CHAPTER 6: CHARACTERIZATION OF SPATIAL AND TEMPORAL NUTRIENT DYNAMICS

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6.1 INTRODUCTION

Primary productivity in marine systems is most often limited by nitrogen (N), but phosphorus (P) can be co-limiting under certain circumstances and systems can vary from N limitation to P limitation over space and time. In estuarine systems, nutrient enrichment can result in algal blooms, changes in algal community composition (including harmful algal blooms) and increases in hypoxia/anoxia (Bricker et al. 2007). In Vieques, lagoon ecosystems are of ecological significance, ranging from bird, fish and crab habitats to the unique dinoflagellate populations of the bioluminescent bay. Furthermore, in tropical systems, excess nutrient loads can cause increases in macroalgal growth and can have deleterious effects on corals, such as macroalgae outcompeting and overgrowing corals. Finally, nitrogen and phosphorus can impact corals directly by lowering fertilization success (Harrison and Ward 2001), and reducing both photosynthesis and calcification rates (Marubini and Davis 1996).

Land based contributions of nutrients come from a variety of sources. Phosphorus and reactive nitrogen can enter the environment from chemical fertilizer (agriculture, lawns, golf courses), industrial sources, animal waste, and human waste (Galloway et al. 2003). Additionally, nitrogen can be contributed from biological nitrogen fixation and atmospheric nitrogen deposition (originating from fossil fuel combustion and ammonia volatilization from agriculture) (Mathews et al. 2002).

Although a comprehensive island wide nutrient budget is beyond the scope of this study, it seems likely that human waste is the largest contributor to the nutrient budget on the island due to a lack of significant agricultural activity and no industrial sources on the island. The wastewater treatment plant (WWTP) in Vieques performs secondary sewage treatment and has a capacity of 0.5 MGD (Navarro 2002). The WWTP is located on the north shore of the island, west of Esperanza and east of the airport (Figure 6.1). Effluent from the WWTP is discharged to a treatment lagoon system consisting of four evaporation/percolation cells, which have no discharge point to the surface waters (NOAA 2007). This type of system relies on a combination of evaporation/volatilization to the atmosphere and a percolation of treated liquid into the groundwater. Volatilization of ammonia from the lagoon system may result in atmospheric deposition of ammonia to the landscape and coastal waters. This singular facility serves a population of 4,000 (less than half the population of the

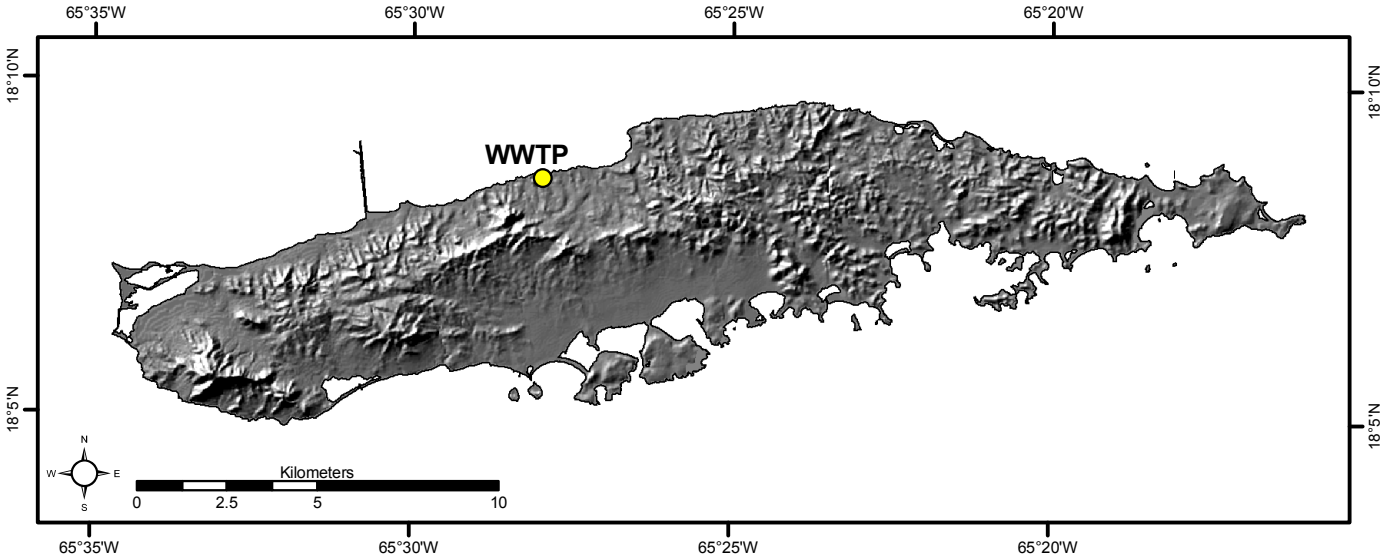

Figure 6.1. Location of wastewater treatment plant (WWTP) site.

island) with the rest of the population not being served by a WWTP. This unsewered population may be especially important to the nutrient budgets of the island.

As the economy of Vieques shifts from being centered around the activities of the U.S. Navy towards tourism, significant development is expected to occur. With development comes the potential for increased nutrient loads. These sources could include increased human waste (with population increases) and increased fertilizer inputs (from golf courses and lawns).

The goals of this part of the ecological characterization project of Vieques were to:

1) Determine if there are any hotspots of nutrient enrichment in the coastal waters;

2) Establish a baseline of nutrient condition against which to measure changes in the future;

3) Characterize the spatiotemporal variability in nutrient concentrations;

4) Characterize the spatiotemporal variability in chlorophyll and turbidity using remote sensing technologies.

6.2 METHODS

Sampling Design

An initial sampling survey of nutrients was conducted in May 2007, in conjunction with the sediment and coral sampling described in previous chapters. Nutrient samples were taken at 138 randomly selected sites. These sites were randomly stratified based on habitat and longitude, as described previously. Results from this initial sampling (Figure 6.2, 6.3) were used to inform a stratified random sampling design for subsequent sampling efforts. Results from the initial sampling suggested that the lagoons were much higher in nutrients than other sites. Because water column nutrient concentrations can vary greatly from season to season, and are often driven by watershed runoff, sampling was conducting in July, August, September, October, November of 2007, and February and March of 2008. The February and March sampling occurred during the dry season, whereas the other sampling dates were during the wet season (Figure 6.4). Forty stratified random sampling sites were selected (Figure 6.5). These samples were stratified by location: inshore (<1.5 km from shore), offshore (>1.5 km from shore) and lagoons, and were evenly distributed between the eastern (uninhabited) and western (inhabited) halves of the island. Due to weather and boat related problems, not all sites could be sampled at every time point. A total of 193 samples were collected during the assessment period.

Sample collection methods

Nutrient samples were collected in high density polyethylene (HDPE) bottles from 0.1 m below the surface. In extremely shallow lagoons (<0.5 m), samples were taken at half the distance to the bottom; in this situation, care was taken to exclude sediment from the samples. Bottles were rinsed three times with site water prior to sampling. Nitrile or latex gloves were worn by field personnel to avoid contamination of the samples during handling. On each sampling mission, replicate samples were collected at four (randomly selected) of the 40 sites to ensure precision in methodology. After collecting the samples, additional data (salinity, temperature, dissolved oxygen) were collected with a YSI 85 handheld water quality meter. Samples were stored on ice, in the dark while in the field and frozen at -20° C upon returning to the lab and not thawed until immediately prior to analysis. Samples were not filtered so that total nutrient levels could be analyzed, rather than only dissolved levels.

Analytical methods used for the analysis of nutrients in water

TDI-Brooks International conducted the nutrient laboratory analyses. Water samples were analyzed for a standard suite of nutrient analytes: nitrate (NO_3^-), nitrite (NO_2^-), orthophosphate ($HPO_4^=$), ammonium (NH_4^+), urea ($(NH_2)_2CO$), total nitrogen and total phosphorus (Table 6.1).

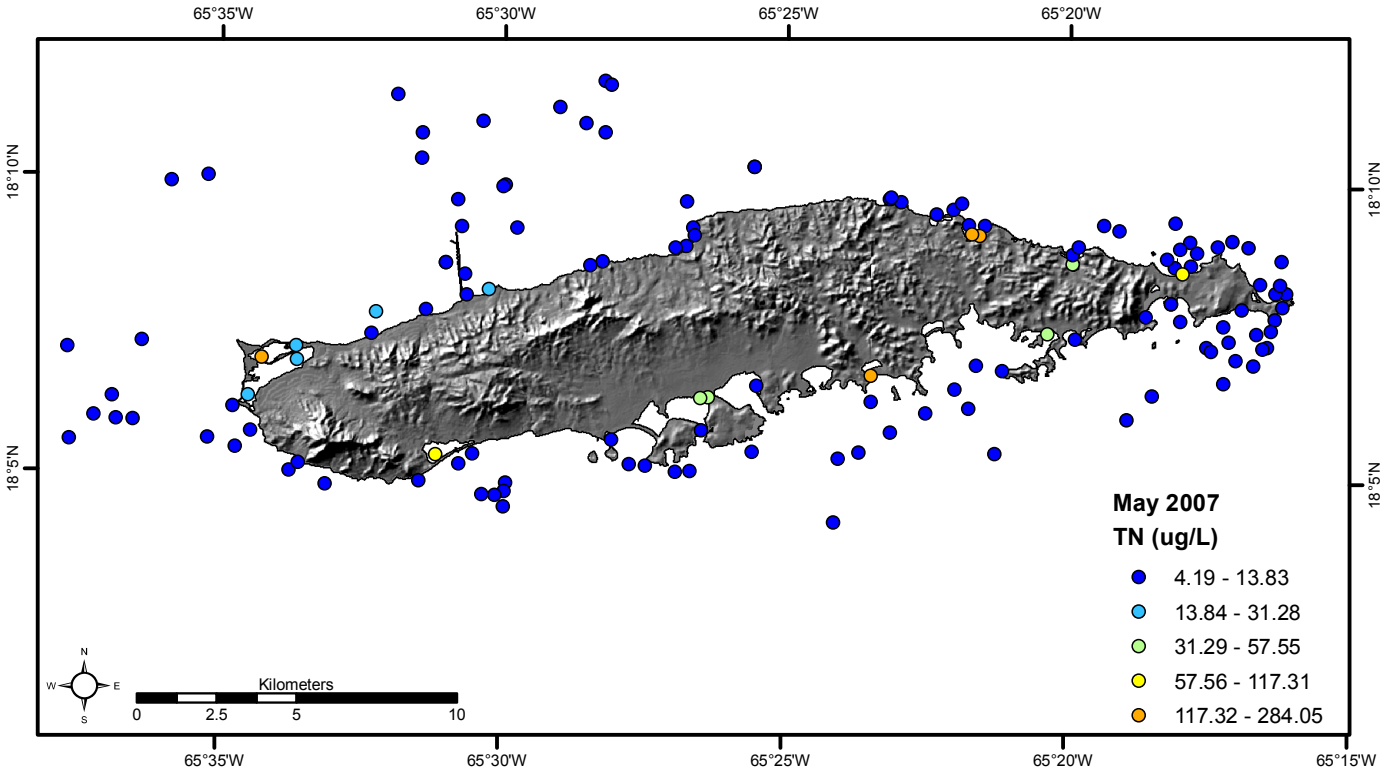

Figure 6.2. Preliminary sampling for total nitrogen (TN) in May 2007.

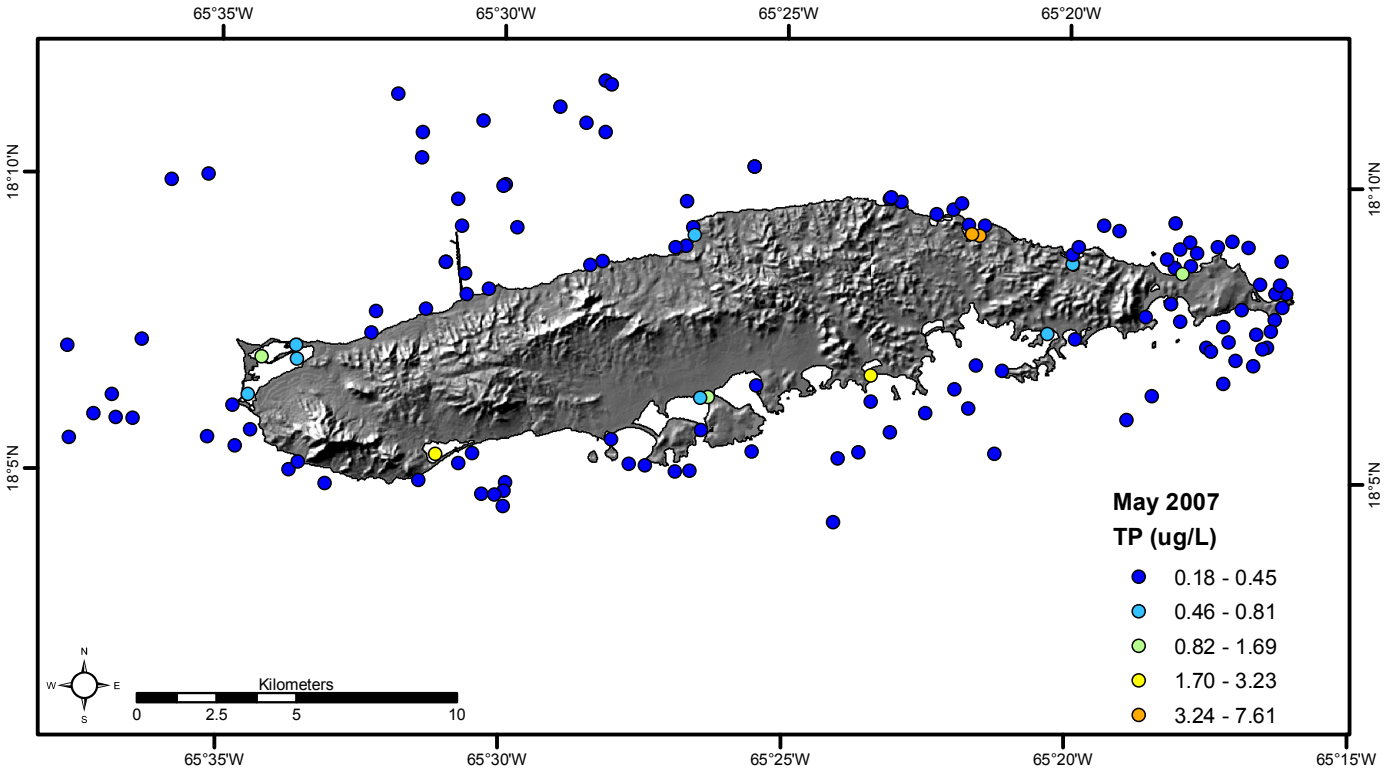

Figure 6.3. Preliminary sampling for total nitrogen (TP) in May 2007.

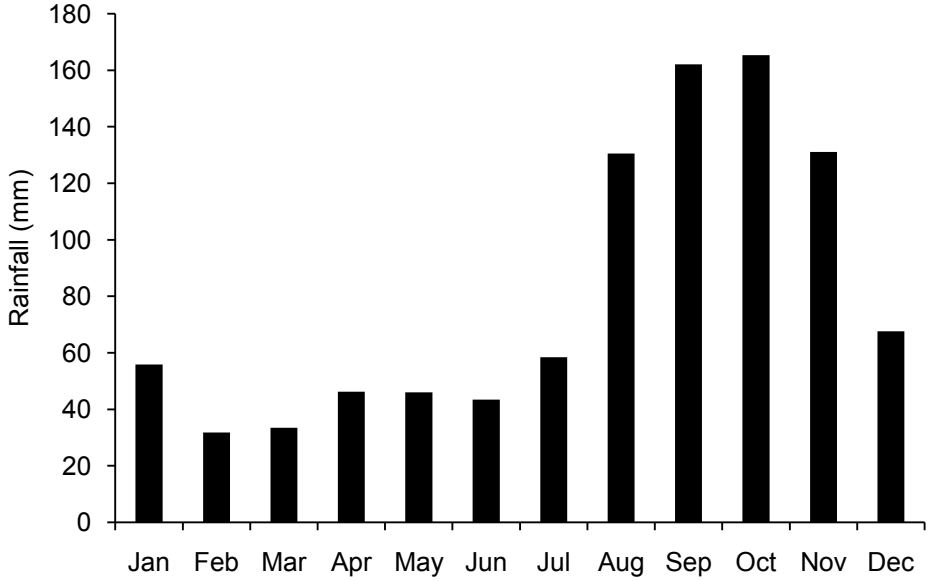

Figure 6.4. Average monthly precipitation in Vieques from 1971-2000 (most recent available data). From: http://cirrus.dnr.state.sc.us/cgi-bin/sercc/cliMAIN.pl?pr9763.

Table 6.1. Details on analytical methods for nutrients

Analyte	Method Detection Limit (µM)	Method Detection Limit (mg/L)	Standard Range (µM)	Standard Range (mg/L)
NO_3^-	0.177	0.010	3.85 - 30.14	0.23 - 1.86
NO_2^-	0.010	0.0004	0.09 - 0.72	0.006 - 0.033
$HPO_4^=$	0.030	0.002	0.35 - 2.18	0.021 - 0.21
$HSIO_3^-$	0.155	0.014	4.05 - 30.08	0.25 - 2.80
NH_4^+	0.070	0.001	0.42 - 3.44	0.026 - 0.062
Urea	0.205	0.012	0.59 - 4.42	0.036 - 0.265

Nitrate and nitrite analyses were based on the methodology of Armstrong et al. (1967). Orthophosphate was measured using the methodology of Bernhardt and Wilhelms (1967) with the modification of hydrazine as reductant. Silicate determination was accomplished using the methods of Armstrong et al. (1967) using stannous chloride. Ammonium analysis was based on the method of Harwood and Kuhn (1970) using dichloro- isocyanurate as the oxidizer. Urea was measured using diacetyl-monoximine and themicarbozide. The total concentrations of nitrogen and phosphorus were determined after an initial decomposition step. This method involves persulfate oxidation while heating the sample in an autoclave (115°C, 20 minutes) (Hansen and Koroleff 1999). After oxidation of the samples, nutrient determination was conducted on the Technicon II analyzer for nitrate and orthophosphate.

Because data were not normally distributed (Shapiro-Wilk W test), non-parametric statistics (Wilcoxon test, α=0.05) were used to evaluate differences between strata and between seasons.

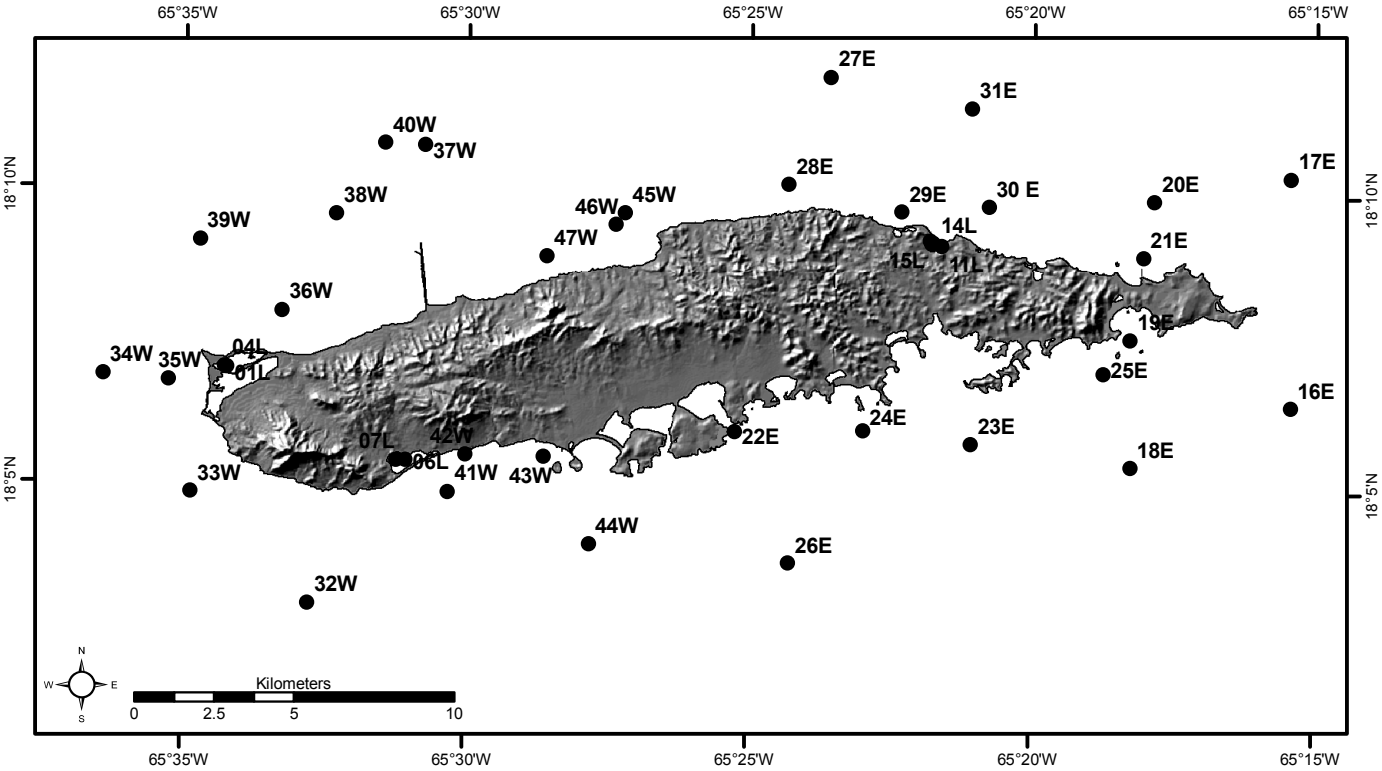

Figure 6.5. Location of sampling sites.

6.3 RESULTS AND DISCUSSION

Summary statistics for all analytes are shown in Tables 6.2a and 6.2b. Data were segregated by lagoon and inshore/offshore because the lagoons are extremely different systems (based on both qualitative observations and water quality/nutrient data) from the nearshore and offshore waters.

Table 6.2a. Lagoon nutrient summary statistics (July 2007 to March 2008). Concentrations in ug/L.

Analyte	Mean	Standard deviation	Minimum	Maximum
HPO_4	30.1	20.6	2.1	112.0
TP	106.8	91.0	2.4	556.7
NH_{4+}	17.2	11.2	1.1	48.8
NO_{3-}	2.7	2.6	0.04	13.5
NO_{2-}	1.7	1.0	0.03	5.0
Urea	31.2	35.5	4.4	172.4
TN	2810.4	1624.9	218.4	7331.4

Table 6.2b. Coastal (inshore and offshore) nutrient summary statistics (July 2007 to March 2008). Concentrations in ug/L.

Analyte	Mean	Standard deviation	Minimum	Maximum
HPO_4	4.3	2.8	1.2	11.5
TP	5.7	2.2	0.5	13.8
NH_{4+}	1.9	1.9	0.06	11.2
NO_{3-}	3.6	1.8	0.04	1.1
NO_{2-}	0.5	0.3	0.04	1.1
Urea	6.0	3.7	1.8	25.2
TN	131.3	229.7	83.6	2766.4

Precipitation Data

Precipitation data during the study period were acquired from the RAWS USA Climate Archive (Desert Research Institute 2009) for the station in Vieques (18° 07' 18", 65° 24' 58"). Precipitation can generate nutrient laden runoff which can be an important driver of nutrient concentrations in some systems.

General Spatial Patterns

In general, maximum observed nutrient concentrations at each site were highest in the lagoons (Figures 6.6-6.11). There were two sites off the south central coast where maximum observed nitrate plus nitrite was also relatively high (Figure 6.6), but it is unclear why these sites had high concentrations. Mean nutrient concentrations were also highest in the lagoons (Figures 6.12-6.17). There were no clear spatial patterns between the eastern (uninhabited) and western (inhabited) sides of the island for either maximum or mean concentrations (Figures 6.6-6.17).

Spatial Patterns by Strata

There were no significant differences among strata for orthophosphate, with higher concentrations of total phosphorus (TP) in the offshore waters than the inshore waters (Figure 6.18). This is somewhat unexpected, but may represent higher uptake of phosphorus by nearshore primary producers. For all nitrogen species, mean concentrations in lagoon samples were an order of magnitude higher and significantly different than either inshore or offshore sites (Figure 6.19). It is likely that these are the natural condition of the lagoons. The lagoons are shallow, poorly flushed and visibly high in humic materials. The lagoons are high in organic matter from the fringing mangroves, and submerged aquatic vegetation (Image 6.1) or benthic microbial mats. There are no statistically significant differences between inshore and offshore nitrogen concentrations (Figure 6.19). This would suggest that, island-wide, there is not a strong land based source of nutrients. Further evidence of this can be seen when comparing the eastern end of the island, which is uninhabited, to the western end of the island, which is inhabited. There are no significant differences in nutrient concentrations between the eastern and western ends of the island, except for urea which is higher in the western zone (Figures 6.20 and 6.21). If anthropogenic land based sources of pollution made up an important portion of the nutrient budget, nutrient concentrations would be expected to be higher on the western end of the island, where the human population resides. Higher concentrations are only seen on the western side of the island for urea. This may represent a human or animal signal, but more investigation would be required to determine why this pattern is not observed in other nutrient species.

Image 6.1 Submerged aquatic vegetation mat in lagoon on Vieques.

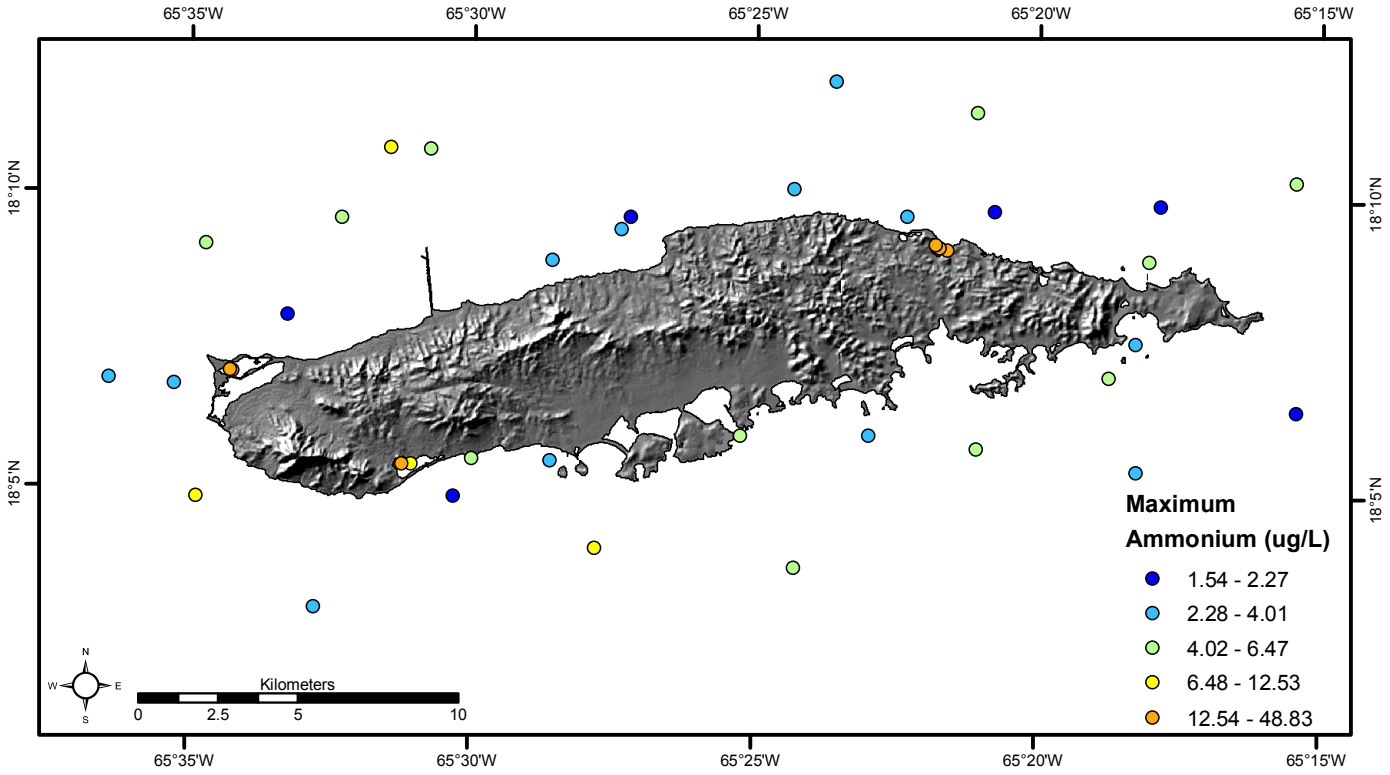

Figure 6.6. Maximum observed ammonium concentrations (ug/L).

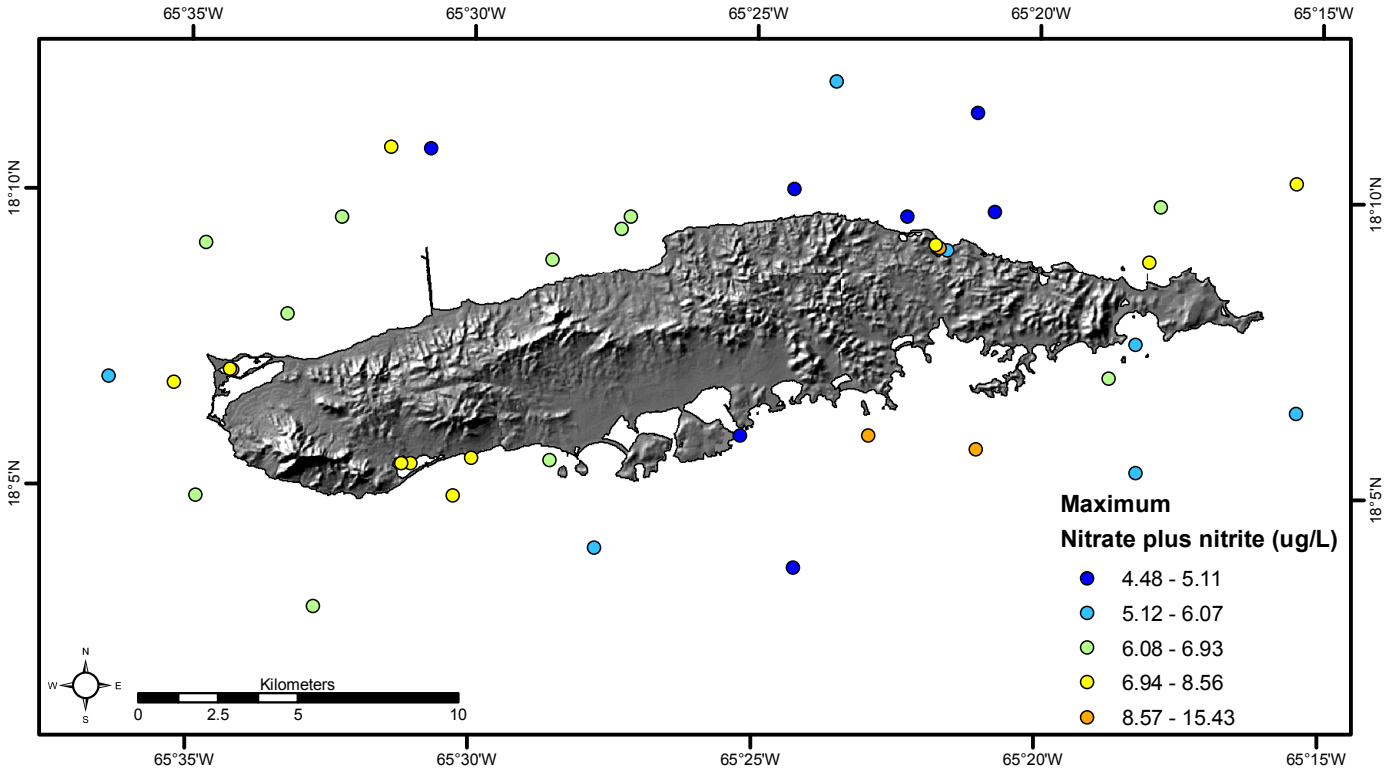

Figure 6.7. Maximum observed nitrate plus nitrite concentrations (ug/L).

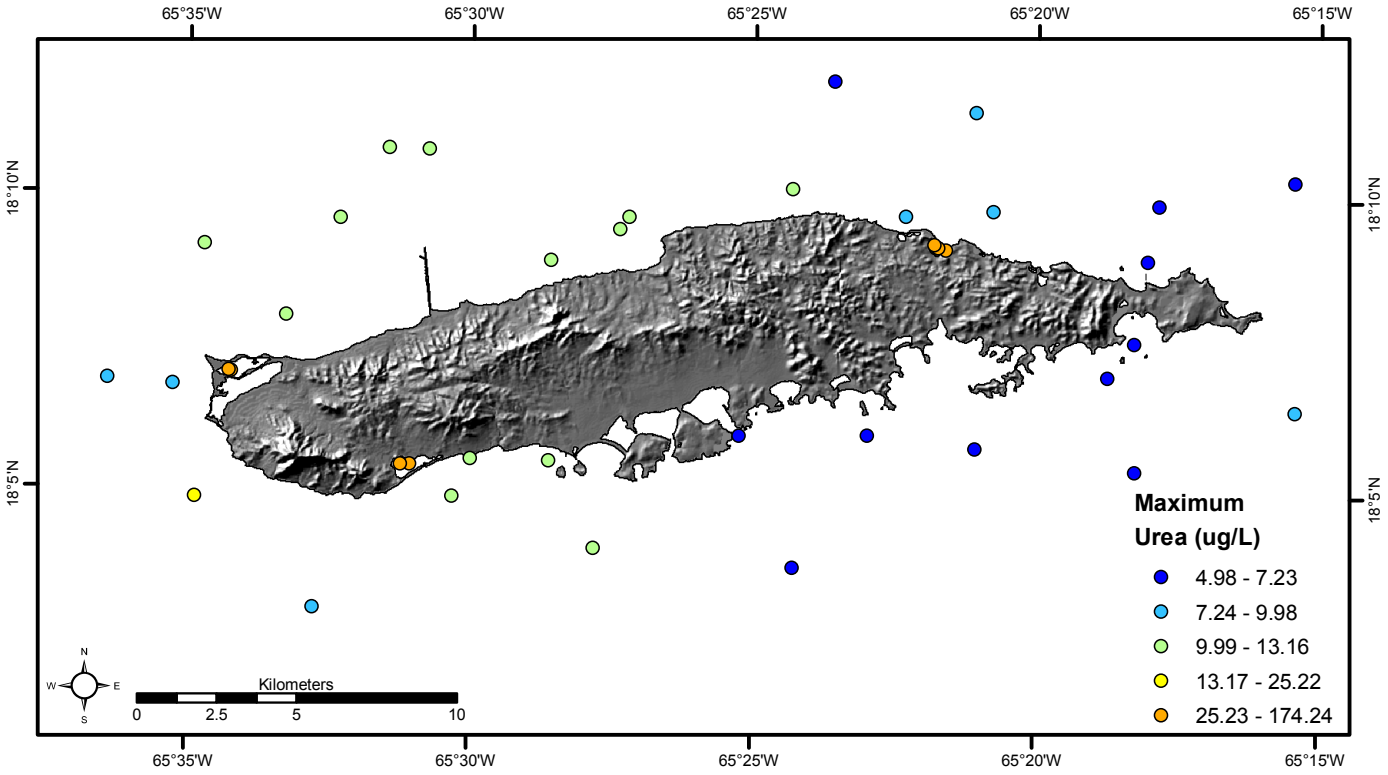

Figure 6.8. Maximum observed urea concentrations (ug/L).

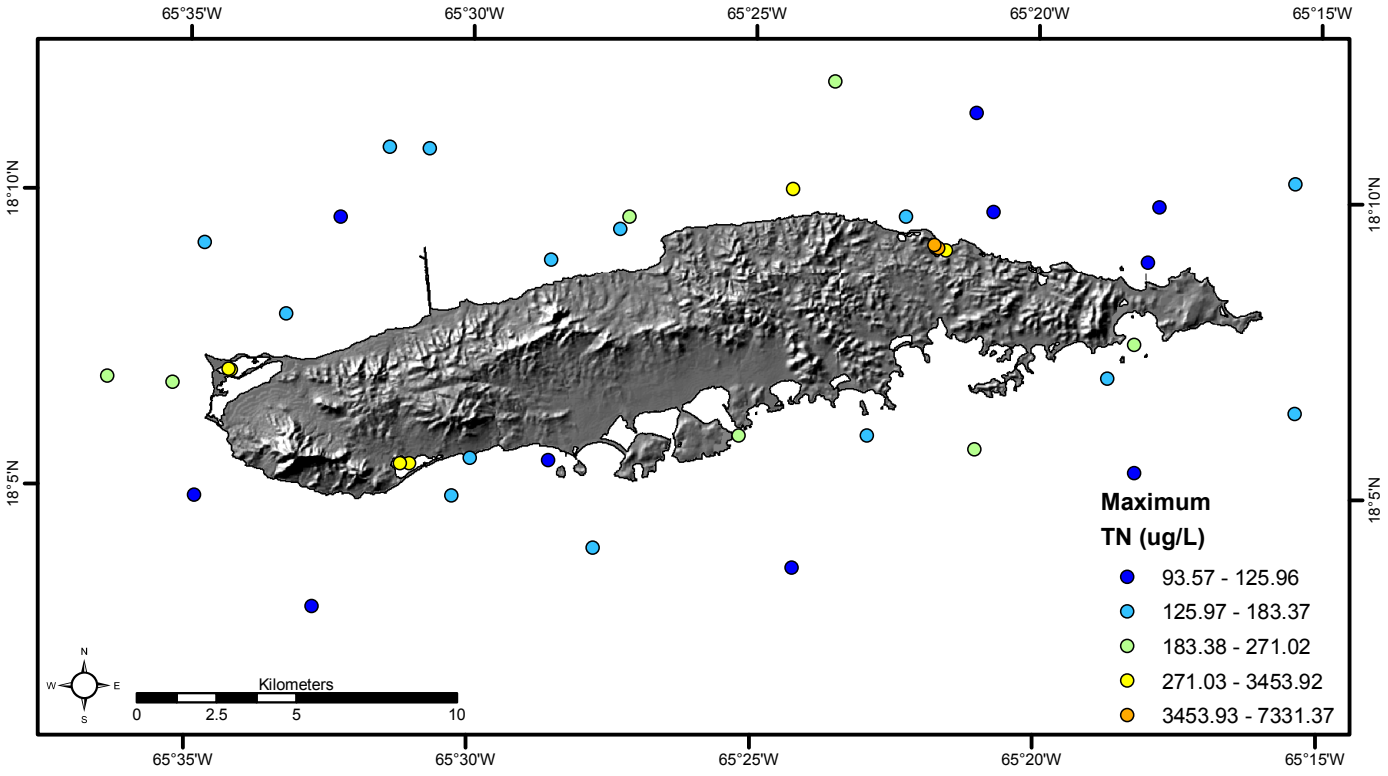

Figure 6.9. Maximum observed total nitrogen (TN) concentrations (ug/L).

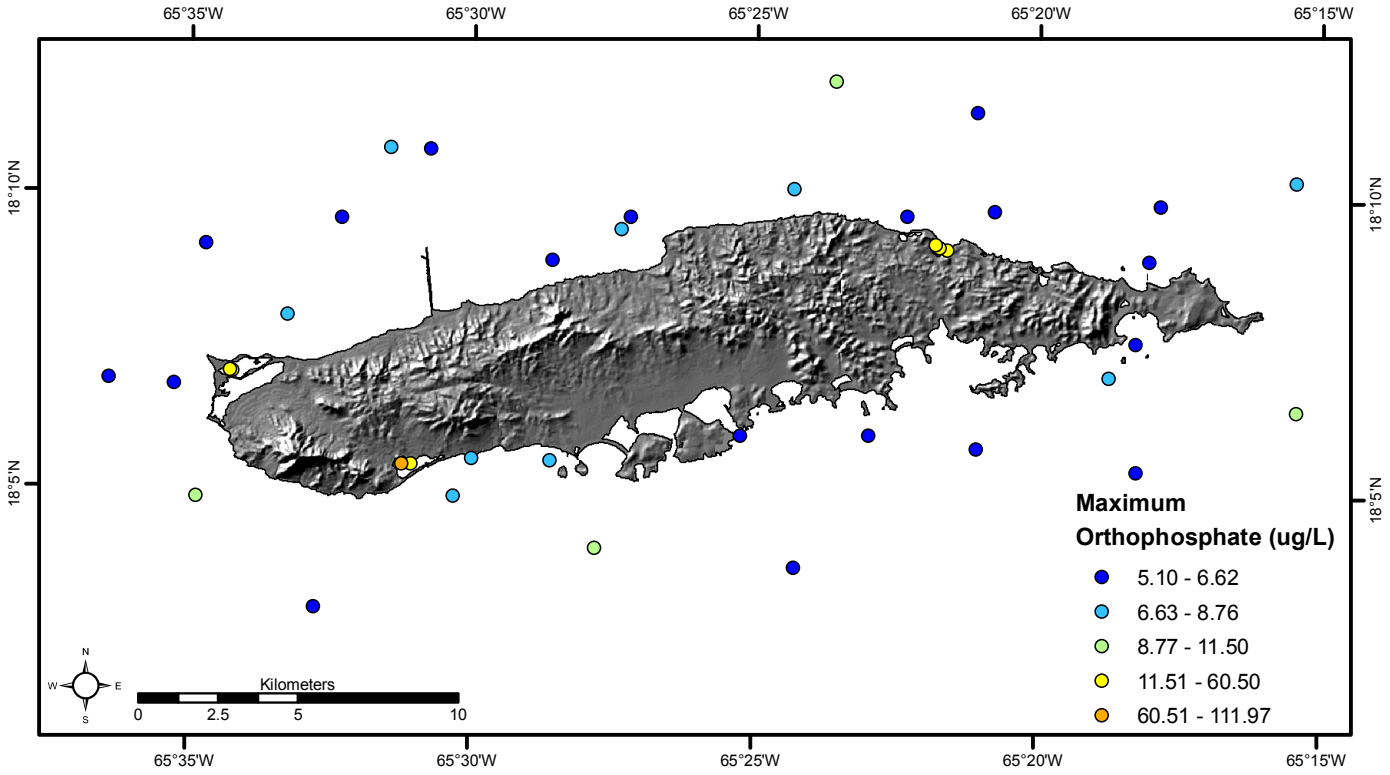

Figure 6.10. Maximum observed orthophosphate concentrations (ug/L).

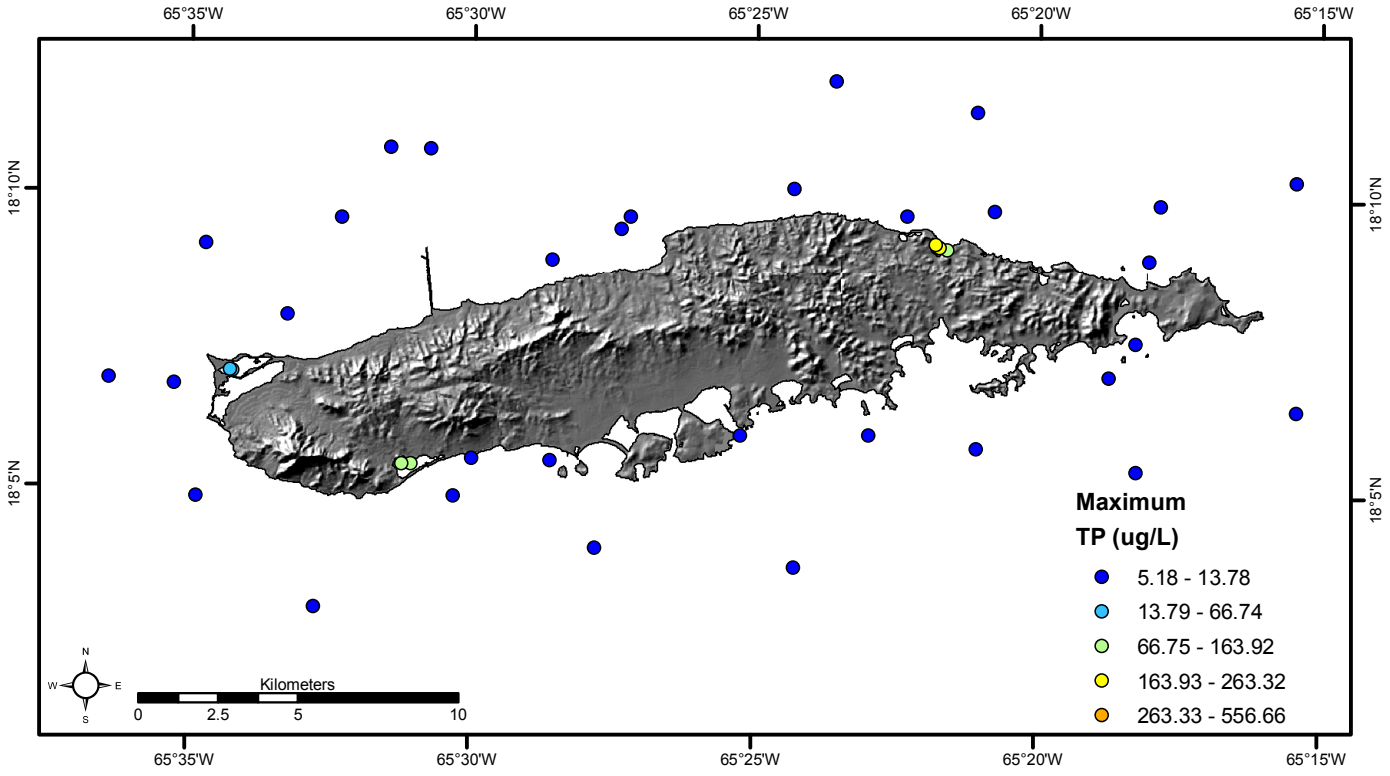

Figure 6.11. Maximum observed total phosphorus (TP) concentrations (ug/L).

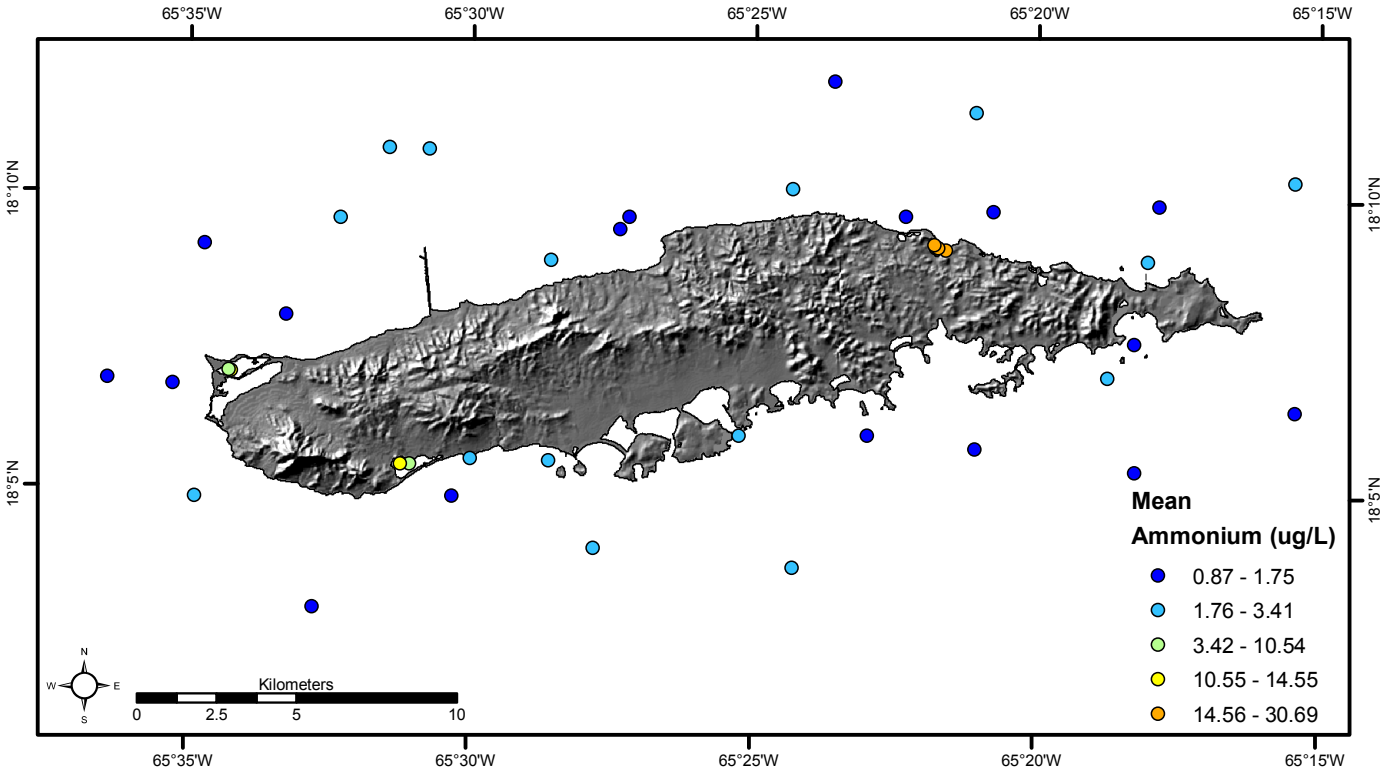

Figure 6.12. Mean observed ammonium concentrations (ug/L).

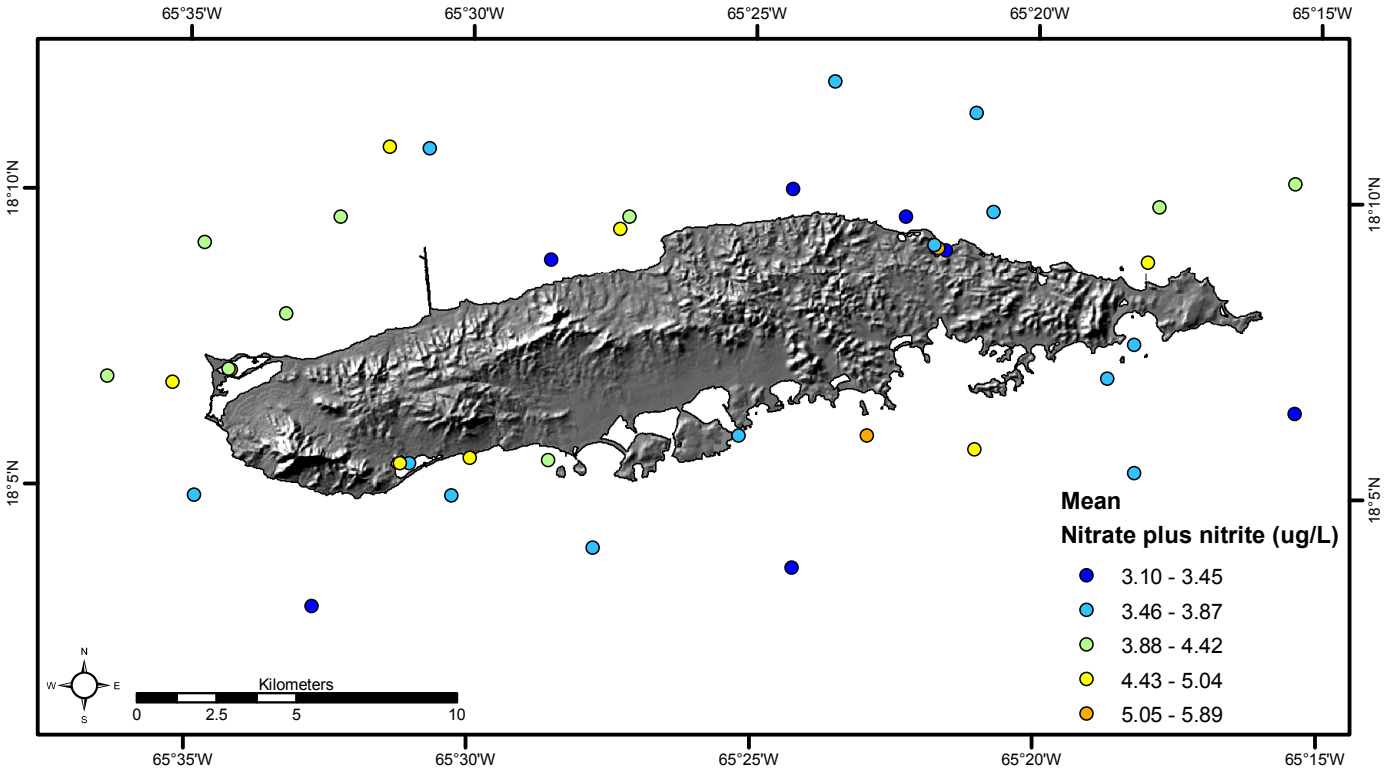

Figure 6.13. Mean observed nitrate plus nitrite concentrations (ug/L).

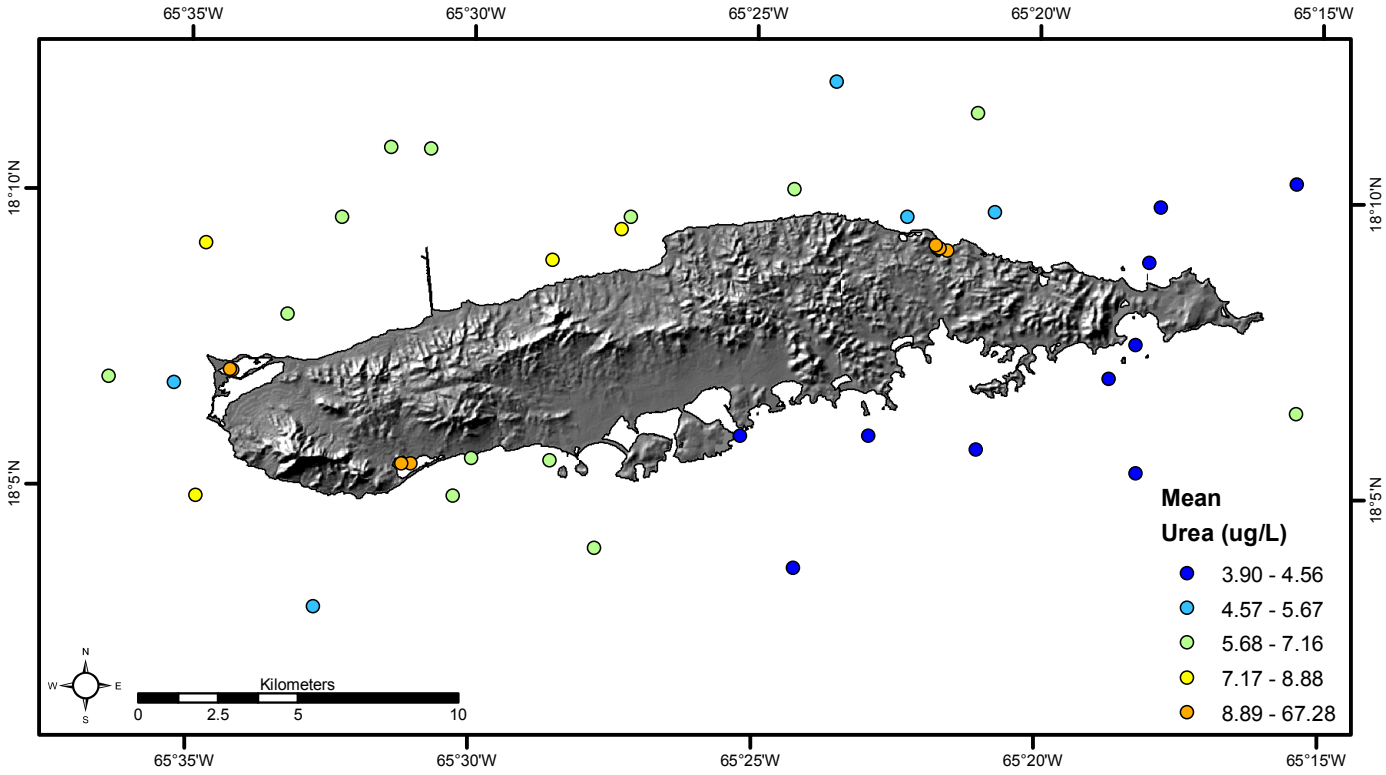

Figure 6.14. Mean observed urea concentrations (ug/L).

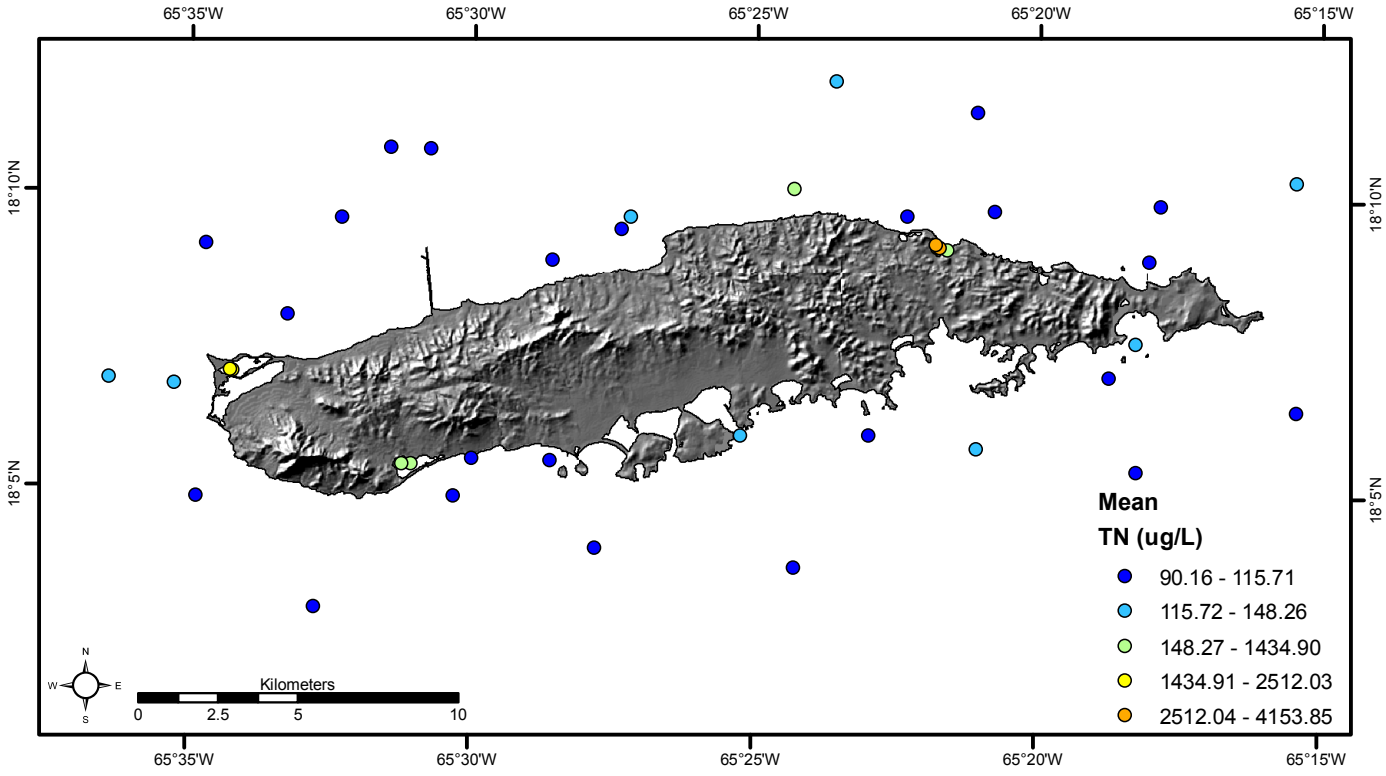

Figure 6.15. Mean observed total nitrogen (TN) concentrations (ug/L).

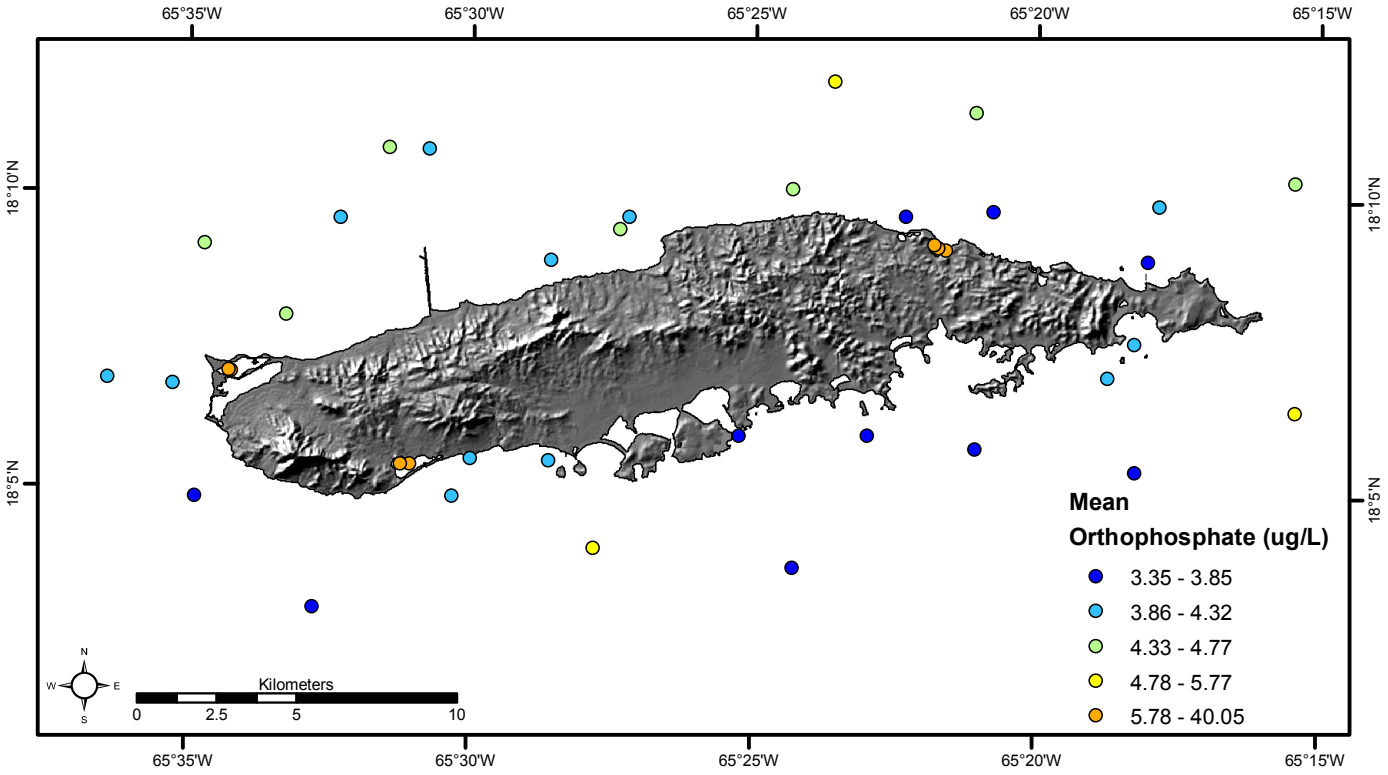

Figure 6.16. Mean observed orthophosphate concentrations (ug/L).

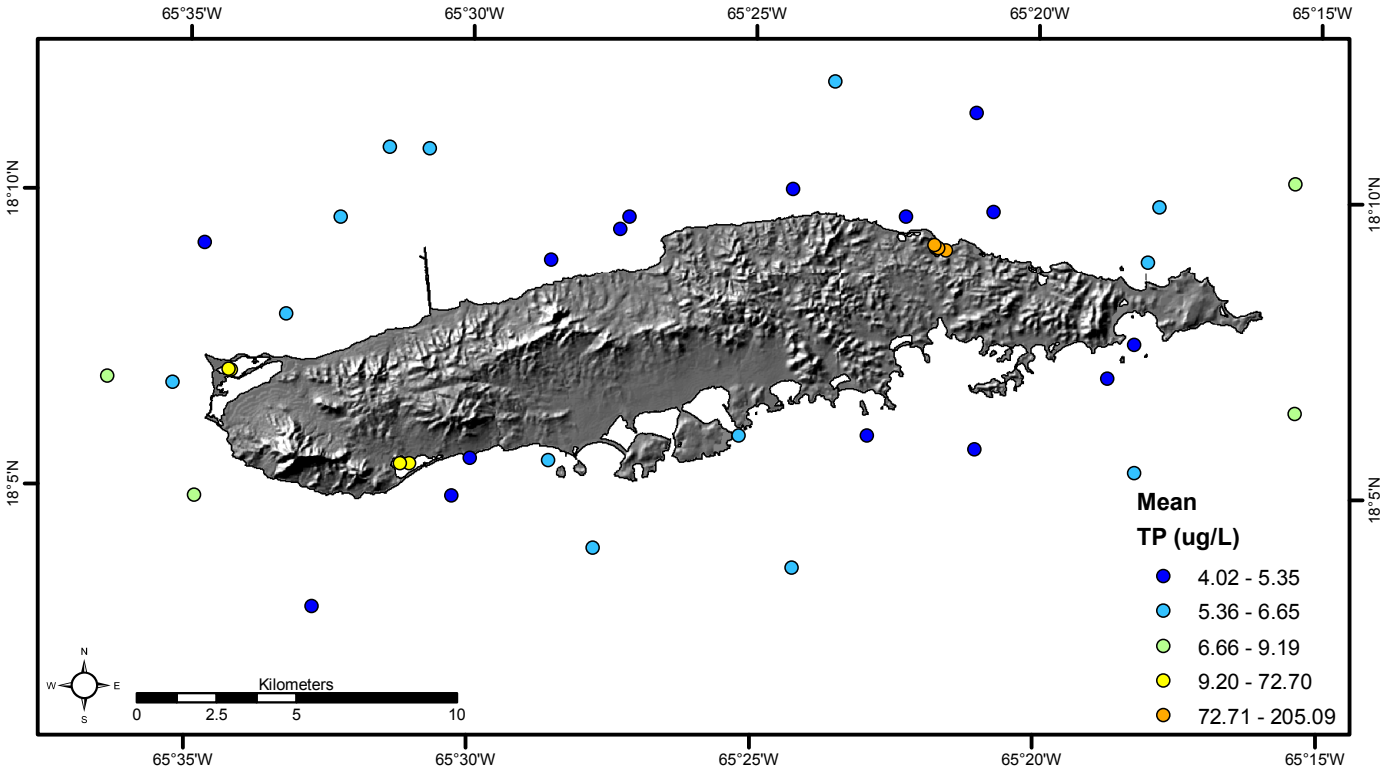

Figure 6.17. Mean observed total phosphorus (TP) concentrations (ug/L).

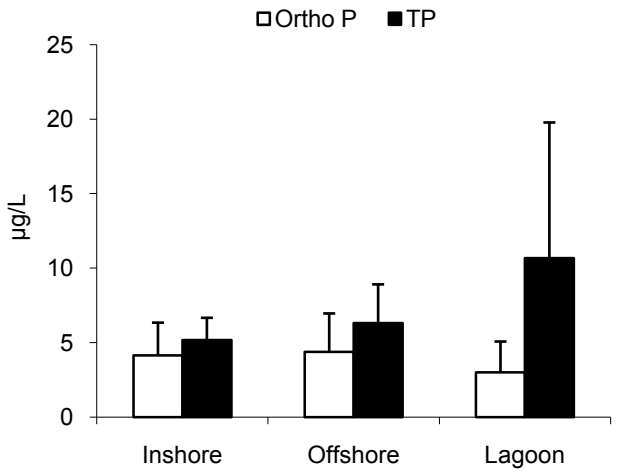

Figure 6.18. Mean concentrations of total phosphorus (TP) and orthophosphate by strata. Error bars are one standard deviation. Offshore TP is statistically higher (α=0.05) than inshore TP (no significant differences among other groups).

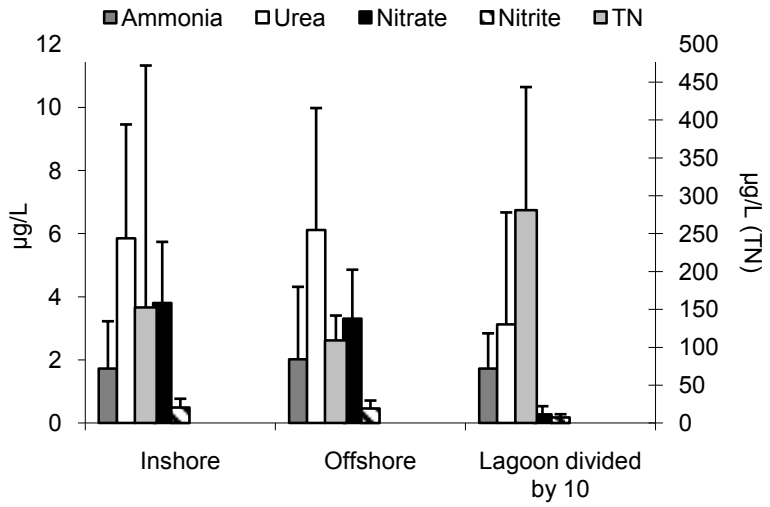

Figure 6.19. Mean concentration of nitrogen by strata. Error bars are one standard deviation. For all analytes, lagoon concentrations are statistically higher (α=0.05) than inshore and offshore.

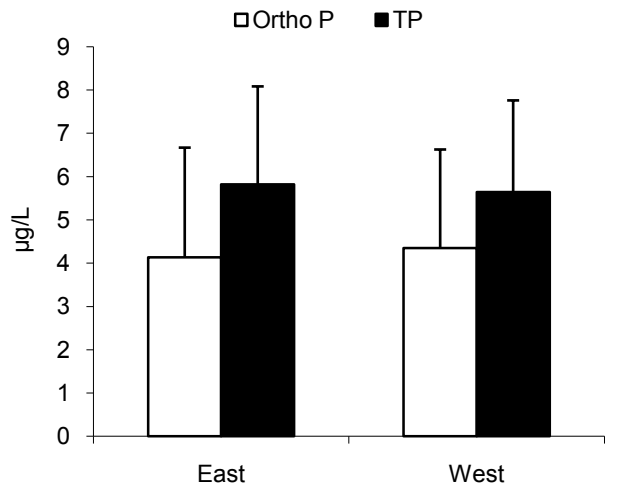

Figure 6.20. Mean concentrations of total phosphorus (TP) and orthophosphate for east versus west. Error bars are one standard deviation. No significant differences between east and west.

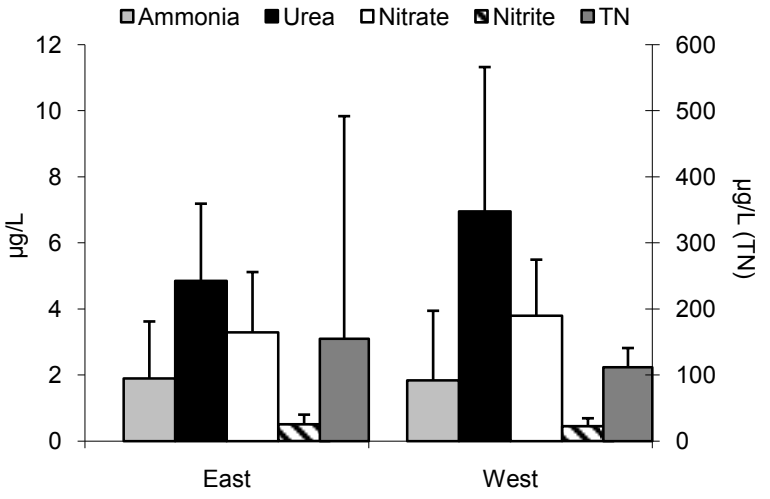

Figure 6.21. Mean concentration of nitrogen for east vs. west for marine (non-lagoon) sites. Error bars are one standard deviation. Urea concentrations on the western part of the island are statistically higher (α=0.05) than on the eastern part of the island. No significant differences for other analytes.

Temporal Patterns

Because there were only two sampling dates during the dry season, and boat/weather problems prevented complete sampling during these dates, it is not statistically valid to compare wet versus dry seasons. Periods of heavy precipitation do not seem to predict nutrient concentrations in lagoon, or inshore and offshore waters (Figures 6.22-6.27, nitrate plus nitrite and orthophosphate data shown). There are sampling points (e.g., August 30, 2007) when very heavy rainfall in the 5 day period before sampling caused elevated concentrations of nitrate plus nitrite, but not concentrations of orthophosphate. This is unexpected because phosphorus is tightly tied to soil particles, so as runoff increases, phosphorus transport would be expected to increase. Conversely, there are sampling points (e.g., January 31st, 2008) when concentrations are elevated but the preceding 5 days were relatively dry. The apparent disconnect between precipitation (and therefore runoff) has several possible explanations. First, it is possible that watershed nutrient inputs are not important to the nutrient budgets of the system. Second, it is possible that biological processes (uptake, denitrification) dampen the runoff signal in coastal waters. Finally, because nutrients can change on the time scale of hours, it is possible that there are shorter term fluctuations in nutrient concentrations that were not captured in this study. Similarly, there could be long term patterns in nutrient concentrations that were not captured during this one year dataset. These research questions could be answered with further study and monitoring.

Comparison with Critical Thresholds

From a regulatory perspective, no nutrient criteria exist for U.S. coastal waters. However, for coral reef ecosystems, it has been suggested that 14 µg-N/L dissolved inorganic nitrogen (DIN) and 31 µg-P/L soluble reactive phosphorus (SRP) are the threshold values above which macroalgal growth can threaten coral reefs (Lapointe, 1997). In Vieques, the inshore and offshore waters never exceeded 14 µg/L of DIN (nitrate + nitrite + ammonium). Although there is no proposed threshold for total nitrogen (TN), TN concentrations in the coastal waters of Vieques did exceed the level for DIN. It should be noted that DIN is much more readily available for plant or phytoplankton uptake than TN, so high TN is not necessarily indicative of an ecological problem. The suggested threshold value for phosphorus (31 µg-P/L) was exceeded only in the lagoons, suggesting that P is not a problem in nearshore or offshore waters.

Comparison with Other Sites in Puerto Rico

Nutrient concentrations observed in Vieques can be compared to observations in other locations in Puerto Rico (Figure 6.28). Coastal (non-lagoon) nutrient concentrations presented here for Vieques are higher than data reported in southwest Puerto Rico (comparing TN and TP; Pait et al. 2007). It should be noted that the southwest Puerto Rico data set was based on a one time sampling in August, so it is possible that this is not representative due to temporal nutrient variability. However, data from a monthly long term dataset for Jobos Bay, Puerto Rico (JBNERR 2009) for orthophosphate, ammonium, nitrate and nitrite, concentrations were very similar to lagoon data for Vieques. Jobos Bay is con-

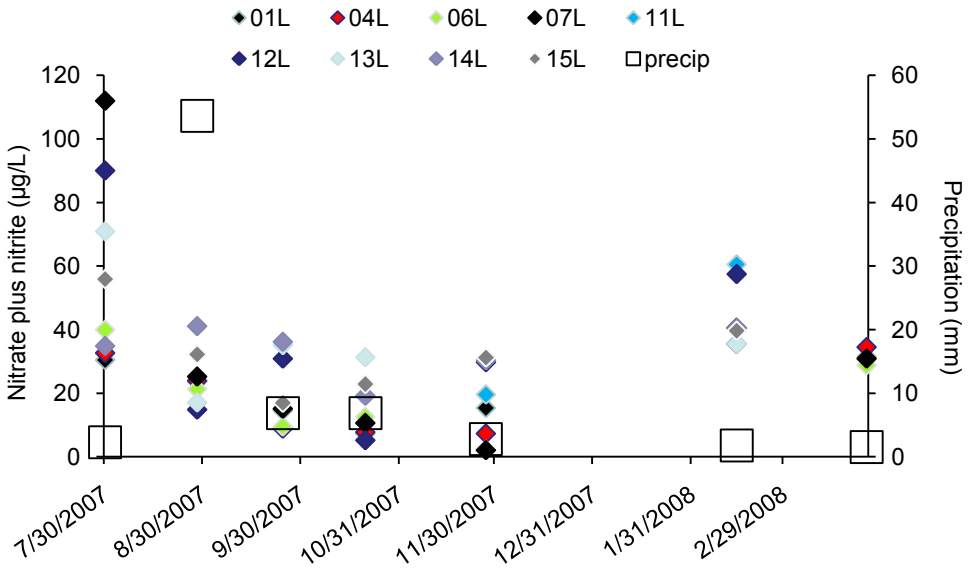

Figure 6.22. Temporal variation in nitrate plus nitrite concentrations in lagoons. Precipitation values show the rainfall in the 5 days preceding sampling.

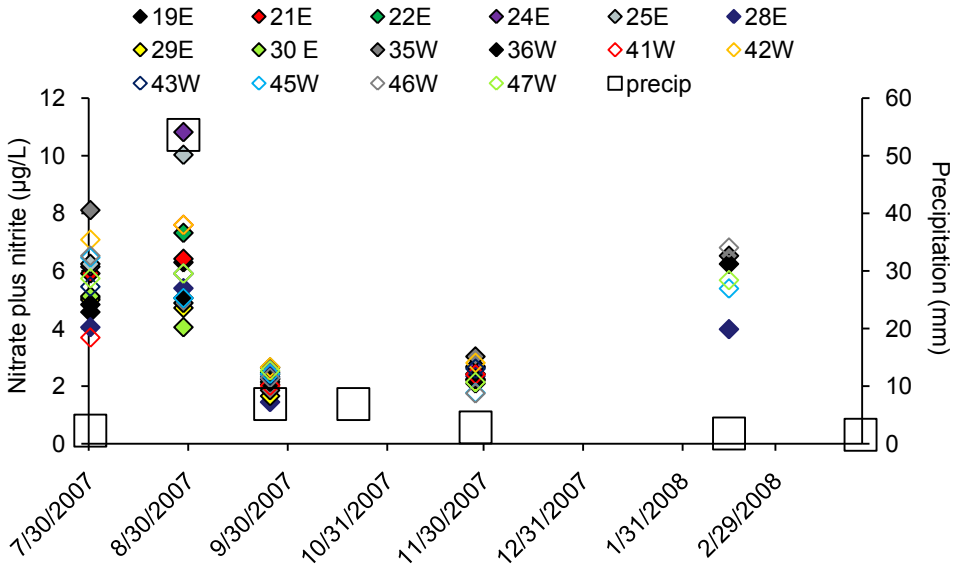

Figure 6.23. Temporal variation in nitrate plus nitrite concentrations inshore. Precipitation values show the rainfall in the 5 days preceding sampling.

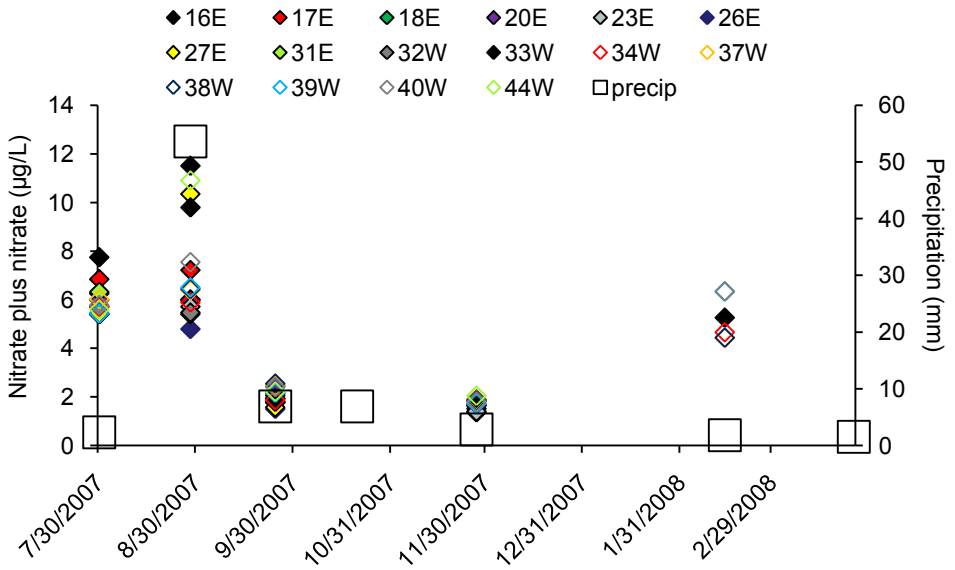

Figure 6.24. Temporal variation in nitrate plus nitrite concentrations offshore. Precipitation values show the rainfall in the 5 days preceding sampling.

sidered to be impacted by both point and non-point source nutrient pollution (Bowen and Valiela 2008). Despite having similar nutrient levels, Jobos Bay is hydrographically and ecologically dissimilar from the lagoons on Vieques, in that Jobos Bay is much larger, much deeper (maximum depth=10m, Jobos Bay Estuarine Profile 2002), better flushed and has less organic matter than the lagoons. It is hypothesized that the high nutrient levels in the Vieques lagoons are the natural state and do not represent anthropogenic enhancement.

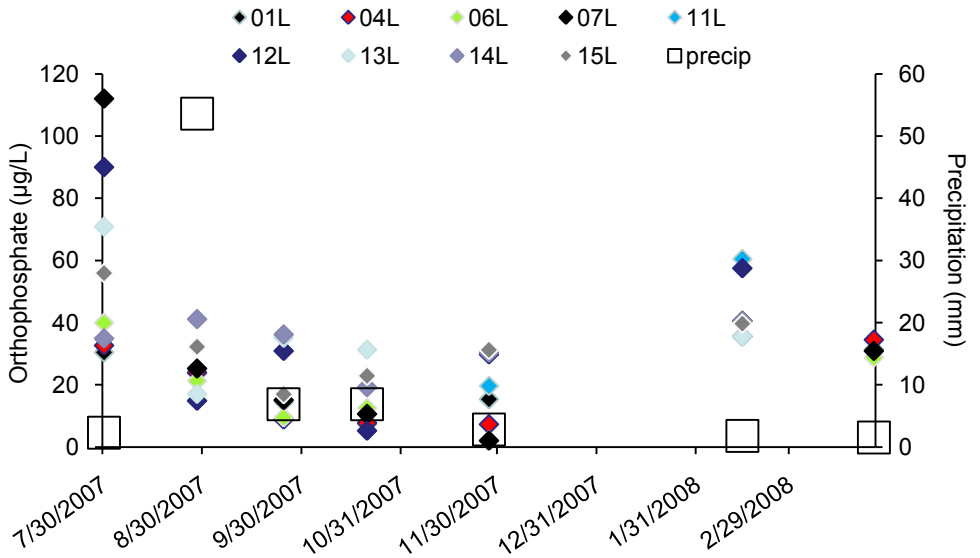

Figure 6.25. Temporal variation in orthophosphate concentrations in lagoons. Precipitation values show the rainfall in the 5 days preceding sampling.

Detecting Changes in Sea Surface Chlorophyll and Turbidity Using Remote Sensing

Nutrient concentrations can affect both benthic macroalgae as well as phytoplankton in the photic zone. Understanding of the temporal variability and annual cycles can be helpful in identifying hot spots. In marine and coastal ecosystems, an understanding of the expected sea surface annual cycle can be used to: (1) identify dominant forcing agents and processes; (2) isolate trends and impacts of anomalous events from seasonal cycles; and (3) plan sampling strategies to resolve important cycles. This can be applied to both chlorophyll, as well as turbidity. Turbidity can be used a proxy for sedimentation rates which can have adverse effects on corals.

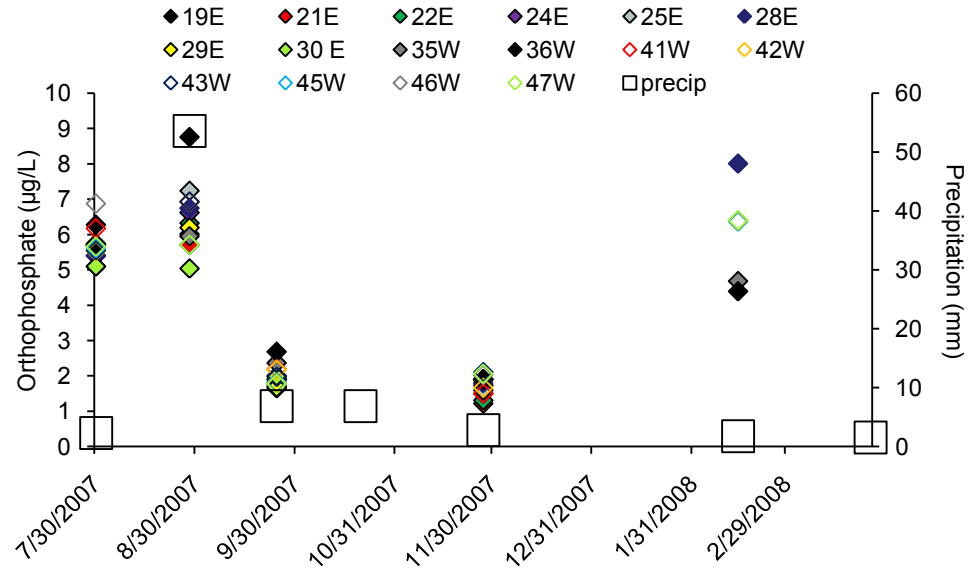

Figure 6.26. Temporal variation in orthophosphate concentrations inshore. Precipitation values show the rainfall in the 5 days preceding sampling.

Currently, there is little *in situ* data to define the annual cycle of sea surface chlorophyll, chlorophyll variability, and water clarity around Vieques. In this study, we utilized the recent advances made in the fields of marine optics and remote sensing to determine fundamental but currently unknown information about the local water quality: namely, the annual cycle of surface chlorophyll and backscattering (a surrogate for turbidity)

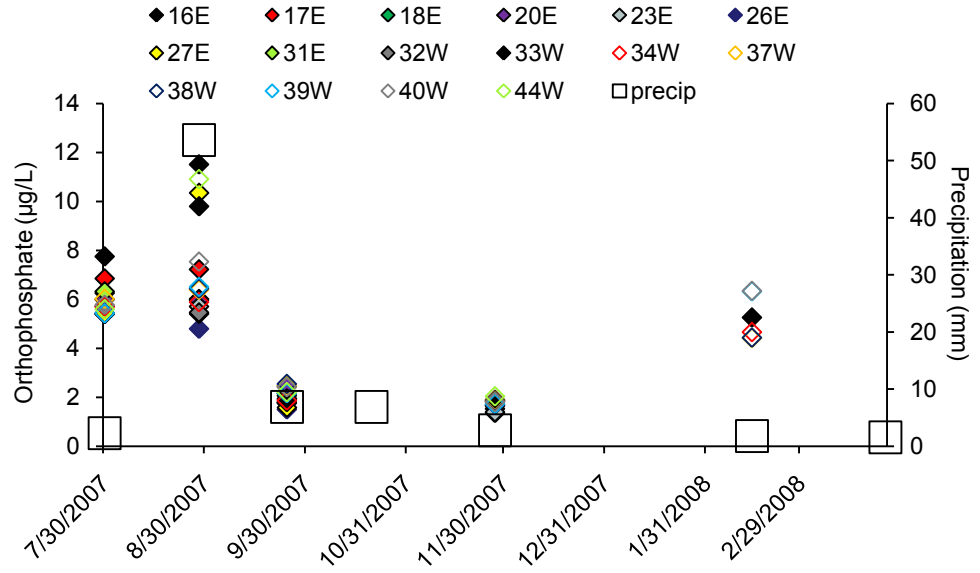

Figure 6.27. Temporal variation in orthophosphate concentrations offshore. Precipitation values show the rainfall in the 5 days preceding sampling.

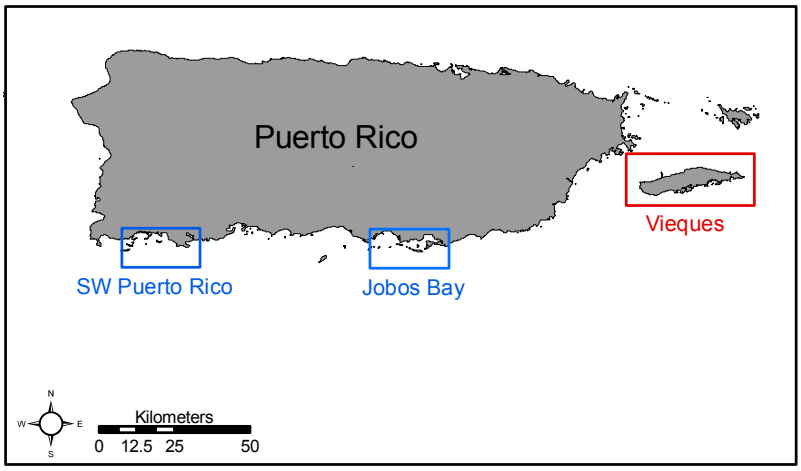

Figure 6.28. Location of other nutrient study sites in Puerto Rico.

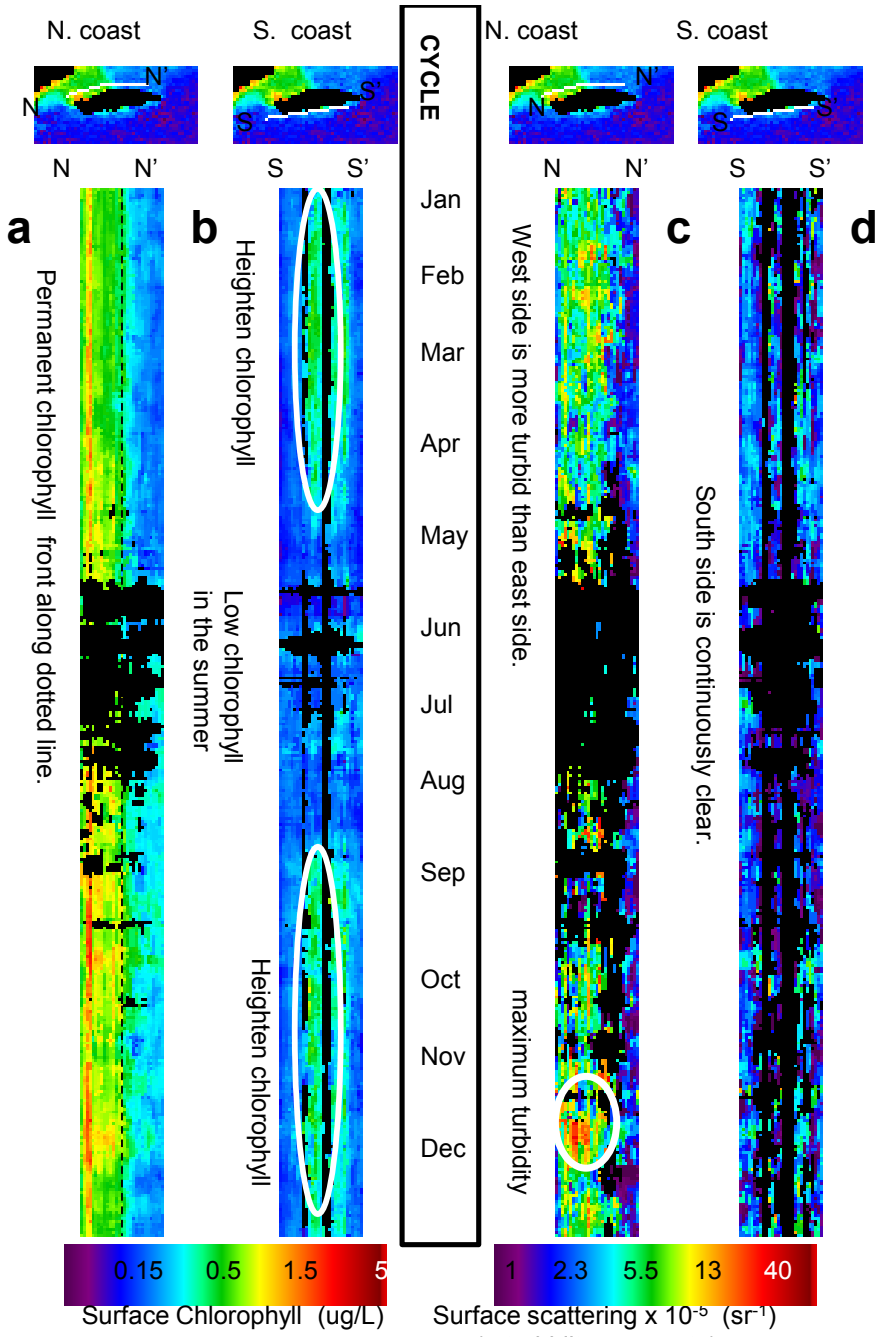

Figure 6.29. Remotely sensed (SeaWIFS) chlorophyll and turbidity patterns.

along the northern and southern coasts of Vieques. Surface chlorophyll and backscattering information were obtained from SeaWiFS (Sea-viewing Wide Field-of- view Sensor) images from 1998 through 2007. We focused on two transects: northern coast (labeled as N to N', Figure 6.29) and southern coast (labeled as S to S', Figure 6.29). They are shown in white in Figure 6.29. Under each map is a Hovmoller diagram (a graph that simultaneously captures temporal and longitudinal variability) that shares the same longitude axis. Each location along the transect consists of 365 expected values, one for each day. An expected value is defined as the median of the data at the same location and Julian day regardless of the year. The cycle shows:

1) Along the northern coast, a chlorophyll front sits near the middle of the island throughout the year (Figure 6.29a). Chlorophyll west of the front is ~ 1 µg/L; that east of the front is ~0.3 µg/L.

2) Along the southern coast, lowest chlorophyll occurs in the summer (Figure 6.29b). In the fall and winter, chlorophyll in the middle of the island is slightly elevated (green, ~ 0.5 µg/L) compared to the tips of the island (~0.15).

3) Along the northern coast, a turbidity front sits slightly off center in the winter (Figure 6.29c). Water is more turbid west of this front.

4) Along the northern coast, annual maximum turbidity usually occurs on the west side of the island in December (Figure 6.29c).

5) Along the southern coast, water is relatively clear throughout the year (Figure 6.29d).

The *in situ* data collected as part of this study are not sufficient to characterize the drivers behind these observed patterns in chlorophyll and turbidity. Further *in situ* studies are required to better understand the driving forces behind these observed patterns in chlorophyll and turbidity, including the relative roles of physical oceanographic forcing factors, storm events and land based sources of pollution.

6.4 SUMMARY AND CONCLUSIONS

Nutrient concentrations in the coastal waters of Vieques are similar in magnitude to what has been observed elsewhere in Puerto Rico. The highest concentrations were found in the lagoons. We hypothesize that this is the natural state of these lagoons, rather than an indication of nutrient pollution hot spots because the lagoons are shallow, poorly flushed and high in organic matter. These data do not suggest that there is currently a problem with anthropogenic nutrient over enrichment in Vieques. However, these data will serve as critical baseline information that will allow coastal managers to take proper steps to insure that development pressure on the island do not increase the nutrient flux to coastal waters, thereby increasing stressors to coral reef ecosystems.

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