A view from the bridge: External and internal forces affecting the ambient water quality of the Florida Keys National Marine Sanctuary (FKNMS)

Joseph N. Boyer[1] *and Ronald D. Jones*[1, 2]
[1]Southeast Environmental Research Center and [2]Department of Biological Sciences,
Florida International University, Miami, FL 33199

boyerj@fiu.edu
305-348-4076 (office)
305-348-4096 (fax)

Running Head: Water Quality in the FKNMS

BOYER, J. N., AND R. D. JONES. (in press) A view from the bridge: External and internal forces affecting the ambient water quality of the Florida Keys National Marine Sanctuary, p. #-#. *In* J. W. Porter and K. G. Porter (eds.), Linkages between ecosystems: the South Florida Hydroscape. St. Lucie Press.

Acknowledgments

We thank all the field and laboratory technicians involved with this project including: J. Absten, O. Beceiro, N. Black, S. Bolanos, C. Covas, D. Diaz, T. Frankovich, B. Gilhooly, S. Kaczynski, E. Kotler, S. Perez, P. Sterling, F. Tam, and especially Pete Lorenzo. We want to thank the captains and crew of the R/V Bellows and R/V Suncoaster of the Florida Institute of Oceanography for their professional support of the monitoring program. We also appreciate the laboratory and lodging support supplied by the Florida Program of the National Underwater Research Center, UNC-Wilmington and FL-DEP Keys Marine Laboratory. This project was possible due to continued funding by the US-EPA under Agreement #X994621-94-0. Funding other portions of the SERC Water Quality Monitoring Network was provided by the South Florida Water Management District and Everglades National Park (SFWMD/NPS Coop. Agreement C-7919 and NPS/SERC Coop. Agreement 5280-2-9017). This is contribution #XX of the Southeast Environmental Research Center at Florida International University.

This publication is dedicated to the memory of Cristina Menendez.

Introduction

The Florida Keys are a archipelago of sub-tropical islands of Pleistocene origin which extend in a NE to SW direction from Miami to Key West and out to the Dry Tortugas (Fig. 1). In 1990, President Bush signed into law the Florida Keys National Sanctuary and Protection Act (HR5909) which designated a boundary encompassing >2,800 square nautical miles of islands, coastal waters, and coral reef tract as the Florida Keys National Marine Sanctuary (FKNMS). The Comprehensive Management Plan (NOAA 1995) required the FKNMS to have a Water Quality Protection Plan (WQPP) thereafter developed by EPA and the State of Florida (EPA 1995). The contract for the water quality monitoring component of the WQPP was subsequently awarded to the Southeast Environmental Research Program at Florida International University and the field sampling program began in March 1995.

The waters of the FKNMS are characterized by complex water circulation patterns over both spatial and temporal scales with much of this variability due to seasonal influence in regional circulation regimes. The FKNMS is directly influenced by the Florida Current, the Gulf of Mexico Loop Current, inshore currents of the SW Florida Shelf (Shelf), and by tidal exchange with both Florida Bay and Biscayne Bay. Advection from these external sources has significant effects on the physical, chemical, and biological composition of waters within the FKNMS, as does internal nutrient loading and freshwater runoff from the Keys themselves. Water quality of the FKNMS may be directly affected both by external nutrient transport and internal nutrient loading sources. Therefore, the geographical boundary of the FKNMS must not be thought of as enclosing a distinct ecosystem but rather as being one of political/regulatory definition.

Ongoing quarterly sampling of >200 stations in the FKNMS and Shelf, as well as monthly sampling of 100 stations in Florida Bay, Biscayne Bay, and the mangrove estuaries of the SW coast, has provided us with a unique opportunity to explore the spatial component of water quality variability. By stratifying the sampling stations according to depth, regional geography, distance from shore, proximity to tidal passes, and influence of Shelf waters we report some preliminary conclusions as to the relative importance of external vs. internal factors on the ambient water quality within the FKNMS.

Methods

Site Characteristics and Sampling Design

A spatial framework for FKNMS water quality management was proposed on the basis of geographical variation of regional circulation (Klein and Orlando 1994). The final implementation plan (EPA 1995) partitioned the FKNMS into 9 segments which was collapsed to 7 for routine sampling (Fig. 1). Station locations were developed using a stratified random design along onshore/offshore transects in Seg. 5, 7, and 9 or within EMAP grid cells in Seg. 1, 2, 4, and 6.

Segment 1 (Tortugas) includes the Dry Tortugas National Park and surrounding waters and is most influenced by the Loop Current and Dry Tortugas Gyre. Segment 2 (Marquesas) includes the Marquesas Keys and a shallow sandy area between the Marquesas and Tortugas called the Quicksands; Segment 4 (Backcountry) contains the shallow, hard-bottomed waters of the gulfside Lower Keys. Segments 2 and 4 are both influenced by water moving south from the Shelf. Segment 6 can be considered as part of western Florida Bay. This area is referred to as the Sluiceway as it heavily influenced by transport from Florida Bay and the Shelf (Smith 1994).

Segment 5 (Lower Keys), 7 (Middle Keys), and 9 (Upper Keys) include the inshore, Hawk Channel and reef tract of the Atlantic side of the Florida Keys. The Lower Keys are most influenced by cyclonic gyres spun off of the Florida Current, the Middle Keys by exchange with Florida Bay, while the Upper Keys are influenced by the Florida Current frontal eddies and to a certain extent by exchange with Biscayne Bay. All three oceanside segments are also influenced by wind and tidally driven lateral Hawk Channel transport (Pitts 1997).

Field Sampling

The period of record of this study was from March 1995 to April 1998 and included 12 quarterly sampling events. For each event, field measurements and grab samples were collected from 150 fixed stations within the FKNMS boundary (Fig. 1). Depth profiles of temperature (°C), salinity (psu), dissolved oxygen (DO, mg l^{-1}), photosynthetically available radiation (PAR, $\mu E\ m^{-2}$), in situ chlorophyll *a* specific fluorescence (FSU), optical backscatterance turbidity (OBS), depth as measured by pressure transducer (m), and density (σ_t, kg m^{-3}) were measured by CTD casts (Seabird SBE 19). The CTD was equipped with internal RAM and operated in stand alone mode at a sampling rate of 0.5 sec. The vertical light attenuation coefficient (K_d, m^{-1}) was calculated at 0.5 m intervals from PAR and depth using the standard exponential equation (Kirk 1994) and averaged over the station depth. This was necessary due to periodic occurrence of optically distinct layers within the water column. During these events, K_d was reported for the upper layer.

In the Backcountry area (Seg. 4, Fig. 1) where it was too shallow to use a CTD, surface salinity and temperature were measured using a combination salinity-conductivity-temperature probe (Orion model 140). DO was measured using an oxygen electrode (Orion model 840) corrected for salinity and temperature. PAR was measured using a Li-Cor irradiance meter equipped with two 4π spherical sensors (LI-193SB) separated by 0.5 m in depth and oriented at 90° to each other. The light meter measured instantaneous difference between sensors which was then used to calculate K_d from in-air surface irradiance.

Water was collected from ~0.25 m below the surface and at ~1 m from the bottom with a teflon-lined Niskin bottle (General Oceanics) except in the Backcountry where it was collected directly into sample bottles. Duplicate, unfiltered water samples were collected using 3x sample rinsed 120 ml HDPE bottles for analysis of total constituents. Duplicate water samples for dissolved nutrients were collected using 3x sample rinsed 150 ml syringes which were then filtered by hand through 25 mm glass fiber filters (Whatman GF/F) into 3x sample rinsed 60 ml HDPE bottles. The wet filters used for chlorophyll *a* (Chl *a*) analysis, were placed in 1.8 ml plastic centrifuge tubes to which 1.5 ml of 90 % acetone/water was added (Strickland and Parsons 1972).

Unfiltered samples were kept at ambient temperature in the dark during transport to the laboratory. During shipboard collection in the Tortugas/Marquesas and overnight stays in the Keys, unfiltered samples were analyzed for alkaline phosphatase activity (APA) and turbidity (see *Analytical*) prior to refrigeration. Filtered samples and filters were kept on ice in the dark during transport. During shipboard collection in the Tortugas/Marquesas and overnight stays in the lower Keys, filtrates and filters were frozen until analysis.

Laboratory Analysis

Unfiltered water samples were analyzed for total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), silicate ($Si(OH)_4$), alkaline phosphatase activity (APA), and turbidity (NTU). TOC was measured by direct injection onto hot platinum catalyst in a Shimadzu TOC-5000 after first acidifying to pH<2 and purging with CO_2-free air. TN was measured using an ANTEK 7000N Nitrogen Analyzer using O_2 as carrier gas to promote complete recovery of the nitrogen in the water samples (Frankovich and Jones 1998). TP was determined using a dry ashing, acid hydrolysis technique (Solórzano and Sharp 1980). $Si(OH)_4$ was measured using the molybdosilicate method (Strickland and Parsons 1972). The APA assay measures the activity of alkaline phosphatase, an enzyme used by bacteria to mineralize orthophosphate from organic compounds. The assay is performed by adding a known concentration of an organic phosphate compound (methylfluorescein phosphate) to an unfiltered water sample. AP in the water sample cleaves the orthophosphate, leaving methylfluorescein, a highly fluorescent compound. Fluorescence at initial and after 2 hr incubation were measured using a Gilford Fluoro IV Spectrofluorometer (excitation = 430 nm, emission = 507 nm) and subtracted to give APA in $\mu M\ h^{-1}$ (Jones 1996). Turbidity was measured using an HF Scientific model DRT-15C turbidimeter and reported in NTU.

Filtrates were analyzed for soluble reactive phosphorus (SRP), nitrate+nitrite (NO_x^-), nitrite (NO_2^-), and total ammonia (NH_4^+) on a four channel autoanalyzer (Alpkem model RFA 300). Filters for Chl *a* content ($\mu g\ l^{-1}$) were allowed to extract for a minimum of 2 days at -20°C before analysis. Extracts were analyzed using a Gilford Fluoro IV Spectrofluorometer (excitation = 435 nm, emission = 667 nm). All analyses were completed within 1 month after collection in accordance to SERC laboratory quality control guidelines.

Some parameters were not measured directly, but were calculated by difference. Nitrate (NO_3^-) was calculated as $NO_X^- - NO_2^-$, dissolved inorganic nitrogen (DIN) as $NO_X^- + NH_4^+$, and total organic nitrogen (TON) defined as TN - DIN. All concentrations are reported as µM unless noted. All elemental ratios discussed were calculated on a molar basis. Percent DO saturation (DO_{sat} as %) was calculated using the equations of Garcia and Gordon (1992).

Statistical Analysis

Stations were grouped four different ways for statistical analysis: by surface or bottom samples, surface by segment, surface by transect distance, and surface by shore type. These groupings were subjectively defined using best available knowledge in an effort to provide information as to source, transport, and fate of water quality components. For the first grouping, stations were selected as being >3 m depth where both surface and bottom samples were collected and stratified by depth. The second grouping included surface samples stratified by segment (Fig. 1) in accordance with the implementation plan (EPA 1995). The third grouping consisted of those surface stations situated on ocean-side transects being aggregated according to their distance from shore: Alongshore, Hawk Channel, or Reef Tract. In addition, we initiated a transect of stations in the Tortugas off Loggerhead Key to serve as a reference. Since sampling at these locations in the Tortugas were only recently set up to address this question, the data is more sparse. Also there are only two “channel” stations in the Tortugas which makes the data more susceptible to outlier conditions.

One of the concerns of this program is to determine the contribution of water movement through the passes of the Keys to the water quality of the reef. To this end we decided to characterize the last grouping of transects as to shore type: those that are adjacent to land off

Biscayne National Park off Old Rhodes Key, Elliot Key and the Safety Valve (BISC), those that abut land in Key Largo, Middle, and Lower Keys (LAND), and those transects which are aligned along an open channel or pass through the Keys (PASS). These grouping strategies may be changed when enough data is collected (ca. 5-7 yr) to be analyzed using a statistically objective, multivariate approach as has been done previously for Florida Bay and Ten Thousand Islands (Boyer et al. 1997; Boyer and Jones 1998).

Typical water quality variables are usually skewed to the left resulting in non-normal distributions. Therefore it is more appropriate to use the median as the measure of central tendency. Data distributions of selected water quality variables are reported as box-and-whiskers plots. The box-and-whisker plot is a powerful statistic as it shows the median, range, the data distribution as well as serving as a graphical, nonparametric ANOVA. The center horizontal line of the box is the median of the data, the top and bottom of the box are the 25th and 75th percentiles (quartiles), and the ends of the whiskers are the 5th and 95th percentiles. The notch in the box is the 95% confidence interval of the median. When notches between boxes do not overlap, the medians are considered significantly different. Outliers (<5th and >95th percentiles) were excluded from the graphs to reduce visual compression. Differences in variables were also tested between groups using the Wilcoxon Ranked Sign test (comparable to *t*-test) and among groups by the Kruskall-Wallace test (ANOVA) with significance set at $P<0.05$.

In an effort to elucidate the contribution of external factors to the water quality of the FKNMS and to visualize gradients in water quality over the region, we combined data from other portions of our water quality monitoring network: Florida Bay, Biscayne Bay, Whitewater Bay, Ten Thousand Islands, and the Shelf (Fig. 1). Data from these 153 additional stations was collected during the same month as the FKNMS surveys and analyzed by SERC personnel using similar methodology and quality control as previously described. Spatial contour maps of median water quality variables (of 12 surveys) were generated in SURFER (Golden Software) using the Kriging algorithm.

Results

Overall Water Quality

Summary statistics for all surface water quality variables including data from all 12 sampling events and all stations for the period of record (Table 1) are shown as median value, minimum value, maximum value, and number of samples measured. Overall, the region was warm and euhaline with a median temperature of 26.7°C and salinity of 36.2 psu. The median DO was 6.2 mg l^{-1}, or ~93 % DO_{sat}. On this coarse scale, the FKNMS exhibited very good water quality with median NO_3^-, NH_4^+, and TP concentrations of 0.10, 0.32, and 0.18 μM, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (~70 %). DIN comprised a small fraction (4 %) of the TN pool with TON making up the bulk (11.4 μM). SRP concentrations were very low (median 0.01 μM) and comprised only 6 % of the TP pool. Chl *a* concentrations were very low overall, 0.25 μg l^{-1}, but ranged from 0.01 to 6.8 μg l^{-1}. Median turbidity was low (0.6 NTU) as reflected in a low K_d (0.206 m^{-1}). This resulted in a median photic depth (to 1 % incident PAR) of ~22 m. Molar ratios of N to P suggested a general P limitation of the water column; median TN:TP = 67 and median DIN:SRP = 49.

Stations Grouped by Depth

Some general differences were observed for those stations >3 m depth where both surface and bottom concentrations were measured. Temperature, DO, TOC, and TON were significantly higher at the surface while salinity, NO_3^-, NO_2^-, NH_4^+, TP, and turbidity were significantly higher in bottom waters. There were no significant differences in SRP, APA, or $Si(OH)_4$ with depth.

Stations Grouped By Segment

NO_3^- was highest in the Backcountry (0.18 µM) followed by the Lower and Middle Keys. Interestingly, NO_3^- concentrations in the Sluiceway (0.08 µM) were not significantly different than the Upper Keys, Tortugas, or Marquesas. Median NO_2^- concentrations in the Tortugas and Marquesas (0.03 µM) were significantly lower than for the other Keys segments. NH_4^+ was highest in the Backcountry (0.46 µM) and lowest in the Tortugas, Marquesas, and Upper Keys (~0.25 µM). The Middle Keys had the most variability in DIN for any of the ocean-side segments.

TP was highest in the Backcountry and Sluiceway (~0.21 µM) and lowest in the Upper Keys (0.15 µM) with the remaining segments being intermediate (Fig. 2). SRP was very low (~0.01 µM) for all areas but was slightly elevated and most variable in the Marquesas and Backcountry. Median $Si(OH)_4$ concentrations were highest in the Sluiceway (4.9 µM), lowest in the Tortugas, Marquesas, and Upper Keys (~0.45 µM), and intermediate in the Backcountry, Lower, and Middle Keys (~1.4 µM). Consistently higher Chl *a* concentrations were observed in the Marquesas (0.36 µg l^{-1}) than for any other area of the FKNMS (Fig. 2). Lowest Chl *a* concentrations were found in the Upper Keys (0.20 µg l^{-1}).

The organic C and N pools as well as APA showed remarkable similarity in relative concentration among segments (Fig. 3). Highest TOC (~260 µM), TON (~15.5 µM), and APA (~0.08 µM h^{-1}) were observed in the Backcountry and Sluiceway which declined SW towards the Tortugas and NE towards the Upper Keys. Median DO_{sat} was relatively similar among segments but was significantly higher and more variable in the Backcountry and Sluiceway (~95 %). This result would not have been evident had we only reported DO in mg l^{-1} as it was not significant across segments.

Salinity was comparable for most segments but was slightly lower in the Sluiceway (Fig. 3). Salinity in the Sluiceway and Backcountry were highly variable and precluded any statistical discrimination from the other segments. Turbidity was highest in the Backcountry (1.0 NTU), Sluiceway (0.85 NTU), and Marquesas (0.83 NTU) with lowest turbidity occurring in the Tortugas segment (0.35 NTU, Fig. 3). The shallow Quicksands area in the Marquesas probably accounted for the elevated turbidity in this segment. The Middle Keys showed high variability in turbidity although the overall median was low.

The Tortugas, Marquesas, and Lower Keys had significantly higher water temperature (~27.3°C) than the other segments (Fig. 4). Light attenuation showed a similar pattern as turbidity with highest K_d in Sluiceway (0.36 m^{-1}) and Backcountry stations (0.31 m^{-1}) and lowest K_d in the Tortugas (0.12 m^{-1}). This works out to respective median photic depths of 13, 15, and 38 m. Median TN:TP ratios in the Tortugas (55) and Marquesas (52) were significantly lower than in the other segments (Fig. 4). Much of this difference was due to decreased TON concentrations in these areas rather than increased in TP. Lowest DIN:SRP ratios were found in the Marquesas (29) followed by the Tortugas (39). Decreased DIN as well as elevated SRP in the Marquesas relative to the Tortugas was responsible for these differences.

Stations Grouped By Distance along Transect

Median concentrations of NO_3^- in the Middle, and Lower Keys were significantly higher in Alongshore stations than those of Hawk Channel and Reef Tract (Fig. 5). Alongshore NO_3^- in the Upper Keys and Tortugas (~0.1 µM) was not nearly as high as found in the Middle and Lower Keys (~2.5 µM). NO_3^-concentrations on the Reef Tract and offshore in the Tortugas, Upper, and Middle Keys were comparable (~0.05 µM) and were all significantly lower than for the Lower Keys. NH_4^+ concentrations followed similar trends as NO_3^- being higher in Alongshore stations in the Middle and Lower Keys and declined with distance offshore (Fig. 5). Alongshore NH_4^+ was highest in the Middle Keys (~0.5 µM). No significant differences in NH_4^+ was seen among Hawk Channel, Reef Tract, and Tortugas groups (~0.3 µM).

Alongshore TP concentrations (~0.18 µM) were significantly higher than the Reef Tract only in the Lower Keys (Fig. 5). The Middle Keys and Tortugas showed no offshore trend while the Upper Keys showed a slight increasing trend in TP from shore to reef. TP concentrations in the Tortugas, Lower, and Middle Keys were comparable (~0.18 µM) while the Upper Keys were lowest overall (~0.16 µM). The major trends in TP were mirrored by SRP but were not statistically significant. Median $Si(OH)_4$ concentrations dropped dramatically with distance offshore in the Middle Keys (Fig. 5). In the Lower Keys, $Si(OH)_4$ was significantly lower only in the Reef Tract stations. There was no difference in $Si(OH)_4$ concentrations in the Upper Keys or Tortugas transects. Alongshore $Si(OH)_4$ concentrations were highest in the Middle Keys (~3 µM) while Reef Tract concentrations were highest in the Lower Keys (~0.5 µM).

There was no significant trend in Chl *a* with distance from land in the Lower Keys (Fig. 6), although there was a slight decline in the Middle Keys and a small increase in the Upper Keys. Chl *a* in the Offshore Tortugas sites was significantly lower than Alongshore and Channel sites and was comparable to levels in the Upper Keys (0.2 $\mu g\ l^{-1}$). TOC in the Lower, Middle, and Upper Keys was elevated Alongshore and declined sequentially through Hawk Channel to the Reef Tract (Fig. 6). There was no significant difference in TOC within Tortugas groups (~170 µM) and was similar to Reef Tract concentrations in the Keys. Highest TOC in Alongshore stations occurred in the Middle Keys (~250 µM). TON concentrations exhibited similar patterns as TOC (data not shown).

Turbidity in all segments declined significantly with distance from land (Fig. 6). All Reef Tract and Offshore Tortugas sites had comparably low turbidity levels (~0.2 NTU). Highest Alongshore turbidity was found in the Middle Keys (1.3 NTU). No significant differences in Alongshore turbidity in the Tortugas, Lower, and Upper Keys were observed (~0.6 NTU). Trends in median salinity with distance offshore were small; trends in salinity variability were large (Fig. 6). Salinity from Alongshore to Reef Tract increased significantly in the Upper Keys whereas in the Lower Keys, salinity actually decreased offshore. No significant change in salinity was observed along Middle Keys, Marquesas, or Tortugas transects. In all segments, Alongshore salinities were much more variable than those of Reef Tract and Offshore. Reef Tract and Tortugas Offshore salinities were not significantly different, therefore, Alongshore salinity in the Lower Keys was higher than local seawater values while Alongshore salinity in the Upper Keys was depressed relative to local seawater values.

Stations Grouped By Shore Type

Ocean-side transects showed marked differences in water quality when grouped by shore type (Fig. 7). Transects situated on open channels (Pass) through the Keys were elevated in NO_3^-,

NH_4^+, TP, $Si(OH)_4$, Chl *a*, TOC, and turbidity relative to those against the island chain (Land). Both salinity and temperature were significantly lower in Pass transects than for Land. Although these differences were statistically significant, the absolute differences were very small being only fractional. We also found that these effects diminished rapidly with distance offshore (data not shown). Interestingly, those transects located along Biscayne National Park (Old Rhodes Key, Elliot Key, the Safety Valve) were lowest of all for NO_3^-, NH_4^+, TP, $Si(OH)_4$, and Chl *a*.

Discussion

Distinguishing internal from external sources of nutrients in the FKNMS is a difficult task. The finer discrimination of internal sources into natural and anthropogenic inputs is even more difficult but most important as anthropogenic inputs may be regulated and possibly controlled by management activities. Advective transport of nutrients through the FKNMS was not measured by the existing fixed sampling plan. However, nutrient distribution patterns may be compared to the regional circulation regimes in an effort to visualize the contribution of external sources and advective transport to internal water quality of the FKNMS.

Circulation in coastal South Florida is dominated by regional currents such as the Loop Current, Florida Current, and Tortugas Gyre and by local transport via Hawk Channel and alongshore Shelf movements (Klein and Orlando 1994). Regional currents may influence water quality over large areas by the advection of external surface water masses into and through the FKNMS (Lee et al. 1994) and by the intrusion of deep offshore ocean waters onto the reef tract as internal bores (Leichter et al. 1996). Local currents become more important in the mixing and transport of freshwater and nutrients from terrestrial sources (Smith 1994; Pitts 1997).

Spatial patterns of salinity in coastal South Florida show these major sources of freshwater to have more than just local impacts (Fig. 8). In Biscayne Bay, freshwater is released through the canal system operated by SFWMD; the impact is clearly seen to affect northern Key Largo by causing a depression in median salinity coupled with high variability in alongshore sites (Fig. 6 and 7). Freshwater entering NE Florida Bay via overland flow from Taylor Slough and C-111 basin in ENP can be seen to mix in a SW direction. The extent of influence of freshwater from Florida Bay on alongshore salinity in the Keys is less than that of Biscayne Bay but it is more episodic. Transport of low salinity water from Florida Bay does not affect the Middle Keys sites enough to depress the median salinity in this region but is manifested as increased variability (Fig. 6). On the west coast, the large influence of the Shark River Slough, which drains the bulk of the Everglades and exits through the Whitewater Bay - Ten Thousand Islands mangrove complex, is clearly seen as impacting the Shelf waters (Fig. 8). The mixing of Shelf waters with the Gulf of Mexico produces a salinity gradient in a SW direction which extends out to Key West. This freshwater source does not seem to impact the Backcountry because of its shallow nature but instead follows a trajectory of entering western Florida Bay and exiting out through the channels in the Middle Keys (Smith 1994). This net transport of lower salinity water from mainland to reef in open channels through the Keys is observed more so as an increase in the range and variability of salinity than as a large depression in salinity (Fig. 7).

In addition to surface currents there is evidence that internal tidal bores regularly impact the Key Largo reef tract (Leichter et al. 1996). Internal bores are episodes of higher density, deep water intrusion onto the shallower shelf or reef tract. Depending on their energy, internal tidal bores can promote stratification of the water column or cause complete vertical mixing as a breaking internal wave of subthermocline water. To determine the extent of stratification we calculated the difference between surface and bottom density, delta sigma-t ($\Delta\sigma_t$), where positive values denoted greater density of bottom water relative to the surface. The resulting graph of $\Delta\sigma_t$ (Fig. 9), shows that the SW area of the Tortugas segment tends to experience the greatest frequency of stratification events. The decreased temperature and increased salinity in bottom waters from intrusion of deeper denser oceanic waters to this region may also account for increases in NO_3^-, TP, and SRP in these bottom waters as well. For example, in April 1998 a mass of colder, nutrient laden water from the Gulf of Mexico moved up onto the Tortugas reefs and fueled a large benthic macroalgae bloom (J. Porter, pers. comm.). This event was observed throughout most of the eastern Gulf as far north as Pensacola (NOAA **????**). At the two most SW stations (Table 2), temperatures dropped ~4°C, NO_3^- increased 3 orders of magnitude, SRP and $Si(OH)_4$ increased by a factor of 100, while TP, turbidity, and in vivo Chl *a* specific fluorescence (measured via CTD) all doubled. As there was only a small increase in NH_4^+ during this event we believe the general case of elevated NH_4^+ and turbidity found in bottom waters throughout the FKNMS is most probably due to benthic flux and resuspension and not to subthermocline advection.

Surface $Si(OH)_4$ concentrations exhibited a pattern similar to salinity (Fig. 10). The source of $Si(OH)_4$ in this geologic area of carbonate rock and sediments is from siliceous periphyton (diatoms) growing in the Shark River Slough, Taylor Slough, and C-111 basin watersheds. Unlike the Mississippi River plume with Chl *a* concentrations of 76 $\mu g\ l^{-1}$ (Nelson and Dortch 1996), phytoplankton biomass on the Shelf (1-2 $\mu g\ l^{-1}$ Chl *a*) was not sufficient to account for the depletion of $Si(OH)_4$ in this area. Therefore, $Si(OH)_4$ concentrations on the Shelf were rapidly depleted by mixing alone allowing $Si(OH)_4$ to be used as a semi-conservative tracer of freshwater in this system (Ryther et al. 1967; Moore et al. 1986). Unlike Florida Bay and the west coast, there was very little $Si(OH)_4$ loading to southern Biscayne Bay, mostly because the source of freshwater to this system is from canals which drain agricultural and urban areas of Dade County.

In the Lower and Middle Keys, it is clear that the source of $Si(OH)_4$ to the nearshore Atlantic waters is through the Sluiceway and Backcountry. $Si(OH)_4$ concentrations near the coast were elevated relative to the reef tract with much higher concentrations occurring in the Lower and Middle Keys than the Upper Keys (Fig. 5). There is an interesting peak in $Si(OH)_4$ concentration in an area of the Sluiceway which is densely covered with the seagrass, *Syringodium* (Fourqurean this issue). We are unsure as to the source but postulate that it may be due to benthic flux.

Visualization of spatial patterns of NO_3^- concentration over South Florida waters provide an extended view of source gradients over the region (Fig. 11). Biscayne Bay, Florida Bay, and the Shark River area of the west coast exhibited high NO_3^- concentrations relative to the FKNMS and Shelf. Elevated NO_3^- in Biscayne Bay is the result of loading from both the canal drainage system and from inshore groundwater (Alleman et al. 1995, Meeder **????**). The source of NO_3^- to Florida Bay is the Taylor Slough and C-111 basin (Boyer and Jones, 1999; Rudnick et al., 1999) while the Shark River Slough impacts the west coast mangrove rivers and out onto the Shelf (Rudnick et al., 1999). The oceanside transects off Biscayne Bay in Seg. 9 exhibited the lowest NO_3^- alongshore compared to the Middle and Lower Keys. A similar pattern was observed in a previous transect survey from these areas (Szmant and Forrester 1996). They also showed an inshore elevation of NO_3^- relative to Hawk Channel and the reef tract which is also demonstrated in our analysis (Fig. 5). Interestingly, NO_3^- concentrations in all stations in the

Tortugas transect were similar to those of reef tract sites in the mainland Keys; there was no inshore elevation of NO_3^- on the transect off uninhabited Loggerhead Key.

Figure 10 also shows that a distinct intensification of NO_3^- occurs in the Backcountry region. Part of this increase may due to a local sources of NO_3^-, i.e. septic systems and stormwater runoff around Big Pine Key (Lapointe and Clark 1992). However, there is another area, the Snipe Keys, that exhibits high NO_3^- which is uninhabited by man. This rules out the premise of septic systems being the only source of NO_3^- in this area. It is important to note that the Backcountry area is very shallow (~0.5 m) and hydraulically isolated from the Shelf and Atlantic which results in its having a relatively long water residence time. Elevated NO_3^- concentrations may be partially due to simple evaporative concentration as is seen in salinity (Fig. 8).

Total dissolved NH_4^+ concentrations were distributed in a similar manner as NO_3^- with highest concentrations occurring in Florida Bay, the Ten Thousand Islands, and the Backcountry (data not shown). NH_4^+ concentrations were very low in Biscayne Bay because it is not a major component of loading from the canal drainage system. NH_4^+ also showed similarities with NO_3^- in its spatial distribution, being lowest in the Upper Keys and highest inshore relative to offshore. There was no alongshore elevation of NH_4^+ concentrations in the Tortugas where levels were similar to those of reef tract sites in the mainland Keys. That the least developed portion of the Upper Keys in Biscayne National Park and uninhabited Loggerhead Key (Tortugas) exhibited lowest NO_3^- and NH_4^+ concentrations is evidence of a local anthropogenic source for both of these variables along the ocean side of the Upper, Middle, and Lower Keys. This pattern of decline implies an onshore source which is diluted with distance from land by low nutrient Atlantic Ocean waters.

Elevated DIN concentrations in the Backcountry, on the other hand, are not so easily explained. We postulate that the high concentrations found there are due to a combination of anthropogenic loading, physical entrapment, and benthic N_2 fixation. The relative contribution of these potential sources is unknown. Lapointe and Matzie (1996) have shown that stormwater and septic systems are responsible for increased DIN loading in and around Big Pine Key. The effect of increased water residence time in DIN concentration is probably small. Salinities in this area were only 1-2 psu higher than local seawater which resulted in a concentration effect of only 5-6%. Benthic N_2 fixation may potentially be very important in the N budget of the Backcountry. Measured rates of N_2 fixation in a *Thalassia* bed in Biscayne Bay, having very similar physical and chemical conditions, were 540 μmol N m^{-2} d^{-1} (Capone and Taylor 1980). Without the plant community N demand, one day of N_2 fixation has the potential to generate a water column concentration of >1 μM NH_4^+ (0.5 m deep). Much of this NH_4^+ is probably nitrified and may help account for the elevated NO_3^- concentrations observed in this area as well. Clearly, N_2 fixation may be a significant component of the N budget in the Backcountry and that it may be a exported as DIN to the FKNMS in general.

Spatial patterns in TP in South Florida coastal waters were strongly driven by the west coast outputs (Fig 12). A declining gradient in TP extended from the inshore waters of Whitewater Bay - Ten Thousand Islands mangrove complex out onto the Shelf and Tortugas. A declining gradient also extended from north central Florida Bay to the Middle Keys. Brand (1997) has postulated that groundwater from a subterranean Miocene quartz sand channel, "the river of sand", containing high levels of phosphorus is the source of TP in this region. However, no evidence of this source exists to date and the data from Florida Bay does not indicate a subterranean source either (Boyer and Jones unpublished data). A very small TP gradient was seen NE Florida Bay signifying that Taylor Slough and the C-111 basin contribute little TP to the system. Finally, there was no evidence of a significant terrestrial source of TP to Biscayne Bay.

In the Keys, there was evidence of elevated TP in alongshore stations of the Middle and Lower Keys but the differences were very small (Fig. 5). The Upper Keys actually showed higher TP concentrations on the reef tract than inshore implying an offshore source. Interestingly, the Tortugas area had higher TP concentrations than the Upper Keys as a result of Shelf water advection.

In South Florida coastal waters, very little of TP is found in the inorganic form (SRP - PO_4^-); most is organic P (TOP). The distribution of SRP on the west coast and Shelf was similar to that of TP with the general gradient from the west coast to Tortugas remaining (Fig 13). However, the SRP distribution was distinctly different from that of TP in Florida Bay, Whitewater Bay, and Biscayne Bay. In central Florida Bay the N-S gradient previously observed for TP was highly diminished for SRP indicating that almost all the TP in central Florida Bay was in the form of TOP. It is unlikely that the source of TOP to this region is from overland flow or groundwater as this is also the region that expresses highest salinity. Alternately, we hypothesize that the presence of the Flamingo channel, running parallel to the southern coastline of Cape Sable, acts as a tidal conduit for episodic advection of inshore Shelf water to enter north central Florida Bay. Subsequent trapping and evaporation then may act to concentrate TOP in this region. The second difference in P distributions was that there was a significant SRP gradient present in NE Florida Bay that was not observed for TP. The sources of SRP to this area are the Taylor Slough and C-111 basin (W. Walker per. communication; Boyer and Jones, 1999; Rudnick et al., 1999).

Whitewater Bay displayed an east-west gradient in SRP concentrations which increased with salinity leading us to conclude that the freshwater inputs from the Everglades were not a source of SRP to this area. Finally, there was evidence of a significant onshore-offshore SRP gradient in southern Biscayne Bay; most probably as a direct result of canal loading and groundwater seepage to this region (A. Lietz personal communication; Meeder et al. 1997).

Concentrations of TOC (Fig. 14) and TON (not shown) are remarkably similar in pattern of distribution across the South Florida coastal hydroscape. The decreasing gradient from west coast to Tortugas was very similar to that of TP. A steep gradient with distance from land was observed in Biscayne Bay. Both these gradients were due to terrestrial loading. On the west coast, the source of TOC and TON was from the mangrove forests. Our data from this area shows that concentrations of TOC and TON increased from Everglades headwaters through the mangrove zone and then decrease with distance offshore. In Biscayne Bay, much of the TOC and TON is from agricultural land use. The high concentrations of TOC and TON found in Florida Bay were due to a combination of terrestrial loading (Boyer and Jones, 1999), in situ production by seagrass and phytoplankton, and evaporative concentration (Fourqurean et al. 1993).

Advection of Shelf and Florida Bay waters through the Sluiceway and passes accounted for this region and the inshore area of the Middle Keys as having highest TOC and TON of the FKNMS (Fig. 7). Strong offshore gradients in TOC and TON existed for all mainland Keys segments (Fig. 6) but not for the Tortugas transect. Part of this difference may be explained by the absence of mangroves in the single Tortugas transect. The higher concentrations of TOC and TON in the inshore waters of the Keys then implies a terrestrial source rather than simply benthic production and sediment resuspension. Main Keys reef tract concentrations of TOC and TON were similar to those found in the Tortugas.

Much emphasis has been placed on assessing the impact of episodic phytoplankton blooms in Florida Bay on the offshore reef tract environment. Spatial patterns of Chl *a* concentrations (Fig. 15) showed that NW Florida Bay, Whitewater Bay, and the Ten Thousand Islands exhibited high levels of Chl *a* relative to Biscayne Bay, Shelf, and FKNMS. The highest Chl *a* concentrations were found in west coast mangrove estuaries (up to 45 $\mu g\ l^{-1}$ in Alligator Bay, TTI). Chl *a* is also routinely high (~2 $\mu g\ l^{-1}$) in NW Florida Bay along the channel connecting the Shelf to Flamingo, ENP. It is interesting that Chl *a* concentrations are higher in the Marquesas (0.36 $\mu g\ l^{-1}$) than in other areas of the FKNMS (Fig. 2). When examined in context with the whole South Florida ecosystem, it is obvious that the Marquesas zone should be considered a continuum of the Shelf rather than a separate management entity. This shallow sandy area (often called the Quicksands) acts as a physical mixing zone between the Shelf and the Atlantic Ocean and is a highly productive area for other biota as well as it encompasses the historical Tortugas shrimping grounds. A Chl *a* concentration of 1 $\mu g\ l^{-1}$ in the water column of a reef tract is considered a problem as it indicates potential of eutrophication. On the other hand, a similar Chl *a* level in the Quicksands indicates a productive shrimp fishery.

The oceanside transects in the Upper Keys (Seg. 9) exhibited the lowest overall Chl *a* concentrations of any zone in the FKNMS. Ocean transects showed a slight increase in Chl *a* on the reef tract in this area (Fig. 6). Transects off the Middle and Lower Keys showed that a drop in Chl *a* occurred only in the reef tract sites; there was no linear decline with distance from shore (data not shown). alongshore compared to the Middle and Lower Keys. Interestingly, Chl *a* concentrations in the Tortugas transect showed a similar pattern as the mainland Keys. Inshore and Hawk Channel Chl *a* concentrations among Middle Keys, Lower Keys and Tortugas sites were not significantly different. As inshore Chl *a* concentrations in the Tortugas were similar to those in the Middle and Lower Keys, we see no evidence of phytoplankton bloom transport from Florida Bay under this type of sampling design. There was however some slight evidence of increased Chl *a* in those stations situated along the major passes in the Keys relative to those abutting land (Fig. 7). The differences between these two groupings were very small (0.25 vs. 0.20 $\mu g\ l^{-1}$).

Along with P concentration, turbidity is probably the second most important determinant of local ecosystem health. The fine, low density carbonate sediments in this area are easily resuspended, rapidly transported, and have high light scattering potential per gram of material. High water column turbidity and transport directly affects filter feeding organisms by clogging their feeding apparatus and by increasing local sedimentation rate. Sustained high turbidity of the water column indirectly affects benthic community structure by decreasing light penetration, promoting seagrasses extinction. Large scale observations of turbidity clearly show patterns of onshore-offshore gradients which extend out onto the Shelf to the Marquesas (Fig. 16). In the last seven years, turbidities in Florida Bay have increased dramatically in the NE and central regions (Boyer et al. 1998) potentially as a consequence of destabilization of the sediment from seagrass die-off (Robblee et al. 1991).

Strong turbidity gradients were observed for all Keys transects (Fig. 6) but reef tract levels were remarkably similar regardless of inshore levels. High alongshore turbidity is most probably due to the shallow water column being easily resuspended by wind and wave action. Inshore stations in the Middle Keys had higher turbidity than other segments. Transects aligned with major passes had slightly greater turbidity than those against land but the difference was not statistically significant (Fig. 7). Light extinction (K_d) was highest alongshore and improved with distance from land (data not shown). This trend was expected as light extinction is directly related to the turbidity of the water.

Using the DIN:SRP ratio is a relatively simple method of determining phytoplankton nutrient limitation status of the water column (Redfield 1967). Most of the South Florida hydroscape was shown to have DIN:SRP values >> 16:1, indicating the potential for phytoplankton to be limited by P at these sites (Fig. 17). The bulk of Florida Bay and both southern and northern Biscayne Bay were severely P limited, mostly as a result of high DIN concentrations. All of the FKNMS is routinely P limited using this metric. Interestingly, the Marquesas/Quicksands area was the least P limited of all zones and exhibited a significant regression between SRP and Chl *a*. Only in the northern Ten Thousand Islands and Shelf did N become the limiting nutrient. The south-north shift from P to N limitation observed in the west coast estuaries has been ascribed to changes in landuse and bedrock geochemistry of the watersheds (Boyer and Jones 1998). The west coast south of 25.4 N latitude is influenced by overland freshwater flow from the Everglades and Shark River Slough having very low P concentrations relative to N. Above 25.7 N latitude the bedrock geology of the watershed changes from carbonate to silicate based and landuse changes from relatively undeveloped wetland (Big Cypress Basin) to a highly urban/agricultural mix (Naples, FL).

The large scale of this monitoring program has allowed us to assemble a much more holistic view of broad physical/chemical/biological interactions occurring over the South Florida hydroscape. Much information has been gained by inference from this type of data collection program: major nutrient sources have be confirmed, relative differences in geographical determinants of water quality have been demonstrated, and large scale transport via circulation pathways have been elucidated. In addition we have shown the importance of looking "outside the box" for questions asked within. Rather than thinking of water quality monitoring as being a static, non-scientific pursuit it should be viewed as a tool for answering management questions and developing new scientific hypotheses. One of the more important management questions to be answered is "Is the water quality better or worse than it used to be?" As it stands, this monitoring program based on quarterly sample intervals may require up to 10 years before small trends may be detected because of seasonal variability and background noise.

Conclusions

Preliminary results of a spatially extensive water quality monitoring program in the FKNMS are reported. Quarterly sampling at 150 fixed stations began in March 1995 and continue at present and consists of 12 sampling events. Stratification of sites according to depth showed that temperature, dissolved oxygen, total organic carbon, and total organic nitrogen were significantly higher at the surface while salinity, nitrate, nitrite, ammonium, total phosphorus, and turbidity were greater in bottom waters. Stratification according to geographical region showed that the Upper Keys generally had lower nutrient concentrations than the Middle or Lower Keys. In the Lower Keys inorganic nitrogen and total phosphorus was elevated in the Backcountry area. The offshore Marquesas/Quicksands area exhibited the highest phytoplankton biomass *(chlorophyll* a*) for any segment of the FKNMS. Declining inshore to offshore trends were observed for nitrate, ammonia, silicate, total organic carbon, total organic nitrogen, and turbidity for all oceanside transects. Total phosphorus concentrations in the Lower Keys transects decreased with distance offshore but increased along transects in the Upper Keys, mostly because of low concentrations alongshore. Stations stratified as being off land or channel/pass showed that those stations situated along channels/passes through the Keys had higher nutrient concentrations, phytoplankton biomass, and turbidity than those stations off land. The differences were statistically significant but the absolute differences were very small and not likely to be biologically important. The water quality of the FKNMS is put in perspective with data from 150 stations sampled in SW Florida Shelf, Florida Bay, Whitewater Bay, Ten Thousand Islands, and Biscayne Bay. It becomes clear from this analysis that the ambient water quality in the Lower Keys and Marquesas is most strongly influenced by water quality of the SW Florida Shelf, the Middle Keys by SW Florida Shelf and Florida Bay transport, the Backcountry by internal nutrient sources, and the Upper Keys from Florida Current intrusion.*

References

ALLEMAN, R. W., ET AL. 1995. Biscayne Bay surface water improvement and management. Technical supporting document. South Florida Water Management District.

BOYER, J. N., J. W. FOURQUREAN, AND R. D. JONES. 1997. Spatial characterization of water quality in Florida Bay and Whitewater Bay by multivariate analysis: Zones of similar influence (ZSI). Estuaries 20: 743-758.

BOYER, J. N., J. W. FOURQUREAN, AND R. D. JONES. 1999. Seasonal and long term trends in the water quality of Florida Bay (1989 - 1997). Estuaries 22: 417-430.

BOYER, J. N., AND R. D. JONES. 1998. Influence of coastal morphology and watershed characteristics on the water quality of mangrove estuaries in the Ten Thousand Islands - Whitewater Bay complex. Proceedings of the 1998 Florida Bay Science Conference. University of Florida Sea Grant.

BOYER, J. N., AND R. D. JONES. 1999. Effects of freshwater inputs and loading of phosphorus and nitrogen on the water quality of Eastern Florida Bay, p. 545-561. *In* K. R. Reddy, G. A. O'Connor, and C. L. Schelske [eds.] Phosphorus biogeochemistry in sub-tropical ecosystems. CRC/Lewis Publishers, Boca Raton, Florida.

BRAND, L. 1998. The role of groundwater in the Florida Bay ecosystem. Proceedings of the 1998 Florida Bay Science Conference. University of Florida Sea Grant.

CAPONE, D. G., AND B. F. TAYLOR. 1980. Microbial nitrogen cycling in a seagrass community, p. 153-161. *In* V. S. Kennedy [ed.], Estuarine perspectives. Academic.

DEPARTMENT OF COMMERCE. 1995. Florida Keys National Marine Sanctuary draft management plan / environmental impact statement. National Oceanic and Atmospheric Administration, Sanctuary Programs Division. 245 p.

ENVIRONMENTAL PROTECTION AGENCY. 1995. Water quality protection program for the Florida Keys National Marine Sanctuary: Phase III report. Final report submitted to the Environmental Protection Agency under Work Assignment 1, Contract No. 68-C2-0134. Battelle Ocean Sciences, Duxbury, MA and Continental Shelf Associates, Inc., Jupiter FL.

FOURQUREAN, J. W., R. D. JONES, AND J. C. ZIEMAN. 1993. Processes influencing water column nutrient characteristics and phosphorus limitation of phytoplankton biomass in Florida Bay, FL, USA: inferences from spatial distributions. Estuar., Coast. Shelf Sci. 36: 295-314.

FRANKOVICH, T. A., AND R. D. JONES. 1998. A rapid, precise, and sensitive method for the determination of total nitrogen in natural waters. Mar. Chem. 60: 227-234.

FROELICH, P. N., JR., D. K. ATWOOD, AND G. S. GIESE. 1978. Influence of Amazon River discharge on surface salinity and dissolved silicate concentrations in the Caribbean Sea. Deep Sea Res. 25: 735-744.

GARCIA, H. E., AND L. I. GORDON. 1992. Oxygen solubility in seawater: Better fitting equations. Limnol. Oceanogr. 37: 1307-1312.

JONES, R. D. 1996. Phosphorus cycling, p. 343-348. *In* G. J. Hurst, G. A. Knudsen, M. J. McInerney, L. D. Stetzenbach and M. V. Walter [eds.], Manual of environmental microbiology. ASM Press.

KIRK, J. T. O. 1994. Light and photosynthesis in aquatic systems, 2nd Ed. Cambridge.

KLEIN, C. J., AND S. P. ORLANDO JR. 1994. A spatial framework for water-quality management in the Florida Keys National Marine Sanctuary. Bull. Mar. Sci. 54: 1036-1044.

LAPOINTE, B. E., AND M. W. CLARK. 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida Keys. Estuaries 15: 465-476.

LAPOINTE, B. E., AND W. R. MATZIE. 1996. Effects of stormwater nutrient discharges on eutrophication processes in nearshore waters of the Florida Keys. Estuaries 19: 422-435.

LEE, T. N., M. E. CLARKE, E. WILLIAMS, A. F. SZMANT, AND T. BERGER. 1994. Evolution of the Tortugas gyre and its influence on recruitment in the Florida Keys. Bull. Mar. Sci. 54: 621-646.

LEICHTER, J. J., S. R. WING, S. L. MILLER, AND M. W. DENNY. 1996. Pulsed delivery of subthermocline water to Conch Reef (Florida Keys) by internal tidal bores. Limnol. Oceanogr. 41: 1490-1501.

MEEDER, J. F., J. ALVORD, M. BYRNS, M. S. ROSS, AND A. RENSHAW. 1997. Distribution of benthic nearshore communities and their relationship to groundwater nutrient loading. Final report to Biscayne National Park.

MOORE, W. S., J. L. SARMIENTO, AND R. M. KEY. 1986. Tracing the Amazon component of surface Atlantic water using ^{228}Ra, salinity, and silica. J. Geophys. Res. 91: 2574-2580.

NELSON, D. M., AND Q. DORTCH. 1996. Silicic acid depletion and silicon limitation in the plume of the Mississippi River: evidence from kinetic studies in spring and summer. Mar. Ecol. Prog. Ser. 136: 163-178.

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION. 1995. Florida Keys National Marine Sanctuary Draft Management Plan/Environmental Impact Statement.

PITTS, P. A. 1997. An investigation of tidal and nontidal current patterns in Western Hawk Channel, Florida Keys. Cont. Shelf Res. 17: 1679-1687.

ROBBLEE, M. B., T. B. BARBER, P. R. CARLSON JR., M. J. DURAKO, J. W. FOURQUREAN, L. M. MUEHLSTEIN, D. PORTER, L. A. YABRO, R. T. ZIEMAN, AND J. C. ZIEMAN. 1991. Mass mortality of the tropical seagrass *Thalassia testudinum* in Florida Bay (USA). Mar. Ecol. Prog. Ser. 71: 297-299.

RUDNICK, D., Z. CHEN, D. CHILDERS, T. FONTAINE, AND J. N. BOYER. 1999. Phosphorus and nitrogen inputs to Florida Bay: the importance of the Everglades watershed. Estuaries 22: 98-416.

RYTHER, J. H., D. W. MENZE, AND N. CORWIN. 1967. Influence of the Amazon River outflow on the ecology of the western tropical Atlantic, I. Hydrography and nutrient chemistry. J. Mar. Res. 25: 69-83.

SOLORZANO, L., AND J. H. SHARP. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnol. Oceanogr. 25: 754-758.

SMITH, N. P. 1994. Long-term Gulf-to-Atlantic transport through tidal channels in the Florida Keys. Bull. Mar. Sci. 54: 602-609.

STRICKLAND, J. D. H., AND T. R. PARSONS. 1972. A practical handbook of seawater analysis. Bull. Fish. Res. Bd. Can. 167: 107-112.

SZMANT, A. M., AND A. FORRESTER. 1996. Water column and sediment nitrogen and phosphorus distribution patterns in the Florida Keys, USA. Coral Reefs 15: 21-41.

List of Tables

Table 1.

	Median	Min.	Max.	*n*
NO_3^-	0.08	0.00	1.61	862
NO_2^-	0.04	0.00	0.22	1180
NH_4^+	0.27	0.01	2.44	1191
TON	9.65	3.64	42.67	1180
TP	0.17	0.01	0.66	1183
SRP	0.01	0.00	0.12	915
APA	0.04	0.01	0.84	1029
Chl *a*	0.25	0.01	6.81	1188
TOC	198.70	86.98	1054.79	1186
$Si(OH)_4$	0.59	0.00	37.36	902
Turbidity	0.46	0.01	12.97	1083
Salinity	36.20	31.80	38.40	1140
Temperature	26.45	17.50	39.60	1146
DO	6.20	4.60	10.40	1123
DO_{sat}	92.50	68.28	150.03	1123
K_d	0.16	0.01	1.12	1138
TN:TP	62.10	15.89	1356.21	1181
DIN:SRP	43.83	1.40	935.33	906
$\%I_o$	17.21	0.00	97.03	1138

Table 2.

	Station #345		Station #350	
	Surface	Bottom	Surface	Bottom
Salinity	36.00	36.00	36.10	36.00
Temperature	24.00	19.70	23.60	20.20
NO_3^-	0.05	3.66	0.00	3.23
NO_2^-	0.01	0.81	0.04	0.35
NH_4^+	0.94	1.14	0.32	0.57
TP	0.23	0.39	0.19	0.40
SRP	0.02	0.22	0.01	0.20
$Si(OH)_4$	0.09	2.07	0.29	2.26
TOC	170.10	155.48	171.42	168.35
TON	4.86	2.25	5.45	4.01
Chl *a*	0.94	1.62	1.10	1.82
Turbidity	0.17	0.50	0.43	1.11
DO_{sat}	94.28	80.91	93.90	78.74

List of Figures

Fig. 1. The SERC Water Quality Monitoring Network showing the FKNMS boundary, segments, and distribution of sampling stations within the FKNMS, Florida Bay, Biscayne Bay, Whitewater Bay, Ten Thousand Islands, and Southwest Florida Shelf.

Fig. 2. Box-and-whisker plots of NO_3^-, NH_4^+, TP, SRP, $Si(OH)_4$, and Chl *a* stratified by FKNMS segment: 1 = Tortugas, 2 = Marquesas, 4 = Backcountry, 5 = Lower Keys, 6 = Sluiceway, 7 = Middle Keys, and 9 = Upper Keys.

Fig. 3. Box-and-whisker plots of TOC, TON, APA, DO_{sat}, salinity, and turbidity by FKNMS segment.

Fig. 4. Box-and-whisker plots of temperature, Kd, TN:TP, and DIN:SRP by FKNMS segment.

Fig. 5. Box-and-whisker plots of NO_3^-, NH_4^+, TP, $Si(OH)_4$ by FKNMS segment and location on transect from land. In the Tortugas segment AS = alongshore, CH = channel, and OS = offshore.

Fig. 6. Box-and-whisker plots of Chl *a*, TOC, turbidity, and salinity by FKNMS segment and location on transect from land.

Fig. 7. Box-and-whisker plots of NO_3^-, NH_4^+, TP, $Si(OH)_4$, Chl *a* , TOC, salinity, and turbidity for ocean-side Keys transects stratified as being located along Biscayne Bay National Park (BISC), against land in Key Largo, Middle and Lower Keys (LAND), or in line with major passes in the Keys (PASS).

Fig. 8. Contour map of median salinity generated from fixed stations (+) in South Florida coastal waters.

Fig. 9. Contour map of median delta sigma-t ($\Delta\sigma_t$ in kg m^{-3}) generated from fixed stations (+) in South Florida coastal waters reported as the median for 12 sampling events. $\Delta\sigma_t$ is the difference in density between surface and bottom waters where positive values mean bottom is more dense than surface.

Fig. 10. Contour map of median $Si(OH)_4$ (μM) generated from fixed stations (+) in South Florida coastal waters.

Fig. 11. Contour map of median NO_3^- (μM) generated from fixed stations (+) in South Florida coastal waters.

Fig. 12. Contour map of median TP (μM) generated from fixed stations (+) in South Florida coastal waters.

Fig. 13. Contour map of median SRP (μM) generated from fixed stations (+) in South Florida coastal waters.

Fig. 14. Contour map of median TOC (µM) generated from fixed stations (+) in South Florida coastal waters.

Fig. 15. Contour map of median Chl *a* ($\mu g\ l^{-1}$) generated from fixed stations (+) in South Florida coastal waters.

Fig. 16. Contour map of median turbidity (NTU) generated from fixed stations (+) in South Florida coastal waters.

Fig. 17. Contour map of median DIN:SRP ratio generated from fixed stations (+) in South Florida coastal waters.

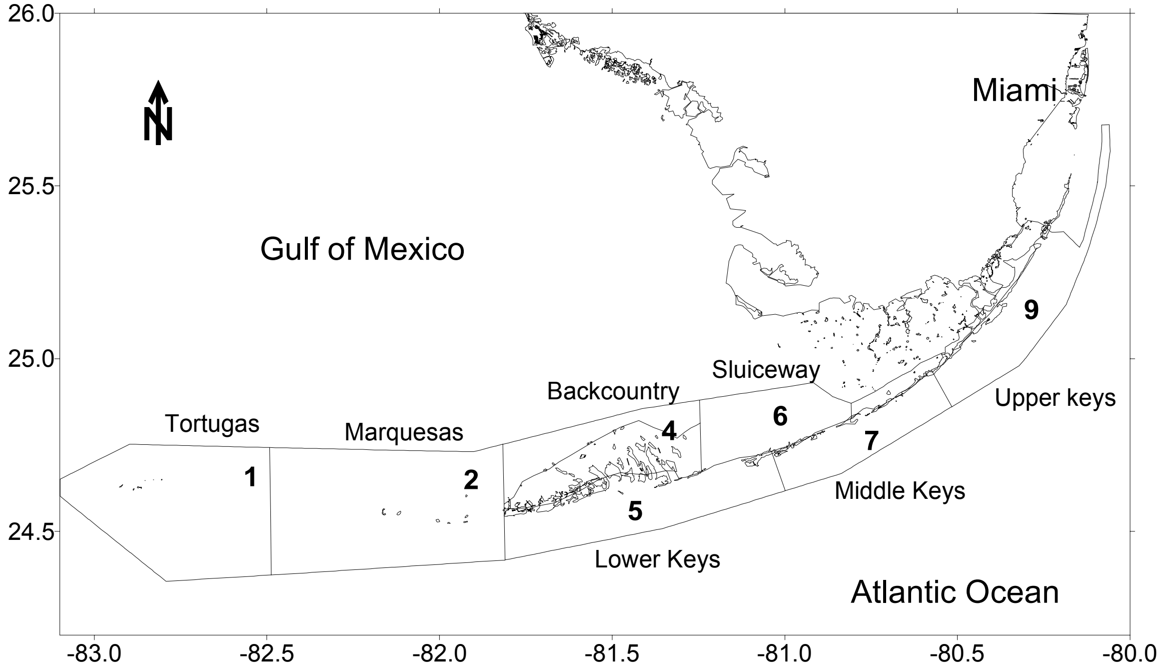

26.0
25.5
25.0
24.5
-83.0
-82.5
-82.0
-81.5
-81.0
-80.5
-80.0
N
Miami
Gulf of Mexico
Sluiceway
Backcountry
Tortugas
Marquesas
Upper keys
Middle Keys
Lower Keys
Atlantic Ocean
1
2
4
5
6
7
9

Figure 1.

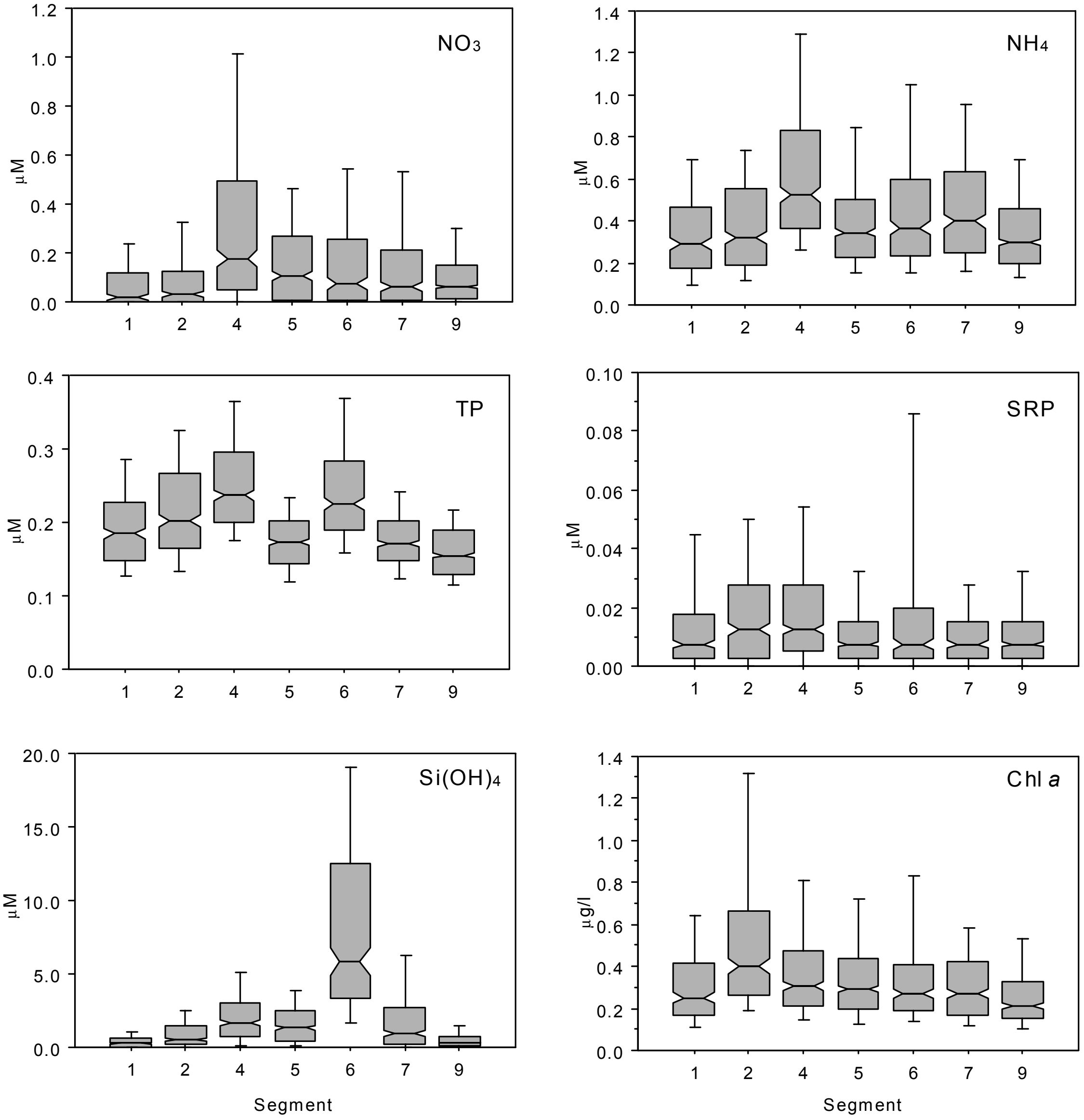

NO3
μM
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1
2
4
5
6
7
9
NH4
μM
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1
2
4
5
6
7
9
TP
μM
0.4
0.3
0.2
0.1
0.0
1
2
4
5
6
7
9
SRP
μM
0.10
0.08
0.06
0.04
0.02
0.00
1
2
4
5
6
7
9
Si(OH)4
μM
20.0
15.0
10.0
5.0
0.0
1
2
4
5
6
7
9
Segment
Chl a
μg/l
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1
2
4
5
6
7
9
Segment

Figure 2.

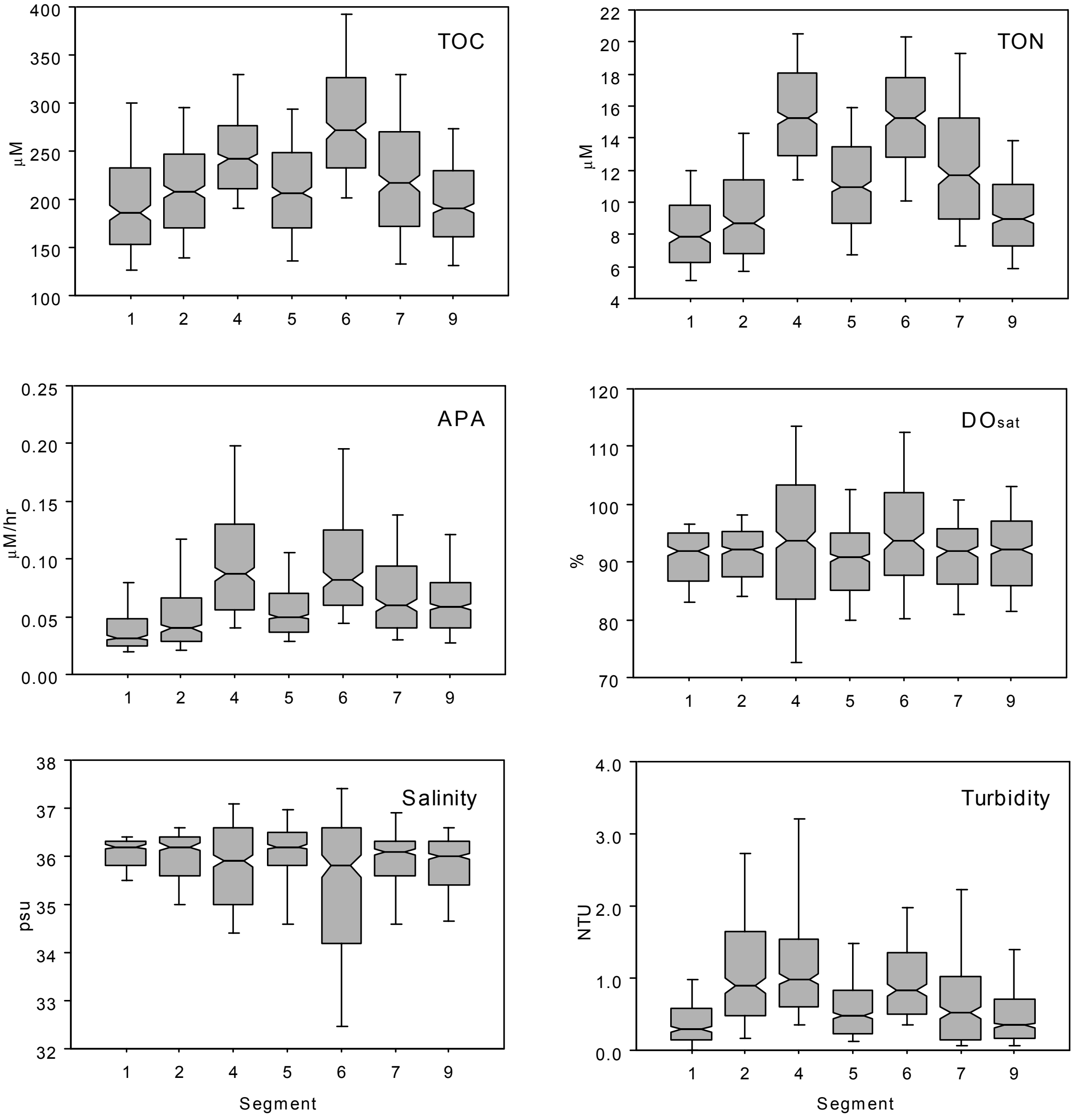

TOC
μM
400
350
300
250
200
150
100
TON
μM
22
20
18
16
14
12
10
8
6
4
APA
μM/hr
0.25
0.20
0.15
0.10
0.05
0.00
DO$_{sat}$
%
120
110
100
90
80
70
Salinity
psu
38
37
36
35
34
33
32
Turbidity
NTU
4.0
3.0
2.0
1.0
0.0
1
2
4
5
6
7
9
Segment
Segment

Figure 3.

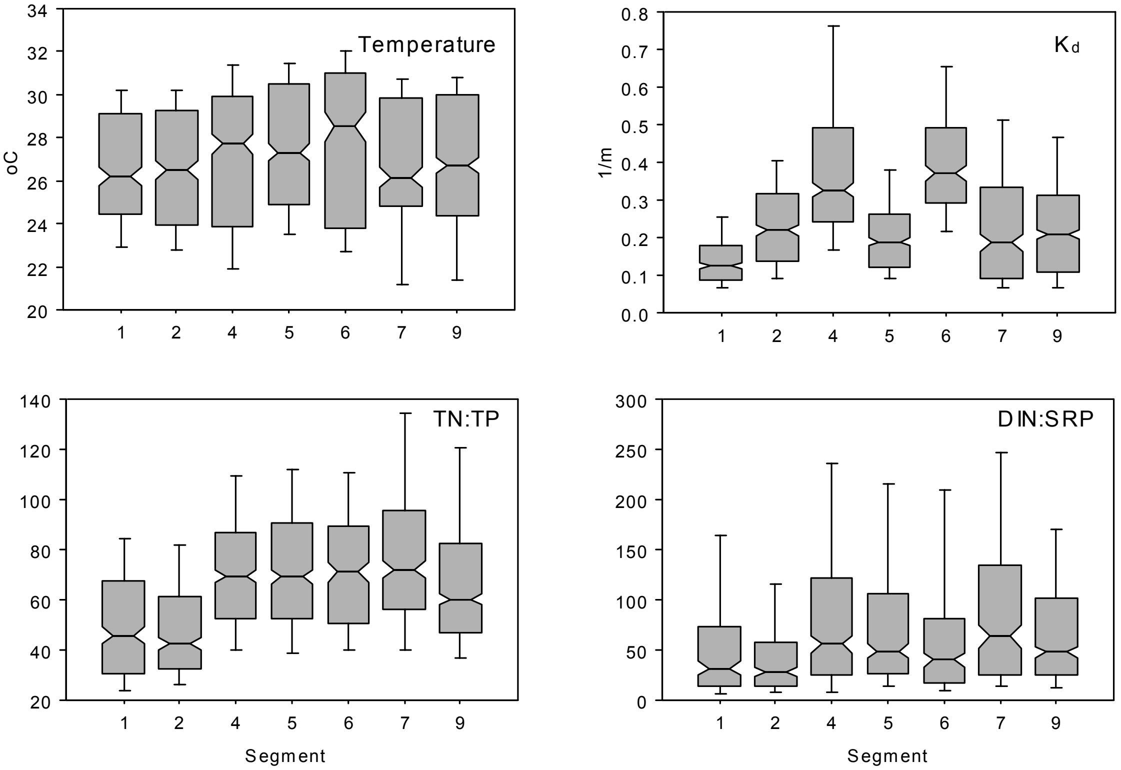

Temperature
oC
34
32
30
28
26
24
22
20
1
2
4
5
6
7
9
Kd
1/m
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
TN:TP
140
120
100
80
60
40
20
DIN:SRP
300
250
200
150
100
50
0
Segment
Segment

Figure 4.

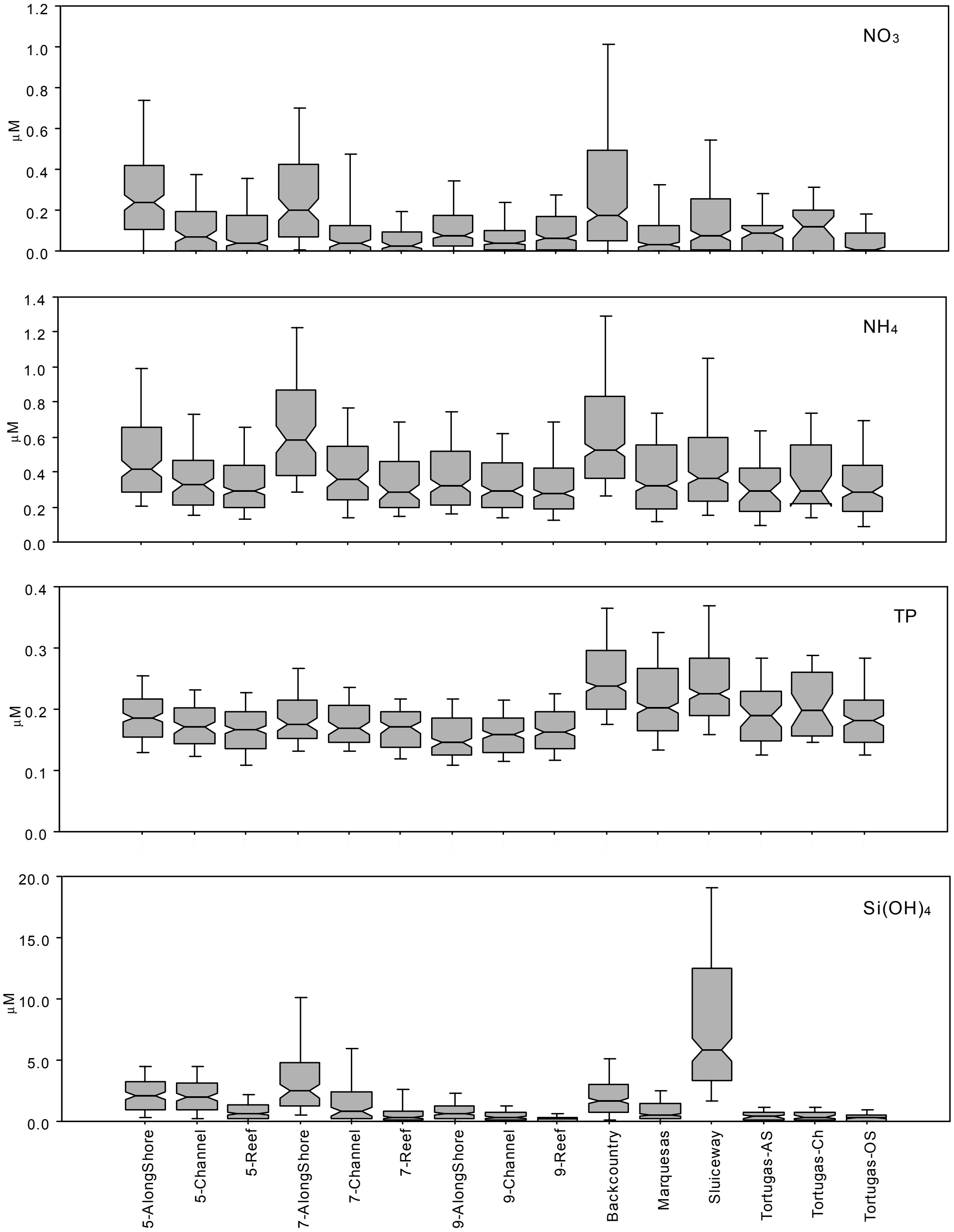
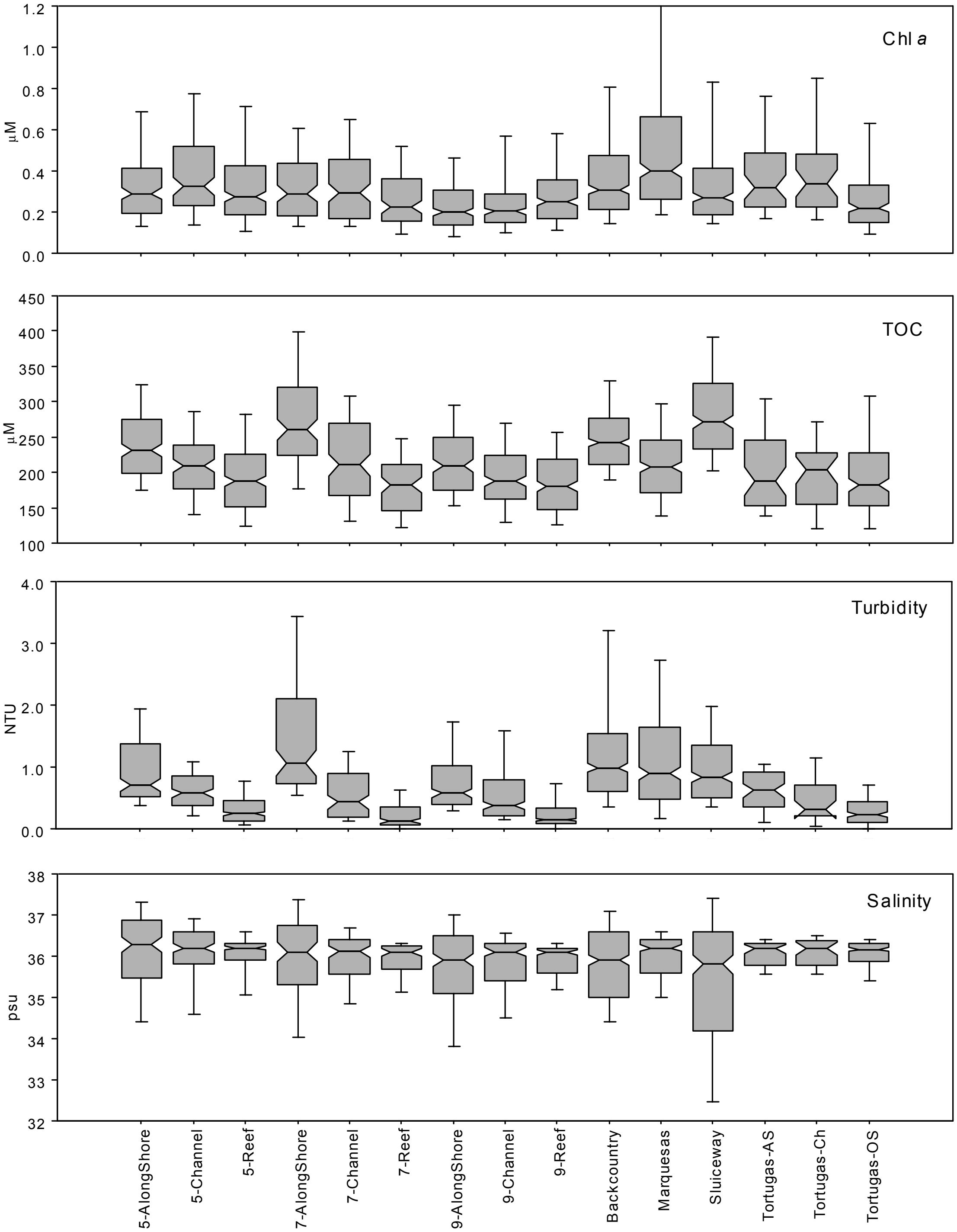

NO₃
NH₄
TP
Si(OH)₄
µM
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.1
0.3
5.0
10.0
15.0
20.0
5-AlongShore
5-Channel
5-Reef
7-AlongShore
7-Channel
7-Reef
9-AlongShore
9-Channel
9-Reef
Backcountry
Marquesas
Sluiceway
Tortugas-AS
Tortugas-Ch
Tortugas-OS

Figure 5.



Chl *a*
μM
1.2
1.0
0.8
0.6
0.4
0.2
0.0
TOC
μM
450
400
350
300
250
200
150
100
Turbidity
NTU
4.0
3.0
2.0
1.0
0.0
Salinity
psu
38
37
36
35
34
33
32
5-AlongShore
5-Channel
5-Reef
7-AlongShore
7-Channel
7-Reef
9-AlongShore
9-Channel
9-Reef
Backcountry
Marquesas
Sluiceway
Tortugas-AS
Tortugas-Ch
Tortugas-OS

Figure 6.

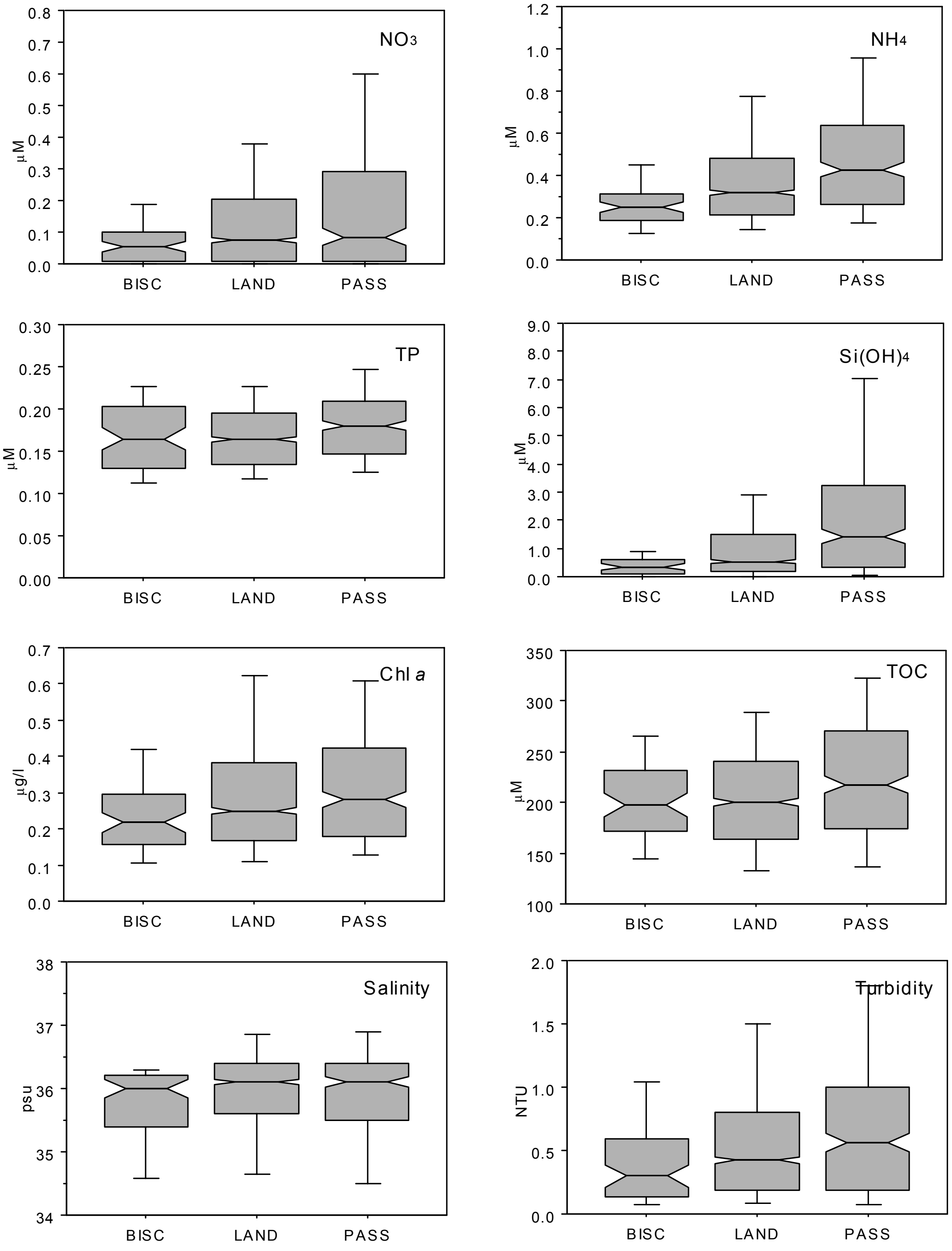

NO3
µM
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
NH4
µM
0.0
0.2
0.4
0.6
0.8
1.0
1.2
TP
µM
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Si(OH)4
µM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
Chl a
µg/l
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
TOC
µM
100
150
200
250
300
350
Salinity
psu
34
35
36
37
38
Turbidity
NTU
0.0
0.5
1.0
1.5
2.0
BISC
LAND
PASS

Figure 7.

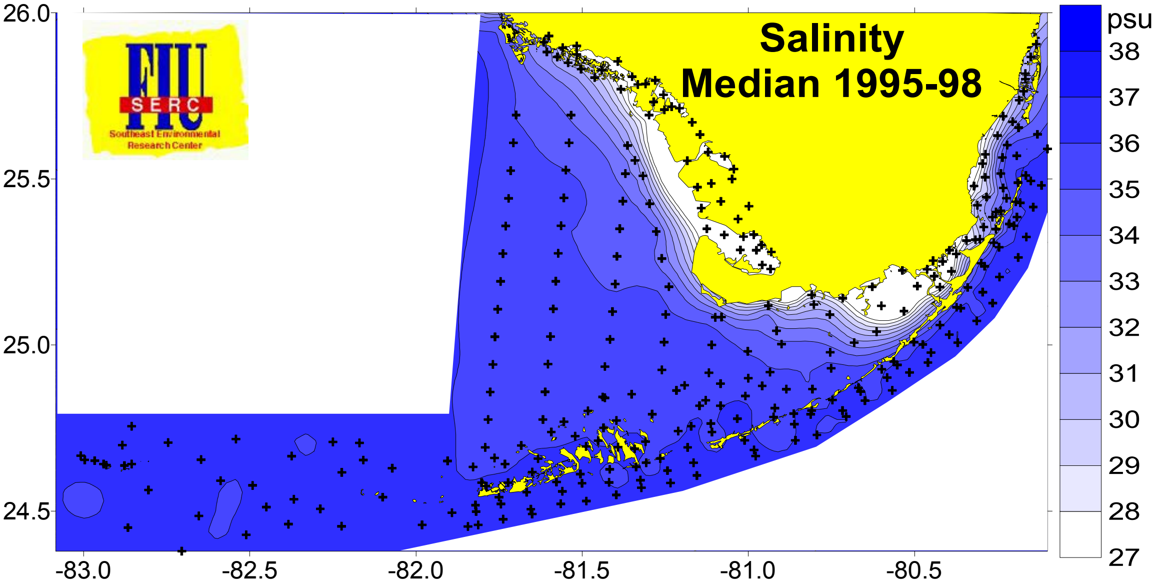


Figure 8.

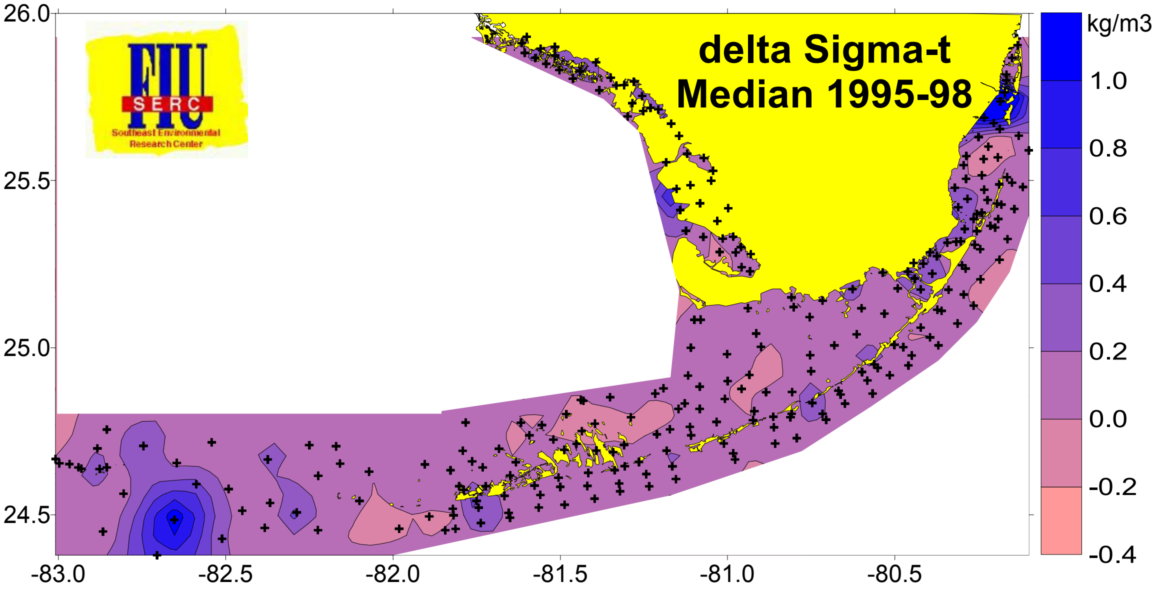


Figure 9.

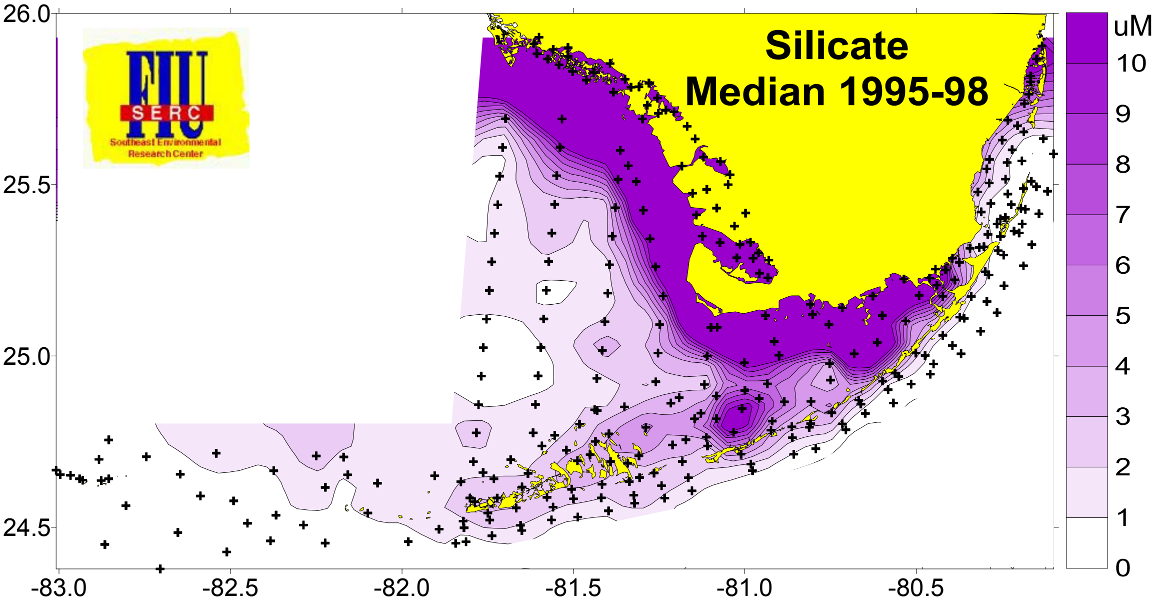


Figure 10.

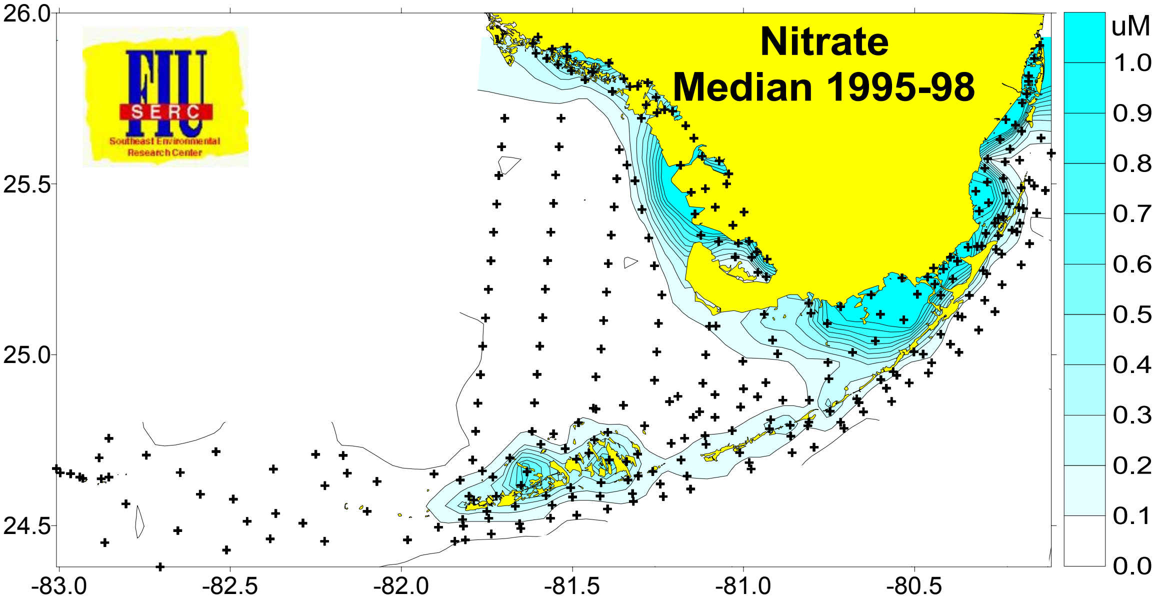


Figure 11.

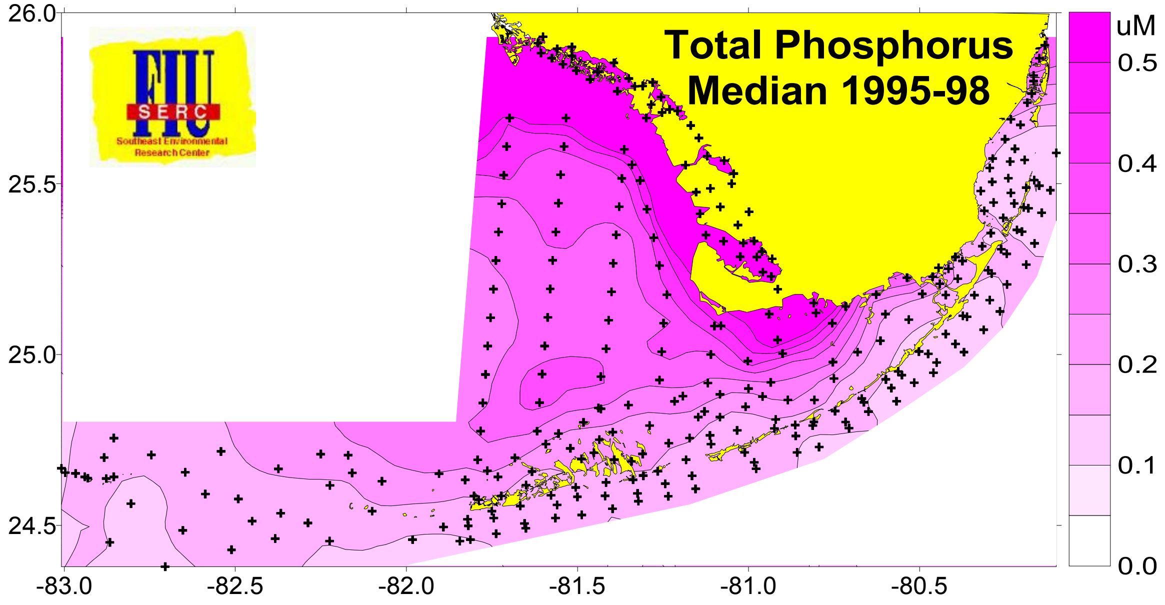


Figure 12.

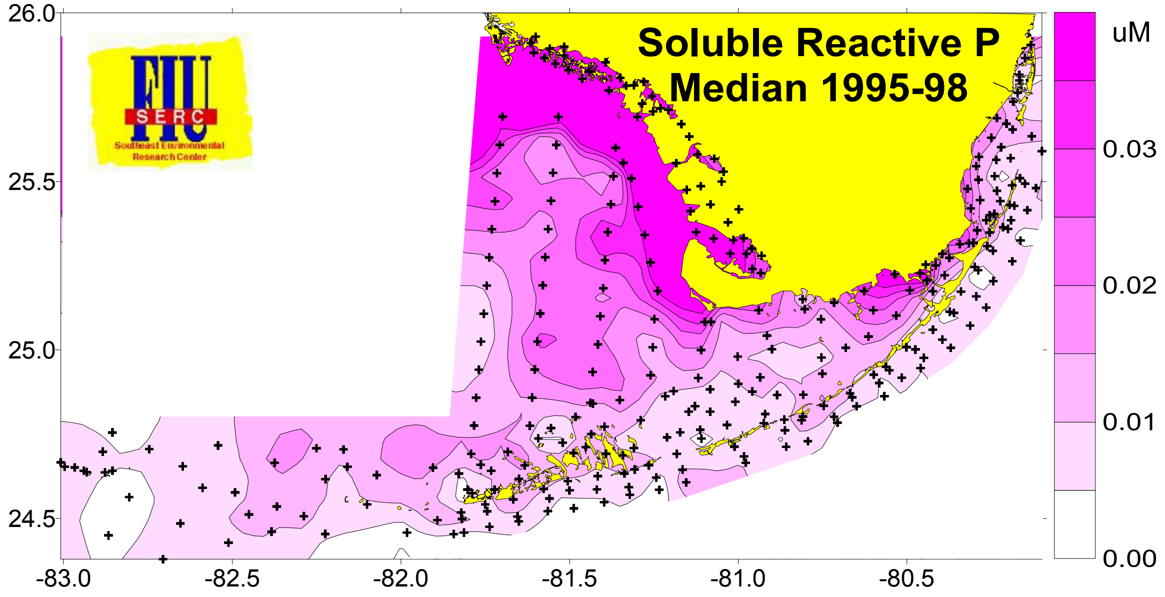


Figure 13.

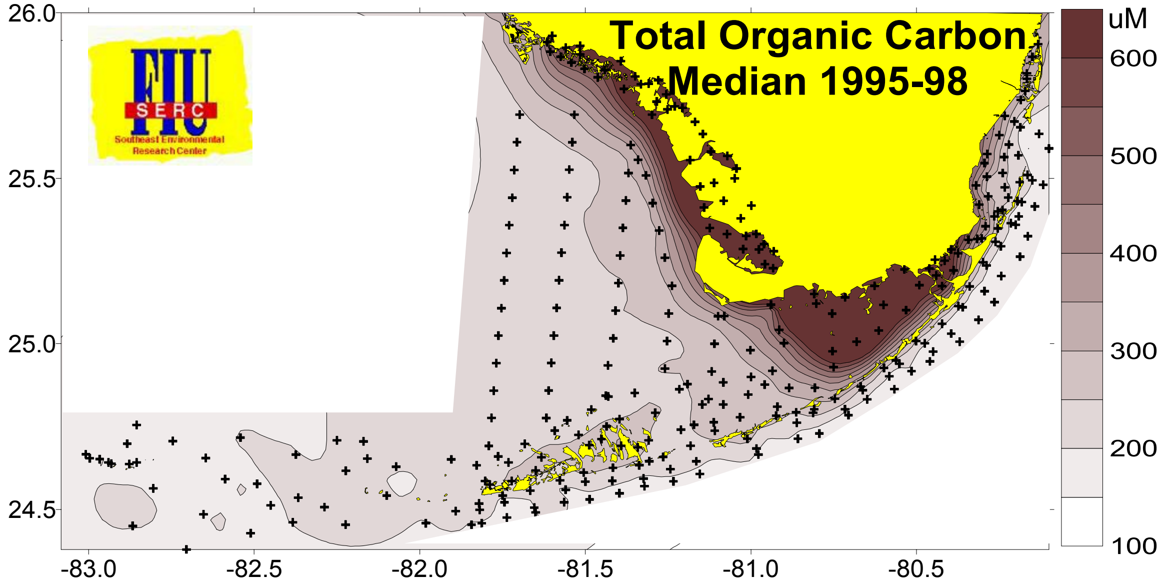


Figure 14.

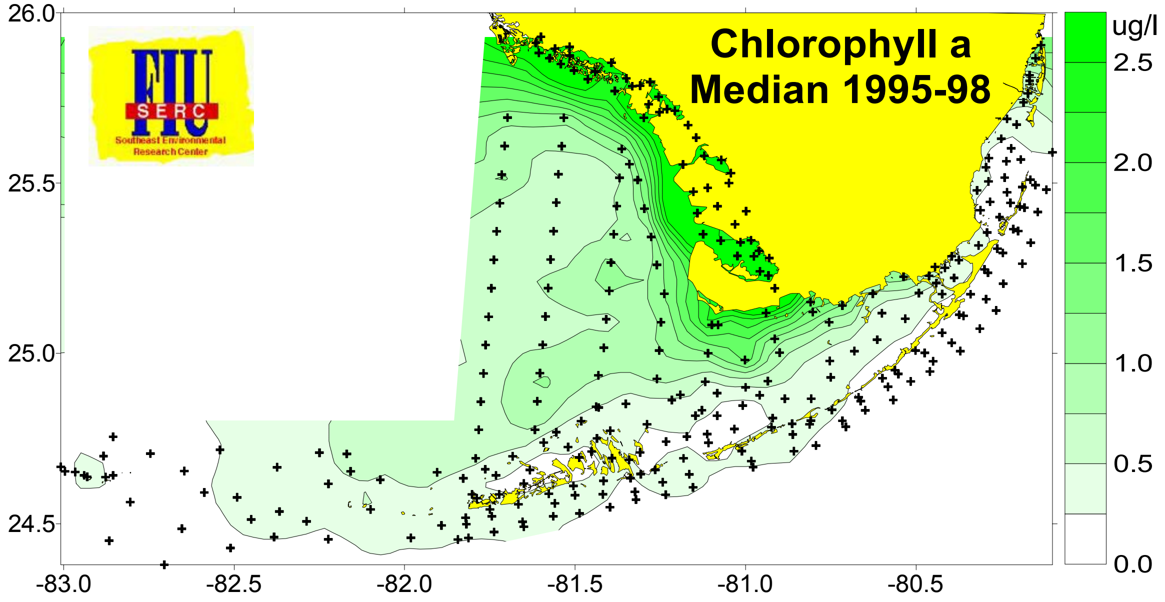


Figure 15.

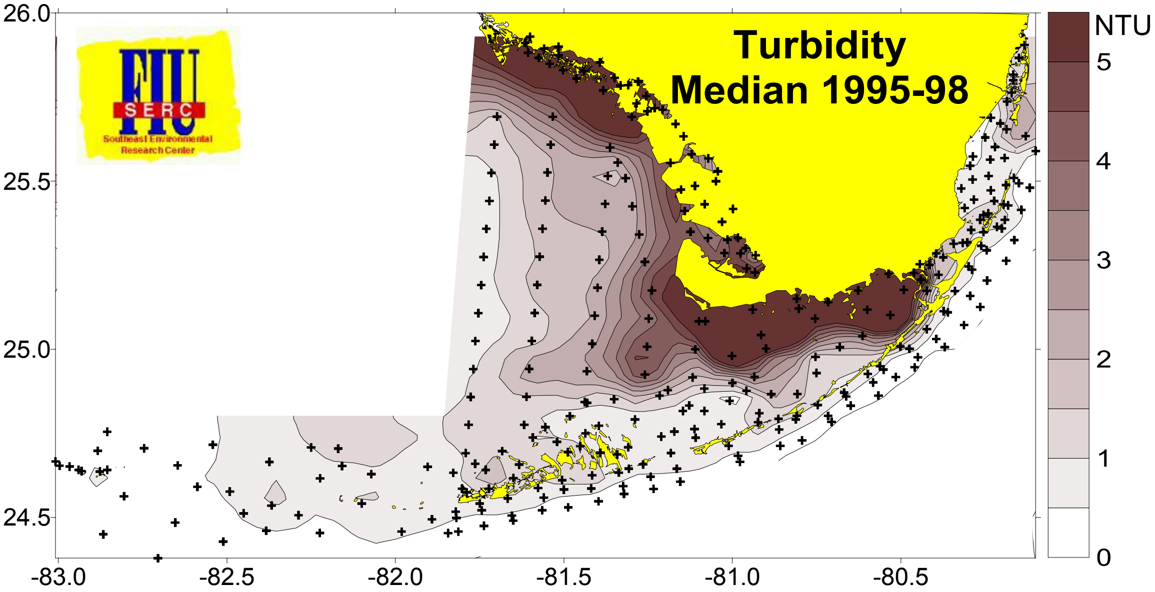


Figure 16.

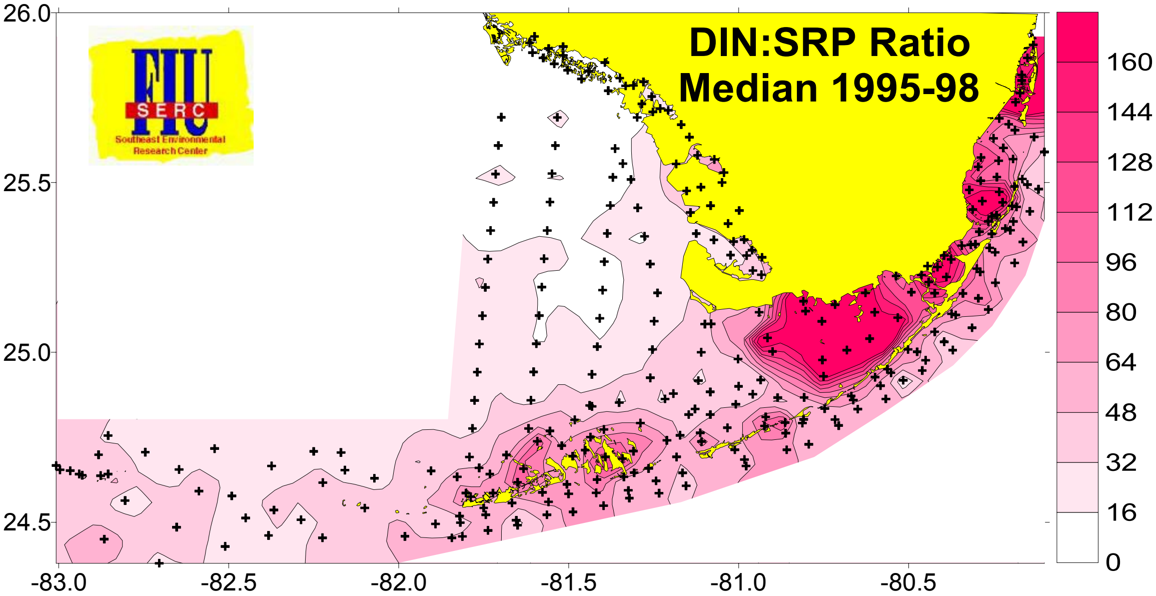


Figure 17.