual ash) materials in the sediment column. Following the method of Heiri et al. (2001), a 4-g quantity of ground sediment was combusted at 550°C in a muffle furnace for 4 h. LOI was computed as follows:

\[
LOI = \frac{W_{\text{dry}} - W_{\text{ash}}}{W_{\text{dry}}} \times 100\%
\]

where \( W_{\text{dry}} \) is the weight of sample previously dried at 100°C, and \( W_{\text{ash}} \) is the weight of the residual ash.

The LOI and porosity data were used to determine the volumetric composition of the sediment column, i.e., the volume of pore space and solids relative to the total volume. The total volume (\( V_t \)) is composed of water-filled interconnected voids (\( V_w \)), mineral solids (\( V_m \)), and organic solids (\( V_o \)) as given by:

\[
V_t = V_w + V_m + V_o
\]

where \( V_w \) is equivalent to \( \phi \) in Eq. 2, \( V_m = (1 - \phi)(1 - \text{LOI}/100) \), and \( V_o = (1 - \phi)(\text{LOI}/100) \).

**Radionuclide Measurements and Geochronology**

To develop chronologies for the sediment column, and to determine rates of sediment accumulation and marsh accretion, measurements of \(^{210}\text{Pb} \) and \(^{137}\text{Cs} \) were made by gamma spectroscopy of the 46.5 and 661.6 keV photopeaks, respectively, using methods adapted from Cutshall et al. (1983) and Wallbrink et al. (2002). Lead-210 (\( t_{1/2} = 22.3 \) yr) is a natural radionuclide of the \(^{238}\text{U} \) decay series and under ideal conditions provides a record of sediment accumulation extending back ~100–125 years from the time of sampling (Robbins, 1978). In contrast, \(^{137}\text{Cs} \) (\( t_{1/2} = 30.1 \) yr) is an impulse tracer introduced to aquatic waters via nuclear weapons testing fallout after 1954 (Ritchie and McHenry, 1990). Both radionuclides are delivered to the marsh surface through a combination of direct atmospheric deposition and lateral
transport by tidal flooding, though the relative contribution of these sources varies widely among marshes in general. Dry, ground samples for radionuclide analysis were placed in a 60-ml plastic jar and counted for 24–48 hr using Canberra Model 2020 low-energy Germanium detectors (LEGe). The radionuclide concentration or activity of excess $^{210}$Pb was determined by subtracting the activity of its parent nuclide $^{214}$Bi (609.3 keV) from the total activity of $^{210}$Pb ($^{210}$Pb$_{ex}$=$^{210}$Pb$_{tot}$–$^{214}$Bi), assuming secular equilibrium between $^{214}$Bi and $^{210}$Pb. Detector efficiencies were determined from counts of NIST Standard Reference Material 4357 (Inn et al., 2001). The counting geometry of the samples was kept identical to that of the NIST standard, so a self-absorption correction for $^{210}$Pb was unnecessary. Note that the activity errors reported with the radionuclide data are propagated one-sigma background, calibration, and counting errors.

Three approaches were used to reconstruct the accumulation history of the marsh sediment column: 1) the Constant Initial Concentration (CIC) $^{210}$Pb model; 2) the constant Rate of Supply (CRS) $^{210}$Pb model; and the $^{137}$Cs activity-depth relationship. In the CIC model a single accretion rate (cm/yr) is derived from the slope of the decay profile of excess $^{210}$Pb (Robbins, 1978; Appleby and Oldfield, 1992). This model assumes that the specific activity (dpm/g) of excess $^{210}$Pb deposited on the marsh surface is constant through time (steady state), specifically, that variations in the rate of sediment deposition do not influence the initial activity of excess $^{210}$Pb. At steady state, excess $^{210}$Pb decreases exponentially with depth in the sediment column following:

$$A = A_o \exp\left(-\frac{\lambda z}{S}\right)$$  \hspace{1cm} (5)

where $A$ (dpm/g) is the excess activity of $^{210}$Pb at depth $z$ (cm), $A_o$ (dpm/g) is the initial activity of excess $^{210}$Pb, $\lambda$ is the decay constant for $^{210}$Pb (0.0311 yr), and $S$ is the vertical accretion rate (cm/yr). On a plot of $\ln A$ versus $z$, the slope of a line fit to the data is proportional to the accretion rate. In this model the age of a sediment interval relative to the year of sampling is derived from a single value of $S$ averaged over the entire profile of excess $^{210}$Pb. The corresponding mass accumulation rate (g/cm$^2$/yr) is derived by plotting $A$ as a function of cumulative mass (g/cm$^2$), which is the product of $\rho_d$ (see Eq. 1) and $z$. In this study $^{210}$Pb provided 80–100 years of sediment accumulation history.
The CRS $^{210}$Pb model relates sediment age and depth by assuming that the *depositional flux* of $^{210}$Pb (dpm/cm²/yr) to the marsh surface is steady state. Sediment age and $^{210}$Pb flux are related by the following:

$$I = I_o \exp(-\lambda t)$$  \hspace{1cm} (6)

where $I$ (dpm/cm²) is the inventory of excess $^{210}$Pb below depth $z$ (cm), $I_o$ (dpm/cm²) is the total inventory of excess $^{210}$Pb in the sediment column, $\lambda$ (0.0311 years) is the decay constant for $^{210}$Pb, and $t$ (yr) is the sediment age at depth $z$. Implied in the CIC model is that the full profile of excess $^{210}$Pb is recovered and thus complete inventory is available for dating. In contrast to the CIC model, which assumes that $A_o$ and $S$ are independent of one another, the CRS model specifies that $A_o$ and $S$ are inversely related such that an increase in $S$ produces a proportional decrease in $A_o$. In essence, the CIC and CRS models represent open and closed systems with respect to $^{210}$Pb supply, transport to the sediment interface, and burial.

Whereas the CIC model yields a single, core-averaged rate of marsh accretion, accretion rates can be calculated as a function of sediment depth (time) using the CRS model, provided the condition of steady-state $^{210}$Pb flux is met. Experience has shown that the CRS model is best suited to tidal marshes that sequester $^{210}$Pb primarily through direct atmospheric deposition and to a lesser extent by allochthonous input from tidal waters. In highly allochthonous marsh systems, the tidal source of excess $^{210}$Pb can exceed the direct atmospheric supply. In this case, the CRS model is contraindicated because the tidally supplied excess is deposited only when the marsh is flooded (non-steady state). As discussed later, the criteria for both the CIC and CRS $^{210}$Pb models were met at the coring sites in Barnegat Bay.

The third method of sediment chronology used in this study is based on the depth of the $^{137}$Cs activity peak in a core relative to the time of maximum atmospheric fallout in ~1964 (Ritchie and McHenry, 1990). Dividing the depth of the $^{137}$Cs peak by the interval between 1964 and the year of sampling (2009 in the present case) gives the accretion rate (cm/yr) averaged over the past ~45 years. The corresponding mass accumulation rate (g/cm²/yr) is determined by plotting $^{137}$Cs activity against cumulative mass. An advantage of $^{137}$Cs chronology over the $^{210}$Pb method is that it can provide a less ambiguous age for sediments deposited after about 1954, specifically, when the activity peak is well-preserved in the sediment column. An advantage of $^{210}$Pb is that it can provide a record of sediment accumulation that exceeds the $^{137}$Cs time frame.
by 25–50 years. When used together these radionuclides provide a robust approach for dating tidal marsh sediments.

Sediment inventories of excess $^{210}\text{Pb}$ and $^{137}\text{Cs}$ were computed to compare the relative amount of radionuclide deposited among the four coring sites (BB-1 through BB-4), and to determine the applicability of the CRS dating model. Radionuclide inventories were computed as:

$$I_i = \sum \rho_d x_i A_i$$

(7)

where $\rho_d$ is the dry-bulk density (g/cm$^3$), $x$ is the sediment interval thickness (cm), $A$ is the radionuclide activity (dpm/g), and the $i$ operator indicates the $ith$ depth interval.

The following conditions are implicit in $^{210}\text{Pb}$ and $^{137}\text{Cs}$ sediment chronology: 1) mixing by burrowing organisms and (or) plant roots has not augmented burial of particles and adsorbed radionuclide; 2) the radionuclide is chemically immobile in the sediment column; and 3) the sedimentary record is complete and not punctuated by prolonged episodes of non-deposition or erosion. As elaborated later, these assumptions appear to have been met at the four marsh coring sites.

**B2.2: Total Organic Carbon and Total Nitrogen**

Total organic carbon and total nitrogen were measured using a CE Flash Elemental Analyzer following the guidelines in EPA 440.0, manufacturer instructions and ANSP-PC SOP. Samples were pre-treated with acid to remove inorganic carbon.

**B2.3: Total Phosphorus**

Total sediment phosphorus was determined using a dry oxidation method modified from Aspila et al. (1976) and Ruttenberg (1992). Solubilized inorganic phosphorus was measured with standard phosphate procedures using an Alpkem Rapid Flow Analyzer. Standard reference material (spinach leaves) and procedural blanks were analyzed periodically during this study. All concentrations were reported on a dry weight basis.

**B2.4: Stable Isotopes of Carbon and Nitrogen**

The stable isotopic composition of sediments was analyzed using a Finnigan Delta XL coupled to an NA2500 Elemental Analyzer (EA-IRMS). Samples were run in duplicate or
triplicate with the results reported in the standard $\delta$ ($\%$o) notation: $\delta X = (R_{\text{sample}}/R_{\text{standard}}) - 1) X 1000\%$; where $X$ is either $^{13}$C or $^{15}$N and $R$ is either $^{13}$C/$^{12}$C or $^{15}$N/$^{14}$N. The $\delta^{15}$N standard was air ($\delta^{15}$N = 0), and for $\delta^{13}$C the standard is the Vienna PeeDee Belemnite (VPDB) limestone that has been assigned a value of 0.0‰. Analytical accuracy was based on the standardization of the UHP N$_2$ and CO$_2$ used for continuous flow-IRMS with IAEA N-1 and N-2 for nitrogen and IAEA sucrose for carbon, respectively. An in-house calibrated sediment standard was analyzed every tenth sample. Generally, precision based on replicate sample analysis was better than 0.2‰ for carbon and 0.6‰ for nitrogen.

**B2.5: Diatoms and Foraminifera**

About 1-g core sediment was subsampled and the organic component was oxidized with 70% nitric acid while heated in a CEM microwave (165°C) for 1.5 h. Diatoms were repeatedly allowed to settle for 24 h and the supernatant was decanted until it reached a neutral pH. A measured amount of digested sample was dripped onto a microscope cover slip and dried. Cover slips were then mounted onto slides using a high refractive index mounting medium (Naphrax™). Diatoms were counted and identified using a Leica DM LB2 microscope equipped with DIC optics. At least four hundred valves were counted for each slide at 1000x magnification, unless diatom concentration was too low to allow a 400-valve count. More details on standard Phycology Section operating procedures for diatom analysis can be found in “Protocols for the analysis of algal samples collected as part of the USGS National Water Quality Assessment Program” (Charles et al., 2002; [http://diatom.ansp.org/nawqa/protocols.asp](http://diatom.ansp.org/nawqa/protocols.asp)). Diatom species identifications were made using the extensive diatom library at ANSP (Charles et al., 2002). Several diatom community metrics were calculated based on species autecological preferences originally assembled by van Dam et al. (1994). Metrics were calculated using the Phyco-Aide program developed at ANSP. Assemblages in each core were analyzed using Principal Component Analysis (PCA). The scores of each taxon along PCA axis 1 were used to order the sequence of taxa in diatom stratigraphic profiles.

**B2.6: Sterol Analysis**

*Aureococcus anophagefferens* is a 2-3 um spherical, non-motile pelagophyte which has caused destructive ‘brown tide’ blooms in northeast and Mid-Atlantic estuaries for two decades (Giner
et al., 2009; Gobler et al., 2005). This species of algae has been shown to be present in the Barnegat Bay during various blooms during the summer months. This alga produces an unusual marine C₃₀ sterol 24-propylidenecholesterol as two isomers (24-E and 24-Z forms). The 24-Z form is thought to be specific for *Aureococcus sp*, however other pelagophyte may also produce this form. While not the main focus of this research, an attempt was made to analyze specific sediment intervals for these isomers to determine time course history of brown tide blooms and to see what correlations (e.g., nutrients, land use, populations etc) can be found for their onset (Gobler et al., 2005).

In brief, four sediment samples from Core BB-4 (2-4 cm, 8-10 cm, 20-22 cm, and 38-40 cm), were extracted using a CH₂Cl₂/MeOH (1:1 v/v) overnight with nonadecanol (C₁₉OH) and docosane (nC₂₂) added as surrogate standards. The extracts were cleaned using silica gel over alumina (deactivated) and then converted to the TMS derivative using BSTFA. The TMS derivatives were analyzed using a GC-MS with an HP5 column in the electron impact mode. In addition, pure compounds of the isomers were graciously provided by Dr. Giner at the Department of Chemistry, SUNY-ESF (Syracuse, NY) to aid in identification.

The results from the analysis were inconclusive. While the standards were detected, the sediment samples did not exhibit detectable amounts of the two isomers (H. White, Haverford College, personal communication). This may be due to analytical problems with extraction and quantification or due to the incorrect selection of the sediment samples. The sedimentation rates were lower than expected (compared to Delaware Bay cores) and intervals were selected that may have not been exposed to this algal species. However, with proper interval selection and confirmation of their presence via sampling during an active bloom, this method may yield important information on the timing of this type of brown tide.

C) Results and Discussion

C1: Sediment Properties and Sediment Accumulation

C1.1: Sediment Bulk Properties

Based on LOI measurements, the organic matter content of the cores ranges from 10 to 70% by weight with a mean for all samples of 38±13% (n=72, 1σ) ([Table 2 and 3; Figures 4–7](#)). This range reflects spatial and temporal variations in marsh plant productivity, organic matter decomposition, and burial of refractory organic matter with allochthonous mineral sediment.
among the coring sites. As is typical for *Spartina* marsh, the organic matter content is highest within the living root zone of the sediment column, generally ~10–20 cm below the surface. The organic matter content varies inversely with dry-bulk density; profiles of LOI and bulk density are mirror images of one another (Figures 4-7). This inverse relationship reflects the dissimilar particle densities of organic matter (1.2–1.5 g/cm³) and mineral grains (2.6–2.7 g/cm³).

Additionally, it demonstrates that the bulk density of the sediment column is influenced more so by temporal variations in the density of particles (ρ, in Eq. 1) deposited on the marsh surface than by post-depositional compaction. Bulk density does not increase systematically with depth (porosity does not decrease), partly because of secondary porosity created by water- and air-filled roots.

Volumetrically, the marsh sediment column at the coring sites is composed mostly of pore space (generally 83–93%), and, to a lesser extent, mineral solids (3–18%) and organic matter (2–7%). At sites BB-2 and BB-4, the solids volume comprises ≤12% of the total, and the relative volume of mineral and organic solids is similar and largely invariant with depth (Figures 4–7). At sites BB-1 and BB-3, the solids volume is somewhat higher at ≤20% of the total with an overall larger fraction of mineral solids (5–18%) relative to organic matter (2–4%) (Figures 4–7). Only in several intervals at the top of core BB-2 does the volume of organics exceed the mineral solids volume.

**C1.2: Sediment Accumulation and Accretion Rates**

Downcore profiles of radionuclide activity and sediment age are presented in Figures 8–11, and the sediment accumulation and marsh accretion rates derived by ²¹⁰Pb and ¹³⁷Cs measurements are listed in Table 4. Excess ²¹⁰Pb activity in all of the cores decreases monotonically with depth, indicative of steady-state sediment accumulation and radioactive decay. Overall, the ²¹⁰Pb rates of sediment accumulation and accretion are 0.039–0.073 g/cm²/yr and 0.16–0.29 cm/yr, respectively. Only in core BB-1 does the shape of the decay profile — an increase in slope at a depth of 25 cm — suggest that there may have been a change (increase) in the rate of sediment accumulation through time (Figure 8). The CIC ²¹⁰Pb age model for BB-1 suggests an age date of ca. 1910 for 25 cm, and the change in slope is consistent with a twofold increase in the rate of accumulation. Regardless, only the whole-core averaged ²¹⁰Pb
accumulation and accretion rates are considered in this report. With the exception of core BB-2, the $^{210}$Pb CIC and CRS age-depth model curves overlap, suggesting that the rates of sediment accumulation have been more-or-less invariant over the period of interest. We cannot explain the large disparity between the two models for core BB-2 (see Figure 9); the CRS model age-depth relationship gives sediment accumulation rates that are significantly larger than CRS and CIC model rates derived for the other cores.

The shape of the $^{137}$Cs profiles for the cores is broadly consistent with the record of $^{137}$Cs atmospheric fallout in U.S. Mid-Atlantic (Olsen et al., 1981) (Figure 8). Activities of $^{137}$Cs increase upcore from the depth of first occurrence (15–25 cm) to a peak centered at 8–15 cm, above which activities decrease to levels just above the minimum detectable activity toward the core top. There is some evidence for "tailing" at the base of the profiles, a form of post-depositional mixing whereby $^{137}$Cs activity is mixed downward by the roots of marsh grass (DeLaune et al., 1978). Downward mixing of $^{137}$Cs can also arise from chemical diffusion of dissolved-phase $^{137}$Cs in porewaters of aquatic sediments (Smith and Comans, 1996). In either case, downward post-depositional migration of $^{137}$Cs can give a false impression of the onset year-depth of $^{137}$Cs deposition in the marsh. However, it has little effect on the position of the $^{137}$Cs activity peak and thus age-depth relations based on the position of the peak.

Mass accumulation and accretion rates calculated from the $^{137}$Cs activity peak (0.048–0.084 g/cm$^2$/yr; 0.16–0.30 cm/yr) are nearly identical to rates computed using the $^{210}$Pb CIC model (Table 4). This level of concordance suggests further that sediment accumulation rates at the marsh sites have not changed measurably after ca. 1954, and it lends further support to the CIC model over the CRS model. Based on this result, and given that $^{210}$Pb provides a longer history of sediment accumulation than $^{137}$Cs, the $^{210}$Pb CIC accretion rates presented in Table 4 were used to convert sediment depth to age for the nutrient-eutrophication histories described later. These age estimates are a key output of this project as they allow us to place the nutrient data into a historical context.

C1.3: Radionuclide Inventories and Focusing Factors

Sediment inventories of excess $^{210}$Pb and $^{137}$Cs were computed to compare the relative amount of radionuclide deposited among the coring sites as a proxy for particle-reactive chemical species in general. Reference inventories of 27.7 dpm/cm$^2$ for $^{210}$Pb and 21 dpm/cm$^2$
for $^{137}$Cs have been determined previously from direct measurements of atmospheric deposition in the U.S. Mid-Atlantic region (Olsen et al. 1985; Graustein and Turekian, 1986). These reference values represent the total amount of radionuclide that could be buried at a site if supplied by atmospheric deposition alone and not subjected to "focusing." Radionuclide focusing is the process by which radionuclides are buried at dissimilar amounts in an environment as a consequence of 1) sediment focusing and 2) boundary scavenging. Sediment focusing refers to preferential transport of fine-grained sediments and adsorbed radionuclide from non-depositional or erosional areas to depositional sites, and it moderates radionuclide inventories through the sediment accumulation rate (Sharma et al., 1987). Boundary scavenging involves repeated resuspension at a location, adsorption of dissolved-phase radionuclide, and redeposition, and it affects radionuclide inventories by modifying the initial activity of the radionuclide ($A_o$ in Eq. 3). In sediment-rich estuarine marshes, sediment focusing is more frequently involved in radionuclide focusing because sediment supplied tidally to the marsh platform carries adsorbed $^{210}$Pb.

Focusing factors for the four marsh sites were calculated by dividing the measured $^{210}$Pb and $^{137}$Cs inventories by the reference inventories. A focusing factor greater than unity implies that atmospherically derived radionuclide has been focused by some combination of sediment focusing or boundary scavenging. In the case of $^{210}$Pb, tidal flooding supplies particle-bound $^{210}$Pb to the marsh platform in addition to that delivered directly by local atmospheric deposition alone. $^{137}$Cs can be similarly focused, but unlike $^{210}$Pb its affinity for suspended particles in brackish and saline waters is limited by competition with cations for sorption sites on suspended particles (Zucker et al., 1984).

Radionuclide inventories and focusing factors for the coring sites are presented in Table 4. Excess $^{210}$Pb inventories range from 22.9 to 62.5 dpm/cm$^2$, which are equivalent to focusing factors of 0.83 and 2.3. At sites BB-1 and BB-2 the focusing factors are close to unity, suggesting that marsh inventory of excess $^{210}$Pb can be supported by the local atmospheric flux alone. However, at sites BB-3 and BB-4 the focusing factors (>1) suggest that other sources of $^{210}$Pb contribute to the inventory probably by sediment focusing or boundary scavenging in waters adjacent to the marsh. Regression analysis suggests that the initial activity of excess $^{210}$Pb deposited on the marsh surface has a stronger influence on the sediment inventories than variations in mass accumulation rate (Figure 12). In other words, boundary scavenging in
Barnegat Bay waters appears to have a greater influence on radionuclide inventories in the marsh than sediment focusing from far-field sources. This interpretation is consistent with physical environment of Barnegat Bay, i.e., a well-mixed, lagoon-type estuary with a limited supply of allochthonous mineral sediment for accumulation in fringing marshes.

Sediment inventories of $^{137}$Cs range from 5.8 to 10.9 dpm/cm$^2$, less than half the reference inventory of 21 dpm/cm$^2$. These low inventories most likely reflect physiochemical factors that limit $^{137}$Cs uptake by particles in brackish and saline waters in general. For this reason $^{137}$Cs activity is unlikely to be focused in the same manner as a more particle-reactive radionuclide such as $^{210}$Pb.

C2: Nutrients/Eutrophication
C2.1: Sediment Organic Carbon, Total Sediment Nitrogen and Total Sediment Phosphorus

Sediment organic carbon (SOC) concentrations for the four cores ranged from 3.2% to 33.7% on a dry weight basis (dw) with an average of 15.7 ± 7.8% SOC (± 1σ); Tables 5-8; Figure 13). Similarly, total nitrogen (TN) ranged from 0.23 to 1.4% N with an overall average of 0.79 ± 0.34%; whereas total sediment phosphorus (TSP) ranged from 0.019 to 0.39% TSP with an overall average of 0.071±0.050%. These concentrations are generally higher than those found in tidal wetlands (salt and freshwater) in the Delaware River and Bay (Velinsky and Sommerfield, unpublished data; Velinsky et al., 2007, 2010abc)

Sediment total nitrogen concentrations were generally highest in the upper section of the cores from sites BB-1, BB-2 and BB-3 (Figure 13). In these cores, below 20 to 30 cm, concentrations remained fairly constant (e.g., BB-4) or were somewhat variable (e.g., BB-1, and BB-2). At BB-3, located in the discharge canal of the power plant, concentrations ranged from 0.27 to 1.2% and were variable with depth. A similar distribution was observed for SOC in all cores except for BB-3 (Figure 13). SOC concentrations were highest in the surface sections of cores, BB-1, BB-2, and BB-4 (up to 28%) decreasing to lower concentrations by approximately 20 cm. In BB-1 and BB-2, there were some slight variations at depth while in BB-3, concentrations generally increased with depth from 15% at the surface to about 30% at 40 cm. As with C and N, total sediment P (TSP) concentrations decreased slightly with depth in all cores (Figure 13). In BB-4, there was a sub-surface maximum at 2-4 cm (0.39%) decreasing to near constant concentrations by 6-8 cm.
The carbon to nitrogen ratio (C/N; atomic units) can be used as a tracer of the source of organic matter to a location and potential diagenetic changes that could occur during burial (Marinucci, 1982; Jasper and Gagosian, 1990; Meyers, 1994; Prahl et al., 1994). Diagenesis is any chemical, physical, or biological change undergone by sediment after its initial deposition (Berner, 1980; Burdige, 2006). In addition, sources such as terrestrial organic matter versus aquatic organic matter can be distinguished. For example, terrestrial material (e.g., trees) are rich in cellulose (i.e., higher C) compared to algae or marsh plants that have less structural material and are higher in proteins (i.e., higher N). Typical marine plants have C to N ratios of ~ 4-10 whereas terrestrial material can have C to N values > 15-20. Diagenesis of recent sediments tends to increase the C to N ratio due to preferential remineralization and release of nitrogen compounds; however, re-incorporation of bacterially-derived N can increase the C to N ratio over time (Fogel et al., 1989; Benner et al; 1991). Marinucci (1982) showed that live *Spartina alterniflora* had C/N values of approximately 25-28 from low and high marshes increasing during initial decomposition than decreasing due to re-incorporation of microbial N. Quirk (unpublished data) measured live *Spartina alterniflora* and *S. patens* leaves and they had C/N values ranging from 24 to 35 (n=4) for marshes in Little Assawoman Creek (DE) with higher values for various root fragments.

In Barnegat Bay, the C to N ratio (atomic) of the marsh sediment ranged from 14 in the bottom sections of BB-4 to 41 in the upper section of BB-2 (*Figure 13*). In core BB-1 the C/N at the surface was 17 increasing to approximately 22 to 28 (24±4), similarly, in BB-4 the C/N was approximately 16.8 in the surface 6 cm increasing slightly to 22 then decreasing to between 14 and 20 (16±2) below 18 cm. In BB-2, the sediment C/N value at the surface was 22, increasing to 42 at 10-12 cm then decreasing to between 22 and 32 (25±3.6) below 12-14 cm. The core from BB-3 had a surface C/N value of 18 increasing with depth through the core to a maximum of 38 at 42-44 cm. In general, the C/N values increased slightly with depth within the root zone of each site then decreased slightly with depth (except for BB-3). The values overall suggest a mixture of *Spartina*-derived organic matter with some additional algal organic matter.

### C2.2: Stable Isotopes of Carbon and Nitrogen

Organic carbon and nitrogen isotopic ratios are useful for distinguishing between marine and continental plant sources of sedimentary organic matter, processing and cycling of nutrients and,
in some instances, the level of system-wide productivity (Fry, 2006 and others). Most photosynthetic plants incorporate carbon into organic matter using the C3 Calvin pathway, which biochemically discriminates against $^{13}$C to produce a $\delta^{13}$C shift of about -20\% to -30\% from the isotope ratio of the inorganic carbon source. C4 plants (e.g., corn, *Spartina*) incorporate CO$_2$ using a different system (PEP) that discriminates against $^{13}$C to produce a $\delta^{13}$C shift of about -8\% to -15\% from the isotope ratio of the inorganic carbon source. Organic matter produced from atmospheric CO$_2$ ($\delta^{13}$C ~ -7\%) by land plants and typical tidal freshwater wetland plants, using the C3 pathway consequently has an average $\delta^{13}$C (PDB) value of about -27\% (O'Leary, 1988), although aquatic wetlands plants can have a large range (see Chmra and Aharon, 1995; Malamud-Roam and Ingram, 2001). In addition, the marsh plant *Juncus roemarianus* is a C3 plant and is reported to have $\delta^{13}$C ranging from -23 to 26\% (Haines, 1976; Hughes and Sherr, 1983; Chmra and Aharon, 1995; Goñi and Thomas, 2000). The source of inorganic carbon for marine algae (C3 plants) is dissolved bicarbonate, which has a $\delta^{13}$C value of about 0\%. Marine organic matter consequently has $\delta^{13}$C values between -20\% and -22\%. The isotopic difference between organic carbon produced by C3 and C4 land plants and marine algae has been used to trace the delivery and distribution of organic matter to sediments in estuarine and coastal areas (Cifuentes et al., 1988; Fogel et al. 1992, Middleburg et al., 1997; Gebrehiwet et al., 2008 and many others).

Carbon isotope ratios can be affected by photosynthetic dynamics and by post-depositional diagenesis (Dean et al., 1986; Fogel et al., 1992; Canuel et al., 1995; Zimmerman and Canuel, 2002), thus isotope data must be interpreted cautiously. A big factor that can impact $\delta^{13}$C values of plant material is the availability of CO$_2$ and rate of production during photosynthesis and the possibility of selective diagenesis of organic matter fractions that are isotopically heavy or light. Although the change in $\delta^{13}$C appears to be small (<2\%) during recent diagenesis (Hayes et al., 1989; Meyers, 1994), shifts due to the availability and rate of production, due to nutrient enrichment or limitation and other factors, can impact on the resultant $\delta^{13}$C values of deposited organic matter (Ember et al., 1987; Fogel et al., 1992; Schelske and Hodell, 1995; Church et al., 2006).

Differences exist between the natural abundances of stable nitrogen isotopes ($\delta^{15}$N, $^{15}$N/$^{14}$N) in dissolved and particulate matter from terrestrial, estuarine, marine, and anthropogenic sources
(Kendall, 1998 and others). Terrestrial-occurring soil nitrogen can have a wide range of values, but in general range from -1 to +4‰, similar to atmospheric nitrogen (0‰). Nitrogen isotopic compositions from marine sources tend to be slightly enriched in the heaver isotope (15N) and are very dependent on the source of dissolved nitrogen and its δ15N, and processing in the system (e.g., ammonification, nitrification, denitrification, etc) at the time of formation. A dominant process in many aquatic environments (and groundwater) is denitrification (Cline and Kaplan, 1975). Denitrification is a microbially-facilitated process of dissimilatory nitrate reduction that ultimately produces molecular nitrogen (N2) through a series of intermediate gaseous nitrogen oxide products. This microbial process uses dissolved nitrate during oxidation of organic matter and as nitrate is consumed there is an enrichment of residual nitrate in the system. Algal/plant production and its δ15N from nitrate would reflect the balance between processes and inputs. There are many points in which nitrogen can be fractionated and its isotopic composition altered. For example, wastewater from treatment facilities has been shown to increase the δ15N of various fish species (Lake et al., 2001) due to the selective removal of the light isotope (14N) nitrogen during treatment. Anthropogenic nitrogen was substantially enriched in watersheds with greater amount of urbanization and wastewater inputs and the nitrogen was shown to be incorporated into the aquatic food web (McCelland et al., 1997).

The isotopic compositions of sediment C and N exhibited interesting changes within each core (Figure 14). The carbon isotopic composition of the sediment ranged from -27 to -13‰ (δ13C average of -18.2±4.5‰). Surface values were similar (~-18.5 to -16‰) and then increased slightly to approximately -14 to -16‰ within the root zone of cores BB-1, BB-2 and BB-4. In core BB-3, located in the discharge canal from the power plant, the δ13C below the root zone decreased to -26.5±0.6‰ from below to the bottom at 44-46 cm. Below the root zone in core BB-1, which is downbay from the Mantoloking Bridge, the δ13C became substantially lighter (more negative) to -22‰ then increased to -15‰ centered around 42-44 cm. Below this depth interval, the δ13C decreased again to approximately -24‰. At BB-2 and BB-4, the δ13C remained fairly constant with depth with only slight variations.

The δ15N of the sediment increased towards the surface to varying degrees in all cores except BB-4 in which the sediment became more enriched in the lighter isotope (Figure 14). The maximum δ15N ranged from 2.7 to 3.1‰ for BB-1, BB-2 and BB-3, while minimum δ15N
values ranged from -0.4 to ~0‰. The δ¹⁵N started to increase between 20 and 30 cm towards the surface and was most pronounced in cores BB-1 and BB-3. In core BB-4, taken near West Creek in the southern part of the Bay, the δ¹⁵N increased with depth from approximately 1.6 to 1.8‰ at the surface to 3.7‰ at the base of the core.

In summary, the carbon isotopic signatures from the cores are indicative of a Spartina-dominated system. *Spartina* is a C4 plant in which the organic carbon produced would have carbon signatures generally around -12 to -14‰ (Long et al., 1975). The decrease with depth in δ¹³C of organic carbon below the surface, especially noted in BB-1 and to a lesser extent BB-2, may be due to decomposition of isotopically heavier polysaccharides which are preferentially degraded first (Benner et al., 1991). Downcore changes in BB-3 may be due to habitat changes due to the nuclear facility construction and the building of the canal. Changes in the δ¹⁵N of organic matter reflect potential changes in the source of N to the Bay. In BB1, BB2 and BB3 the δ¹⁵N increased starting around 30 cm towards the surface, while in BB-4 the δ¹⁵N decreased. It is not clear as to the cause for this decreased in δ¹⁵N, but it may be due to changes in the cycling and source of organic matter to this part of Barnegat Bay. Cores obtained from farther downstream may help in this analysis. The relationship between time and the changes in the carbon and nitrogen stable isotopes is presented below.

**C2.3: Diatom Analysis and Assemblages**

Diatoms are microscopic, photosynthetic algae with a siliceous structure. They contain yellow-brown pigments and therefore are also referred to as golden algae. Comprising one of the most common types of algae, they are found in a diverse range of environments from freshwater to marine. Diatom species are differentiated by their shape and characteristics of their siliceous structure. The main forms are centric (i.e., circular, radial symmetry), and pennate (i.e., having bilateral symmetry). They exhibit two main living modes in the environment: planktonic and benthic (i.e., living on or in the bottom substrate).

Diatoms are one of the most powerful water quality indicators; they colonize virtually every aquatic microhabitat and many diatom species have very strict ecological requirements, with well-defined optima and tolerances for environmental variables such as pH, nutrient concentration, salinity, water transparency and physical habitat. Because of their strong relationships with environmental conditions, diatoms are used to derive inference models for
many environmental factors. The inference models are developed using calibration sets of both diatoms and measured environmental variables for specific geographic regions. To produce robust quantitative models, the calibration sets require at least 30 sampling sites that maximize the gradient length covered by the variable of interest (e.g., phosphorus concentration, pH, etc.). These models can then be used to infer environmental parameters of interest, and have been used successfully to reconstruct reference conditions and assess the impact of anthropogenic activities on aquatic systems (e.g., Cooper et al., 1993; 1995; Bennion et al., 2001).

Diatom assemblages have been shown to be important indicators of nutrient concentration within freshwater and marine environments (Janousek, 2009; Sullivan, 1975; Sullivan and Currin, 2000). Due to the fact the diatoms respond quickly and directly to nutrients, they have been used for many years as indicators of nutrient changes in aquatic systems (Potapova et al., 2004; Potapova and Charles, 2007; Ponader et al., 2008). Diatom diversities in sediment cores from marine aquatic systems have been used to evaluate nutrient and land use changes over time (Cooper et al., 1993; 1995; Bennion et al., 2001; Janousek, 2009; Sullivan, 1975; Sullivan and Currin, 2000; Velinsky et al., 2010abc). In this study we take a first approach using diatom metrics calculated using species-ecological models developed by van Dam et al. (1994). While this data set is mostly based on freshwater species it does contain some marine diatoms. It provides ecological information for both diatoms and water characteristics that is not currently available for Barnegat Bay and has been used for recent studies in other marshes by this research group (Velinsky, et al., 2010abc).

Fifty-one sections were analyzed for diatom composition from four Barnegat Bay cores (BB-1, BB-2, BB-3, and BB-4). At least 400 valves were counted for each sample and over 300 taxa (Appendix I) were identified in these samples, allowing a robust analysis for nutrient and ecological conditions. The distribution of key diatom species (those occurring with more than 5% relative abundance) in each of the cores is presented in Figures 15-18. Brief descriptions of the species’ stratigraphic distribution and major shifts in diatom assemblages are provided below for each core.

**Core BB-1:** 145 freshwater and coastal-brackish benthic diatom species were identified in 11 sections from core BB-1, of which 17 species occurred with abundances > 5% in at least 1 sample. The most abundant species were: *Staurosira construens* var. *venter* (maximum relative abundance 17%), *Stauroforma exiguiformis* (17%), *Denticula subtilis* (17%), *Planothidium*
frequentissimum (15%), Luticola mutica (15%) and Pseudostaurosira brevistriata (14%). Four zones of diatom assemblages were identified: Zone 1 (1783-1886), is represented by a very diverse assemblage at the core bottom (52-54 cm) with mostly high nutrient freshwater taxa (Nitzschia vasta, Diploneis parma, and Planothidium frequentissimum), but also including a small number of brackish benthic species and some undescribed Navicula species; Zone 2 (1886 – 1937), between 16 and 30-cm core depth, where species diversity declined sharply. Within this zone, Navicula sp. 1 MUR DME, along with the freshwater benthic species Staurosira construens var. venter, Pseudostaurosira brevistriata and Stauroforma exiguiformis, became dominant. Denticula subtilis and Ctenophora pulchella (coastal brackish species), Nitzschia nana (brackish, but also an indicator of freshwater intermittently dry and wet), and Cocconeis placentula (an indicator of macrophyte growth) occurred with low abundances within this zone. In Zone 3 (1937-1988), between 6 and 16-cm depth, Denticula subtilis, a brackish coastal species that is also abundant in water waste flow, and Luticola mutica, an aerophilic species, reached maximum relative abundances (17% and 15%, respectively). Other species occurring within this zone were Planothidium frequentissimum, Nitzschia spp. and Navicula perminuta, indicating high nutrient freshwater or brackish conditions. Stauroforma exiguiformis, a freshwater, circumneutral to slightly acidic species, abruptly decreased within this zone. Zone 4 (1988 – 2009) spans the top 0 to 6-cm of the core and is represented mostly by freshwater high nutrient benthic species; Luticola mutica disappeared and Denticula subtilis declined. Within this zone, Planothidium frequentissimum reached its maximum relative abundance (15%) and Staurosira construens var. venter, Pseudostaurosira brevistriata and Nitzschia microcephala were present in high abundances. Navicula sp. 1 MUR DME, the undescribed species that occurred with sustained relative abundances within the previous three zones, declined within this zone (Figure 15).

Core BB-2: 172 species were identified in 11 sections from this core with 21 species present at > 5% relative abundance in at least 1 sample. The most abundant species were: Luticola mutica (maximum relative abundance 35%), Melosira nummuloides (32%), Navicula sp. 1 MUR DME, Denticula subtilis (19%), Diploneis smithii (17%) and Planothidium frequentissimum (16%) (Figure 16). Three zones were identified in this core. In Zone 1 (1721-1963), between 6 cm depth and core bottom, diatoms were highly diverse with cosmopolitan brackish marine or high
electrolytic freshwater species (e.g., *Navicula cincta, N. phylepta, N. digitoradiata*), species common in salt marshes (e.g., *Tryblionella debilis*), or marine sediments (e.g., *Paralia sulcata*). *Navicula cincta*, considered a pollution-tolerant species, reached its highest abundance at 14-16 cm depth (early 1900s). Zone 2 (1963-19890, between 2-6 cm, retained some of the species common in Zone 1, but species diversity decreased sharply. *Melosira nummuloides*, an epiphytic/planktonic marine species, became very abundant between 4 and 6-cm core depth. *Luticola mutica* occurred in high abundance within this zone. In Zone 3 (1989-2009), at the top of the core, most of the species present in previous zones declined or disappeared, while the freshwater *Planothidium frequentissimum* and the coastal-marine, pollution-tolerant *Denticula subtilis* reached their highest abundances in the stratigraphic record.

**Core BB-3:** In this core, 181 species were identified, of which 21 species were present with relative abundances > 5%. The most abundant species occurring in this core were: *Denticula subtilis* (30%), *Pseudostaurosira subsalina* (29%), *Cosmioneis pusilla* and *Nitzschia bacillum* (24%), *Fragilaria zeilleri* var. *elliptica* (20%) and *Pinnularia divergentissima* (19%). Diatom assemblages displayed three main changes in species composition that defined four zones. Zone 1 (1854-1903) was the core bottom (44-46 cm) and was represented by highly abundant freshwater benthic (*Pinnularia divergentissima, Cosmioneis pusilla*) and planktonic (*Aulacoseira crassipunctata, A. spp.*) species. In Zone 2 (1903-1937), between 20-32 cm, a major shift in species composition took place at 32-cm depth. The planktonic *Aulacoseira* spp. and benthic *P. divergentissima* were replaced by benthic species indicative of low (*Frustulia saxonica*) to medium electrolyte (*Rhopalodia acuminata, Caloneis silicula*), slightly acidic freshwater or brackish waters (*Diploneis smithii, Fragilaria zeilleri* var. *elliptica*). Zone 3 (1937-1992), between 4-18 cm depth was mainly characterized by sustained abundances of *Pseudostaurosira subsalina* and the decline or disappearance of freshwater species from previous zones. Two subzones, 3a and 3b were separated at 12-cm depth (1965) by an approximately 2x increase in *P. subsalina* relative abundance and a peak in *Nitzschia nana*, which seems to indicate an environment with high osmotic oscillations or increased salinity. Zone 4 (1992-2009), the top 4 cm of the core, was defined by the appearance of *Nitzschia bacillum* and high abundances of *Denticula subtilis, Planothidium frequentissimum, Nitzschia frustulum* and *Navicula salinicola*, indicating high nutrient or polluted environment.
Core BB-4: In this core, 138 species were identified, 22 occurring with abundances > 5% in at least 1 sample. Species occurring in highest abundances were: *Navicula* sp. 7 BB DME (45%), *Navicula* sp. 3 BB DME (30%), *Denticula subtilis* (27%) and *Navicula* sp. 1 MUR DME (26%). Many other species are present throughout the core with lower relative abundances (e.g., *Planothidium delicatum, Navicula phyllepta, N. perminuta*). Important shifts in relative abundances of species defined two zones. Zone 1 (1800-1903), the lower part of the core between 34 and 70 cm, was characterized by high abundances of *Denticula subtilis*, a brackish coastal species that can also be abundant in waste water flow. Other species occurring within this zone are also characteristic of brackish or electrolyte rich freshwaters (*Navicula perminuta, N. phyllepta*) and tidal flats, salt marshes or polluted sites (*Navicula digitoradiata, N. cineta*). Above 34 cm, in Zone 2 (1903-2009), *Navicula* sp. 1 MUR DME appeared with high, but fluctuating, abundances up to the top of the core. Other undescribed species were also very abundant within this zone: *Navicula* sp. 7 BB DME at 20-22 and 12-14-cm depth, and *Navicula* sp. 3 BB DME above 10-cm core depth. Other species identified within this zone suggest a brackish coastal or average to high electrolyte content waters (*N. microdigitoradiata, F. pygmaea, N. salinicola*). Many undescribed *Navicula* species were present in high abundances in this core, and their autecology is impossible to establish at this time (Figure 18). It is possible that these species, or some of them, characterize undisturbed or less impacted environments, such as the southern rural or semi-rural part of Barnegat Bay.

Diatom assemblages identified in the four cores collected from Barnegat Bay wetlands varied in species composition, but they are all characterized by sharp historical changes. The shifts in diatom species composition varied across sites, with greatest changes in the northern and slightest in the southern part (core BB-4). One major change took place at the end of the 19th (core BB-1) or beginning of 20th century (cores BB-3 and BB-4). This change is marked by a shift from mixed freshwater/brackish to freshwater species (core BB-1) or from high energy, turbulent, to shallower and slightly acidic freshwater species in BB-3 or appearance of abundant, unknown *Navicula* species in core BB-4.

A second major shift in diatom species took place in 1937 in cores BB-1 and BB-3. In core BB-1, diatoms displayed a decline in freshwater species, replaced by brackish or aerophilic species. This change appears to be triggered by the construction of the Point Pleasant Canal,
which opened between 1926 and 1931, and continued, with expansion of residential development in the area. In core BB-3, the 1937 change is marked by disappearance of the brackish *Fragilaria zeilleri* var. *elliptica* and the system became dominated almost exclusively by freshwater species.

The next major shift took place in core BB-3 in 1965 with the loss of freshwater, slightly acidic species (e.g., *Frustulia saxonica*, *F. krammeri*, *F. vulgaris*) and replacement with abundant brackish *Pseudostaurosira subsalina*. Similar to core BB1, this change appears to be induced by the construction of the Forked River canal, prior to the construction of the Oyster Creek Nuclear Generating Station (OCNGS). The observed change induced by canal construction in types of diatoms in these two cores is consistent with previous observations by Kennish et al. (1984) who mention original low salinity, slightly acidic habitats, similar to low flow streams in the New Jersey Pine Barrens. The authors also found that after the construction of the intake and discharge canals of the OCNGS, the environment became brackish, similar to the Bay. Intensive studies were also conducted in the area to assess the impact of the OCNGS, which induced changes in bathymetry, bottom composition and water quality and flow in Oyster Creek. Loss of diversity and phytoplankton biomass were found in Oyster Creek in comparison to other areas of the Bay (Mountford 1971; Hein 1977) and these findings are consistent with the observed loss of diversity in diatom species, replaced by *P. subsalina* dominant, a type of diatom assemblage unique to core BB-3. However, no pollution-tolerant or nuisance species were recorded by the authors at that time.

In core BB-2, the most important change in diatom species took place in 1963 and is marked by a drastic loss of species diversity. This change appears to be related to the rapid growth in residential development and related activities taking place in this area. The rapid population growth induced an increase in discharge of domestic sewage and non-point source runoff, causing loss in wetland habitat, which was likely responsible for the loss in diatom species diversity, as well. Abundant brackish (*Melosira nummuloides*) and aerophilic (*Luticola mutica*) species suggest important changes in water quality, which may be related to extensive use of freshwater for residential purposes with concomitant lowering of water tables and saline water infiltration.

A final change that took place recently (late 1980s or early 1990s) was identified in all study cores except BB-4, and is represented by a shift to more pollution-tolerant species (e.g.,
Denticula subtilis, Nitzschia inconspicua, Planothidium frequentissimum). This change is notably pronounced in core BB-3 and may indicate cumulative effects from the OCNGS, or for all other sites, combined effects from residential development, commercial and recreational activities, and impacts from recent climate change. The recent change in diatom composition is also contemporaneous with the observed brown-tide events in Barnegat Bay over the last two decades. Diatom species Skeletonema costatum, Thalassiosira pseudonana and Prorocentrum spp. were found coincidental with these events (Olsen and Mahoney, 2001). Unfortunately, these marine planktonic species were not found or were very rare in the study cores, thus making it difficult to establish a clear relationship to the brown-tide events.

The samples collected in the Barnegat Bay wetlands span a range of marine-brackish to freshwater diatom species, making detailed analysis complex. To extract the ecological information contained in the diatom data identified in this region, various trophic state metrics were calculated (van Dam et al., 1994; USGS NAWQA; Hall and Smol, 1999). These metrics are often used to assess freshwater rivers and streams in the U.S. All of these metrics have strengths and weaknesses that vary with the quality of the ecological information available for the taxa found in each of the cores. Because most marine or brackish species present in the Barnegat Bay region do not occur in van Dam et al. (1994) data sets, metric calculations were based mostly upon the freshwater species occurring in these cores. The van Dam et al. (1994) summary and synthesis of ecological characteristics of taxa is based primarily on samples from Western Europe, and generally include taxa with wide geographic distributions. The van Dam et al. (1994) autecological values for many taxa have been revised to be more relevant for the U.S., and are contained in a data compilation developed for the USGS National Water Quality Assessment (NAWQA) program by Porter (2008) and Porter et al. (2008).

The van Dam et al. (1994) diatom metrics showed an abrupt increase in the proportion of eutrophentic (i.e., high nutrient species) in cores BB-1, BB-2, and meso-eutrophic species in BB-3, above approximately 20 cm, respectively (Figure 19; Tables 9-12). Below this depth range, meso-eutrophic species were present in BB-1 and oligotrophic in BB-3. In BB-2, the proportion of eutrophic species was usually higher than the other categories; however, it was lower in the mid and upper sections. In these intervals, mesotrophic and meso-eutrophic species were also present, while oligotrophic species were absent or very rare. Core BB-4 had a high number of undescribed species with unknown ecological preferences (85-95%), and the calculated trophic
indices are not as reliable. However, it is clear that in this core, situated in the southern part of the study area, diatom assemblages displayed fewer changes in species composition since the early 1900s, in comparison to the northern, more populated sites, suggesting a less impacted location. Only with a detailed calibration (diatom-nutrient) would this assessment be stronger (see Recommendation Section below).

C3: **Historical Analysis**

A major focus of this study was to determine the changes in the loadings of nitrogen and phosphorus over time within the Barnegat Bay system. These changes are thought to have occurred in the early to mid 1960s due to population increases, fertilizer increase usage and inputs from wastewater treatment facilities. In the mid to late 1970s, the point source discharges were re-directed offshore of the barrier islands by suburban development and fertilizer usage increased substantially. For example, Hunchak-Kariouk and Nicholson (2001) showed that sub-watersheds with higher levels of urban development had higher concentrations of dissolved nitrate+nitrite in export to the Bay. In addition, an objective was to determine if there was any indicator of an ecosystem change (e.g., change in plant flora, oxygen dynamics, marsh production, etc.) as a result of the nutrient changes. Lastly, we wanted to determine if the marshes along the tidal river are a sink for N and P via sediment burial and how this relates to other inputs.

It is important to recognize that both nitrogen and phosphorus can undergo substantial biogeochemical processing and diagenetic changes during burial (Figure 1; see for example Berner, 1980; Howes et al., 1984; Hopkinson and Schubauer, 1984; Hines et al., 1989; Koretsky et al., 2008 and many others). In brief, inorganic forms of N and P are taken up by marsh plants, phytoplankton and benthic algae and incorporated into marsh sediments. During burial, microbial activity (both oxic and anoxic) can release organic nitrogen and phosphorus into the porewaters of the sediments which can then move back into the overlying waters via advection and diffusion processes. A major sink or loss reaction for nitrogen is denitrification which converts oxidized nitrogen to nitrogen gas which is then removed from the system. These nutrients, along with externally introduced nutrients, are then transported to the Bay or taken up again during photosynthesis. This recycling of nutrients in a marsh is a major process that impacts overall marsh/estuarine productivity and transport to coastal areas. In this regard,
depending on the environment and specific characteristics, such as the magnitude of nutrient loadings, sedimentation rates, oxic/anoxic conditions, it may or may not be possible to measure changes in nitrogen or phosphorus accumulation rates that reflect inputs from external sources such as with chemicals that do not undergo significant biogeochemical reactions (e.g., PCBs, Pb, Zn, etc).

C3.1. Changes in Nutrients Concentrations in Barnegat Bay Cores with Time

In Barnegat Bay, total nitrogen in sediments over time varied among core locations (Figure 20). At the upper coring site (BB-1), TN concentrations gradually increased from ~ 0.8%N starting in 1920s reaching maximum concentrations starting around 1990 with levels between 1.38 and 1.41%N. Similarly, in BB-2 TN concentrations started to increase in the 1910s to highest levels in the 1980s and early 1990s. Similarly, at BB-4, concentrations of TN increased slightly in the first half of the 20th century and then increased in the mid-1960s to higher concentrations by 2000. At BB-3, concentrations of TN showed a slight bi-modal distribution over time with concentrations slightly lower in the early 1900s and early 1990s and higher concentrations in the late 1800s and mid-1900s. It is unclear as to why the profile at BB-3 was different than the other locations; however, the stable isotopes of carbon suggest that this site may not have been a tidal marsh until extensive reworking of the landscape for the construction of the nuclear power plant at Oyster Creek (see below).

The stable isotopes of sediment nitrogen may give some indication as to changes in the source of nitrogen and biogeochemical cycling within the Bay. Ulseth and Hershey (2005), Leavitt et al. (2006) and Velinsky (unpublished data) show that higher $\delta^{15}N$ of the nitrogen is associated with higher inputs from urban sources and waste water. Bratton et al. (2003) showed similar trends in cores from the Chesapeake Bay. Similarly, Elliot and Brush (2006) showed a correlation between the $\delta^{15}N$ of tidal wetland core sediments and estimates of nitrogen wastewater loadings over time. Lastly, in Woodbury Creek and Oldmans Creek marshes in New Jersey, an increase in $\delta^{15}N$ observed in sediment cores was attributed to both increased nitrogen loading and changes in the way nitrogen is processed in wastewater treatment plants (Church et al., 2006). However, in the Murderkill River marshes within Delaware Bay, there was a pronounced increase in the $\delta^{15}N$ of the sediment nitrogen in dated sediment cores (Velinsky et al., 2010abc). The increase in the $\delta^{15}N$, from < 1 ‰ to between 3 and 10 ‰ at the surface,
started in the 1950s and were not directly related to the introduction of waste water from a large facility constructed in the mid-1970s. Down core variations of $\delta^{15}N$ are somewhat difficult to interpret given the number of biogeochemical processes influencing nitrogen and variations of sources over time. In the Barnegat system, starting in the early 1900s, there was a general increase in the $\delta^{15}N$ of sediment N. This was evident in the three upbay cores (BB-1, BB-2 and BB-3) with highest $\delta^{15}N$ of 2.7 to 3.9‰. At the downstream site, BB-4, even as the TN increased over time, the $\delta^{15}N$ decreased throughout the core (from ~4‰ to ~2‰ at present). It is unclear as to why this trend is occurring but this site is less influenced from terrestrial sources as the major rivers into the Bay are located farther upstream above Toms River.

Concentrations of total sediment phosphorus (TSP) changed slightly over time at all coring locations to some degree (Figure 21). At BB-1, concentrations of TSP exhibited a gradual increase over time reaching a peak concentration of 0.065% P at 1978. Concentrations then decreased slightly and increased again at the surface to 0.11% P. At the two mid-bay sites (BB-2 and BB-3) and downbay site (BB-4) there was a less gradual increase in TSP concentrations over time with highest concentrations found at or just below the surface of the marsh. There is a large increase in TSP in the late 1990s in BB-4 to some the highest levels measured in all of the sites. In general, concentrations below the surface sections (pre-1990s) were generally similar and averaged 0.060±0.02% P. Overall, in all cores from the bay there was some increase in concentration towards the surface.

Schelske and Hodell (1991; 1995), and Perga and Gerdeaux (2004) have shown a relationship between the concentration of P in the sediments or water column and the isotopic composition of carbon ($\delta^{13}C-OC$) in the sediments or in fish scales over time, respectively. The fish scales were an integrator of the base of the food web (i.e., phytoplankton) and reflect nutrient inputs. Similarly, Church et al. (2006) showed a relationship between sedimentary P and $\delta^{13}C-OC$ in a marsh core from Woodbury Creek, New Jersey. It is thought that as P levels increase, primary productivity increases to a point at which there is reduced isotopic fractionation during enzymatic uptake of dissolved CO$_2$. This reduced fractionation would result in higher isotopic compositions of organic matter (i.e., more $^{13}C$-enriched) and would suggest that P was helping to control aquatic productivity. Therefore, if phosphorus is limiting production, the $\delta^{13}C$ of the organic carbon in a core may reflect a system-wide change in productivity. However, while this relationship was shown in a tidal freshwater marsh.
(Woodbury Creek), it is has not been clearly evident in other tidal marshes within Delaware Bay, suggesting-site specific conditions may be most important (Velinsky, et al., 2010abc). Other factors, such as the relationship between mineral and organic matter deposition within a marsh, organic matter decomposition and inputs of allochthonous material can be significant (Middleburg et al., 1997; Gebrehiwet et al., 2008).

In Barnegat Bay, there was no consistent trend in the \( \delta^{13}C \) of organic carbon with time. This indicates that productivity within the Bay over time cannot be assessed using a \( \delta^{13}C \)-TSP relationship as shown in Great Lake sediments (Schelske and Hodell (1991; 1995) and in Woodbury Creek (Church et al., 2006). It may be that P is controlling overall system productivity (see debate over nitrogen versus phosphorus in marine waters) or site-specific factors (e.g., low sedimentation rates; loading rates of N and P; see Conley et al., 2009) may be a factor. Interestingly, at the upbay site (BB-1), the very lower portion of the core (Figures 14 and 21) exhibited \( \delta^{13}C \) of approximately -25‰ increasing to -15‰ in the early 1800s. As stated earlier, the light \( \delta^{13}C \) (i.e., less \( ^{13}C \), more \( ^{12}C \)) is an indication of C3 plant, algal or terrestrial organic matter inputs as \textit{Spartina} is a C4 plant and has a \( \delta^{13}C \) of \( \sim -12\text{-}14‰ \). Starting around the early 1900s, the \( \delta^{13}C \) shifts back to -15.7±0.5‰ and increases slight at the surface to -19‰. While the timing is different, a somewhat similar profile is evident at BB-3, within the discharge canal of the Oyster Creek Nuclear Facility. The upper portion of the core (> 1980) reflects mostly \textit{Spartina} inputs while before that time period the \( \delta^{13}C \) reflects either terrestrial or algal inputs of organic matter (i.e., low \( \delta^{13}C \)). Historical images from the 1930s (NJ DEP, www.state.nj.us/dep/gis/geowebsplash.htm) indicate that the current coring location was more of an upland site and not a tidal salt marsh. During the construction of the facility (mid-1960s), the creek was re-aligned and the site became a wetland area and now dominated by \textit{Spartina}. At both sites BB-2 and BB-4 the marsh sediment over time reflect major contributions from \textit{Spartina} plants as indicated by the \( \delta^{13}C \) of between -14 to -16‰ on average. There was no relationship between TSP and \( \delta^{13}C \) of the organic carbon, suggesting that phosphorus may not be limiting in this system and that other factors are controlling the \( \delta^{13}C \) of the organic carbon in the sediments. As mentioned above changes in the source of organic matter to the marshes (i.e., terrestrial-upland material versus \textit{in situ}-local production), or that \textit{in situ} marsh processes and plant communities may have changed over time.
C3.2: Nitrogen and Phosphorus Accumulation Rates over Time

Sediment cores can be used to calculate the mass of nitrogen (N) and phosphorus (P) accumulating in the marsh over time (Burdige, 2006; Kahn and Brush, 1994; Hartzell et al., 2010). Using the mass accumulation rate and concentration of nitrogen and phosphorus (% TN and % TSP) in each interval, the N and P accumulation rate (mg N or P/cm²-yr) for each year can be obtained. It should be noted that missing intervals that were not analyzed for N and P were linearly interpolated from the interval concentrations above and below. The accumulation rates can then be applied to estimate of wetland area to provide an estimate of the amount of N and P removed (via burial) by wetland processes. Other removal/transport processes (e.g., denitrification, recycling, sediment movement) would need to be determined to provide a complete N and P cycle of the Bay.

Nitrogen accumulation rates for the four locations presently range from approximately 0.33 to 0.82 mg N/cm²-yr. There was a slight trend of increase accumulation rates with time at some of the locations (Figure 22). It was anticipated that a reduction of the rate would be evident in the period after the point source discharge was re-directed off shore, but this was not evident from the cores, suggesting that other sources continued to increase over time or that the system (i.e., surface waters, ground waters) was discharging substantial levels of nitrogen. In the upbay core, BB-1, the rate doubled from the 1940s to the present (ca. 0.4 to 0.8 mg N/cm²-yr). In the other three cores there was an increase with time, but the increase was less pronounced.

Phosphorus accumulation rates ranged from 0.013 to 0.26 mg P/cm²-yr. In all cores, rates were higher in the surface section of each core (0.04 to 0.16 mg P/cm²-yr; Figure 22). At BB-1 the rate was variable over time (bimodal) with a sub-surface peak around 1975, prior to the P ban in detergents and the re-direction of point sources. The rate then decreased until the late 1990s, but exhibited a higher rate in the surface section. This core, taken in the upbay area, would be exposed to higher nutrient concentrations since the loadings and ambient concentrations are higher in the upper sections of the Bay due to the proximity to the Metedeconk and Toms rivers. At BB-2 the rate was similar over time until recently, while in BB-3 and BB-4 the rate increased to the present. The accumulation rates of both N and P reveal slightly higher rates over time, but these rates must be balanced against diagenesis the potential to remobilize or solubilize bound N and P during initial burial (~ top 0-10 cm).
C3.3: Diatom Changes in Barnegat Bay Sediments

The diatom metrics used to assess eutrophication for each core are plotted against time in Figure 23. It appears that there were two separate trends occurring in the cores from the various sites. At sites BB-1 and BB-2 there was an increase in the index for eutrophic conditions starting in the late 1940s to 1960s. The index then decreased in the late 1980s to the present. At BB-3, the meso/eutrophic index increased substantially in the 1950s (peak at ~ 1975) and then decreased sharply in the late 1980s. The decreases in eutrophentic and meso/eutrophentic species after the 1980s may be an indicator of the changes in nitrogen and phosphorus loadings from various sources, or may indicate combined effects with recent climate change. There was no substantial change in the trophic indices at BB-4 over time, (but see above discussion about undescribed species present in this core). The downbay location may be less impacted compared to the sites (BB-1 and 2) that are influenced by greater freshwater discharge (i.e., Toms and Metedeconk rivers).

To evaluate how nutrient conditions may have impacted the diatom species and metrics in each core, total sediment N and P and N and P accumulation rates were plotted against the metrics for eutrophentic and meso/eutrophentic species (Figures 24-25). The trends for these cores were evaluated as one data set. Both isotope and diatom metrics were log-transformed to meet normality requirements. Statistical analysis was performed using JMP v. 7.0 (SAS Institute Inc.). The strongest relationships were found between eutrophentic diatoms and $\delta^{15}$N ($r^2_{adj} = 0.78, p=0.0004$), OC ($r^2_{adj}=0.35, p=0.03$), and TSP ($r^2_{adj}=0.31, p=0.04$) in core BB1. In this core, both diatom metrics and sediment isotopes seemed to indicate strong impact from land use and population growth, as well as loss of freshwater species related to Point Pleasant Canal construction in 1926. Eutrophentic species from BB-2 were found strongly related to TN ($r^2_{adj}=0.4, p=0.02$). In core BB3, oligotrophentic species displayed significant relationships with OC ($r^2_{adj}=0.7, p=0.0001$), TN ($r^2_{adj}=0.4, p=0.01$) and TSP ($r^2_{adj}=0.3, p=0.03$).

For %TN, there was a significant relationship ($p<0.01$) between percent N in the sediment and the meso/eutrophentic diatom indices and the sum of the eutrophentic ($r^2= 0.17; p<0.002$) and meso/eutrophentic ($r^2 = 0.26; p<0.0002$). However, percent N only explains 17% and 25% of the diatom metrics, respectively, and other factors, such as salinity, temperature, and water depth would be important. In addition, nitrogen accumulation was significantly related to the
meso/eutrophentic index for all cores combined, but explained only 10% of the metric. Only P accumulation rates were (not percent TSP) significantly related to both the eutrophentic (\(r^2 = 0.069; p<0.05\)) and the sum of the eutrophentic+ meso/eutrophentic (\(r^2 = 0.17; p<0.007\)).

The strong relationships found between diatom autecology and sediment stable isotopes suggest important changes in nutrient inputs and biogeochemical processes taking place within the tidal Barnegat Bay through time. Both measured and diatom-inferred nutrients indicate impact from increased residential development starting in the 1950s, which caused an increase in treated and untreated sewage and non-point source runoff (Kennish et al. 2007). Human development is considered the main source of habitat loss, alteration, and pollution in Barnegat Bay and the tidal wetlands (Kennish 2001). The impact on diatom assemblages appears to be greatest in northern sites, which are also characterized by urban and sub-urban land use, versus the rural and semi-rural southern townships.

If Barnegat Bay was found in fair condition in the earlier studies (Kennish 1984) and later moderately eutrophic (Seitzinger and Pilling 1993), the changes displayed by diatom assemblages from tidal wetland cores show that up to now, regulation efforts have not succeeded in restoring this protected area to its original, pre-human settlement condition. Diatom assemblages revealed irreversible shifts in habitat characteristics and water properties consistent with increasing human activities. Unfortunately, the most recent changes in diatom composition and sediment nutrients suggest an increase in water pollution since the 1990s, with potential changes in the source of nutrient loadings, and combined effects from climate change. The diatom-inferred changes in top cores are in agreement with recent findings on organic pollutants in Barnegat Bay (Kennish et al. 2007; Vane et al. 2008).

Importantly, because of the high number of undescribed species found in the study cores, a more comprehensive study of diatom-nutrient relationships needs to be developed for Barnegat Bay and adjacent wetlands to optimize the use of these types of data for future management purposes (e.g., similar approach used by Reavie et al. (2006) for the Great Lakes and adjacent wetlands).

**C3.4 Fate of Nutrients Entering Barnegat Bay: Marsh Burial**

The rate of nitrogen and phosphorus accumulation and burial can be viewed in the context of inputs into Barnegat Bay. These data can help determine the potential for present-day tidal
marshes within Barnegat Bay to provide a service (i.e., ecosystem services) with regard to nutrient removal and to help justify the protection and enhancement of tidal wetlands. Removal or sequestration of nutrients by coastal marshes can be important, and is dependent on many factors including the areal extent of marshes, accretion rate, nutrient inputs and biogeochemical processes. Nutrients taken up by plants and some heterotrophs are removed on a seasonal basis, but these can be remineralized and recycled to the water column (Mitch and Gosselink, 1993). Sediment profiles of nitrogen, phosphorus and carbon reflect many biogeochemical factors, including biological uptake and transformation and physical processes such as advection and diffusion of dissolved nutrients and sediment accretion. Many of these processes are substantially active in the upper sections of a marsh (e.g., root zones; 0-15 cm) and concentrations and accumulation rates in this interval may not reflect longer-term burial. For example, concentrations of both N and P in the surface sections are generally elevated compared to concentrations at depths greater than 10-20 cm. This is due to processes mentioned above as well as changes in nutrient loadings to the Bay. As such, it is necessary to determine an average concentration of N and P in each core in order to account for diagenetic changes as well as loading changes over time. For this, concentrations of N and P were multiplied by the dry sediment density (g/cm³) at each interval and then divided by the total mass of sediment that represents the past 60 years (i.e., 1950 to present). The average concentrations were then used along with the bulk accumulation rate (g/m²-yr) derived from the constant-input-concentration model (CIC) to provide an average accumulation rate for the past 60 years. The depth-integrated rates ranged from 4.5 to 6.0 g N/m²-yr (average = 5.2±0.7 g N/m²-yr) for nitrogen and 0.33 to 1.0 g P/m²-yr (0.51±0.33 g P/m²-yr) for phosphorus, and were slightly lower than those calculated for the surface section (3.3 to 7.6 g N/m²-yr and 0.43 to 1.6 g P/m²-yr; Figure 22).

An estimation of the area of tidal coastal wetlands fringing Barnegat Bay is 26,000 acres (1.1 X 10⁸ m²; Lathrop and Haag, 2007; www.crssa.rutgers.edu/projects/lc/). Using this area and the depth-integrated and core-top rates for N and P accumulation yields current burial rates (gross rates) of 5.5 and 6.5 X 10⁵ kg N/yr, and 0.54 and 0.88 X 10⁵ kg P/yr, respectively (Table 13). Using recent input estimates for nitrogen (Wieben and Baker, 2009) and phosphorus (BBNEP, 2003), coastal tidal marshes in the Bay can potentially sequester 79 to 94% of the nitrogen and 54 to 88% of the phosphorus (Table 13). Using the depth-integrated N and P rates over the past 50 years allows for the burial of 79±11% and 54±34% of the current input rate into the Bay.
Similar burial rates and relative importance of marsh burial were shown by Greene (2005) for the Patuxent River (Maryland) and Velinsky et al. (2010c) for the Murderkill River (Delaware) and Craft (2007) for marshes in coastal Georgia. These calculations show that marsh accumulation can sequester a majority of the P and N loads from the various sources (i.e., point sources and non-point sources). However, sediment recycling of N and P (Berner, 1980; Burdige, 2006) are not accounted for in these estimates and will modify and most likely reduce these estimates (i.e., Burial – Recycling = Net Burial). These estimates provided above show that the marshes as well as subtidal areas (Seitzinger, 1992) have a potential to trap both N and P before being exported to the Bay from the non-tidal watershed and highlight the importance of ecosystem services that marshes provide (i.e., water filtration) and the potential cost of water treatment if marsh areas are reduced by either land development or sea level rise.

C4. Sea Level Rise and Barnegat Bay Marsh Accretion

Coastal wetland ecosystems, such as salt marshes and tidal freshwater wetlands, are particularly vulnerable to rising sea level because they fall within about a meter of mean sea level. The generally accepted estimate for global (eustatic) sea level rise ranges from 0.2 to 1 m over the next 100 years, and over this period the rate of eustatic sea level rise is expected to accelerate from its current rate of 1–2 mm/yr (IPCC, 2007). As sea level rises, the landward edge of the marsh can be eroded and a new marsh formed if topographic features allow for marsh migration. However, in many coastal areas, topography and developed lands hinder marsh migration, and the services provided by coastal wetlands are lost.

NOAA tide gauge records for Cape May, Atlantic City, and Sandy Hook indicate relative sea-level rise rates of 4.06±0.74, 3.99±0.18, and 3.9±0.25 mm/yr, respectively (Zervas, 2001). Because tide gauges are fixed to the land surface, rates of relative sea level rise include the particular effects of eustatic sea level rise and land subsidence in the vicinity of the gauge. Subsidence in the Barnegat Bay area is due to collapse of the glacial forebulge and perhaps human activities such as groundwater withdrawal (Davis, 1987). For the Sandy Hook gauge, Snay et al. (2007) used satellite GPS data for 1995-2005 to determine a local subsidence rate of 2.2±0.7 mm/yr. This gives an absolute local rate of sea level rise of 1.7±0.7 mm/yr (3.9 mm/yr plus -2.2 mm/yr), which falls within the generally accepted range for eustatic sea level rise (1–2 mm/yr; IPCC, 2007). Subsidence rates for the other gauges are unknown, but they probably fall
in the range of -1 to -2 mm/yr based on other data presented by Snay et al. (2007). Indeed, for two sites along the New Jersey coast, Engelhart et al. (2009) reported subsidence-corrected rates of sea level rise of 1.3±0.2 and 1.4±0.7 mm/yr, averaged over the past 4000 yr. These rates are somewhat lower than those indicated by New Jersey tide gauges, but this is to be expected given the large difference in averaging periods and perhaps spatial variations in subsidence rates.

Marsh accretion rates at the four coring locations ranged from 1.8 to 3.0 mm/yr, based on the average of site-specific rates determined through 137Cs and 210Pb chronology (Table 4). Note that these net accretion rates do not account for subsidence. Net accretion rates determined for this study are comparable to rates reported for other barrier-lagoon marshes of the Mid-Atlantic coast (Reed et al., 2009), but they are somewhat lower than those for sediment-rich estuaries such as tidal Delaware River and Bay estuary (Sommerfield and Velinsky, unpublished data).

Although the Barnegat Bay marshes are accreting in advance of eustatic sea-level rise, they fall on a landscape that appears to be subsiding at a higher rate. If we assume that the marshlands are subsiding in accord with the Sandy Hook gauge (-2.2 mm/yr; Snay et al., 2007), then the absolute rates of accretion (net accretion rate plus subsidence) range from -0.4 (Site BB-2) to 0.8 mm/yr (BB-3 and 4). Hence, with respect to the local rate of sea level rise (1.7 mm/yr), there is an apparent accretionary deficit of 0.9 to 1.3 mm/yr at the coring sites. Here it should be noted that subsidence rates tend to be highly variable on small spatial scales, so the -2.2 mm/yr value could be invalid in the present case. Over the next few years, local subsidence rates in the marshlands will be determined directly from bench mark re-leveling at three sites in the Bay (Quirk, Kreeger, Maxwell-Doyle and Velinsky, unpublished data), which should provide data needed to place the accretion rates in the context of sea-level rise. In summary, with the data in-hand we conclude that the Barnegat Bay marshes are accreting at, to just below, local rates of relative sea level rise. The fact that they are not accreting in advance of rising sea level makes them vulnerable to inundation should the rate of sea level rise accelerate in the future.
D) Summary and Conclusions

This study involved the chemical analyses of sediments sub-sampled from four sediment cores taken from tidal marshes in Barnegat Bay, New Jersey. The goal was to determine the chronology of carbon, nitrogen, and phosphorus deposition, nutrient loading histories, and related ecological responses based on preserved diatom assemblages and stable isotope signatures of carbon (δ\textsuperscript{13}C-OM) and nitrogen, (δ\textsuperscript{15}N-TN). Cores were collected from marsh sites upstream from below Mantoloking Bridge (Reed marsh, BB-1) to downstream near West Creek (BB-4), and dated using \textsuperscript{210}Pb and \textsuperscript{137}Cs radiometric methods. All cores provided sufficient temporal coverage (> 50-80 yr) for detailed chemical analyses.

Major findings of this study include:

- Sediment mass accumulation rates determined from the mean of \textsuperscript{210}Pb- and \textsuperscript{137}Cs-derived rates ranged from 0.048 to 0.081 g/cm\textsuperscript{2}/yr, and corresponding accretion rates ranged from 0.18 to 0.30 cm/yr. Overall these rates are lower, but comparable to, accumulation and accretion rates measured in marshes of neighboring Delaware Estuary. When compared to rates of relative sea level rise from nearby tide gauges, rates of accretion for Barnegat Bay suggest that marsh vertical growth is barely sufficient to keep up with sea level rise.

- Sediment concentrations of C, N and P are typical for tidal fresh and marine marshes throughout the region, especially marshes within a back barrier island system such as Barnegat Bay. Sediment organic carbon (SOC) concentrations ranged from 3.2% and 33.7% dw, total nitrogen (TN) ranged from 0.23 to 1.4% N and total sediment phosphorus (TSP) ranged from 0.02 to 0.39% P. Sediment nitrogen concentrations increased towards the surface in three cores (BB-1, BB-2 and BB-4), while TSP concentrations showed only a small increase towards the surface at three sites, but a larger increase in BB-4, the most downstream location. Sediment organic carbon exhibited highest levels in the surface sections of BB-2 and to some extent BB-4, with lower concentrations at BB-3.

- Sediment N accumulation rates increased twofold at the upbay site (BB-1) starting in the mid-1950s while the other locations exhibited small or no increase with time. Phosphorus accumulation increased only slightly with time. Rates increased between the 1940s and 1950s in cores BB-1 and BB-3, with only a slight increase, at the surface, for
BB-2. In core BB-4, the downbay-most location, there was an abrupt increase starting in the early 1990s.

- Changes in diatom assemblages reveal a first shift in late 1880s-early 1900s, prior to human settlement in the Barnegat Bay area. This shift may be a signal of indirect impact (atmospheric deposition or riverine transportation of nutrients and other pollutants) of post-industrial activities (post-1850) from other areas in New Jersey.

- The analyses of the diatom assemblages and associated metrics indicate major shifts toward more eutrophic or mesotrophic conditions starting in the 1940-1950s (cores BB-1, BB-2 and BB-3). These changes are consistent with an increase in sediment nutrients found in the same cores and appear to indicate impacts from increasing population and land use in the northern part of Barnegat Bay, an area with urban and sub-urban land use. The highest impacts were found in cores BB-1 and BB-3 which appear to strongly respond also to the construction of Point Pleasant Canal (BB-1) and Forked River Canal for the OCNGS (BB-3). These two cores revealed a change from freshwater to brackish and aerophilic diatom species, indicating that major changes took place in wetland hydrology with influx of brackish water and high osmotic oscillations after canal construction. This may also reflect combined effects from lowering of the water table following extensive use of potable ground water by a growing demand from population increase, which may allow for salt water intrusion into area aquifers. The southern site BB4, situated in a rural or semi-rural area, was the least impacted with a change in species composition in early 1900, but without the major shifts displayed by the northern sites throughout the 20th century. This core also included abundant species that have not been described in the literature. Their ecological preferences are unknown at this time, but they may be indicative of undisturbed, or less impacted environmental conditions in Barnegat Bay wetlands.

- Diatoms from all cores indicate a more recent shift starting in late 1980-early 1990; this last shift may represent combined effects from water pollution, nutrient inputs and climate change. This last shift is also contemporaneous with recent proliferation in *Aureococcus* (brown-tide events), but the relationship to diatom assemblages from tidal wetlands is impossible to establish at this point. Study of diatoms in Barnegat Bay sediments may provide more information on this phenomenon.
• Overall, the irreversible shifts recorded by diatom species in cores BB-1, BB-2 and BB-3 suggest, that despite the fact that the Barnegat Bay wetlands are protected by both federal and state laws, these sites remain impacted by anthropogenic disturbances and have not returned to their natural, reference conditions. On the contrary, the most recent changes suggest an increase in habitat deterioration and pollution. Thus, the changes recorded in diatom species convey a strong message to decision makers and managers to identify and limit sources that contribute to the continuous degradation of the estuary and its watershed.

• Recent estimates suggest that current burial rates in the marsh can remove a substantial fraction of both N and P; however, recycling rates and other sinks need to be considered for more accurate estimates of net burial rates in the tidal wetlands of Barnegat Bay. This study provides important data and results that can be incorporated into an ecosystem model for Barnegat Bay to help determine potential water quality changes in the future.

• Preliminary investigation was conducted on foraminiferans from core BB-4. This investigation revealed that species composition remained fairly constant throughout the stratigraphic record. Changes in foraminiferan species can be used successfully to determine sea level, salinity and surface temperature changes (Kemp et al. 2009; Eichler et al. 2010), while anomalies in their shell morphology can be used to assess contaminant and pollution effects (Scott et al. 2005, Vance et al. 2006). Thus, the analysis of foraminiferan species composition and anomalies of their test morphology in existing cores can potentially be used to assess the impact of pollution in Barnegat Bay and possibly assess in which way the algal blooms may impact their species composition.

Recommendations for Future Research and Monitoring

• Since many species found in Barnegat Bay sediment samples have not yet been described in the literature, it is necessary to characterize the undescribed species and determine their autecology. We started investigating these diatoms and their ecological significance in collaboration with Dr. Mike Sullivan (Florida State University) and Dr. Sherry Cooper (Bryn Athyn College), both scientists with extensive knowledge of diatoms from coastal wetlands, including Delaware Bay. This work is in progress and we would like to continue working with them and improve our wetland diatom-based ecological
knowledge, if funding will be available in the future. This will help directly by improving our ability to interpret water quality changes based on existing diatom stratigraphies.

- Develop a surface-sample diatom calibration dataset for Barnegat Bay and adjacent wetlands and use it to determine the ecological preferences of diatom species from this area. This work will imply collection of both surface sediment and water chemistry samples (Atlantic coastal marshes) at several points along the salinity/nutrient gradient (north-south transect), and analysis of relationships between diatoms and measured chemical variables.

- Analyze the cores for additional indicators of nutrient enrichment, harmful algal blooms, and ecosystem change. While preliminary research was performed on sterols (a form of naturally produced hydrocarbons) that indicate brown tide (*Aureococcus anophagefferens*), a specific project should be undertaken to assess the history of blooms in the Bay. This along with other algal metrics (e.g., dinoflagellate analysis) can help understand the timing and development of nutrient enrichment.

- Results of this project revealed that Barnegat Bay marshes can bury a substantial portion of the nitrogen entering the Bay. Burial is only one method for nitrogen sequestration that these marshes can perform. To better assess the total removal potential from coastal wetlands, additional cores (n<5) need to be obtained to broaden the data set and strengthen the data set and estimate. In addition, denitrification studies and measurements should be undertaken in marshes across the salinity gradient of the Bay. Denitrification is a microbial process that converts dissolved nitrate, a dominant form of nitrogen, to nitrogen gas. These ecosystem services are an important component of nutrient management and TMDLs.
E) Acknowledgments

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Van Breemen et al. 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the NE USA. *Biogeochemistry* 57/58: 267-293.


Table 1. Core locations and collection dates for Barnegat Bay field work.

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<th>ID</th>
<th>Date</th>
<th>General Location</th>
<th>Lat (N)</th>
<th>Long (W)</th>
<th>Depth (cm)</th>
<th>Chem IDs</th>
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<td>74 04.797&quot;</td>
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<td>74 15.614'</td>
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Stations are listed from upbay to downbay.
Table 2. Bulk sediment properties and radioisotope data for core BB-1 and BB-2.

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<th>Interval (cm)</th>
<th>Midpoint (cm)</th>
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<th>LOI (%)</th>
<th>Total Pb-210 (dpm/g)</th>
<th>Excess Pb-210 (dpm/g)</th>
<th>Excess Pb-210 error (dpm/g)</th>
<th>Cs-137 (dpm/g)</th>
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Table 3. Bulk sediment properties and radioisotope data for BB-3 and BB-4.

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Table 4. Summary data for radioisotope analysis and dating.

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<th>CIC Pb210 mass accumulation (g/cm²/y)</th>
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CRS- Constant rate of supply model; CIC – Constant initial concentration model
Table 5. Concentrations of various parameters for Core BB-1B.

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Concentrations on a dry weight basis. NA- Not analyzed.
Sedimentation rate (210Pb, CIC) = 0.25 cm/yr
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Concentrations on a dry weight basis. NA- Not analyzed.
Sedimentation rate (210Pb, CIC) = 0.16 cm/yr
Table 7. Concentrations of various parameters for Core BB-3B.

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Concentrations on a dry weight basis. NA- Not analyzed.
Sedimentation rate ($^{210}$Pb, CIC) = 0.29 cm/yr
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Concentrations on a dry weight basis. NA- Not analyzed.
Sedimentation rate (210Pb, CIC) = 0.28 cm/yr
Table 9. Diatom Metrics determined from species identification: BB-1B.

<table>
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<th>Core ID/Depth Interval (cm)</th>
<th>Mid-Depth (cm)</th>
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<th>Mesotrophic</th>
<th>Oligotrophic</th>
<th>Oligo/mesotrophic</th>
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Metrics based on van Dam et al. (1994)
Table 10. Diatom Metrics determined from species identification: BB-2A.

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<th>Mesotrophic</th>
<th>Oligotrophic</th>
<th>Oligo/mesotrophentic</th>
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Metrics based on van Dam et al. (1994)
Table 11. Diatom Metrics determined from species identification: BB-3B.

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Metrics based on van Dam et al. (1994)
Table 12. Diatom Metrics determined from species identification: BB-4B.

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<th>Oligo/mesotrophentic</th>
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<td>0.0</td>
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<td>9.5</td>
<td>0.3</td>
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</table>

Metrics based on van Dam et al. (1994)
Table 13. Comparison of Barnegat Bay marsh nitrogen and phosphorus burial rates measured in this study to rates of nitrogen and phosphorus inputs to the Barnegat Bay.

<table>
<thead>
<tr>
<th></th>
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<th>Phosphorus (kg/yr (\times 10^5))</th>
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</tr>
<tr>
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</tr>
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<td>Core Top Concentration</td>
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<td>0.88</td>
</tr>
<tr>
<td>Avg Concentration (50yrs)</td>
<td>5.48</td>
<td>0.54</td>
</tr>
<tr>
<td><strong>Burial as % of Inputs</strong></td>
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<td></td>
</tr>
<tr>
<td>Core Top Concentration</td>
<td>94%</td>
<td>88%</td>
</tr>
<tr>
<td>Avg Concentration (50yrs)</td>
<td>79±11%</td>
<td>54±34%</td>
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</tbody>
</table>

Nitrogen inputs ranged from 6.5 to 7.65 \(\times 10^7\) kg/yr (Hunchak, 2001; Wieben and Baker, 2009; Kennish et al., 2007) while phosphorus input is derived from the Barnegat Bay Characterization Report. Wetland area (26,000 acres, 1.1 \(\times 10^8\) m\(^2\)) are obtained from [www.crssa.rutgers.edu/](http://www.crssa.rutgers.edu/) projects/lc/.
Figure 1a,b. Generalized schematic of nitrogen and phosphorus cycling in wetlands. SOP – soluble organic phosphorus. In marine sediments, dissolved sulfide (from sulfate reduction) can bind reduced iron, allowing for greater movement of porewater P from the sediments to the overlying water. (Images taken from Mitch and Gosselink, 1993)
Figure 2. Coring locations within the Barnegat Bay system.
Figure 3. Tripod and pulley system used to retrieve push-piston cores from marshes in Barnegat Bay. Upper picture is from the Forked River marsh (BB-3) while the lower picture is from BB-4, near West Creek.
Figure 4. Profiles of dry-bulk density (DBD), loss-on-ignition (LOI), and volume composition of the sediment column at site BB1B. The volume composition shown in this and subsequent figures was computed using Equation 4 in the text.

Figure 5. Profiles of dry-bulk density (DBD), loss-on-ignition (LOI), and volume composition of the sediment column at site BB2A.
Figure 6. Profiles of dry-bulk density (DBD), loss-on-ignition (LOI), and volume composition of the sediment column at site BB3B.

Figure 7. Profiles of dry-bulk density (DBD), loss-on-ignition (LOI), and volume composition of the sediment column at site BB4B.
Figure 8. Profiles of excess $^{210}\text{Pb}$ and $^{137}\text{Cs}$ activity for core BB1B and age-depth models for the sediment column derived using the two $^{210}\text{Pb}$ models described in the text. The $^{210}\text{Pb}$ profile suggest a possible increase in sediment accumulation rate at depth of 25 cm (arrow), which is concordant with ca. 1910–1915. Note that sediment ages based on the CIC model are used in this report to construct the nutrient chronologies.

Figure 9.Profiles of excess $^{210}\text{Pb}$ and $^{137}\text{Cs}$ activity for core BB2A and age-depth models for the sediment column derived using the two $^{210}\text{Pb}$ models.
Figure 10. Profiles of excess $^{210}$Pb and $^{137}$Cs activity for core BB3B and age-depth models for the sediment column derived using the two $^{210}$Pb models.

Figure 11. Profiles of excess $^{210}$Pb and $^{137}$Cs activity for core BB4B and age-depth models for the sediment column derived using the two $^{210}$Pb models.
Figure 12. Scatter plots of excess $^{210}$Pb inventory versus excess $^{210}$Pb initial specific activity (left) and mass accumulation rate (right). Note that a $p$-value <0.5 suggests a statistically significant relationship between the two variables. The regression results indicate that the $^{210}$Pb inventory is to a greater extent affect by the initial $^{210}$Pb activity of the sediment than by the sediment accumulation rate. This can be interpreted to mean that boundary scavenging has a stronger influence on the inventories than sediment focusing.
Figure 13. Sediment organic carbon, C to N, total nitrogen, and sediment phosphorus distribution with depth in the marshes of the Barnegat Bay.
Figure 14. Depth distribution of the isotopic composition of sediment N ($\delta^{15}$N) and C ($\delta^{13}$C) from the Barnegat Bay.
Figure 15. Stratigraphic diagram of diatom species with relative abundances > 5% in at least a sample from core BB-1. Dashed lines represent shifts in diatom assemblages. On average approximately 48±15% of the diatoms counted were not identified.
Figure 16. Stratigraphic diagram of diatom species with relative abundances > 5% in at least a sample from core BB-2. Dashed lines represent shifts in diatom assemblages. On average approximately 67±11% of the diatoms counted were not identified.
Figure 17. Stratigraphic diagram of diatom species with relative abundances > 5% in at least a sample from core BB-3. Dashed lines represent shifts in diatom assemblages. On average approximately $51\pm18\%$ of the diatoms counted were not identified.
Figure 18. Stratigraphic diagram of diatom species with relative abundances $>5\%$ in at least a sample from core BB-4. Dashed line represents the major shifts in diatom assemblages with apparition of abundant *Navicula* spp. On average approximately $85\pm5\%$ of the diatoms counted were not identified.
Figure 19. Diatom metrics with depth for the Barnegat Bay cores using the van Dam et al. (1994) indices. On average approximately 65±20% of the diatoms counted were not identified.
Figure 20. Concentrations of total sediment nitrogen (TN) and the nitrogen isotopic composition of TN ($\delta^{15}$N-TN) from the 1800 to 2009.
Figure 21. Concentrations of total sediment phosphorus (TSP) and the carbon isotopic composition of organic carbon ($\delta^{13}$C-OC) from 1800 to 2009.
Figure 22. Nitrogen and phosphorus accumulation rates over time in tidal wetlands in the Barnegat Bay. Linear interpolation was used for sections of sediment that were not analyzed for N or P. The dotted line is at approximately 1970 for reference.
Figure 23. Diatom metric for eutrophic and meso/eutrophic species through time in Barnegat Bay cores.
Figure 24. Relationship between total sediment N and P, and the diatom metric for eutrophentic species in each core.
Figure 25. Relationship between the accumulation rate of sediment N and P and the diatom metric for eutrophentic species in each core.
Appendices

Excel File with Data and QA
(upon request)