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Modern Nutrient Limitation and Geologic Record of Organic Matter Sources in the Bioluminescent Bays of Vieques, Puerto Rico

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A departmental senior thesis submitted to the Department of
Geosciences at Trinity University in partial fulfillment of the
requirements for graduation with departmental honors.

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ABSTRACT

The factors contributing to the success of the bioluminescent dinoflagellate, *Pyrodinium bahamense* var. *bahamense* in the bays of Vieques, Puerto Rico, are not fully understood, although the dinoflagellate's success is closely tied to its environment and the nutrients within that environment. Exploring the present and past nutrient concentrations and sources of organic material within the bioluminescent bays of Vieques assists in determining the status of and potential threat to the population of *Pyrodinium bahamense var. bahamense*. Modern carbon, nitrogen, and phosphorus nutrient concentrations were measured, primarily in the seagrass *Thalassia testudinum*, to evaluate the distribution and potential limitation of those nutrients. As a primary producer, the seagrass is the first biota to reflect any changes in the nutrient availability of the ecosystem. All seagrass samples were within healthy C:N:P ranges as defined for the species, but trends in relative limitation were established. Puerto Ferro had lower nitrogen availability relative to Puerto Mosquito, while Puerto Mosquito had lower phosphorus availability. Relative phosphorus and nitrogen availability also exhibited trends related to distance from shore; phosphorus availability increased with greater distance from shore while nitrogen availability decreased by the same measure. The hydrodynamics in the bays, especially Puerto Mosquito, could be the cause of the spatial trends in nutrient availability as well as the higher nutrient content of the bays relative to larger bodies of water with more interaction with the open ocean. The relative isolation of Puerto Mosquito is a potential factor limiting nutrient flushing, allowing the nutrient content that supports the present dinoflagellate population to thrive.

In addition, $\delta^{13}C$ values were measured in numerous samples of seagrass and mangrove, two primary sources of organic material, in order to establish their isotopic compositions. With these isotopic and nutrient data, in addition to isotopic data from the third primary source of organic matter, suspended particulate matter (SPM), three end member N:C and $\delta^{13}C$ values were established. $\delta^{13}C$ isotopic analysis of sediment cores revealed overall temporal shifts in organic matter source from mangrove in the past to seagrass and suspended particulate matter in the recent to present-day environment.

The evaluation of the past and present habitat of the bioluminescent bays suggests that the bays experienced a sea level transgression approximately 3000 years B.P. and that the dinoflagellate did not thrive until recently. The relatively recent success suggests that human involvement might not be the only source dictating the future success or failure of the species in the bays of Vieques. Future development within the watersheds of the bays, as well as natural habitat change, could force changes to established nutrient cycles, organic matter sources, and therefore, the success of the dinoflagellate. The protected nature of the bays, from natural and commercial change is a primary reason the dinoflagellate demonstrates its present success. In the future, this isolation could have hazardous implication for dinoflagellate populations, as isolated habitats can have difficulty adapting to change.

Introduction

In the summer of 2007, I traveled to the Puerto Rican island of Vieques to participate in a summer field research project for undergraduate students sponsored by the Keck Geology Consortium. Three bays on the south shore of the island support some of the world's highest concentrations of *Pyrodinium bahamense var. bahamense*, a species of bioluminescent planktonic dinoflagellate. Two of the bays, Puerto Mosquito and Puerto Ferro, served as the focus of the study due to their similar physical attributes but contrasting dinoflagellate populations. The student projects were designed to explore the past and present environmental attributes that are necessary to support these populations and are an extension of Keck research completed in the summer of 2006. Keck students are analyzing the bays across several disciplines. These include study of: 1) the organic and inorganic composition and cycling of the water; 2) the hydrodynamic interaction between the bay and open ocean; 3) the overall stratigraphy and depth of the bays; and 4) the taphonomy of the bays and how past organisms interacted with the bays. These projects will shed light the ecosystems of Vieques that support such high concentrations of *Pyrodinium bahamense* var. *bahamense*.

The primary objectives of my project were to investigate carbon, nitrogen, and phosphorus nutrient concentrations and $\delta^{13}C$ values of modern biota as well as nutrient and isotopic compositions of present and past sedimentary organic matter from Puerto Mosquito and Puerto Ferro. Nutrient status within a bay's ecosystem directly affects the dinoflagellate population (Phlips et al., 2006), so by studying the present and past nutrient concentrations and sources of organic material within the bays, I can help constrain the status of and potential threat to the population of *Pyrodinium bahamense var. bahamense*.

Primary producers, such as the seagrass *Thalassia testudinum*, play an especially important role within the bays' ecosystems. As autotrophs, primary producers form the base of the food web and therefore are the first to reflect changes in nutrient availability. For this reason, the seagrass has been the primary focus of my investigation of modern biota. Spatial variations in nutrient availability (N and P) as well as average nutrient ratios relative to other, larger studies, reveal both the relative health of the seagrasses in the bays as well as the potential sources of these nutrients.

Since suspended particulate matter, seagrasses, and mangroves are the primary sources of organic material in a modern tropical lagoonal ecosystem (e.g., Gonneea et al., 2004), nutrient and isotopic compositions of these end members can provide detailed information regarding modern nutrient cycling within the bays. Samples from each of the main sources of organic matter (sediment, segrasses, and mangroves) were analyzed for C:N ratios and carbon isotopic composition. These analyses provide group-specific reference values which can be used to monitor past sources of organic material recorded in layers of sediment. When sediment compositional analyses are combined with changes in both types and rates of sedimentation, these data reveal a great deal about changes in the past habitat.

My study of the past and present nutrient exchange systems of the bays and other Keck studies focusing on the bays' water chemistry, ecology, and geology all highlight processes that could affect the dinoflagellate populations within the bays. These studies assist in the identification of potential threats to dinoflagellate habitat. These threats include changes in the distribution of biota, changes in nutrient levels, and changes to the physical shape and bathymetry of the bays, any of which could lead to the bays' ecological destabilization.

Geologic history of Vieques

The islands of Puerto Rico and Vieques sit on the northeast portion of the Caribbean plate, part of the Antilles island arc that stretches east and south, to almost present-day South America (Fig. 1). Dominated by oceanic crust, this relatively small plate is bordered by the North American plate to the north, the South American plate to the south, and by the Cocos and Nazca plates to the west. Volcanic activity, the result of subduction of the North American plate under the Caribbean plate, formed the islands of Puerto Rico and Vieques (Schellekens, 1999). The timing of volcanic initiation is unknown, but it is thought to have begun in the Mid-Cretaceous, based on the age of subaerial volcanic activity soon after the Aptian-Albian boundary (Donnelly, 1989). Once emergence occurred, sedimentation and the still-active volcanism sped the growth of the islands. Volcanic activity on Vieques ended around 45 million years ago due a shift in subduction zone to the Cayman Trench (Schellekens, 1999).

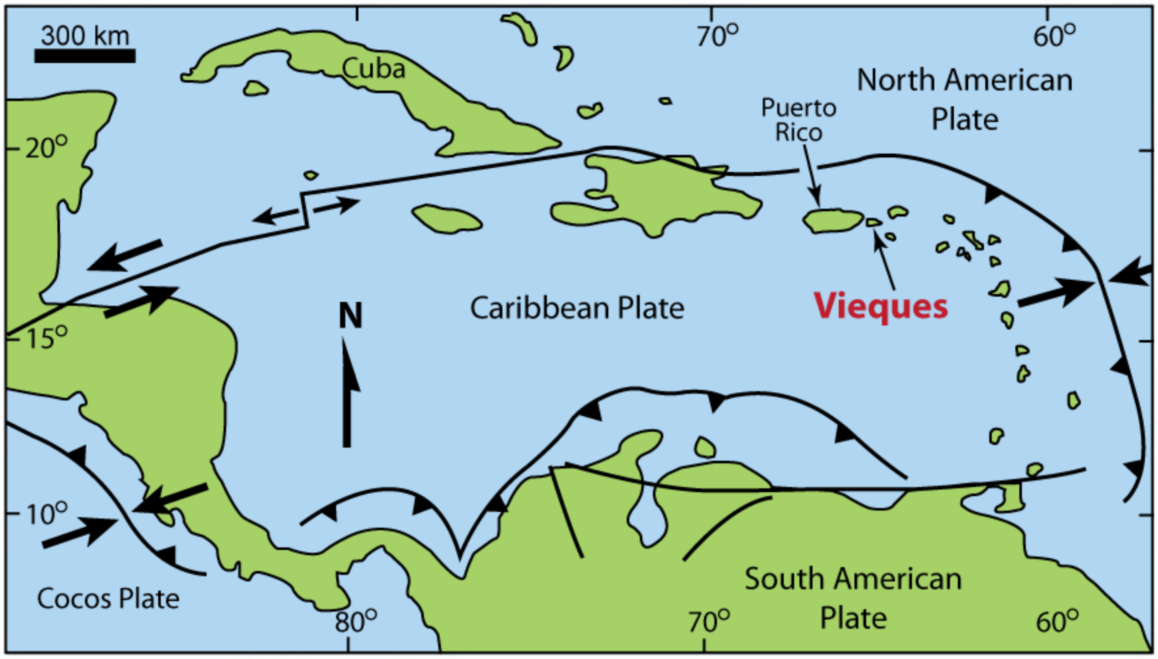


Figure 1. Tectonic map of the Caribbean region. Arrows indicate relative motion between plates. Vieques, on the Caribbean Plate, is indicated in red.

The resulting bedrock of Vieques is made up mostly of granodiorite and quartz diorite (KTd), with some Cretaceous volcanic assemblages and marine sandstones (Kv) exposed on the eastern third of the island (Fig. 2). Marine limestone (Tl), beach deposits (Qb), and alluvial deposits (Qa) make up the area surrounding the bays. The amount and composition of carbonate found in the sediment deposited within the bays confirms the sedimentary rock of the island as the source of the carbonate found there (Armstrong and Gilbes, 2007).

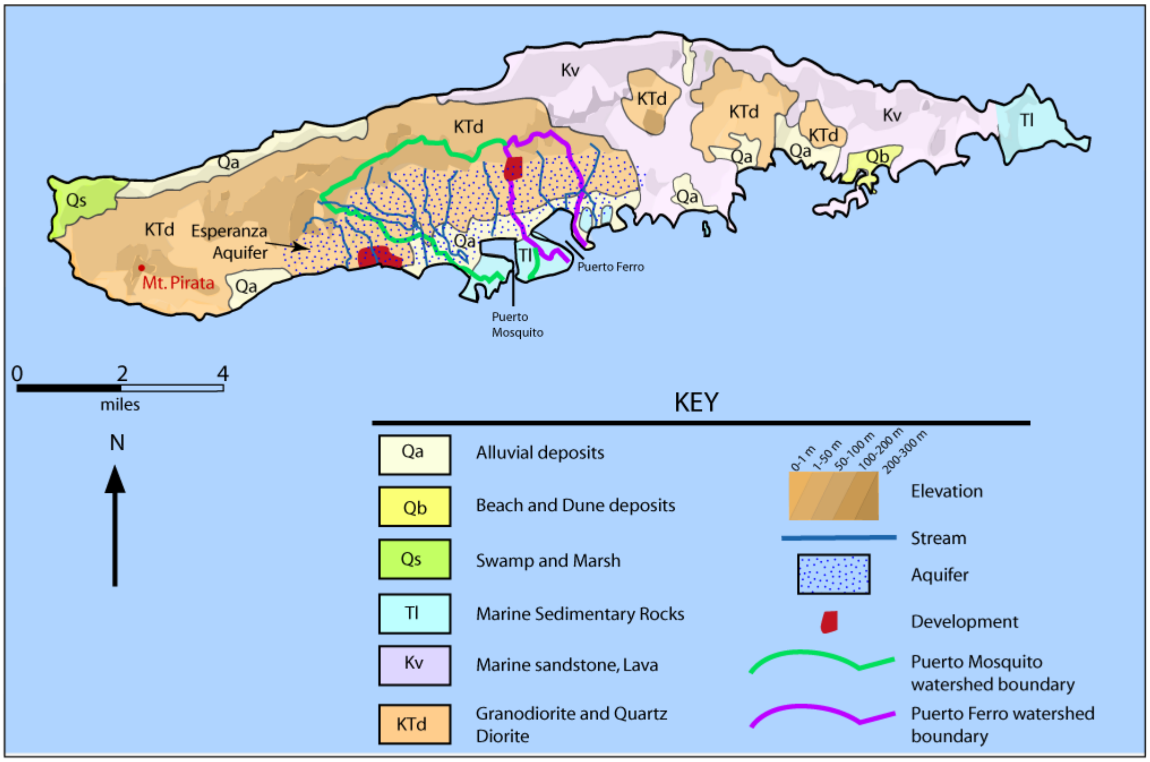


Figure 2. Geologic and elevation map of Vieques, Puerto Rico with watersheds, streams, and development near Puerto Mosquito and Puerto Ferro.

Environmental setting

The people of Vieques and environmental scientists are concerned about how future agricultural and commercial development will affect the overall ecosystems of Puerto Mosquito and Puerto Ferro as well as the populations of the dinoflagellates. For much of the bays' existence, there was little or no development nearby. In the early 1940's, the U.S. Navy acquired two-thirds of Vieques to use for military exercises, which included weapons testing. In 2003, the Navy returned the virtually undeveloped land to the Puerto Rican people. While portions of the bays coastlines are protected, many see an opportunity to develop any unprotected areas to their full commercial potential.

Climate

The island of Vieques covers approximately 125 km^2 and has a tropical marine climate. Due to the proximity of the island to the equator there is little variation in temperature throughout the year. The mean maximum temperature for the year is 29.7˚ C while the mean minimum is 19.4˚ C (Daly et al., 2003). The surrounding warm ocean water gives the island very high humidity, which instigates a relatively high rate of precipitation; the island accumulates a mean annual precipitation of 168.7 centimeters (Daly et al., 2003).

Cloud cover and the distribution of precipitation are primarily controlled by topography and terrain (Daly et al., 2003). Mt. Pirata, the island's highest peak at 301 meters, sits on the western third of the island (Fig. 2), which consequently receives 30% more rain than the other two-thirds of the island (Alusio et al., 1988). Despite significant amounts of precipitation there are no permanent rivers or streams on the island.

Groundwater dynamics

The island of Vieques has multiple natural aquifers that at one time were viable and supplied the island with drinking water. Use of the Esperanza aquifer (Fig. 2), covering roughly 10 mi^2, was discontinued in 1978, due to increased salinity. A pipeline connected to the main island of Puerto Rico was built to bring drinking water to Vieques. Infiltration from ephemeral streams nourished by storms and direct rainfall are sources of recharge for the aquifer. Rates of recharge are up to 5 percent of total annual rainfall (Veve and Taggart, 1996). Much of the Esperanza is composed of an alluvium deposit and acts as a recharge zone; the relative rate of infiltration increases towards the interior of the island. The interior is dominated by a sandy or clayey soil, and organic-rich material from decaying mangrove forests. This deposit contains a 5 foot thick clay layer at approximately 25 foot depth, creating an artesian aquifer below and limiting the depth of infiltration (Veve and Taggart, 1996). This clay layer increases in thickness toward the coast, which further limits recharge of the aquifer near the bays. Transmissivity of the aquifer increases from 200 ft^2/d in the east to 2000 ft^2/d in the west (Veve and Taggart, 1996).

Soil erosion

Erosion is another problem associated with soils surrounding the bays. Higher rainfall rates increase erosion and consequently deposition toward the coast, especially in areas of decreased vegetation. Commercial development on the island could result in loss of vegetation and possible amplification of erosion and therefore rates of sediment deposition into the bays. Both water and sediment in the bays' ecosystems are significant components of the nutrient cycle, which provides nutrients that support the dinoflagellate *Pyrodinium bahamense* var. *bahamense* in Puerto Mosquito and Puerto Ferro. Disturbances to any part of the nutrient cycle could affect the success of the dinoflagellate.

Physical attributes of Puerto Mosquito and Puerto Ferro

The sharing and distribution of nutrients between biota, including mangrove, seagrass, and dinoflagellates, are affected by the physical attributes of the bays. Though surrounded by similar environments, Puerto Mosquito and Puerto Ferro differ in their physical and chemical attributes (Fig. 3). Those physical attributes, such as shape, size, and bathymetry, control hydrodynamics and might affect the dinoflagellate populations.

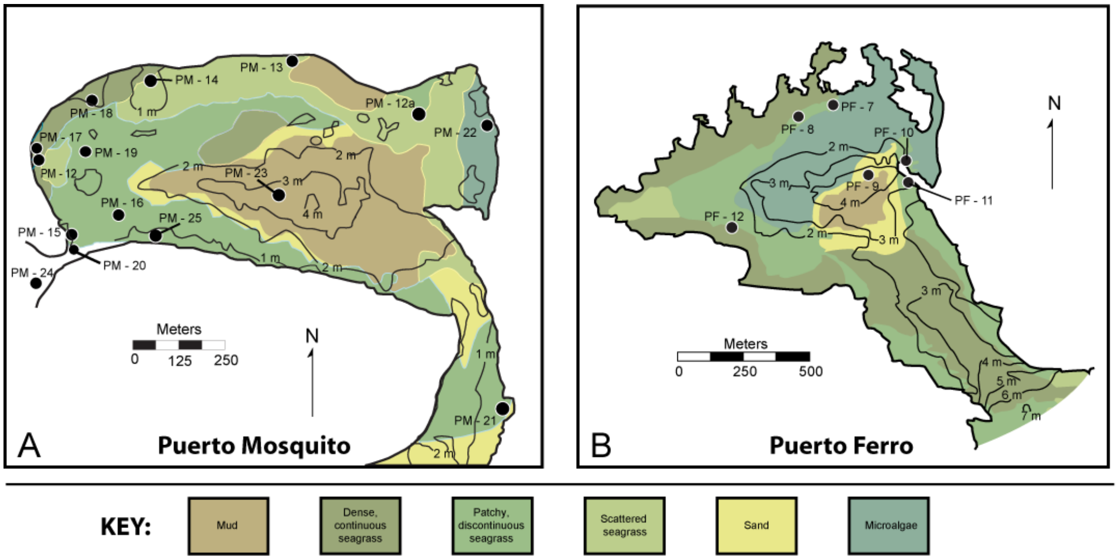


Figure 3. Sediment core locations, seagrass density distribution, and bathymetry of Puerto Mosquito (A) and Puerto Ferro (B). Modfied from NOAA (1999).

Puerto Mosquito (PM) is smaller than Puerto Ferro (PF) (PM = 784,000 m^2; PF = 29,000 m^2) (Fig. 3), and although both bays reach depths of 4 – 5 meters in their centers, the area at that depth is much larger in Puerto Ferro (Fig. 3). Puerto Ferro also reaches a much greater depth (8 – 9 meters) at its canal mouth while the mouth of Puerto Mosquito is much shallower (2 – 3 meters) (Tainer, 2007). In addition, the ocean channel of PM is narrower than PF (130 m vs. 250 m); both the lesser width and depth of the ocean channel of PM might reduce the interaction of the bay with the ocean, affecting salinity and pH values of the bays. Puerto Mosquito (PM) has a slightly higher average salinity and pH than PF (PM = 37.61 psu and 8.15; PF = 36.22 psu and 8.00).

A portion of Puerto Mosquito is a tidal flat, covered with 470,000 m^2 of dead mangroves, connected to the back part of the bay only by a very small canal (Britney Channel) (Fig. 4). This tidal flat maintains higher water residence times and evaporation rates, and as a consequence, salinity and pH in the tidal flat is significantly higher than the main bay, measuring 40.00 psu and 8.48.

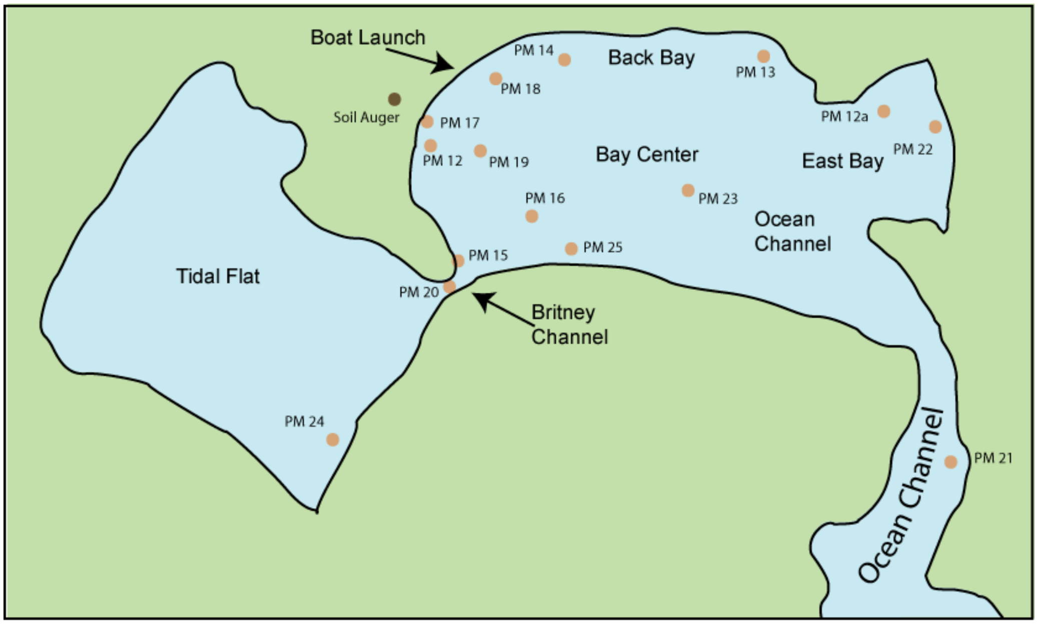


Figure 4. Core sites and bay area names of Puerto Mosquito on Vieques, Puerto Rico.

The composition of exposed sediments of Puerto Mosquito varies across the bay. The hypersaline, relatively stagnant salt flat is dominated by terrigenous material, with almost no carbonate and a low percentage of organic material (Ku et al., 2008). Near Britney Channel, water flow is somewhat restricted, contains a higher percentage of organic material relative to the salt flat, 30-40% carbonate material, and approximately 60% terrigenous material. Below this material is a blue-green carbonate-free clay. Closer to the opening of the bay, where flow becomes increasingly turbid, the carbonate material increases to 50-60% while the organic material decreases. Again a blue-green carbonate free clay is present below. At the deepest region of the bay, carbonate material is coarser grained and comprises approximately 80% of the sediment volume. The lower clay layer has greater amounts of carbonate and is more gray-green. Along the channel outlet carbonate ranges from 75-95% and the clay is fine grained and olive gray (Ku et al., 2008). The marginal areas of the bays have higher turbidity relative to the center of the bays or the ocean channel (e.g., Nelson, 2007), suggesting a higher suspended sediment load near shore, which might impact seagrass density.

Biology of the bays

Life in the bioluminescent bays exists on many levels, each supporting and competing with one another. Most of these interactions occur through the exchange of nutrients. Nutrient cycles exist in delicate balances in marine coastal systems. The dinoflagellate *Pyrodinium bahamense* is supported by nutrients cycling through the bay's system; this system includes all organisms, sediments, and water within the bay. The burial of organic matter is also a significant process in the cycling of nutrients through a bay ecosystem. Any disturbance to parts of the nutrient systems in the bay, such as mangrove or seagrass populations, would in turn affect the dinoflagellate. Studying nutrient ratios and isotopic contents of each of the three possible biological sources (seagrasses, mangroves, and particulate matter), allows tracing of organic matter (OM) sources through the bays (Gonneea et al., 2004). In this study the seagrass, mangrove, and particulate matter elemental ratios and isotopes were used together to trace the OM source through time in the bays' systems.

Seagrasses and primary production

The seagrass, *Thalassia testudinum*, acts as a primary producer in the bioluminescent bays of Vieques. Primary producers transform available inorganic material into organic compounds to use as food. The resulting organic material can also be used as energy for higher organisms, such as fish, which in turn provide energy for humans. Because primary producers self-manufacture usable forms of energy for themselves and other organisms they are referred to as autotrophs. This energy fabrication is performed in the most common method, photosynthesis, using sunlight as the catalyst; one of the products of photosynthesis is carbohydrates, which higher organisms can convert into energy (Garrison, 2002).

The net primary productivity for marine autotrophs is significantly higher than that of their terrestrial counterparts. Photosynthetic productivity can be limited by four primary factors water, carbon dioxide, sunlight, and nutrients (Garrison, 2002) as well as multiple secondary factors including zooplankton grazing and the presence of toxins. Both sunlight and carbon dioxide can be eliminated as primary factors due to the widespread and constant availability in Puerto Mosquito and Puerto Ferro. While the seagrass *Thalassia testudinum* is a widespread primary producer, both mangroves and phytoplankton may also play important roles, acting both as sources and sinks for nutrients.

Generally, the density of seagrass plants is greatest near the shore, with plant density decreasing with increasing distance from shore and with increasing depth (Fig. 3). All seagrass samples were taken at depths of less than two meters, because the seagrass did not grow below that depth (Fig. 3), the result of light limitation and/or substrate disturbance through bioturbation (Nelson, 2007). In the past, seagrass distribution (Fig. 3) was thought to have been most influenced by turbidity and water depth, and turbidity in turn by the proportion of fine sediment (Nelson, 2007); however, the relationships between nutrient availability and seagrass distribution in Puerto Mosquito and Puerto Ferro had not been explored. Scattered seagrass grows along the north and east shore in Puerto Mosquito and the western shore in Puerto Ferro (Fig. 3). Scattered growth is associated with high turbidity which decreases light availability, limiting primary biota growth. This high turbidity is associated with terrigenous mud and areas of the bays of increased terrigenous sedimentation (Nelson, 2007). Dense seagrass beds grow along the northwest shore of Puerto Mosquito as well as an isolated area in the north central part of the bay, and along the north and west shores as well as the ocean channel in Puerto

Mosquito (Fig. 3). These seagrass beds are associated with areas of low turbidity, allowing increased light availability and are often areas of low terrigenous sedimentation and dominated by Halimeda sand (Nelson, 2007).

Mangroves

Both bays are surrounded by mangrove forests, which protect the bays from pollution and excess sediment accretion and are sources for organic carbon and nutrients (Gonneea et al., 2004). A marine tree, mangroves take root in the shallows of bays with portions of their roots exposed above the water line. Below the water line, the root systems are often home to shellfish. Three species of mangrove (named for their bark color) inhabit Vieques: *Rhizophora mangle* (Red), *Laguncularia racemosa* (White), and *Avicennia germinans* (Black). Puerto Ferro, though a larger bay, has only 353,000 m^2 of mangrove forest while Puerto Mosquito has a larger surrounding mangrove forest, covering 764,000 m^2 (Cintron and Maddux, 1972). The total area for Puerto Mosquito includes a tidal flat, which is made up of mostly dead mangroves.

The extensive mangrove coverage demonstrates the relatively protected nature of Puerto Mosquito, because mangroves prefer calm hydrologic conditions. These mangrove forests not only offer natural protection for the bays but also present areas for organic carbon burial are themselves sources for organic carbon and nutrients. Mangrove forests are significant sources for organic carbon, with an average productivity of 2500 mg C $m^{-2}d^{-1}$ (Gonneea et al., 2004). Their position between the bay and inland areas also provide the bay protection from terrestrial pollutants and excess sediment accretion (Gonneea et al., 2004). Their role in sediment accretion affords the capability for long-term organic carbon sequestration (Gonneea et al., 2004). Since organic matter from mangroves is likely to play a significant role in the nutrient cycles within Puerto Mosquito and Puerto

Ferro, it was important to characterize the C:N:P ratios and isotopic composition of the mangroves in this area.

Dinoflagellate habitat and red tides

The blue-tinted bioluminescence in the waters of Vieques is attributed exclusively to the dinoflagellate *Pyrodinium bahamense var. bahamense* (Fig. 5). The etymology of the name is Greek: *pyros* means fire and *dinos* means whirling. The name stems from dinoflagellates' ability to whirl, facilitated by flagella (Bernache-Baker, 1995). While the purpose of bioluminescence in other organisms, such as the firefly, is to promote reproduction, its role in *Pyrodinium bahamense* is not known. It is widely accepted, however, that they are asexual; therefore reproductive signaling would be deemed unnecessary (Usup and Azanza, 1998).

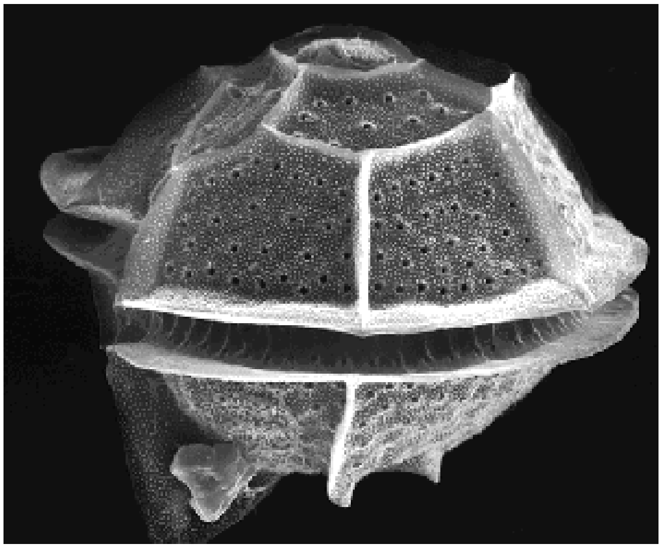


Figure 5. The dinoflagellate *Pyrodinium bahamense var. bahamense*, the cause of the bioluminescence in the bays of Vieques (FDA, 2007).

Toxic blooms, called red tides, have long been associated with *Pyrodinium bahamense* var. *compressum*, but have not been observed in var. *bahamense.* Although nontoxic, the blooms observed in var. *bahamense* occurred over a greater range of conditions than previously thought (Phlips et al., 2006). Even nontoxic blooms can be harmful, upsetting the fragile nutrient balance of their habitat and the endangering the organisms within it. The integral role of nutrient cycling and limitation is displayed in the toxin accumulation that often occurs after episodes of heavy rainfall (Usup and

Azanza, 1998). Heavy rainfall and the resulting runoff are responsible for marine influx of land-dominant nutrients, such as phosphorus, and if timed correctly could maximize planktonic growth resulting in toxic algal blooms (Usup and Azanza, 1998). Increased plankton growth, or a plankton bloom, depletes nutrients available to other organisms. Plankton blooms in common ecosystems with dinoflagellate populations can induce toxin accumulation, negatively affecting other organisms, including humans. Studies examining the habitat of these dinoflagellates will play an important role in understanding the capacity of *Pyrodinium bahamense* var. *bahamense* for toxic and non-toxic blooms.

A morphologically similar variety *compressum* is native to the Pacific Ocean. Previously, it was universally accepted that only this variety had the ability to produce a potent neurotoxin, saxitoxin (Phlips et al., 2006). To date, all naturally occurring toxic red tides associated with *Pyrodinium bahamense* are attributed to only this var. *compressum*. Recently however, saxitoxin accumulation in var. *bahamense* has been documented in a river lagoon environment along Florida's coastline (Phlips et al., 2006). The factors controlling such toxic accumulations seemed tied to conditions that favor dinoflagellate blooms. These include nutrient availability, hydrologic environment (i.e.salinity, flow, dissolved gas content), and biological interactions (Phlips et al., 2006). Phlips and others (2006) hypothesize that some combination of changes in these factors stimulate saxitoxin acculumation. Possibilities include: (1) environmentally-induced limitations on physiological success, such as temperature and salinity tolerances; (2) regulation of physiological and overall population growth through nutrient availability; and (3) competitive advantages for survival parallel to other species (Phlips et al., 2006).

Keck studies have placed emphasis on the comparison between Puerto Mosquito and Puerto Ferro because of the significant difference in dinoflagellate populations. Puerto Mosquito supports a larger dinoflagellate population; populations have been reported to range from 20,000 to 150,000 organisms per liter; the maximum measured in 2007 was 54,600 organisms per liter (Gasparich, 2007). The concentrations in Puerto Ferro were determined to range from 2-3 orders of magnitude below the concentrations in Puerto Mosquito, with a maximum of 400 organisms per liter (Gasparich, 2007). The dinoflagellate population within Britney channel, connecting the tidal flat to Puerto Mosquito proper, has been measured at 0; however, the tidal flat dinoflagellate population has not been measured, so the effect of high salinity levels on the dinoflagellate population is unknown (Gasparich, 2007).

Though the adjacent bays have different concentrations of dinoflagellates, they experience some of the same trends in concentration distribution. Both bays exhibit smaller concentrations of the organisms at the bay mouths, while concentrations are higher in the back, more stable areas of the bay (Gasparich, 2007). This concentration variation is hypothesized to be a result of the turbid interaction of the bays with the open ocean (Gasparich, 2007).

C:N:P ratios and nutrient limitation

Nutrient levels of an ecosystem can be evaluated through nutrient ratios such as the well-known Redfield ratio. The Redfield ratio, 106:16:1, describes the average ratio of marine carbon, nitrogen, and phosphorus in plankton; this ratio is measured in plankton growing at maximum rates without significant nutrient limitation (e.g., Redfield et al., 1963; Atkinson and Smith, 1983). Deviations from this standard are often seen in phytoplankton populations, which may be due to either the presence of particular types of phytoplankton that have slightly different normal nutrient ratios (Arrigo et al., 1999) or as a product of the plankton's primary growth environment, because nutrient deprivation during growth results in non-standard ratios. Nitrogen deprived phytoplankton show N:P ratios of <10:1, while phosphorus deprived plankton show N:P ratios to be >30:1 (Atkinson and Smith, 1983).

Redfield (1958) suggested phosphorus alone can limit primary production. For this reason, *Thalassia testudinum*, a common marine grass and primary producer, is commonly used to investigate nutrient ratios. The Redfield ratio established for phytoplankton is not suitable for analysis of benthic plants, such as *Thalassia testudinum*, due to the increased complexity and structure of benthic plants (Fourqurean and Zieman, 1992). Atkinson and Smith (1983) suggest an alternate ratio of 550:30:1 for benthic plants. Accepted ratios for specifically *T. testudinum* range from 445:32:1 to 601:20:1 (Patriquin, 1972). As with plankton, variation from this ratio range can be used identify limited nutrient(s) in benthic plants. Specifically, C:N ratios, if well-preserved after burial, can be used to trace the different sources of organic matter because both terrestrial and marine organisms have ratios specific to their species that are preserved with burial (Gonneea et al., 2004). Previous investigations involving *Thalassia testudinum* suggest that the variance in the density of seagrass beds is the direct result of nutrient availability (Fourqurean and Zieman, 1992)

Carbon isotopes

One can use stable isotopes to trace carbon through ecosystems because carbon exists naturally as three stable isotopes; ^{12}C makes up 98.89% of total carbon; ^{13}C makes up 1.11%; and ^{14}C makes up 1×10^{-10}% (Siegenthaler and Sarmiento, 1993; Kwon and Schnoor, 1994,). Photosynthetic biotas prefer the lightest carbon isotope available from the source of CO_2. Therefore, the percentage of ^{13}C in photosynthetic organisms will always be less than the percentage of the original C from CO_2 (Siegenthaler and Sarmiento, 1993; Kwon and Schnoor, 1994). In aquatic ecosystems, the photosynthetic autotrophs draw carbon into the water making it available for use by other biota. In many aquatic ecosystems, the phytoplankton have carbon isotope ratios that are distinct from both large aquatic plants such as seagrasses, and from terrestrial plants such as mangroves. Isotope analysis can be used with C:N ratios to distinguish between organic matter sources and to trace the organic matter through ecosystems.

To correctly use isotopes in determining organic matter sources the end members must be clearly defined (Gonneea et al, 2004). In my study, these end members are seagrass, mangroves, and particulate matter. In order for C:N ratio and carbon isotope analysis to be useful for identifying end members and tracing sediment organic matter sources, two conditions must be met. All three end members must have distinct C:N ratios and/or carbon isotopic compositions, and the C:N ratios and isotope compositions must not be significantly altered post burial (Gonneea et al., 2004). Isotopic composition of inorganic matter can be used to determine the material's geologic origin. Sediment isotopes can be used to trace the development of the environment in which those sediments exist and where they might have originated. However, since this study focused on the sources of organic matter within the sediment, the inorganic portion of the sediment was removed, and only the remaining organic material was analyzed. Tracing the development of the bays through organic matter use and deposition can help us understand how these specific bays became so hospitable to the dinoflagellates, and help us determine if organic matter inputs to the system have changed significantly over time.

Nutrient cycling, limitation, and organic matter sources

The marine nutrient cycle gives the ocean the ability to support a plethora of organisms. Nutrients are constantly being recycled and reused, passed from organism to organism, even returning to land or being trapped in rock. The three most essential nutrients to marine organisms are carbon, nitrogen, and phosphorus. Unlike carbon, nitrogen and phosphorus exist in short supply here on earth and throughout the universe. (Ingmanson and Wallace, 1989). The ratios in which nutrients exist can determine both the type of and abundance of life that can be supported in that system. Puerto Mosquito and Puerto Ferro are interesting systems because of the bioluminescent dinoflagellate populations they support. Nutrient and isotope ratios give insight to organic matter sources and possible limiting nutrients for *Pyrodinium bahamense* var. *bahamense*. Analyzing the ratios and relative abundances across both bays leads to greater understanding of the environment and the support for dinoflagellates.

Carbon cycling

The global carbon cycle is one of the most intricate and complex of the nutrient cycles (Fig. 6). This is in part due to the many terrestrial and marine sinks, or reservoirs, that are available for carbon storage and is also due to the abundance of carbon itself. This cycle also sparks public interest because of the role of CO_2 as a green house gas and as part of the global carbon cycle. This cycle can be described as many smaller cycles working concurrently to create one large-scale cycle. It can be broken into two actions, the movement of carbon from a source into a sink and the movement of carbon back out of that sink. Four of the largest carbon reservoirs are: sedimentary rocks, 1,000,000 Giga tons of carbon (Gt C); the deep ocean, 38,000 Gt C; the atmosphere, 750 Gt C; and warm ocean surfaces, 620 Gt C (Siegenthaler and Sarmiento, 1993; Kwon and Schnoor, 1994).

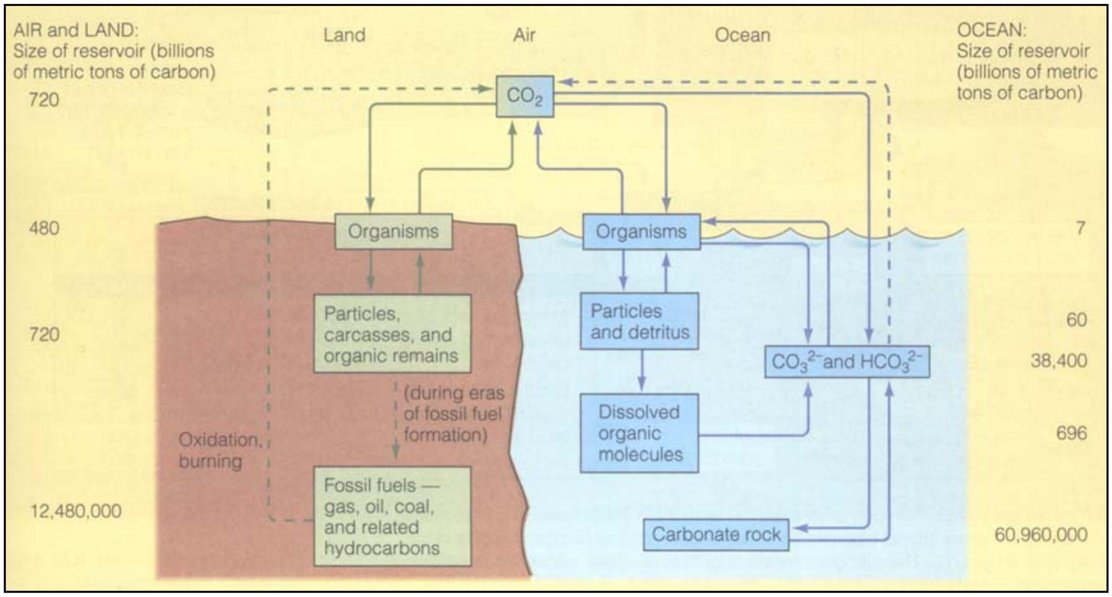
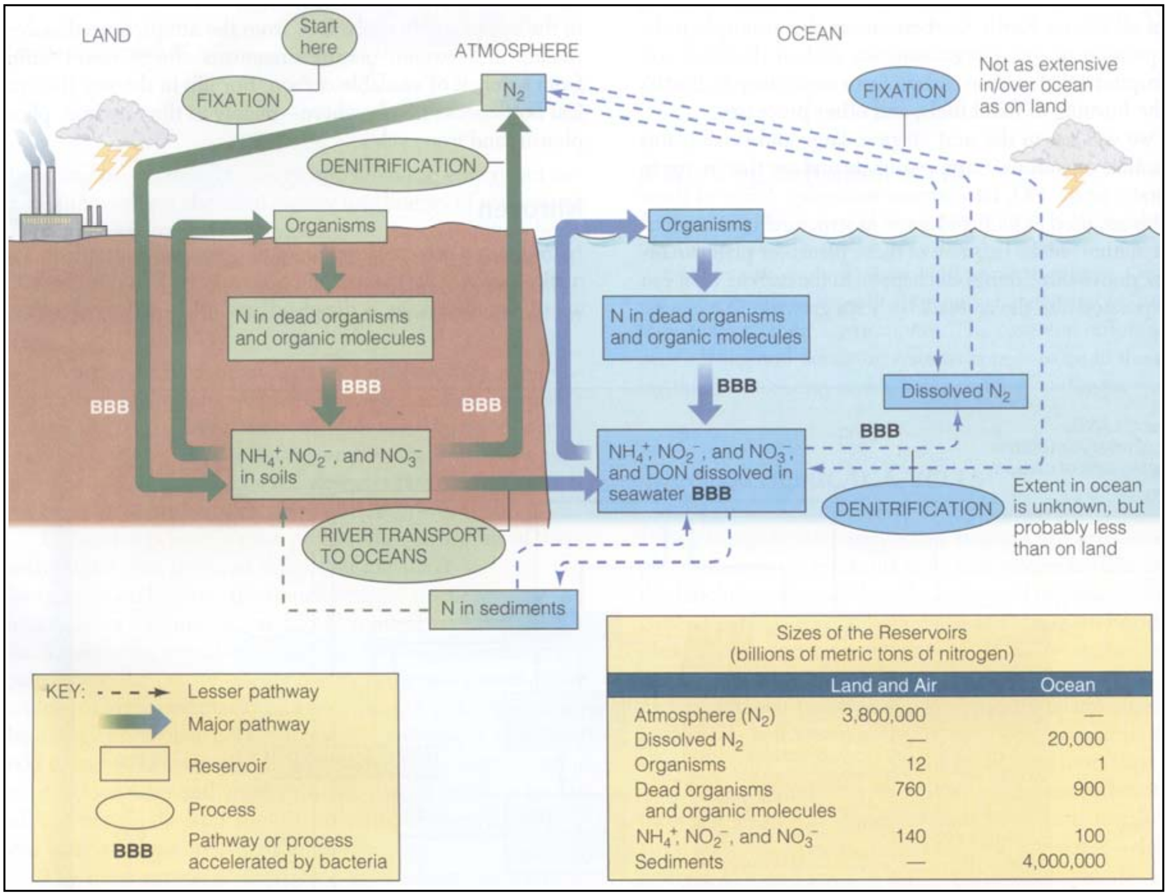


Figure 6. The carbon cycle. The figure above shows the possible pathways for carbon. These pathways involve terrestrial, marine, and atmospheric interactions.

Some of the ways carbon is released from these sinks includes: upwelling of deep ocean water, release of CO_2 by warm surface ocean water and photosynthesis by terrestrial and marine biota. When photosynthesis is performed by biota within an ecosystem, interdependent life forms such as *Pyrodinium bahamense*, seagrasses, and mangroves become carbon sinks themselves. When such organisms die they sink to the bottom of the bays and a small but varied percentage of the dead biomass is buried creating large carbon sinks. The bulk of biomass is broken down and recycled by bacteria. These sinks are only depleted through upwelling, uplift and exposure (Siegenthaler and Sarmiento, 1993; Kwon and Schnoor, 1994). Therefore, carbon passes through almost every geological, geographical and organic cycle on earth, including those which exist in the bioluminescent bays (Fig. 6). For this reason and due to its overall abundance, carbon is rarely the limiting reagent for ecosystems (e.g., Fourqurean and Zieman, 1992), and is an ideal standard to measure relative abundances of nitrogen and phosphorus.

Nitrogen cycling

The majority of nitrogen exists as N_2, nitrogen gas, a form that is unsuitable for most organisms. Gaseous nitrogen can be transformed into a form that organisms can use, nitrate (NO_3^-), by three agents: lightning, photochemical processes, and nitrogen-fixing bacteria (Fig. 7). Nitrogen-fixing bacteria, most of which are found on land, are responsible for completing the majority of this conversion on earth. Nitrate is taken up by plants, which strip the nitrate of its three oxygens for use in multiple biochemicals within the plant. The plant retains the bulk of these biochemicals for its own use unless it dies or is eaten; in which case a minute portion can be passed on to any animal that eats the plant. When a nitrogen bearing organism dies, decomposer bacteria release the nitrogen atom as ammonium (NH_4^+,), which can be actively used by “nitrite” bacteria.



Sizes of the Reservoirs
(billions of metric tons of nitrogen)

	Land and Air	Ocean
Atmosphere (N_2)	3,800,000	—
Dissolved N_2	—	20,000
Organisms	12	1
Dead organisms and organic molecules	760	900
NH_4^+, NO_2^-, and NO_3^-	140	100
Sediments	—	4,000,000

Figure 7. The nitrogen cycle. The figure above shows the possible pathways and sizes of reservoirs for nitrogen. These pathways involve terrestrial, marine, and atmospheric interactions.

These bacteria convert the ammonium to nitrite (NO_2). “Nitrate” bacteria transform the nitrite into nitrate thus completing the cycle (Ingmanson and Wallace, 1989). Due to the limited availability of nitrogen in a usable form it is often a limiting nutrient for an ecosystem. Systems depleted in nitrogen would become less productive than those with abundant nitrogen. Exploring the nitrogen availability in the primary producer *Thalassia testudinum* utilizing C:N ratios will help determine if nitrogen is limited within the bays of Vieques.

Phosphorus cycling

The majority of phosphorus is stored in rock as phosphate (PO_4^-). Igmanson and Wallace (1989) describe the phosphorus cycle as generally a one-way trip, from terrestrial rock to the ocean to marine rock, only returning to the land over very long time scales (Fig. 8). Sediment can act as either a sink or source of phosphate ions, though this has yet to be determined in Puerto Mosquito and Puerto Ferro. The determination of this portion of the phosphorus cycle is specifically location dependent.

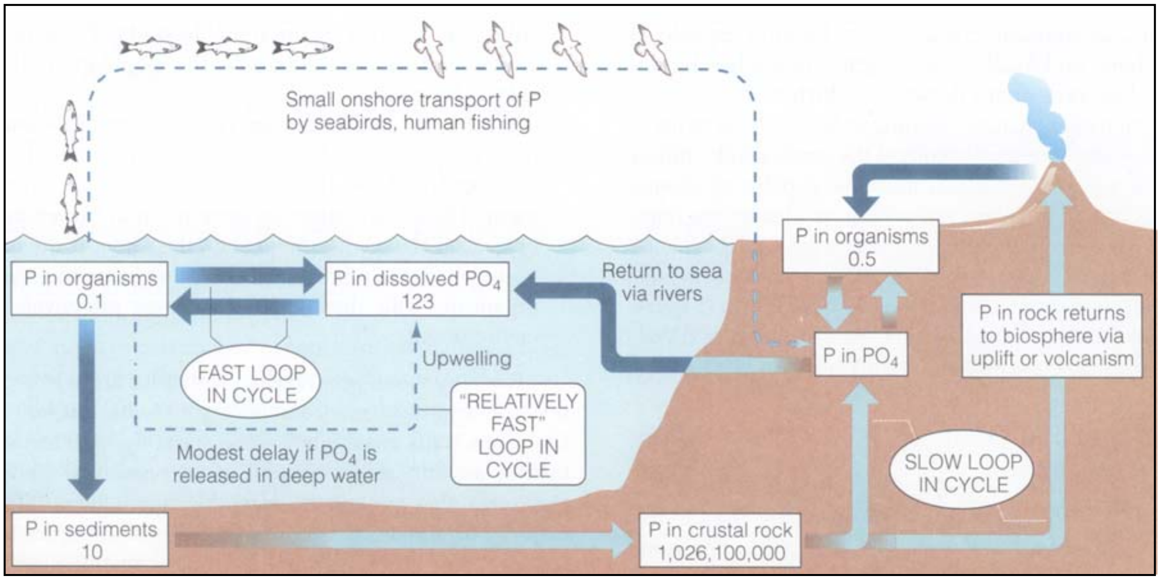


Figure 8. The phosphorus cycle. The figure above shows the possible pathways for phosphorus. These pathways involve terrestrial, marine, and atmospheric interactions.

Unlike the nitrogen cycle, the phosphorus cycle is heavily dependent on the movement of water. The inorganic phosphate trapped in rock can be absorbed by plants on land and in the ocean only if it is first dissolved in water. The plants are able to convert it to an organic phosphate which they use in their own biochemical pathways. Once the phosphate has been taken up by a plant, it can move through the food chain as animals consume portions of the plant. The decomposition of any organic phosphorus by bacteria reverts the phosphorus to an inorganic form, which can be dissolved in water for re-use or stored in rock.

There are relatively few pathways through which phosphorus can return to land once it reaches the ocean. These include: uplift of the sea floor resulting in erosion, subduction resulting in volcanic activity, or the removal of organisms containing phosphorus (e.g., the fishing industry). Due to the global asymmetry of the cycle, the amount of phosphorus on land and in the ocean is unbalanced (Ingmanson and Wallace, 1989). On a smaller scale, phosphorus is commonly the limiting nutrient for an ecosystem. This is due in part to the asymmetry of the global phosphorus cycle, because small changes in influx can result in large changes to the entire cycle. It is also a common limiting nutrient because it is in such a limited supply globally. Due to the significant role of water in the phosphorus cycle as well as the overall limited availability of the nutrient, understanding its distribution in lagoonal systems such as Puerto Mosquito and Puerto Ferro is important. The limitation in phosphorus availability on Vieques can be determined using the C:P ratio in primary producers such as the seagrass *Thalassia testudinum*.

Previous Work

Previous studies of nutrient availability, dinoflagellate populations, affects of development on lagoonal ecosystems, and of ecosystems similar to the Vieques bays provide important background for the interpretation and analysis of my data. The analysis of Florida Bay (Fourqurean and Zieman, 2002) explores nutrient ratios and cycling in bay ecosystems using *Thalassia testudinum*, which can compare to the nutrient cycling of both the bioluminescent bays of Vieques. Phlips and others (2006) also explore nutrient cycling and availability along the coast of Florida, focusing on how that might affect dinoflagellate health and population. The La Parguera case study (Armstrong and Gilbes, 2007) explores potential cause and effect of disturbances in the ecosystem of a bioluminescent bay and how the populations of dinoflagellates might be enhanced or deteriorated by those disturbances. Gonneea and others (2004) trace organic sources in lagoonal systems through time using isotopic analysis of three end members.

Nutrient availability

Forqurean and Zieman (2002) conducted nutrient analysis in Florida Bay, a large body of water situated between the Florida Keys and mainland Florida. Extensive sampling of *Thalassia testudinum* was conducted across all areas of the large bay. These samples were evaluated for their C, N, and P content in order to establish the spatial distribution of these nutrients. Trends in the relative availability of each nutrient were established for all nutrients. However, no correlation between the distribution of N and P could be documented. Ratio analysis with C indicated increased N availability toward the coast with increased P availability further from the coast. Ratio analysis of N and P indicate the coast as predominantly P-limited while greater distance from the coast as predominantly N-limited; a ratio value of less than or greater than 30 was chosen to determine the limiting reagent (Fourqurean and Zieman, 2002).

Nutrient availability and dinoflagellate populations

The distribution and concentration of *Pyrodinium bahamense* var. *bahamense* has been correlated to factors including temperature, salinity, and nutrient availability, along the coast of Florida by Phlips and others (2006). Generally, populations of *bahamense* off the coast of Florida were only documented in water temperatures greater than 20° C while blooms (rapid population growth) were limited to temperatures greater than 25° C (Phlips et al., 2006). Phlips and others (2006) also confirmed that population amplification occurred in periods of high rainfall, which in Florida occur in the summer. The bays or lagoons that had tropical/subtropical temperatures year round were able to support *Pyrodinium bahamense* var *bahamense* year round while bodies of water where the temperature fluctuated could only support populations in the warm months (Phlips et al., 2006). This variety of dinoflagellate thrives within a wide salinity perimeter, ranging from 14-46 and forms blooms from 16 – 42 (Phlips et al., 2006). This dinoflagellate, var. *bahamense,* was also associated with bodies of water with relatively long residence times, ranging from one to multiple weeks (Phlips et al., 2006). Finally, there was no significant correlation between overall population levels and phosphorus levels; *Pyrodinium bahamense* var *bahamense* was detected in environments with mean levels ranging from 8 $\mu g\ 1^{-1}$ to 100 $\mu g\ 1^{-1}$ (Phlips et.al, 2006). However, it was determined that abnormally high phosphorus levels, ranging up to 330 $\mu g\ 1^{-1}$, were directly related to peak dinoflagellate populations, with concentrations greater than 100,000 organisms/L. Though less evident, a direct relationship between high nitrogen levels and dinoflagellate peak populations could be illustrated, with a population peak occurring at nitrogen levels around 600 µg 1^{-1} (Phlips et al., 2006).

This combination of environmental factors, as well the involvement and interaction of shore use and development, can profoundly influence *Pyrodinium bahamense* var *bahamense* populations. The negative effect of a toxic bloom in the Gulf of Mexico or Caribbean would be felt by many organisms. The role nutrients play in supporting or limiting those blooms is important because small changes in those cycles can still have large scale effects.

Development, sediment influx, and dinoflagellate population

La Parguera, a bioluminescent bay on the main island of Puerto Rico, similar to the bioluminescent bays on Vieques, is experiencing a declining dinoflagellate population, potentially related to development (Armstrong and Gilbes, 2007). La Parguera, Puerto Mosquito, and Puerto Ferro offer a valid comparison for the potential influence of development on bay ecosystems. The hope is to uncover the leading causes of the waning dinoflagellate concentrations and how to best protect habitats where this population is stable (e.g., Puerto Mosquito and Puerto Ferro). Armstrong and Gilbes (2007) found that the amount of suspended sediment was significantly higher in La Parguera, amounting to approximately 320 grams/liter compared to the 270grams/liter in Puerto Mosquito. La Parguera's higher suspended sediment load is in part due to increased terrestrial sediment influx. This disparity is also the result of hydrodynamics and the grain size and composition variability of the sediment between the bays. From the differences in suspended sediment load, it might be inferred that La Parguera has a higher deposition rate compared to Puerto Mosquito. However, the sediment in La Parguera is mostly terrigenous and much finer grained, and thus can be suspended in the water much longer. Lastly, and possibly most important to the preservation of the bioluminescent bays, boat traffic and coastal development is much more extensive in La Parguera (Armstrong and Gilbes, 2007).

Organic matter sources

Gonneea and others (2004) explored carbon burial rates and organic matter sources in lagoonal systems in the Yucatan Pennisula of Mexico, similar to those on Vieques. Mangrove sediments were sampled to obtain C and N isotopes as well as C:N ratios. Three possible organic matter sources were identified: seagrass, mangroves, and phytoplankton. Based on the $\delta^{13}C$ values and C:N ratios of organic matter preserved in the lagoon sediments, the organic matter sources and any change in the relative contributions of the sources throughout time could be established. Mangroves and phytoplankton were the predominant sources near the lagoon shorelines where carbon burial rates were higher. The central lagoon area source was seagrass, and carbon burial rates were much lower. In the lagoons of the Yucatan, the burial rate is directly related to the level of mangrove source contribution (Gonneea et al., 2004).

Field and Laboratory Methods

A temporary lab was set up on Vieques for on-site sample preparation. The rest of the analyses were carried out at Wesleyan University and at Trinity University. Sediment core as well as mangrove, seagrass, and suspended particulate matter samples were taken from June 3 – 15, 2007.

Sediment

A total of fourteen cores were collected, four from Puerto Ferro and ten from Puerto Mosquito (Fig. 3). Cores ranged in length from 20 cm to 370 cm. We used two methods for core sampling determined by water depth and desired sample length: for shallower samples (< 2 meters water depth), we used the pushcore method, which yielded 25-100 centimeters sediment; for deeper samples, vibracoring was used, yielding up to almost four times the thickness of sediment. The positions of vibracore samples were chosen to most completely represent sediment and nutrient variation in the bays. At most cores the location, water temperature, percent O_2, and water depth were measured. In the field lab, the sedimentological characteristics were identified based on changes in color, grain size, and overall visual appearance and thoroughly described (Appendix A). Cores were physically divided into 2.0 centimeter depth increments and any organic material within the core was removed from the sediment for further analysis.

At the Wesleyan Geochemistry laboratory, cores were chosen for further analysis based on their location, sediment length, and sediment composition. From each core at least two samples were taken from each facies and dried in an oven. Once dried, the samples were crushed to a homogenous powder using a mortar and pestle. Portions of each sample were weighed analyzed for organic C, N, and P concentrations by coulometry, flash combustion, and spectrophotometry at Wesleyan University and Trinity University. After the removal of carbonate carbon, with 10% acetic acid, sediment from selected depths was analyzed for C isotopes at Indiana University.

Biota

Seagrass, mangrove, and particulate matter samples were collected at most core sites (Fig. 3 and Appendix C), although not all core sites had seagrass or mangrove growth. The seagrass was hand-pulled from the bay floor, making sure roots were intact, and multiple samples were bagged at each site. Only the leaves were used for analysis. Mangrove samples were cut using plant shears. Each sample contained multiple leaves attached to approximately 3 inches of stem. Again, multiple samples were taken from each site, and from multiple locations on each tree. Multiple seagrass and mangrove samples from each site ensured that any variation between samples would be recognized. In the field laboratory on Vieques, seagrass and mangrove samples were all cleaned, dried, and frozen within 48 hours of collection to prevent decomposition. All epiphytes, other organisms, and sediment on the plants were removed with razor blades.

Once back in the Wesleyan laboratory all plant material was freeze dried. The green leafy component of both the seagrass and mangrove was sampled and weighed for analysis by taking hole punches of each sample, avoiding discoloration. The weighed samples of seagrass were analyzed for phosphorus levels using the method outlined in Fourqurean and Zieman (1992). As with the sediment core samples, flash combustion was used to measure C:N values in the biota. Inorganic C levels were determined using a coulometer and organic C by calculating the difference between total C and inorganic C.

Seawater samples were also taken at each core site to obtain particulate matter. The samples were taken in 500 mL plastic bottles at approximately 1 meter depth by holding an open bottle under the water. If the water was deeper than 1 meter, multiple samples were taken at 0.5 meter intervals to the sea floor, avoiding sediment stirred up from the bottom. In the field lab, water was filtered through a precombusted 0.45 um GF/F glass filter with pore size of 0.7 microns to obtain particulate matter. The filters were frozen at the field lab and at the Wesleyan Geochemistry lab the filters were dried in an oven for approximately 1 hour.

Data and analysis

The data presented here is evaluated in conjunction with other studies that focus on other aspects of the bays' systems in order to more fully understand the habitat and history of the bays. Nutrient ratios obtained from seagrass, mangrove, particulate matter, and the shallowest sediments were used to determine basic trends in the modern distribution and limitation of nutrients within each bay. The possible limiting nutrients are nitrogen and phosphorus, because carbon is widely available in bay ecosystems (e.g., Fourqurean and Zieman, 1992). By studying C:N:P ratios of the seagrass *Thalassia testudinum*, I assessed potential modern nutrient limitations of primary producers in the Vieques bays. The changes in sediment nutrient ratios and carbon isotopic composition reveal the sources of organic carbon though time.

Modern sediment accumulation

Based on initial data, sedimentation rates in Puerto Mosquito are related to water depth. Shallow sites, along the western shore of the bay, exhibited recent average rates ranging from 0.41 cm/yr to 0.63 cm/yr, and 0.08 cm/yr in deeper water (Ku et al., 2008). The shallow depositional sites also exhibit higher terrigenous and carbonate marine sedimentation rates relative to deeper sites (Ku et al., 2008). This variation in rates has implications for present nutrient input into the bays as well as recording past nutrient influx.

Seagrass nutrient analysis

A C:N:P ratio (by weight) of between 445:32:1 and 601:20:1 for *Thalassia testudinum* represents the ratio of a healthy organism growing without nutrient limitation (Patriquin, 1972). The C:N:P ratios of all seagrass sampled in this study fall within that range. However, trends in relative N and P ratios suggest spatial variation in seagrass density within the both bays might be affected by nutrient availability, as suggested by Fourqurean and Zieman (2002).

Within Puerto Mosquito, the three seagrass samples nearest the boat launch (Fig. 4), in the western, back-bay exhibit the lowest C:N ratios, which indicated higher nitrogen levels (C:N ratios = 11.74 – 14.15) (Fig. 3 and Table 1). As the distance from the boat launch increases, the C:N ratio also increases, suggesting lower nitrogen availability. The highest ratio in the bay is along the southern coast, near the middle of the bay (Fig. 4 and Table 1). This sample (PM – 16) exhibits a ratio of 26.99 but might be an outlier. Other than sample PM – 16, the highest C:N ratio was in the channel connecting the bay to the ocean (PM – 21). This C:N ratio of 18.98 indicates low nitrogen availability relative to other points within the bay. This trend is in agreement with Fourqurean and Zieman (2002), which stated that, on a much larger scale, nitrogen availability decreased from inshore waters out, so this aspect of the C:N ratio might be scale invariant. Puerto Ferro exhibited similar trends in nitrogen availability across the bay, but the data set from PF is smaller (Fig. 3 and Table 1). In addition to the observed inshore-offshore availability, average C:N values were slightly higher in PF relative to PM (Table 2), suggesting that Puerto Ferro has decreased nitrogen availability relative to Puerto Mosquito. Relative to Florida Bay the averages and ranges of C:N ratios were generally lower

Sample	C:N	C:P	N:P	C:N:P
PM 13	19.12	334.9	17.52	335:18:1
PM 14	17.82	453.8	25.47	454:25:1
PM 15	17.31	535.5	30.94	536:31:1
PM 16	26.99	402	15.21	402:15:1
PM 17	12.01	407.8	33.96	408:34:1
PM 18	14.15	481.6	34.04	482:34:1
PM 19	11.74	347.1	29.85	347:30:1
PM 21	18.98	487.9	26.04	488:26:1
PM ave.	17.27	431.33	26.63	431:27:1
PF 8	16.97	501.2	29.54	501:30:1
PF 12	20.25	373.7	18.52	373:19:1
PF ave.	18.61	437.45	24.03	437:24:1

Table 1. Nutrient ratios for Thalassia testudinum samples from Puerto Mosquito and Puerto Ferro, Vieques, Puerto Rico.

Ratio	Site	Min	Max	Mean
C:N	**Florida Bay**	11.1	47.1	24.6
	Pt. Mosquito	11.7	26.0	17.3
	Pt. Ferro	17.0	20.3	18.6
C:P	**Florida Bay**	373.4	1901.3	937.4
	Pt. Mosquito	334.9	535.5	431.3
	Pt. Ferro	373.7	501.2	437.5
N:P	**Florida Bay**	15.4	107.1	40.2
	Pt. Mosquito	15.21	34.4	26.6
	Pt. Ferro	18.6	29.5	24.0

Table 2. Comparisons of C:N, C:P, and N:P nutrient ratios. Data from Fourqurean and Zieman (2002) and this study.

in Puerto Mosquito and Puerto Ferro (Table 2). This difference indicates that there is greater nitrogen availability in the Vieques bioluminescent bays relative to Florida Bay.

The trend of C:P ratios within both Puerto Mosquito and Puerto Ferro was opposite that of the C:N ratios. The maximum ratios, therefore lowest phosphorus availability, were seen in the back part of Puerto Mosquito (PM - 15 and 18; C:P = 535.5 - 481.6) (Fig. 4 and Table 1). The increased ratios were concentrated in more protected areas of the bay and areas of denser seagrass distribution. The only other location of low phosphorus availability was at PM – 21, in the ocean channel (C:P = 481.9) (Fig. 4 and Table 1). These ratios loosely suggest phosphorus availability increases with distance from shore. Puerto Ferro had a similar average ratio to Puerto Mosquito although no spatial trend could be seen possibly due to limited data. Both averages and ranges of C:P ratios in Puerto Mosquito and Puerto Ferro were again near the low end of the ranges found in Florida Bay (Table 2).

The N:P ratios of PM indicate relative phosphorus limitation near shore (PM - 15, PM - 17, PM - 18) and relative nitrogen limitation farther from shore (PM - 16) (Fig. 3; Table 1), which is consistent with the C:N and C:P data. This spatial relationship could not be evaluated in PF, where both samples are near shore (Fig. 3). Although the N:P ratios from PM suggest relative P limitation near shore and relative N limitation farther from shore, greater sampling density is required for validation of this hypothesis.

Sediment isotope and nutrient composition

The isotopic analysis and interpretation of Puerto Mosquito sediments were conducted using three core samples. The cores, PM - 14, PM - 23, and PM – 21, were selected for isotopic analysis based on the hydrologic conditions of their locations (Fig. 3). PM - 14 is located in the back bay (Fig. 4), a location with areas of both dense and patchy *Thalassia testudinum*. PM – 23 is located in the central bay, which is dominated by mud with no seagrass is present. PM – 21 is located in the ocean channel, which today has patchy, discontinuous seagrass. The different locations and conditions of these samples offer a better picture of the isotopic and sedimentation distribution across the entire bay.

Changes in the total organic C and N (assumed to be organic N), δ^{13}C, as well as C:N ratios with core depth can be correlated with sedimentary facies changes. The top sediment layer in PM cores is an organic-rich, mixed carbonate-siliciclastic mud, though thickness varies with core location (Fig. 9). Below the top organic rich layer is a sedimentary layer dominated by molluscan shells and gravelly shell hash (Fig. 9), possibly related to a transgressive lag or a storm deposit in deeper water (e.g., Nelson, 2007). Below the gravelly shell hash is a gray or green-blue terrigenous mud. In PM - 23, the shortest core, a gray terrigenous mud with low $CaCO_3$ content (0.75 wt.%) was present at the base (Fig. 9).

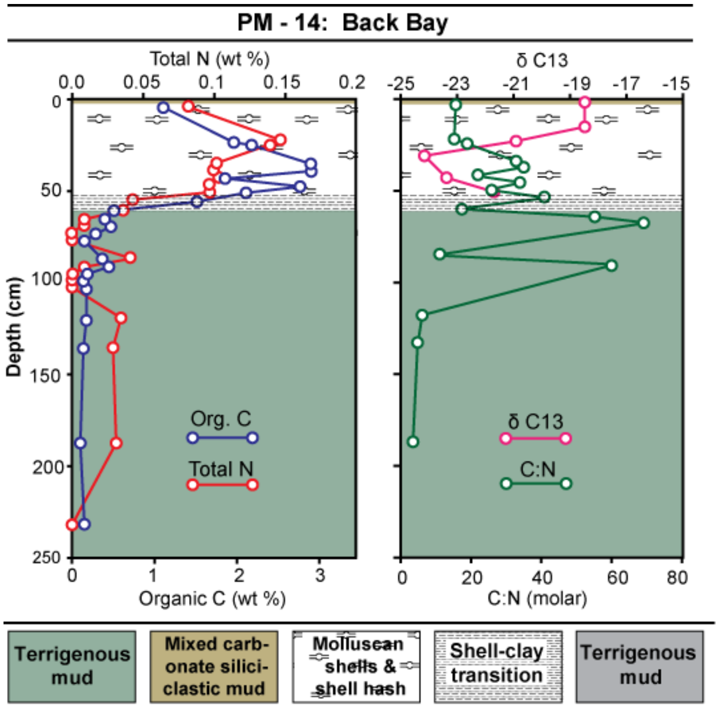


Figure 9. Down core analyses for PM - 14. Core depth (cm) vs. N, organic C, C:N, and δ^{13}C, with sedimentary facies shown for reference.

PM - 14 contains the thinnest layer of organic-rich, mixed carbonate-siliciclastic mud of the three cores, reaching to only 6 centimeters depth. This facies contained lower total N (0.06%) and organic C (1.6%) compared to the gravelly shell hash. The gravelly shell hash layer thickness is similar in all cores as are the total N (0.1%) and organic C (1-2%) contents in this layer (Fig. 9). In PM – 14, the gravelly shell hash extends to a depth of 56 centimeters where it begins a transition to a blue-green terrigenous mud. At 68 centimeters the core is exclusively the blue-green terrigenous mud, which extends to the bottom of the core at 235.5 centimeters. The total nitrogen and organic carbon content of this facies is lower than both the above facies and is relatively constant with depth. Total nitrogen ranges from (0%) to (0.04%) while total organic carbon from (0.11%) to (0.48%) (Fig. 9). δ^{13}C values for the cores are affected by changes in sedimentation. δ^{13}C values for PM - 14 steadily increase with depth, from approximately 30 centimeters to 50 centimeters, where the shell hash grades into terrigenous mud (Fig. 9).

PM - 23, from the central bay, has a much thicker top organic-rich mixed carbonate-siliciclastic mud layer, compared to PM – 14, extending to a depth almost 27 centimeters. The total nitrogen and organic carbon for this facies is relatively high (Fig. 10). Nitrogen values begin at (0.3%) and decrease to approximately (0.25%) at approximately 20 centimeters depth, while carbon begins around (3%) and falls to approximately (2.25%) at approximately 20 centimeters depth. A facies shift occurs at 25 centimeters, from the

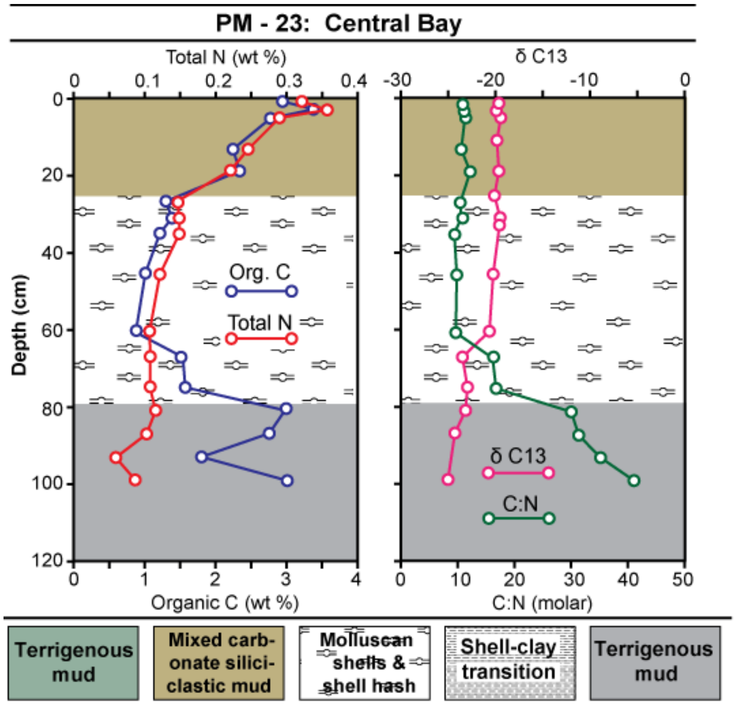


Figure 10. Down core analyses for PM - 23. Core depth (cm) vs. N, organic C, C:N, and δ^{13}C, with sedimentary facies shown for reference.

organic-rich top layer to the gravelly shell hash. In the gravelly shell hash facies, which extends to a depth of around 80 centimeters, the total nitrogen (0.15%) and organic carbon (1.5%) are steady throughout, very similar to the gravelly shell hash in PM - 14. The PM – 23 top layer values are unlike those in PM – 14, where total nitrogen and organic carbon are lower in the organic-rich mud, although the values in the gravelly shell hash are similar to the values from both PM – 23 and PM – 14. PM - 23 δ^{13}C values are similar to PM - 14 near the top of the core (approximately [-20‰]). Around 30 centimeters, just after the facies shift to the gravelly shell hash, the isotope values decrease to below (-20‰). This is a small fluctuation, as values return to above (-20‰) by 35 centimeters. At around 40 centimeters, a steady decrease in δ^{13}C begins, with values decreasing below (-20‰) (Fig. 10). At 60 centimeters, there is a large jump in values to (-25‰) where they remain down to 100 centimeters depth.

The top organic rich layer in PM – 21, similar to PM – 23 and unlike PM - 14, has relatively high total nitrogen (0.35%) and organic carbon (3%) compared to the gravelly shell hash below (Fig. 11). This facies ends at approximately 25 centimeters, shifting to the gravelly shell hash, where the total nitrogen and organic carbon falls to around (0.225%) and (1.75%) respectively. At depths greater than 50 centimeters, there are only small fluctuations in total nitrogen (0.06% – 0.15%) and

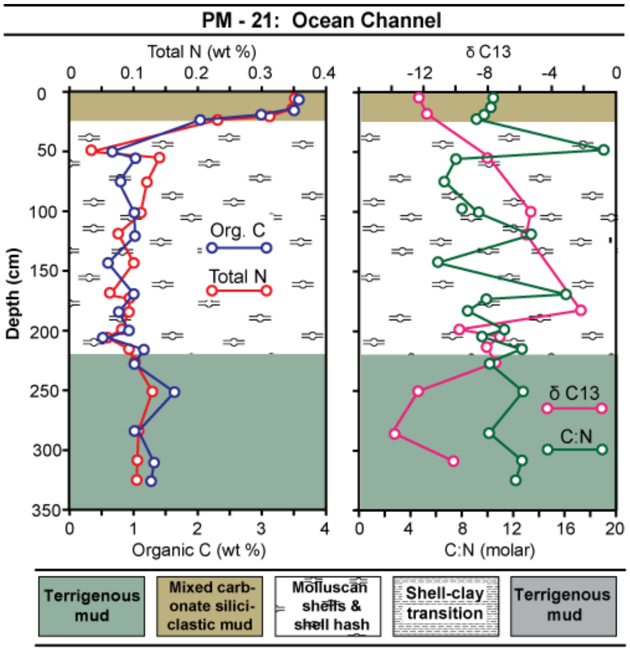


Figure 11. Down core analyses for PM - 21. Core depth (cm) vs. N, organic C, C:N, and δ13C, with sedimentary facies shown for reference.

organic carbon (0.5% – 1%). However, there is a facies shift at approximately 221 centimeters to the blue-green terrigenous mud (Fig. 9). $\delta^{13}C$ values (-12‰) in the organic-rich top layer of PM – 21 are higher than PM - 14 or PM - 23 (Fig. 11) and the values continue to increase in the shell hash. At 180 cm, $\delta^{13}C$ reaches approximately (-3‰); however, $\delta^{13}C$ values more than (- 5‰) might indicate error due to carbonate carbon contamination (Ku et al., 2008). The terrigenous mud at the base of PM-21 exhibits $\delta^{13}C$ values below (-10‰) (Fig. 11).

In PM – 21, $\delta^{13}C$ values begin and remain at approximately (-12‰) for the organic-rich mixed carbonate-siliciclasitc mud layer. This facies transitions to the gravelly shell hash at 25 centimeters depth and the $\delta^{13}C$ values increase to as much as (-2‰). However, $\delta^{13}C$ values greater than (-5‰) could indicate carbonate contamination. The facies shift to blue-green terrigenous mud (221 centimeters) correlates to a shift in isotopic values. At that depth the values shift to values ranging from (-8‰) to (-14‰).

Organic matter sources in Puerto Mosquito and Puerto Ferro

The N:C and $\delta^{13}C$ values for modern seagrass and mangrove from both Puerto Mosquito and Puerto Ferro were plotted with the organic matter source end members established by Gonneea and others (2004) (Table 3). Seagrass $\delta^{13}C$ values from this study ranged from (-7.6‰) to (-14.0‰) while the N:C values ranged from (0.03%) to (0.08%) (Fig. 10 and Table 4). The majority of the seagrass samples from Vieques fell within the seagrass end member from Gonneea and others (2004), but they were concentrated at higher $\delta^{13}C$ values relative to the earlier study. Mangrove $\delta^{13}C$ values ranged from (-25.56‰) to (-31.51‰) and the N:C values ranged from (0.008%) to (0.029%) (Fig. 12 and Table 3). The majority of the sample values fell at the high end for the $\delta^{13}C$ and the low end for the N:C mangrove end member defined by Gonneea and others (2004). No data were available to establish suspended particulate matter (SPM) values for Vieques, but the similarities between the two environments permits the assumption that the SPM in the Vieques bays would also be dominated by phytoplankton, and therefore would be similar to the SPM measured in the Yucatan lagoons. This assumption is dependent on the fact that both study locations are environmentally similar as well as supportive of large dinoflagellate populations.

Sample	N:C	δ13C ‰	δ15N ‰
Seagrass			
PM – 21	0.05269	-9.7	-0.6
PM – 19	0.08518	-9.8	1.4
PM – 18	0.07067	-11.1	3.1
PM – 17	0.08326	-14.0	1.9
PM - 16	0.03705	-9.4	0.5
PM – 15	0.05777	-9.4	0.4
PM – 14	0.05612	-8.9	2.6
PM – 13	0.05230	-9.6	2.5
PF – 12	0.04938	-10.3	3.3
PF – 8	0.05893	-7.9	1.2
Mangrove			
PM – 22	0.008401	-26.91	
PM – 21	0.016766	-28.27	
PM – Britney Channel	0.029197	-31.51	
PF – 19	0.018353	-27.36	
PF – 18	0.013659	-27.44	
PF – 17	0.014601	-27.07	
PF - 7	0.020096	-25.56	

Table 3. N:C, δ^{13}C, and δ^{15}N data for all seagrass and mangrove samples from Puerto Mosquito and Puerto Ferro.

The N:C values from the sediment cores, based on total C and N (wt. %), were used in conjunction with δ^{13}C values to determine the organic matter sources of sediment through time (Fig. 12). The values were plotted on the previously discussed ternary diagram modified from Gonneea and others (2004) (Fig. 12) with seagrass and mangrove end member data from Vieques. The N:C and δ^{13}C values for the first 50 centimeters of PM – 14 ranged from (0.04) to (0.06) and (-18.5‰) to (-23.4‰). This range was closest to the seagrass end member established by Gonneea and others (2004) (Fig. 12) and the values established in this study. δ^{13}C values for PM - 14 are approximately (-19‰) within the organic-rich mud (Fig. 9). Below this layer, from a depth of 6 centimeters until just past 50 centimeters, δ^{13}C values decrease to approximately (-24‰).

PM – 23, of the three cores, exhibited the greatest shift in organic matter source. The lower core (80 – 100 centimeters) range in values for N:C and δ^{13}C are (0.024) to (0.033) and (-23‰) to (-25‰) respectively (Fig. 12). These values are most similar to the mangrove end member established by Gonneea and others (2004) and this study.

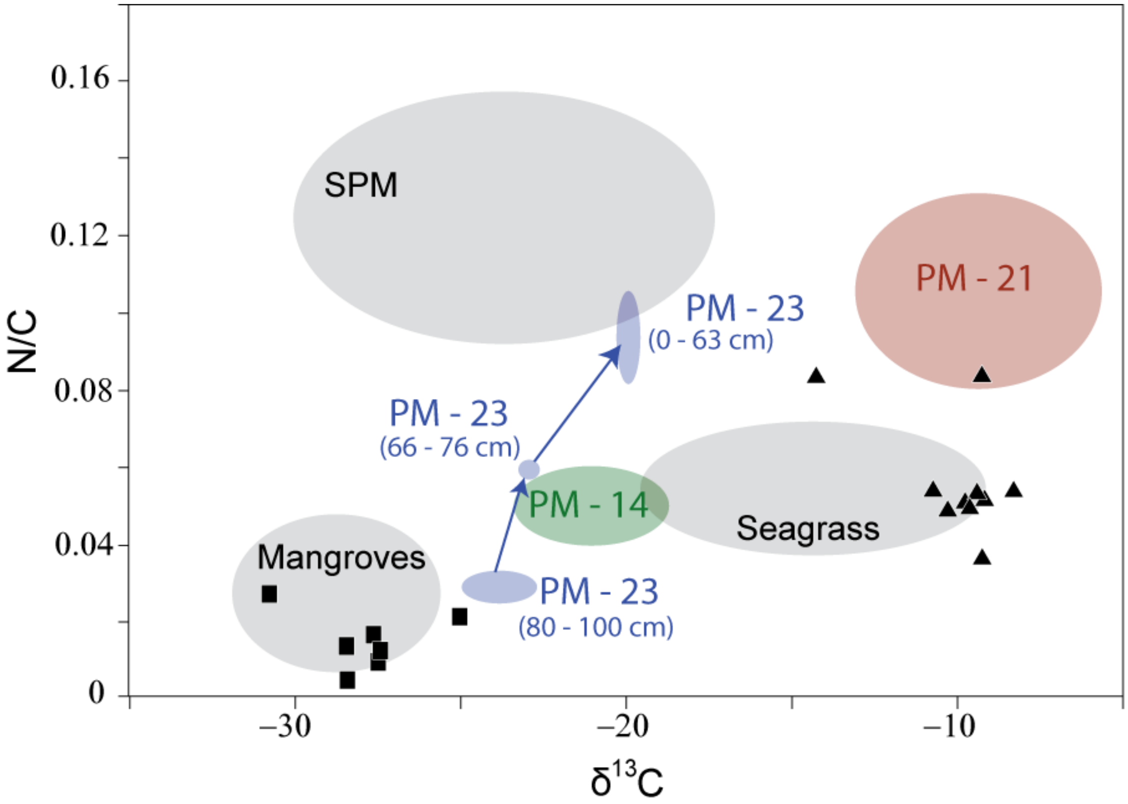


Figure 12. N/C vs. δ^{13}C with data from Puerto Mosquito and Puerto Ferro seagrass (solid triangles) and mangrove (solid squares) and cores PM-14 (green), PM-21 (red), and PM-23 (blue). The ranges in values for potential sources of organic material are indicated by grey ovals (SPM, seagrass, and mangrove) from a study performed in a similar lagoonal ecosystem by Gonneea and others (2004). Figure modified from Gonneea and others (2004).

This middle core (66 – 76 centimeters) shifts away from the mangrove source toward seagrass and SPM. The range in N:C and δ^{13}C values in this portion of the core are approximately N:C (0.06) and δ^{13}C (-23‰) (Fig. 12). However, the values do not fall near enough to any of the three end members to definitively indicate one primary source; most likely the organic matter source was a combination of all three end members. The organic matter source continues to shift in the upper core (0 – 63 centimeters). N:C

(0.081 to 0.105) and $\delta^{13}C$ (-19.43‰ to -20.56‰) values were closest to the SPM end member source (Fig. 12).

The organic matter source for core PM – 21 is relatively constant for the entire length of the core, with N:C values from (0.079) to (0.13) and $\delta^{13}C$ values from (-2‰) to (-13‰) (Fig. 12). This is closest to the seagrass end member but suggests some suspended particulate matter source, as defined by Gonneea and others (2004).

Discussion and conclusions

The nutrient availability in the lagoonal systems of Vieques helps explain the relatively high concentrations of bioluminescent dinoflagellates. The present-day nutrient contents of *Thalassia testudinum* in this study exhibit average C:N and C:P ratios near the minimum observed in a larger study performed in Florida Bay (Fourqurean and Zieman, 2002) (Table 3), suggesting higher relative availability of both nitrogen and phosphorus. The waters of the bioluminescent bays of Vieques are more isolated from the open ocean than Florida Bay, so hydrodynamics might influence the observed difference. Also, terrestrial sources are the main suppliers of phosphorus and nitrogen for marine ecosystems (e.g., Fourqurean and Zieman, 2002), so increased interaction with the land could be another factor that influences the differences in ratios, since all samples in this study were taken less than 200 meters from shore. Relative to similar studies of *Thalassia testudinum* my data set is limited by sparse distribution, but my data permit isolation of broad trends pertaining to the nutrient systems of Puerto Mosquito and Puerto Ferro.

The relative availability of phosphorus and nitrogen could be the result of multiple factors. First, the bioluminescent bays are more contained and isolated compared to Florida Bay, with increased mangrove covered shoreline. Since terrestrial sources are the main suppliers of phosphorus and nitrogen, increased interaction with the land could be one explanation for lower ratios. Within the bays, the spatial distribution of nitrogen content appears similar to the distribution in Florida Bay. Fourqurean and Zieman (2002) observed decreased nitrogen availability with increasing distance from shore, similar to observations made in this study, permitting the hypothesis that C:N ratios are scale invariant. While light availability is known to decrease both C:P and C:N ratios (Abal et al. 1994; Grice et al. 1996), the shallow depths of both bays and less turbid water near the deepest portions of the bays (Nelson, 2007) suggest that light availability is not a factor.

Areas of decreased P availability are concentrated in protected areas of Puerto Mosquito and areas of denser seagrass distribution. Another location of low phosphorus availability was the ocean channel (Fig. 4). Thus phosphorus availability appears to increase with distance from shore; opposite of what is expected, assuming that terrestrial sources provide most phosphorus. However, Fourqurean and Zieman (2002) suggest offshore sources of P are as important as terrestrial sources. Although difficult to evaluate in PM or PF, phosphorus limitation in Florida Bay was correlated with smaller grain size, due to the increased surface area allowing increased P-sorption (Fourqurean and Zieman, 2002).

The N:P ratios of both Puerto Mosquito and Puerto Ferro, if PM – 13 and PM – 16 are considered outliers, suggest that Puerto Ferro is more nitrogen limited compared to Puerto Mosquito (Table 2). The N:P ratio limitation values established for Florida Bay (Fourqurean and Zieman, 2002) have not been used in this study. Though similar in environment, the size discrepancy between Vieques and Florida Bay as well as the overall increased nutrient availability of the bays of Vieques suggest that the N:P cutoff values used to determine limitation might be different on Vieques.

Sources of sediments that accumulate in Puerto Mosquito originate from both terrestrial and marine sources (Ku et al., 2008). Both marine and terrestrial sediment sources accumulate at higher rates along the shores of Puerto Mosquito. The majority of N_2 conversion to nitrate, the nitrogen species used by plants, also occurs on land (Garrison, 2002). The Puerto Mosquito watershed is approximately twice the size of the Puerto Ferro watershed (Fig.2), which could account for its relative abundance of nitrogen and the relative limited availability in Puerto Ferro. The relative phosphorus limitation in Puerto Mosquito compared to Puerto Ferro cannot be related to the watershed alone. Fourqurean and Zieman (2002) suggest that marine phosphorus sources could be just as or even more influential than terrestrial sources alone. Therefore, the smaller ocean canal of Puerto Mosquito would greatly limit the marine phosphorus source while the much larger, open canal of Puerto Ferro would not (Fig. 4).

Terrestrial phosphorus and nitrogen sources could also be enhanced or disrupted by alteration to the bays' watersheds, such as agricultural and commercial development (Fig. 2). Nitrogen or phosphorus inundation within the bays could result in algal blooms, which have been shown to be toxic in the *Pyrodinium bahamense* var. *compressum* (e.g. Phlips et al., 2003). Small amounts of the toxin have been measured in some var. *bahamense* off the coast of Florida brought on by excess nitrogen runoff (Phlips et al., 2003), though the ability of this variety to produce enough toxin to become lethal is unknown. If the terrestrial nutrient source decreased or was cut off, the supply of nutrients to the bays and therefore, the success of the dinoflagellate *Pyrodinium bahamense* var. *bahamense* would be greatly reduced, possibly leading to the species' extinction within the bays. One explanation for the recent continual success of the dinoflagellate in Puerto Ferro and Puerto Mosquito could be the U.S. Naval occupation of portions of Vieques. For approximately 60 years, this greatly limited the development on the island, protecting the bays from possible disruption to the nutrient cycles within the watersheds.

All three cores, PM – 14, PM – 21, and PM – 23 differ in their hydrodynamic environments (Fig. 3). Therefore, there are both similarities and differences in their sedimentological characteristics in both their recent and distant histories. PM – 14 top layer is much thinner and the total organic C and N is lower than PM – 23 and 21 (Fig. 9). The disparity might be related to a dilution effect caused by higher rates of terrigenous sediment deposition at PM - 21 and PM - 23, resulting in lower organic C concentrations (Ku et al., 2008). The gravelly shell hash below the organic-rich top layer is more similar in thickness across the bay, with small discrepancies in the depth of deposition (Fig. 9). This shell dominated layer does not occur anywhere else in the cores (Fig. 9) nor do they reside in the bay today, as it is dominated by dinoflagellate. The cause, whether related to a gradual or a catastrophic event, of the disappearance of the mollusks is unknown; however, their habitat does not appear to have supported dinoflagellates. The terrigenous mud layer below is blue-green in both PM – 14 and PM – 21 and gray in PM – 23. This discrepancy might be due to the depth of sample, as PM – 23 is by far the shortest. Therefore there is a possibility the blue-green clay underlies PM – 23 but at a greater depth than sampled. A blue-green terrigenous mud was documented in the soil auger, onshore (Fig. 4), and the Esperanza aquifer is underlain by a similarly described clay layer that extends to the bays (Veve and Taggart, 1996). Further exploration is needed to determine if this is a continuous layer.

This layer, whether extending into the bays or not, has possible implications for the nutrient cycling within them. The clay layer limits infiltration into the aquifer and therefore increases run-off into the bays. Increased run-off has the potential to flush nutrients out of the bay; the seasonality of rainfall and therefore seasonal nutrient flushing could impose cyclic dinoflagellate blooms or seagrass growth. This could be one factor facilitating the greater success of the dinoflagellate population within Puerto Mosquito compared to Puerto Ferro. The size shape of the canal of Puerto Mosquito could limit nutrient flushing as it limits interaction with the open ocean, protecting the dinoflagellates from seasons of decreased nutrients. For this reason, increased run off into Puerto Mosquito could result in nutrient flooding and possible saxitoxin accumulation and toxic algal blooms. Therefore, the hydrodynamics of the bay system and all other factors controlling onshore nutrient concentrations must be taken into consideration when implementing development upstream of the bioluminescent bays.

The N and C percentage and $\delta^{13}C$ values for the first 50 centimeters of PM – 14 ranged from (0.04%) to (0.06%) and (-18.5‰) to (-23.4‰) (Fig. 10), which indicates sediment dominated by seagrass as a source for sediment organic matter based on previous work by Gonneea and others (2004). Due to limited samples only the recent sedimentation history can be discussed for PM – 14. However, the trends in $\delta^{13}C$ decrease in value with depth, indicating that the percentage of mangrove as an organic matter source increases (Fig. 9 and Fig. 10). Therefore, it is likely that in the back bay of Puerto Mosquito (PM – 14) mangrove was the dominant organic matter source in the past, and more recently the primary source of organic matter shifted to seagrass, as we see in the top 50 centimeters of PM - 14 (Fig. 10). Based on these data and the known habitats of mangrove and seagrass, the trends in PM-14 indicate possible sea level transgression (Fig. 10), with increasing water depth through time.

The greatest shift in organic matter (OM) source is recorded in core PM – 23, sampled from the center of Puerto Mosquito (Fig. 4). The oldest recorded source, in the lower core (80 – 100 centimeters), is approximately 70% mangrove and 30% seagrass, using the end members established by Gonneea and others (2004) (Fig. 10). This places the lower core sediment in a marine, terrestrial transition zone and relatively shallow water, where mangroves are found. In the middle core (66 – 76 centimeters) the OM source shifts to approximately equal percentages of mangrove, seagrass, and suspended particulate matter (Fig. 10). The OM sources dictate a sedimentation location of increasing water depth and therefore increasing distance from shore. Like PM – 14, the shift in OM source and assumed shift in sedimentation environment suggests a possible sea level transgression in Puerto Mosquito. In the upper core (0 – 63 centimeters) the OM source shifts again, dominated almost completely by SPM. This is consistent with the top sediment seen in the central part of Puerto Mosquito, because there is no seagrass currently growing there (Fig. 3). From its current location (Fig. 3) and OM source data (Fig. 10) it can also be inferred that no sea level regression has occurred.

The core at PM - 21 samples a much thicker portion of sediment than the other two and therefore represents more of the bay's sedimentation history. The organic matter source values for PM - 21 are also very different compared to PM – 23 and PM - 14 (Fig. 10). The OM source is relatively constant throughout the core, indicating approximately 60% seagrass and 40% SPM (Fig. 10). Neither the habitat changes and inferred sea level transgression observed in cores PM – 14 and PM – 23 are recorded in core PM – 21. This is most likely due to its position in the bay. It is in the channel that connects the open ocean to Puerto Mosquito while PM – 14 and PM – 23 are deeper within the bay (Fig. 3). The locations of PM – 14 and PM – 23 would more likely be affected by sea level changes and experience the greatest habitat alteration as a result of those changes relative to the position of core PM – 21.

In recent history (approximately the last 40 – 200 years), sediment accumulation in Puerto Mosquito, with higher sedimentation rates focused in the shallow, western bay and lower rates in deeper water, seems to imply that terrigenous sediment is confined to the shallows of the bay, never reaching the center. The sediment history, sedimentation rate based on ^{210}Pb data (Ku et al., 2008), as well as the shifts in organic matter source indicate a sea level transgression about 1800 – 2300 years ago. Based on sedimentation data (the organic-rich layer), the conditions that have supported the dinoflagellate population are a recent phenomena, beginning 300 – 1900 years ago (Ku et al., 2008). This is recorded in the shifts of OM source in PM – 23, where no SPM was present in the past, it is the dominant source today. Therefore, while the present-day habitats of Puerto Mosquito and Puerto Ferro show great ability to support dinoflagellate populations, past changes in the bays' environment that might have influenced the success of the dinoflagellate appear to be natural. So while protection of the habitat from future development is important, further exploration related to the natural evolution of dinoflagellate population success as well as the influence of outside variables is required to fully understand how to support long-term success of the species in the bays of Vieques.

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Appendix A – Sediment core descriptions

PM 14 Depth (cm)	**Description**	**Color**	**Dissolved O_2**	**Temperature (°C)**
0 - 6	Soupy, clay matrix with small broken shells Much darker underneath	5 GY 2/1	Surface - 6.3 mg/l 100 %	Surface - 30.2
6 - 29	Contains shells ranging from 1 – 6 cm in length	5 Y 4/1	90 cm – 5.8 mg/l 94%	90 cm – 30.1
29 - 56	Contains smashed shells	5 G 2/1		
56 - 68	Gradational clay	5 G 3/1		
68 – 235.5	Mainly greenish clay Also brown with modeling at the edges Clay – modeling, fine grain sizes, not sandy but some sand grains attached to roots present - Bioturbation near the bottom, white feel at 196 cm - Grades between fine clay and sand at 164 cm	5 G 5/7 5 GY 3/1		

PM 21 Depth (cm)	**Description**	**Color**
0 - 25	Dark, soupy	
25 - 108 108 - 171 171 - 188 188 - 221	Carbonate sand with shells and plant material. Plant material concentrated at 40-52 cm Carbonate sand with larger shells, < 4 cm with plant material Sandy carbonate with fewer large shells Sandy with broken larger shells, approximately 5 cm	5 Y 6/1 5 GY 4/1
221 - 268	Finer grain sand, no large shells, light olive gray	
268 - 336	Finer grains with increased plant material throughout	

PM 23* Depth (cm)	**Description**	**Color**	**Dissolved O_2**	**Temperature (°C)**
0 - <27	Very soupy (0-2cm) Dark gray gradually grades into very fine grained	N4	Surface – 5.7 mg/l, 92% 3.0 meters – 5.5 mg/l, 89%	Surface – 29.9 3.0 meters – 29.8
~27 - ~40	Essentially same color matrix throughout, gritty Band of shell fragments at 27 – 37.5	5 Y 5/1		
? - ?	Many shells, ≤ 4cm Sandy			
	Color similar to above facies, whole shells with fragments, 1mm – 1.5mm Roots present			
? – 100 cm	Medium dark gray			
* Notebook water damaged, some notes could not be deciphered				

Appendix B – Core locations

Core	Latitude (N)	Longitude (W)
Puerto Mosquito		
PM - 25	18.10022	65.44678
PM -24	18.09589	65.45297
PM - 23	18.10145	65.44475
PM - 22	18.10248	65.43972
PM – 21	18.0995	65.45042
PM - 16	18.10087	65.44779
PM – 15	18.1001	65.45022
PM – 14	18.10387	65.44784
PM – 13	18.10488	65.44022
Puerto Ferro		
PF – 12	18.106183	65.431839
PF - 11	18.106528	65.424447
PF - 8	18.109433	65.429239
PF - 7	18.109767	65.427475

Appendix C – Nutrient data for biota

Sample	**Total C (wt.%)**	**Total N (wt.%)**	**C:N (org C:total N) molar**
PM 13 SG*	31.98	1.95	19.12
PM 14 SG	34.17		17.82
PM 15 SG	31.48	2.120	17.31
PM 16 SG	30.52	1.350	26.99
PM 17 SG	33.86	3.290	12.01
PM 18 SG	31.32	2.580	14.15
PM 19 SG	33.69	3.380	11.74
PM 21 SG	33.35	2.080	18.98
PM 21 M**	45.83	0.900	59.65
PM 22 M	43.19	0.420	119.03
PM 24 M	42.60	1.910	26.07
Britney Channel M	38.08	1.300	34.25
PF 7 M	37.36	0.880	49.76
PF 8 SG	34.03	2.340	16.97
PF 12 SG	33.08	1.910	20.25
PF 17 M	42.97	0.730	68.49
PF 18 M	41.74	0.700	73.21
PF 19 M	41.50	0.890	54.49

*SG = seagrass
**M = mangrove

Appendix D – Nutrient data for core sediment

Sample	Interval (cm)	CaCO3 (wt%)	Inorg. C (wt.%)	Total C (wt.%)	Total N (wt.%)	Organic C (wt.%)	C:N (org C:total N) molar	Terrig. sediment (non-carb, non-organic) wt.%	Organic Matter (approx. wt.%)
PM12A	0-2	29.77	3.57	6.30	0.292	2.72	10.86	64.8	5.45
PM12A	2-4	33.36	4.00	6.76	0.319	2.76	10.09	61.1	5.51
PM12A	6-8	27.56	3.31	5.75	0.282	2.44	10.10	67.6	4.88
PM12A	8-10	26.07	3.13	6.06	0.281	2.93	12.15	68.1	5.85
PM12A	12-14	24.30	2.92	6.00	0.278	3.08	12.91	69.5	6.16
PM12A	18-20	32.72	3.93	6.12	0.206	2.20	12.41	62.9	4.39
PM12A	22-24	34.75	4.17	6.14	0.139	1.97	16.51	61.3	3.94
PM12A	26-28	36.46	4.38	7.19	0.146	2.81	22.39	57.9	5.62
PM12A	34-36	39.18	4.70	6.31	0.110	1.61	17.02	57.6	3.22
PM12A	44-46	4.61	0.55	1.39	0.06	0.84	17.48	93.7	1.67
PM12A	48-50	1.26	0.15	0.77	0.029	0.62	25.22	97.5	1.24
PM12A	66-68	0.14	0.02	0.28	0.004	0.26	85.31	99.3	0.53
PM12A	68-70	5.91	0.71	1.28	0.041	0.57	16.26	92.9	1.15
PM 13	0-8	47.60	5.71	11.41	0.298	5.70	22.29	41.0	11.40
PM 13	8-10	44.80	5.38	10.46	0.287	5.08	20.63	45.0	10.16
PM 13	12-14	14.84	1.78	8.76	0.411	6.98	19.80	71.2	13.95
PM 13	16-18	23.95	2.87	8.74	0.307	5.86	22.26	64.3	11.73
PM 13	20-22	18.06	2.17	8.04	0.327	5.88	20.97	70.2	11.75
PM 13	28-30	25.65	3.08	9.47	0.374	6.39	19.91	61.6	12.78
PM 13	46-48	45.54	5.46	12.17	0.353	6.70	22.15	41.1	13.41
PM 13	72-74	50.67	6.08	11.08	0.271	5.00	21.57	39.3	10.01
PM 13	84-86	58.96	7.07	10.86	0.233	3.78	18.97	33.5	7.56
PM 13	112-114	55.51	6.66	10.40	0.167	3.74	26.11	37.0	7.48
PM 13	126-128	53.92	6.47	8.25	0.105	1.78	19.79	42.5	3.56
PM 13	140-145	49.78	5.97	7.71	0.049	1.74	41.68	46.7	3.48
PM 13	175-180	37.00	4.44	6.23	0.046	1.79	45.46	59.4	3.57
PM 13	200-204	14.28	1.71	2.17	0.038	0.45	14.08	84.8	0.91
PM 13	222-224	2.49	0.30	0.67	0.021	0.37	20.05	96.8	0.73
PM 13	236-238	5.74	0.69	1.04	0.023	0.35	18.17	93.6	0.70
PM 13	252-254	1.02	0.12	0.34	0.013	0.21	18.79	98.6	0.43
PM 14	3-5	76.12	9.13	10.25	0.080	1.11	16.27		
PM 14	22-24	58.47	7.02	9.01	0.147	1.99	15.86	37.5	3.99
PM 14	24-26	54.09	6.49	8.69	0.138	2.20	18.62	41.5	4.40
PM 14	34-36	21.53	2.58	5.51	0.102	2.93	33.38	72.6	5.85

Sample	Interval (cm)	CaCO3 (wt%)	Inorg. C (wt.%)	Total C (wt.%)	Total N (wt.%)	Organic C (wt.%)	C:N (org C:total N) molar	Terrig. sediment (non-carb, non-organic) wt.%	Organic Matter (approx. wt.%)
PM 14	38-40	4.04	0.49	3.42	0.099	2.94	34.57	90.1	5.88
PM 14	42-44	4.01	0.48	2.37	0.102	1.89	21.55	92.2	3.78
PM 14	46-48	3.64	0.44	3.26	0.096	2.83	34.23	90.7	5.65
PM 14	50-52	2.83	0.34	2.47	0.097	2.13	25.73	92.9	4.26
PM 14	54-56	2.08	0.25	1.78	0.043	1.53	41.79	94.8	3.07
PM 14	60-62	1.04	0.13	0.66	0.036	0.54	17.33	97.9	1.07
PM 14	64-66	1.15	0.14	0.55	0.009	0.41	55.44	98.0	0.82
PM 14	68-70	0.07	0.01	0.48	0.008	0.48	70.20	99.0	0.95
PM 14	72-74	0.13	0.02	0.32	0.000	0.31		99.2	0.62
PM 14	76-78	0.08	0.01	0.17	0.000	0.16		99.6	0.31
PM 14	86-88	0.03	0.00	0.38	0.042	0.37	10.45	99.2	0.74
PM 14	90-92	0.04	0.01	0.48	0.009	0.47	64.08	99.0	0.95
PM 14	94-96	0.06	0.01	0.18	0.000	0.18		99.6	0.35
PM 14	98-100	0.07	0.01	0.15	0.000	0.14		99.6	0.28
PM 14	102-104	0.03	0.00	0.18	0.000	0.17		99.6	0.35
PM 14	118-120	0.05	0.01	0.20	0.034	0.19	6.61	99.6	0.38
PM 14	134-146	0.77	0.09	0.22	0.029	0.13	5.00	99.0	0.25
PM 14	186-188	0.44	0.05	0.16	0.031	0.11	4.09	99.3	0.22
PM 14	230-232	0.00	0.00	0.14	0.000	0.14		99.7	0.28
PM 16	0-5	46.17	5.54	7.85	0.241	2.31	11.17	49.2	4.61
PM 16	10-15	51.60	6.19	8.17	0.167	1.98	13.79	44.4	3.95
PM 16	25-30	64.99	7.80	9.10	0.145	1.30	10.47	32.4	2.60
PM 16	45-50	68.36	8.20	9.72	0.138	1.52	12.81	28.6	3.04
PM 16	65-70	66.25	7.95	10.26	0.142	2.31	19.00	29.1	4.63
PM 16	85-90	64.90	7.79	9.26	0.123	1.48	14.04	32.2	2.95
PM 16	105-110	52.64	6.32	7.36	0.105	1.04	11.51	45.3	2.08
PM 16	115-120	59.48	7.14	7.91	0.094	0.78	9.59	39.0	1.55
PM 16	135-140	75.23	9.03	10.33	0.107	1.31	14.24	22.2	2.61
PM 16	154-156	74.65	8.96	10.70	0.145	1.74	13.94	21.9	3.48
PM 16	182-184	81.72	9.81	11.42	0.155	1.62	12.15	15.0	3.24
PM 16	220-222	0.93	0.11	4.70	0.115	4.59	46.60	89.9	9.18
PM 16	270-272	20.80	2.50	3.04	0.058	0.54	10.86	78.1	1.09
PM 16	310-312	19.59	2.35	2.73	0.040	0.38	11.00	79.6	0.76
PM 16	368-370	19.24	2.31	2.45	0.046	0.15	3.67	80.5	0.29
PM 21	0-10	75.34	9.04	12.16	0.353	3.12	10.32	18.4	6.25
PM 21	10-16	78.09	9.37	12.44	0.350	3.07	10.22	15.8	6.13

Sample	Interval (cm)	CaCO3 (wt%)	Inorg. C (wt.%)	Total C (wt.%)	Total N (wt.%)	Organic C (wt.%)	C:N (org C:total N) molar	Terrig. sediment (non-carb, non-organic) wt.%	Organic Matter (approx. wt.%)
PM 21	18-20	79.46	9.53	12.17	0.315	2.63	9.73	15.3	5.26
PM 21	22-24	85.62	10.27	12.08	0.232	1.81	9.09	10.8	3.61
PM 21	48-50	1.76	0.21	0.82	0.037	0.61	19.00	97.0	1.22
PM 21	54-56	89.05	10.68	11.61	0.143	0.92	7.54	9.1	1.84
PM 21	74-76	89.19	10.70	11.40	0.123	0.70	6.61	9.4	1.40
PM 21	100-102	89.62	10.75	11.65	0.113	0.90	9.30	8.6	1.80
PM 21	118-120	89.47	10.74	11.64	0.079	0.91	13.38	8.7	1.82
PM 21	142-144	91.42	10.97	11.51	0.102	0.54	6.12	7.5	1.07
PM 21	168-170	90.54	10.86	11.76	0.065	0.89	16.04	7.7	1.79
PM 21	172-174	90.49	10.86	11.69	0.097	0.83	9.93	7.9	1.66
PM 21	182-184	89.90	10.79	11.48	0.095	0.69	8.50	8.7	1.39
PM 21	198-200	89.32	10.72	11.53	0.084	0.82	11.30	9.1	1.63
PM 21	204-206	91.00	10.92	11.42	0.062	0.51	9.58	8.0	1.01
PM 21	214-216	87.23	10.47	11.50	0.096	1.04	12.59	10.7	2.07
PM 21	226-228	87.60	10.51	11.42	0.105	0.91	10.08	10.6	1.81
PM 21	250-252	84.20	10.10	11.55	0.133	1.45	12.74	12.9	2.90
PM 21	285-286	87.90	10.55	11.50	0.109	0.95	10.11	10.2	1.90
PM 21	308-310	88.67	10.64	11.81	0.108	1.17	12.69	9.0	2.35
PM 21	324-326	87.34	10.48	11.61	0.108	1.13	12.15	10.4	2.25
PM 22	0-4	70.04	8.40	10.33	0.200	1.93	11.22	26.1	3.85
PM 22	6-8	45.39	5.45	10.07	0.223	4.62	24.20	45.4	9.24
PM 22	12-14	85.14	10.22	10.76	0.192	0.54	3.29	13.8	1.08
PM 22	18-20	75.14	9.02	10.89	0.132	1.88	16.55	21.1	3.75
PM 23	0-2	37.28	4.47	7.42	0.321	2.95	10.71	56.8	5.89
PM 23	2-4	32.31	3.88	7.26	0.357	3.39	11.08	60.9	6.77
PM 23	6-8	44.09	5.29	8.07	0.289	2.78	11.24	50.3	5.57
PM 23	12-14	47.55	5.71	7.96	0.245	2.25	10.70	47.9	4.51
PM 23	18-20	49.92	5.99	8.32	0.222	2.33	12.28	45.4	4.67
PM 23	26-28	70.95	8.51	9.82	0.146	1.30	10.42	26.4	2.61
PM 23	30-32	65.25	7.83	9.19	0.149	1.37	10.69	32.0	2.73
PM 23	34-36	69.88	8.38	9.60	0.149	1.21	9.48	27.7	2.43
PM 23	43-48	77.28	9.27	10.28	0.120	1.01	9.79	20.7	2.02
PM 23	58-63	77.56	9.31	10.19	0.107	0.88	9.59	20.7	1.76
PM 23	66-68	71.89	8.63	10.13	0.108	1.51	16.25	25.1	3.02
PM 23	74-76	68.74	8.25	9.81	0.108	1.56	16.85	28.1	3.13
PM 23	80-82	37.90	4.55	7.53	0.116	2.98	29.86	56.1	5.96

Sample	Interval (cm)	CaCO3 (wt%)	Inorg. C (wt.%)	Total C (wt.%)	Total N (wt.%)	Organic C (wt.%)	C:N (org C:total N) molar	Terrig. sediment (non-carb, non-organic) wt.%	Organic Matter (approx. wt.%)
PM 23	86-88	14.50	1.74	4.50	0.103	2.76	31.26	80.0	5.52
PM 23	92-94	46.80	5.62	7.43	0.060	1.81	35.04	49.6	3.62
PM 23	98-100	0.75	0.09	3.10	0.086	3.01	40.99	93.2	6.02
PM 24	0-6	0.00	0.00	0.84	0.080	0.84	12.31	98.3	1.68
PM 24	8-10	0.00	0.00	0.81	0.074	0.81	12.74	98.4	1.62
PM 24	12-14	0.00	0.00	1.27	0.083	1.27	17.87	97.5	2.53
PM 24	18-20	0.24	0.03	3.57	0.194	3.54	21.31	92.7	7.08
PM 24	36-38	0.02	0.00	0.83	0.058	0.83	16.71	98.3	1.66
PM 24	52-54	0.00	0.00	0.42	0.034	0.42	14.32	99.2	0.84
PM 24	68-70	0.00	0.00	0.24	0.002	0.24	126.42	99.5	0.48
PM 24	78-80	0.00	0.00	0.23	0.005	0.23	52.09	99.5	0.46
PM 24	88-90	0.00	0.00	0.22	0.004	0.22	73.21	99.6	0.45
PM 24	94-96	0.08	0.01	0.35	0.035	0.34	11.55	99.2	0.69
PM 24	116-118	11.63	1.40	1.64	0.014	0.24	21.11	87.9	0.49
PM 24	138-140	26.04	3.12	3.38	0.037	0.26	8.17	73.4	0.52
PM 24	152-154	2.23	0.27	0.49	0.003	0.22	94.16	97.3	0.44
PM 24	168-170	1.57	0.19	0.39	0.031	0.20	7.63	98.0	0.41
PM 25	0-2	46.43	5.57	8.20	0.287	2.63	10.69	48.3	5.26
PM 25	2-4	63.71	7.64	8.60	0.178	0.96	6.28	34.4	1.91
PM 25	6-8	49.42	5.93	7.58	0.150	1.65	12.75	47.3	3.29
PM 25	12-15	54.12	6.49	7.80	0.109	1.31	14.02	43.3	2.61
PM 25	15-20	66.47	7.98	8.87	0.124	0.89	8.36	31.7	1.78
Soil Auger 1		0.03	0.00	0.73	0.079	0.73	10.74	98.5	1.46
Soil Auger 2		0.00	0.00	0.20	0.030	0.20	7.55	99.6	0.39
Soil Auger 3		0.00	0.00	0.30	0.044	0.30	7.99	99.4	0.61
Soil Auger 4		0.00	0.00	0.33	0.052	0.33	7.28	99.3	0.65
Soil Auger 5		0.00	0.00	0.31	0.037	0.31	9.71	99.4	0.62
Soil Auger 6		0.00	0.00	0.17	0.027	0.17	7.35	99.7	0.34
Soil Auger 7		0.00	0.00	0.32	0.038	0.32	9.91	99.4	0.64
Soil Auger 8		0.00	0.00	0.16	0.030	0.16	6.13	99.7	0.31
Soil Auger 9		0.00	0.00	0.12	0.035	0.12	4.00	99.8	0.24
PF 7	0-2	62.65	7.52	10.63	0.332	3.11	10.93	31.1	6.22
PF 7	2-4	64.42	7.73	10.90	0.356	3.17	10.40	29.2	6.34
PF 7	6-8	68.15	8.18	10.94	0.286	2.76	11.25	26.3	5.52
PF 7	12-14	70.45	8.45	10.92	0.266	2.46	10.79	24.6	4.93
PF 7	18-20	69.31	8.32	11.33	0.322	3.01	10.91	24.7	6.03

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PF 7	22-24	74.29	8.91	11.97	0.313	3.05	11.36	19.6	6.10
PF 7	28-30	76.69	9.20	11.55	0.250	2.35	10.95	18.6	4.69
PF 7	46-48	82.02	9.84	11.85	0.215	2.01	10.90	14.0	4.02
PF 7	68-70	83.95	10.07	11.65	0.165	1.58	11.17	12.9	3.16
PF 8	0-5	72.80	8.73	11.10	0.269	2.37	10.25	22.5	4.73
PF 8	5-10	69.30	8.32	10.94	0.283	2.63	10.82	25.4	5.25
PF 8	10-15	66.10	7.93	10.73	0.269	2.80	12.16	28.3	5.60
PF 8	15-20	68.11	8.17	10.82	0.279	2.65	11.07	26.6	5.30
PF 8	55-60	82.62	9.91	12.07	0.240	2.15	10.44	13.1	4.30
PF 8	70-75	80.86	9.70	11.74	0.206	2.04	11.56	15.1	4.08
PF 11	10-15	89.56	10.75	10.74	0.127	0.00	-0.02	10.4	0.00
PF 11	15-20							100.0	0.00
PF 11	55-60	91.23	10.95	11.87	0.088	0.92	12.21	6.9	1.84
PF 11	80-85	90.52	10.86	11.69	0.080	0.83	12.05	7.8	1.65
PF 11	110-115	89.66	10.76	11.54	0.103	0.79	8.92	8.8	1.57
PF 11	122-124	87.92	10.55	11.98	0.118	1.43	14.17	9.2	2.86
PF 11	130-135	87.58	10.51	11.92	0.141	1.41	11.66	9.6	2.83
PF 11	146-148	90.40	10.85	12.14	0.085	1.30	17.82	7.0	2.59
PF 11	165-170	92.27	11.07	11.82	0.063	0.75	13.95	6.2	1.50
PF 11	190-195	91.67	11.00	11.88	0.087	0.88	11.88	6.6	1.77
PF 11	210-215	93.11	11.17	11.97	0.085	0.80	10.97	5.3	1.59
PF 11	245-250	91.95	11.03	12.15	0.094	1.12	13.84	5.8	2.23
PF 11	320-325	90.40	10.85	11.81	0.075	0.96	14.97	7.7	1.92
PF12	0-2	72.56	8.71	11.74	0.350	3.04	10.10	21.4	6.07
PF12	2-4	71.32	8.56	11.53	0.326	2.98	10.63	22.7	5.95
PF12	10-15	63.81	7.66	10.68	0.308	3.02	11.46	30.1	6.05
PF12	15-20	64.74	7.77	11.30	0.324	3.53	12.72	28.2	7.06
PF12	25-30	74.12	8.89	11.08	0.216	2.19	11.83	21.5	4.38
PF12	40-45	71.46	8.57	10.01	0.155	1.44	10.82	25.7	2.87
PF12	60-65	66.05	7.93	9.14	0.103	1.21	13.70	31.5	2.43
PF12	70-75	66.56	7.99	9.41	0.132	1.42	12.58	30.6	2.85