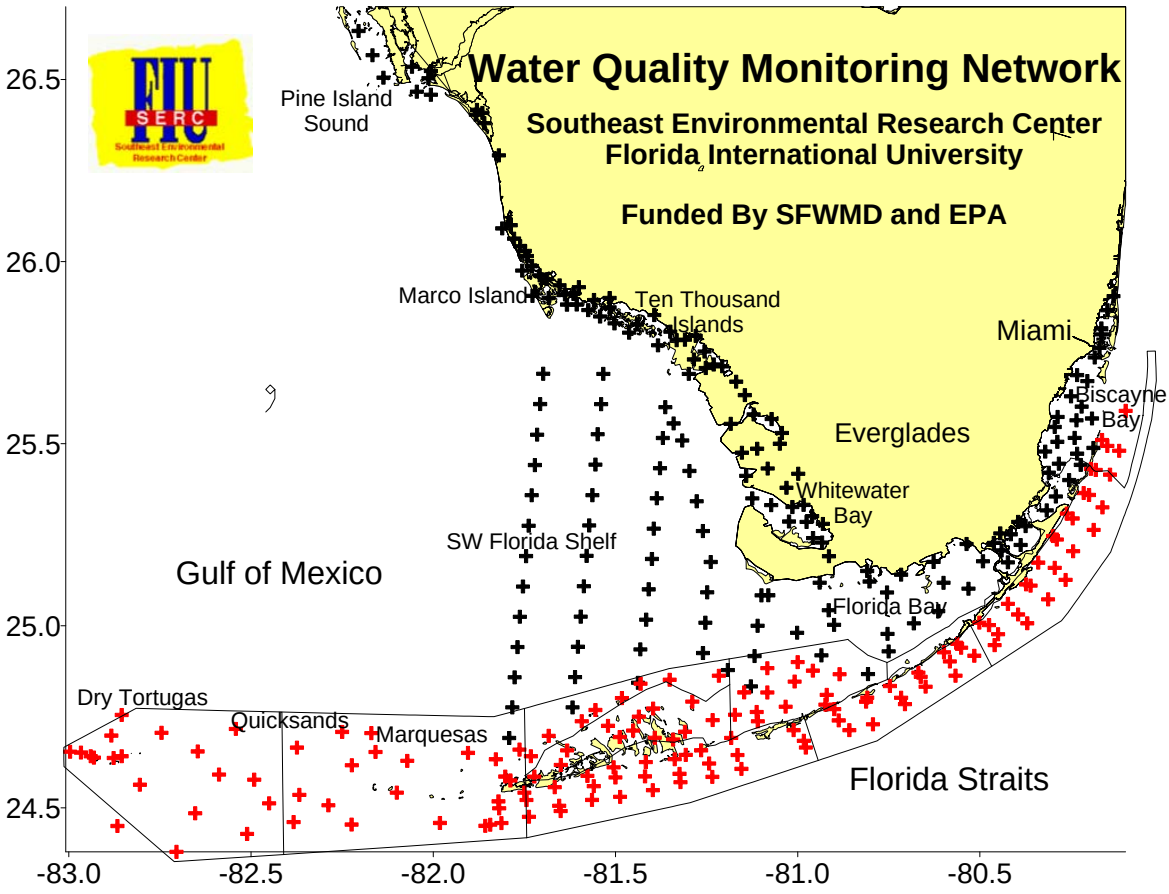
2007 ANNUAL REPORT OF THE WATER QUALITY MONITORING PROJECT

FOR THE WATER QUALITY PROTECTION PROGRAM

OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY



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EXECUTIVE SUMMARY

This report serves as a summary of our efforts to date in the execution of the Water Quality Monitoring Project for the FKNMS as part of the Water Quality Protection Program. The period of record for this report is Mar. 1995 – Dec. 2007 and includes data from 50 quarterly sampling events at 154 stations within the FKNMS including the Dry Tortugas National Park.

Field parameters measured at each station include salinity (practical salinity scale), temperature (ºC), dissolved oxygen (DO, mg l^{-1}), turbidity (NTU), relative fluorescence, and light attenuation (K_d, m^{-1}). Water quality variables include the dissolved nutrients nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), dissolved inorganic nitrogen (DIN), and soluble reactive phosphate (SRP). Total unfiltered concentrations of nitrogen (TN), organic nitrogen (TON), organic carbon (TOC), phosphorus (TP), silicate (SiO_2) and chlorophyll *a* (CHLA, μg l^{-1}).

The EPA developed Strategic Targets for the Water Quality Monitoring Project which state that through 2011, beginning in 2008, annually maintain the overall water quality of the near shore and coastal waters of the FKNMS according to 2005 baseline. For reef sites, chlorophyll *a* should be less than or equal to 0.2 micrograms/l and the vertical attenuation coefficient for downward irradiance (Kd, i.e., light attenuation) should be less than or equal to 0.13 per meter. For all monitoring sites in FKNMS, dissolved inorganic nitrogen should be less than or equal to 0.75 micromolar and total phosphorus should be less than or equal to 0.2 micromolar. Table 1 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2007.

Table 1. 2007 Comparison to Strategic Targets.

49 of 136 reef values	>0.2 ug/l CHLA	(36.0%)
25 of 136 reef values	>0.13/m Kd	(18.4%)
348 of 620 total values	>0.75 uM NH_4^+	(56.1%)
362 of 620 total values	>0.20 uM TP	(58.4%)

Several important results have been realized from this monitoring project. First, is documentation of elevated nitrate in the inshore waters of the Keys (Fig. 1). This result was evident from out first sampling event in 1995 and continues to be a characteristic of the ecosystem. Interestingly, this gradient was not observed in a comparison transect from the Tortugas (no human impact). This type of distribution implies an inshore source which is diluted by low nutrient Atlantic Ocean waters. Presence of a similar gradient in TOC and decreased variability in salinity from land to reef also support this concept. There were no trends in either TP or CHLA with distance from land.

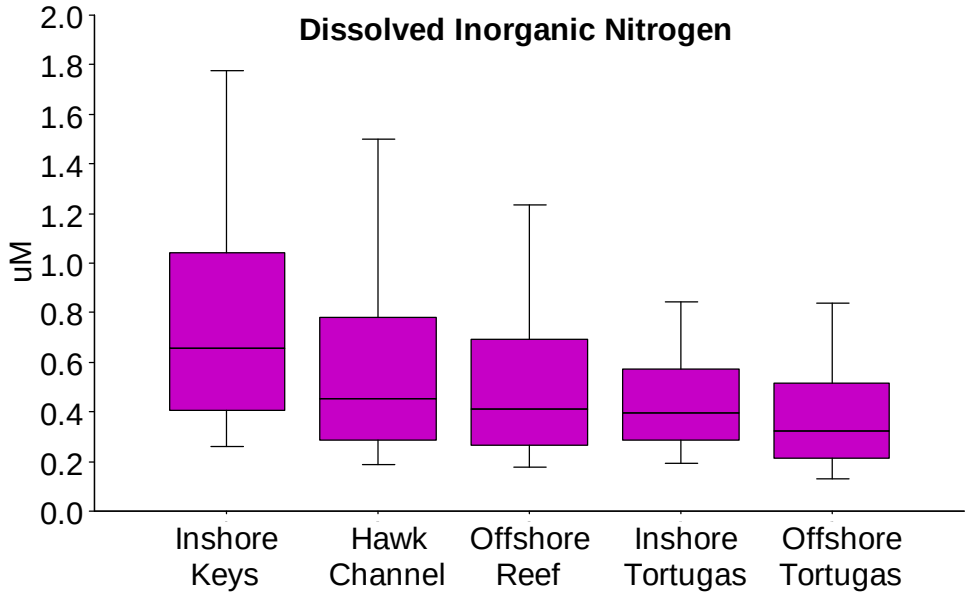

Figure 1.

Some variables showed noteworthy differences over the period of record (Fig2). Since the 2005 hurricane season, DIN, especially NH_4^+ has been elevated throughout the region.

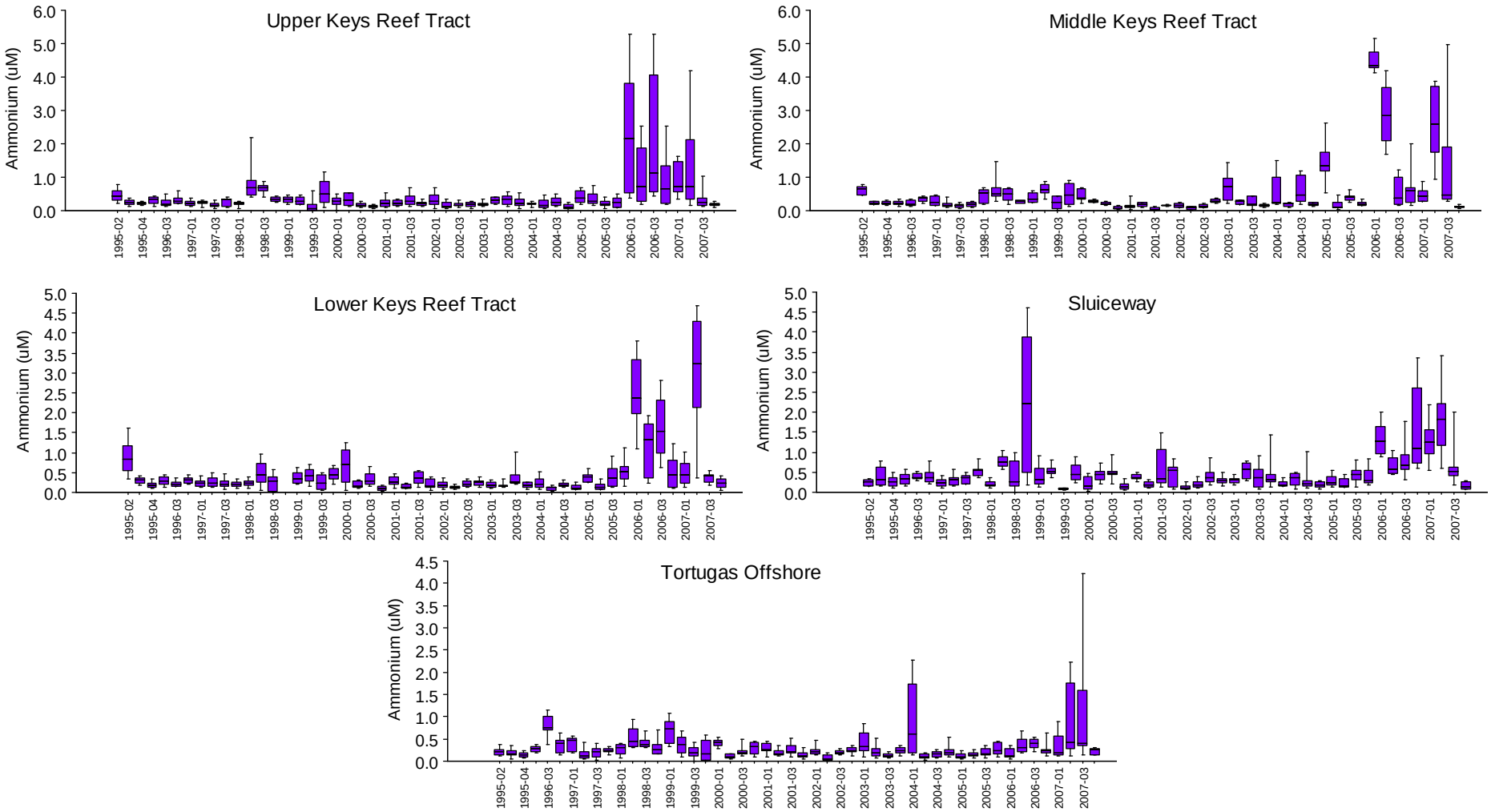
Upper Keys Reef Tract
Middle Keys Reef Tract
Lower Keys Reef Tract
Sluiceway
Tortugas Offshore
Ammonium (uM)

Figure 2.

This brings up another important point; when looking at what are perceived to be local trends, we find that they seem to occur across the whole region but at more damped amplitudes. This spatial autocorrelation in water quality is an inherent property of highly interconnected systems such as coastal and estuarine ecosystems driven by similar hydrological and climatological forcings. It is clear that trends observed inside the FKNMS are influenced by regional conditions outside the Sanctuary boundaries.

In all regions of the FKNMS, DIN (mostly as NH_4^+) was elevated relative to the long term median, while DO and turbidity were lower (Fig. 3). The changes were small but significant. Overall, TOC and TON were lower than the long term median mostly because they have been declining over the years. TP, CHLA, salinity, and temperature showed little variation from the overall median.

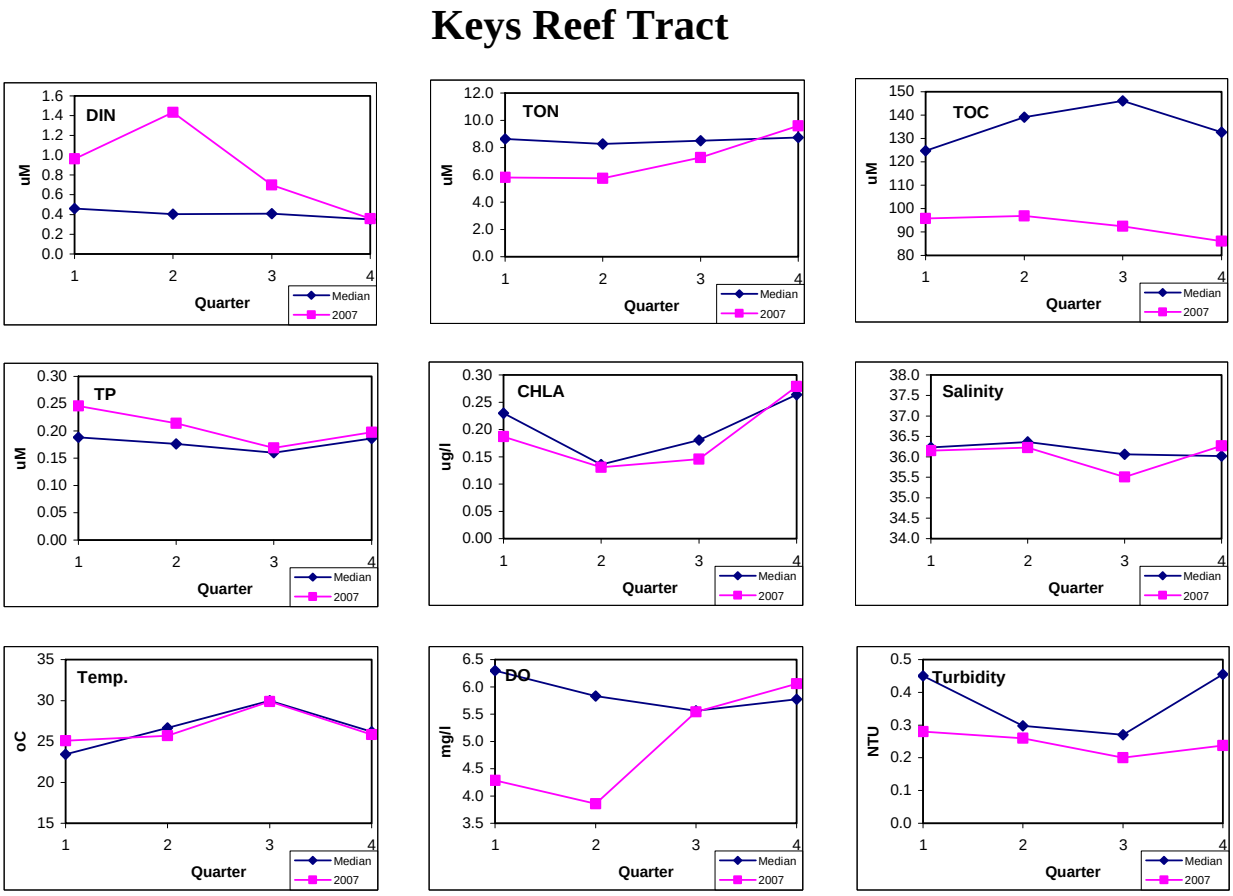

Figure 3.

We believe that the FKNMS experienced very different water masses than seen in previous years leading to anomalous water quality conditions. This year, deviations from long term conditions occurred both on the oceanside and gulfside of the Keys. We believe that these differences were due to a change in waters of SW Shelf water moving through the passes. Gulf waters transported south by the Loop Current west of the Tortugas could have been entrained in the Florida Current. Better integration with physical circulation models of the Gulf of Mexico and South Atlantic Basin may provide some clues as to the source.

Finally, we would have expected that such large increases in DIN and TP should have caused increases in CHLA by stimulating phytoplankton growth and production. That we saw declines in CHLA is especially puzzling.

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.

We continue to maintain a website (http://serc.fiu.edu/wqmnetwork/) where data from the FKNMS is integrated with the other parts of the SERC water quality network (Florida Bay, Whitewater Bay, Biscayne Bay, Ten Thousand Islands, and SW Florida Shelf) and displayed as downloadable contour maps, time series graphs, and interpretive reports.

One note of importance is that the South Florida Water Management District cancelled all funding for monitoring of the SW Florida Shelf effective Oct.1, 2007. We thank the FKNMS Sanctuary Advisory Committee and EPA for their letter of support

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1. Project Background

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.

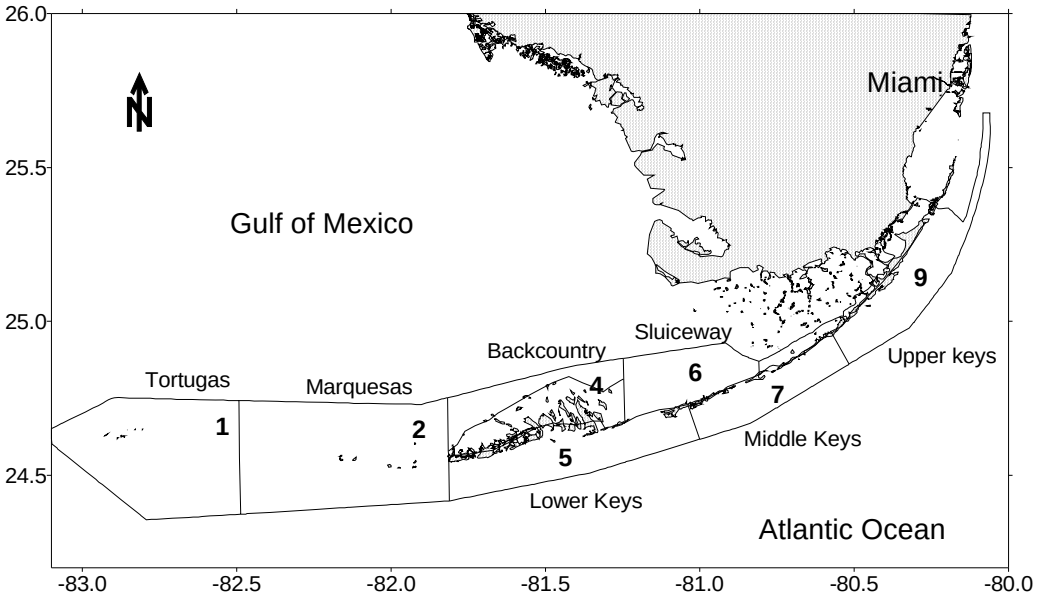

Figure 1. *Map of FKNMS boundary including Segment numbers and common names.*

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), discharge from the Everglades through the Shark River Slough, and by tidal exchange with both Florida Bay and Biscayne Bay (Lee et al. 1994, Lee et al. 2002). Advection from these external sources has

significant effects on the physical, chemical, and biological composition of waters within the FKNMS, as may internal nutrient loading and freshwater runoff from the Keys themselves (Boyer and Jones 2002). Water quality of the FKNMS may be directly affected both by external nutrient transport and internal nutrient loading sources. Therefore, the geographical extent of the FKNMS is one of political/regulatory definition and should not be thought of as an enclosed ecosystem.

A spatial framework for FKNMS water quality management was proposed on the basis of geographical variation of regional circulation patterns (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 Segment 5, 7, and 9 or within EMAP grid cells in Segment 1, 2, 4, and 6.

Segment 1 (Tortugas) includes the Dry Tortugas National Park (DTNP) and surrounding waters and is most influenced by the Loop Current and Dry Tortugas Gyre. Originally, there were no sampling sites located within the DTNP as it was outside the jurisdiction of NOAA. Upon request from the National Park Service, we initiated sampling at 5 sites within the DNTP boundary. 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 on the gulfside of the Lower Keys. Segments 2 and 4 are both influenced by water moving south along the SW Shelf. Segment 6 can be considered as part of western Florida Bay. This area is referred to as the Sluiceway as it strongly influenced by transport from Florida Bay, SW Shelf, and Shark River Slough (Smith, 1994). Segments 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).

We have found that water quality monitoring programs composed of many sampling stations situated across a diverse hydroscape are often difficult to interpret due to the “can’t see the forest for the trees” problem (Boyer et al. 2000). At each site, the many measured variables are

independently analyzed, individually graphed, and separately summarized in tables. This approach makes it difficult to see the larger, regional picture or to determine any associations among sites. In order to gain a better understanding of the spatial patterns of water quality of the FKNMS, we attempted to reduce the complicated data matrix into fewer elements which would provide robust estimates of condition and connection. To this end we developed an objective classification analysis procedure which grouped stations according to water quality similarity.

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 (Fig.2), 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.

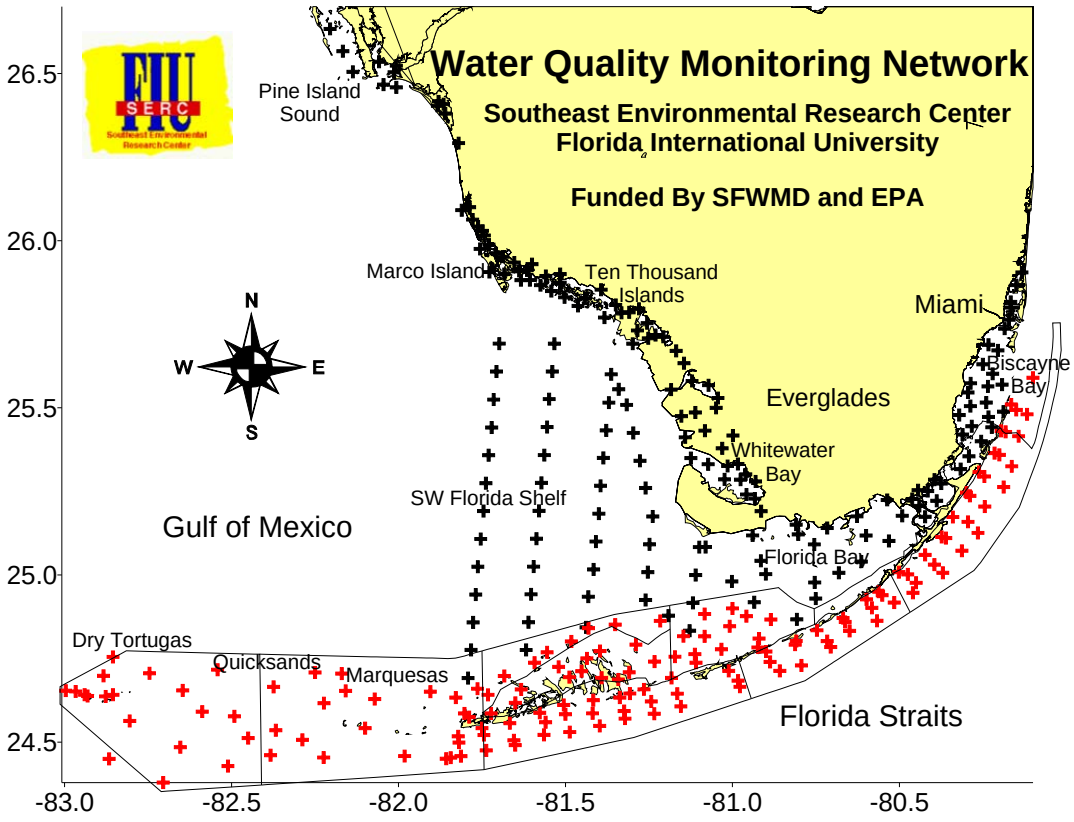

Figure 2. *The SERC Water Quality Monitoring Network showing the distribution of fixed sampling stations (+) within the FKNMS, Florida Bay, Biscayne Bay, Whitewater Bay, Ten Thousand Islands, and Southwest Florida Shelf.*

2. Methods

2.1.Field Sampling

The period of record of this study was from March 1995 to December 2007 which included 50 quarterly sampling events. For each event, field measurements and grab samples were collected from 154 fixed stations within the FKNMS boundary (Fig. 2). Depth profiles of temperature (°C), salinity (practical salinity scale), dissolved oxygen (DO, mg l^{-1}), photosynthetically active radiation (PAR, µE m^{-2} s^{-1}), *in situ* chlorophyll *a* specific fluorescence (FSU), optical backscatterance turbidity (OBS), depth as measured by pressure transducer (m), and density (σ_t, in 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 attenuation coefficient for downward irradiance (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. To determine the extent of stratification we calculated the difference between surface and bottom density as delta sigma-t ($\Delta\sigma_t$, in kg m^{-3}), where positive values denoted greater density of bottom water relative to the surface. A $\Delta\sigma_t$ >1 is considered weakly stratified, while any instances >2 is strongly stratified.

In the Backcountry area (Seg. 4, Fig. 1) where it is too shallow to use a CTD, surface salinity and temperature were measured using a combination salinity-conductivity-temperature-DO probe (YSI 650 MDS display-datalogger with YSI 600XL sonde). DO was automatically corrected for salinity and temperature. PAR was measured using a Li-Cor LI-1400 DataLogger 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 approximately 0.25 m below the surface and at approximately 1 m from the bottom with a teflon-lined Niskin bottle (General Oceanics) except in the Backcountry and Sluiceway where surface water was collected directly into sample bottles. Duplicate, unfiltered water samples were dispensed into 3x sample rinsed 120 ml HDPE bottles for analysis

of total constituents. Duplicate water samples for dissolved nutrients were dispensed into 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 resulting wet filters, used for chlorophyll *a* (CHLA) 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).

All samples were kept on ice in the dark during transport to the laboratory. During shipboard collection in the Tortugas/Marquesas and overnight stays in the lower Keys, filtrates and filters were frozen until further analysis.

2.2. Laboratory Analysis

Unfiltered water samples were analyzed for total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), silicate (SiO_2), and turbidity. 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). SiO_2 was measured using the molybdosilicate method (Strickland and Parsons 1972). Turbidity was measured using an HF Scientific model DRT-15C turbidimeter and reported in NTU.

Filtrates were analyzed for nitrate+nitrite (NO_x^-), nitrite (NO_2^-), ammonium (NH_4^+), and soluble reactive phosphorus (SRP) by flow injection analysis (Alpkem model RFA 300). Filters for CHLA 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 QA/QC 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. DO saturation in the water column (DO_{sat} as %) was calculated using the equations of Garcia and Gordon (1992).

2.3. Objective Classification Analysis

Stations were stratified according to water quality characteristics (i.e. physical, chemical, and biological variables) using a statistical approach. Multivariate statistical techniques have been shown to be useful in reducing a large data sets into a smaller set of independent, synthetic variables that capture much of the original variance. The method we chose was a type of objective classification analysis (OCA) which uses principal component analysis (PCA) followed by k-means clustering algorithm to classify sites as to their overall water quality. This approach has been very useful in understanding the factors influencing nutrient biogeochemistry in Florida Bay (Boyer et al., 1997), Biscayne Bay, and the Ten Thousand Islands (Boyer 2006). We have found that water quality at a specific site is the result of the interaction of a variety of driving forces including oceanic and freshwater inputs/outputs, sinks, and internal cycling.

Briefly, data were first standardized as Z-scores prior to analysis to reduce artifacts of differences in magnitude among variables. PCA was used to extract statistically significant composite variables (principal components) from the original data (Overland and Preisendorfer 1982). The PCA solution was rotated (using VARIMAX) in order to facilitate the interpretation of the principal components and the factor scores were saved for each data record. Both the mean and SD of the factor scores for each station over the entire period of record were then used as independent variables in a cluster analysis (k-means algorithm) in order to aggregate stations into groups of similar water quality. The purpose of this analysis was to collapse the 154 stations into a few groups which could then be analyzed in more detail.

2.4. Box and Whisker Plots

Typically, water quality data are skewed to the left (low concentrations and below detects) resulting in non-normal distributions. Therefore it is more appropriate to use the median as the measure of central tendency because the mean is inflated by high outliers (Christian et al. 1991). Data distributions of 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 a *t*-test) and among groups by the Kruskall-Wallace test (ANOVA) with significance set at $P<0.05$.

2.5. Contour Maps

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, SW Shelf, and Marco Island – Ft. Meyers (see example in Fig. 10 and http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm for all other maps). Data from these 153 additional stations were collected during the same month as the FKNMS surveys and analyzed by the SERC laboratory using identical methods. Contour maps were produced using Surfer (Golden Software). The most important aspect of generating contour maps is the geostatistical algorithm used for interpolating the data values. Care should be taken in the selection of the algorithm because automated interpolation to a regular rectangular grid can produce artifacts, especially around the edges and when the area of interest is irregularly shaped. The kriging algorithm was used because it is designed to minimize the error variance while at the same time maintaining point pattern continuity (Isaaks & Srivastava, 1989). Kriging is a global approach which uses standard geostatistics to determine the "distance" of influence around each point and the "clustering" of similar samples sites

(autocorrelation). Therefore, unlike the inverse distance procedure, kriging will not produce valleys in the contour between neighboring points of similar value.

2.6. Time Series Analysis

Individual site data for the complete period of record were plotted as time series graphs (see http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm) to illustrate any temporal trends that might have occurred. Temporal trends were quantified by simple regression with significance set at $P<0.05$.

3. Results

3.1. Overall Water Quality of the FKNMS

Summary statistics for all water quality variables from all 50 sampling events are shown as median, minimum, maximum, and number of samples (Table 1). Overall, the region was warm and euhaline with a median temperature of 27.0°C and salinity of 36.2; oxygen saturation of the water column (DO_{sat}) was relatively high at 87.8%. On this coarse scale, the FKNMS exhibited very good water quality with median NO_3^-, NH_4^+, and TP concentrations of 0.095, 0.305, and 0.195 μM, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (~70 %). However, DIN comprised a small fraction (4 %) of the TN pool with TON making up the bulk (median 10.8 μM). SRP concentrations were very low (median 0.022 μM) and comprised only 6 % of the TP pool. CHLA concentrations were also very low overall, 0.223 μg l^{-1}, but ranged from 0.01 to 15.2 μg l^{-1}. TOC was 173.8; a value higher than open ocean levels but consistent with coastal areas.

Median turbidity was low (0.69 NTU) as reflected in a low K_d (0.191 m^{-1}). This resulted in a median photic depth (to 1 % incident PAR) of ~22 m. Overall, 30% of incident light (I_o) reached the bottom. Molar ratios of N to P suggested a general P limitation of the water column (median TN:TP = 57.9) but this must be tempered by the fact that much of the TN is not bioavailable.

Table 1. *Summary statistics for each water quality variable in the FKNMS for the period of record. Data are summarized as median (Median), minimum value (Min.), maximum value (Max.), and number of samples (n).*

Variable	Depth	Median	Min.	Max.	*n*
NO_3^-	Surface	0.18	0.00	2.19	618
(μM)	Bottom	0.12	0.00	1.84	375
NO_2^-	Surface	0.04	0.00	0.33	618
(μM)	Bottom	0.03	0.00	0.19	375
NH_4^+	Surface	0.49	0.03	7.57	618
(μM)	Bottom	0.30	0.01	3.34	375
TN	Surface	10.25	3.90	49.42	617
(μM)	Bottom	8.65	3.17	96.98	373
TON	Surface	8.83	0.00	49.11	618
(μM)	Bottom	7.90	1.92	96.60	370
TP	Surface	0.22	0.10	1.47	607
(μM)	Bottom	0.20	0.09	0.59	365
SRP	Surface	0.03	-0.01	0.78	618
(μM)	Bottom	0.03	-0.03	0.68	375
CHLA ($\mu g\ l^{-1}$)	Surface	0.19	0.00	9.18	614
TOC	Surface	111.33	0.00	1310.8	608
(μM)	Bottom	96.57	53.29	1018.3	374
$Si(OH)_4$	Surface	0.49	0.00	226.39	617
(μM)	Bottom	0.30	0.01	29.87	374
Turbidity	Surface	0.51	0.00	10.73	590
(NTU)	Bottom	0.37	0.01	5.78	356
Salinity	Surface	36.25	23.49	47.3	603
	Bottom	36.37	33.68	38.9	601
Temperature	Surface	26.96	18.87	33.2	603
(^oC)	Bottom	26.75	18.80	33.0	602
DO	Surface	5.26	2.07	9.5	601
($mg\ l^{-1}$)	Bottom	4.88	2.97	8.0	603
K_d		0.12	0.00	2.320	448
TN:TP	Surface	44.22	9.08	175.0	606
DO Saturation	Surface	80.05	0.00	134.7	602
(%)	Bottom	73.34	0.00	119.3	602
I_o (%)		40.72	0.00	100.00	383
$\Delta\sigma_t$		0.03	-8.37	23.1	595
Si:DIN	Surface	0.67	0.00	681.11	618

3.2. Objective Classification Analysis

PCA identified five composite variables (hereafter called PC1, PC2, etc.) that passed the rule N for significance at $P<0.05$ (Overland and Preisendorfer 1982) indicating five separate modes of variation in the data (Table 2). These five principal components accounted for 56.8 % of the total variance of the original variables. PC1 had high factor loadings for NO_3^-, NO_2^-, NH_4^+, and SRP and was named the "Inorganic Nutrient" component. PC2 included TP, CHLA, and turbidity and was designated as the "Phytoplankton" component. The covariance of TP with CHLA implies that, in many areas, phytoplankton biomass may be limited by phosphorus availability. This is contrary to much of the literature on the subject which usually ascribes nitrogen as being the limiting factor for phytoplankton production in coastal oceans. TOC and SiO_2 were included in PC3 as the "Terrestrial Organic" component. Interestingly, this implies that much of the silicate in the system is delivered from terrestrial, or at least Gulf of Mexico, sources. Temperature and DO were inversely related in PC4. Finally, PC5 included salinity and TON, implying a source of TON from marine waters. In past analyses, TON has been a member of the Terrestrial PC3. We are unsure as to the reason for its change in association.

Table 2. *Results of principal component analysis are shown as factor loadings (correlations between the raw variables and the principal components) for the first four principal components after VARIMAX rotation. For clarity, loadings with a magnitude >0.450 are shown in boldface type.*

Variable	PC1	PC2	PC3	PC4	PC5
NO_3^-	**0.670**	0.054	-0.030	0.078	-0.182
NO_2^-	**0.774**	-0.008	0.051	-0.068	0.179
NH_4^+	**0.769**	-0.039	0.067	-0.001	0.021
TON	0.099	0.072	0.162	-0.183	**0.568**
TP	0.043	**0.578**	-0.097	-0.041	0.101
SRP	0.289	0.169	-0.283	0.087	-0.363
CHLA	-0.109	**0.682**	0.071	-0.013	-0.281
TOC	0.103	0.117	**0.704**	-0.002	0.043
Silicate	0.001	-0.050	**0.754**	0.028	-0.006
Turbidity	0.102	**0.622**	0.001	-0.242	0.036
Salinity	-0.054	0.038	-0.221	0.238	**0.730**
Temp.	-0.035	-0.045	0.161	**0.790**	0.084
DO	-0.106	0.001	0.121	**-0.752**	0.132
%Variance Explained	17.4	13.7	9.9	8.8	7.0

Spatial distributions of the mean factor score for each station indicated how the average water quality varied over the study area. The "Inorganic Nutrient" component had two peaks: in the Backcountry and bayside of the Middle Keys. The "Phytoplankton" component described a N to S gradient in the Backcountry and Sluiceway which extended west across the northern Marquesas. The "Terrestrial Organic" component was highest in eastern Sluiceway extending into the Backcountry and was also distributed as a gradient away from land on the Atlantic side of the Keys. Temperature and DO showed a distribution heavily loaded in the oceanside. Finally the salinity/TP component showed lower loadings in the alongshore Upper Keys and bayside Sluiceway extending through most Atlantic sites of the Middle and Lower Keys.

The k-means clustering algorithm used the mean and SD of the four factor scores of each station to classify all 150 sampling sites into 8 groups having robust correspondence in water

quality (Fig. 3). The bulk of the stations fell into 6 large clusters (1, 3, 5, 6, 7, and 8) which described a gradient of water quality throughout the FKNMS. Although the differences among them were very subtle, they were statistically significant and allowed us to say that the overall nutrient gradient, from highest to lowest concentrations, was cluster 7, 8>1>5>6>3 (Table 3 in Appendix).

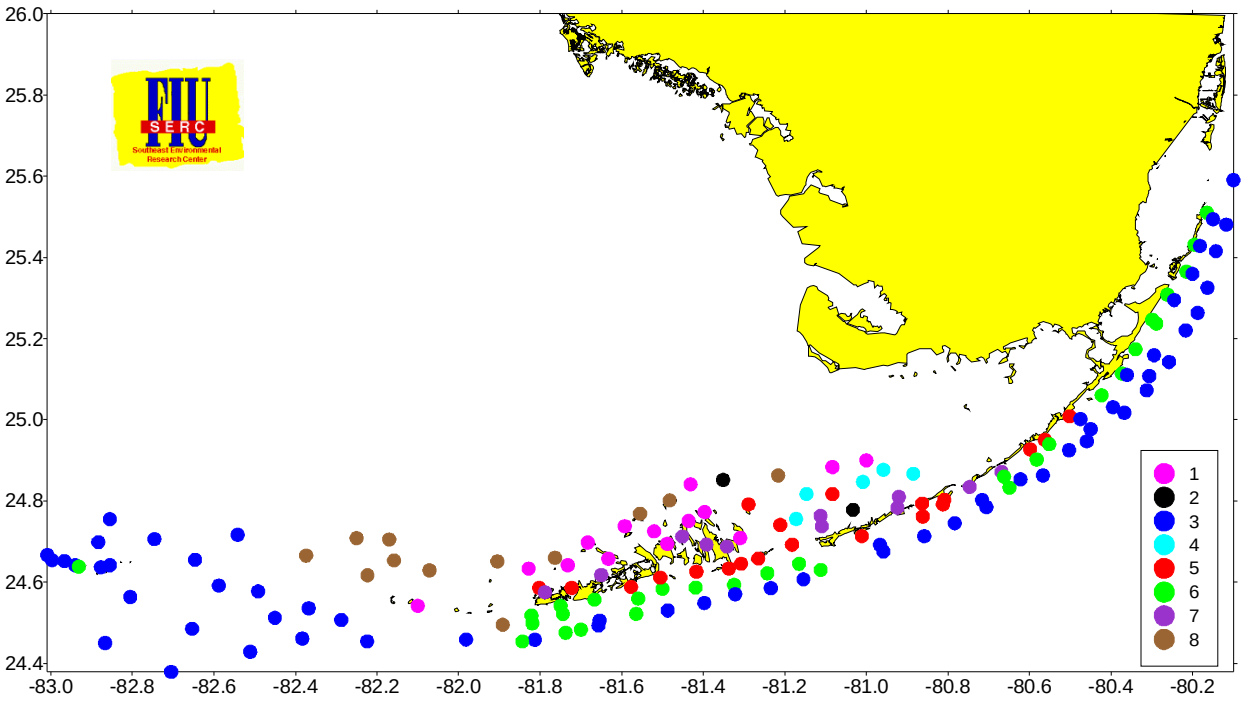

Figure 3. *Results of objective analysis showing station membership in distinct water quality groups.*

Cluster 7 (●) was composed primarily stations located inside the Backcountry, bayside Middle Keys, and the inshore sites off Lower Matecumbe Key. This group was highest in inorganic nutrients, especially NO_3^-, as well as TOC and TON (Fig. 4). We expect that there are different reasons for the distribution of these sites. In the shallow Backcountry sites we expect that benthic flux of nutrients might be very important, whereas elevated DIN at inshore Lower Matecumbe sites may be the result of anthropogenic loading.

Cluster 8 (●) included the northernmost sites in the Sluiceway, Backcountry and Marquesas. It had the highest TP, CHLA, and turbidity but was low in inorganic nutrients, DON, and DOC. We believe that the water quality in Cluster 8 was primarily driven by Shelf circulation patterns.

Cluster 1 (●) was composed of 2 sites in the northern Sluiceway and 12 sites in northern Backcountry extending out to the Marquesas. This group was high in TP, CHLA, and turbidity.

The main distinction between Cluster 1 and 8 was higher in CHLA and lower in TOC. So Clusters 8 and 1 may be viewed as a gradient of high TP Shelf water being attenuated by uptake of nutrients within the Backcountry and/or mixing with Atlantic Ocean waters.

Clusters 5, 6, and 3 may be interpreted as representing an onshore-offshore nutrient gradient. Cluster 5 (●) included the most of the inshore sites of the Keys, excluding the northernmost and southernmost ones. They were elevated in DIN relative to the Hawk Channel and reef tract sites. Cluster 6 (●) was made up of sites in Hawk Channel of the Lower Keys and alongshore sites in the Upper Keys. This group was slightly lower in nutrients than Cluster 5. Cluster 3 (●) was made up of outer reef tract and Tortugas stations. These sites had lowest nutrients, CHLA, turbidity, and TOC of any in the FKNMS. A clear gradient of elevated DIN, TP, TOC, and turbidity from alongshore to offshore was observed in the Keys with the Upper Keys being lower than the Middle and Lower Keys. No significant onshore-offshore gradient was observed for CHLA.

Sites making up Cluster 4 (●) were located in the Sluiceway and were similar to other Sluiceway sites except that they had the greatest range in salinity. Cluster 2 (●) was composed of only 2 sites in the Sluiceway and will not be discussed.

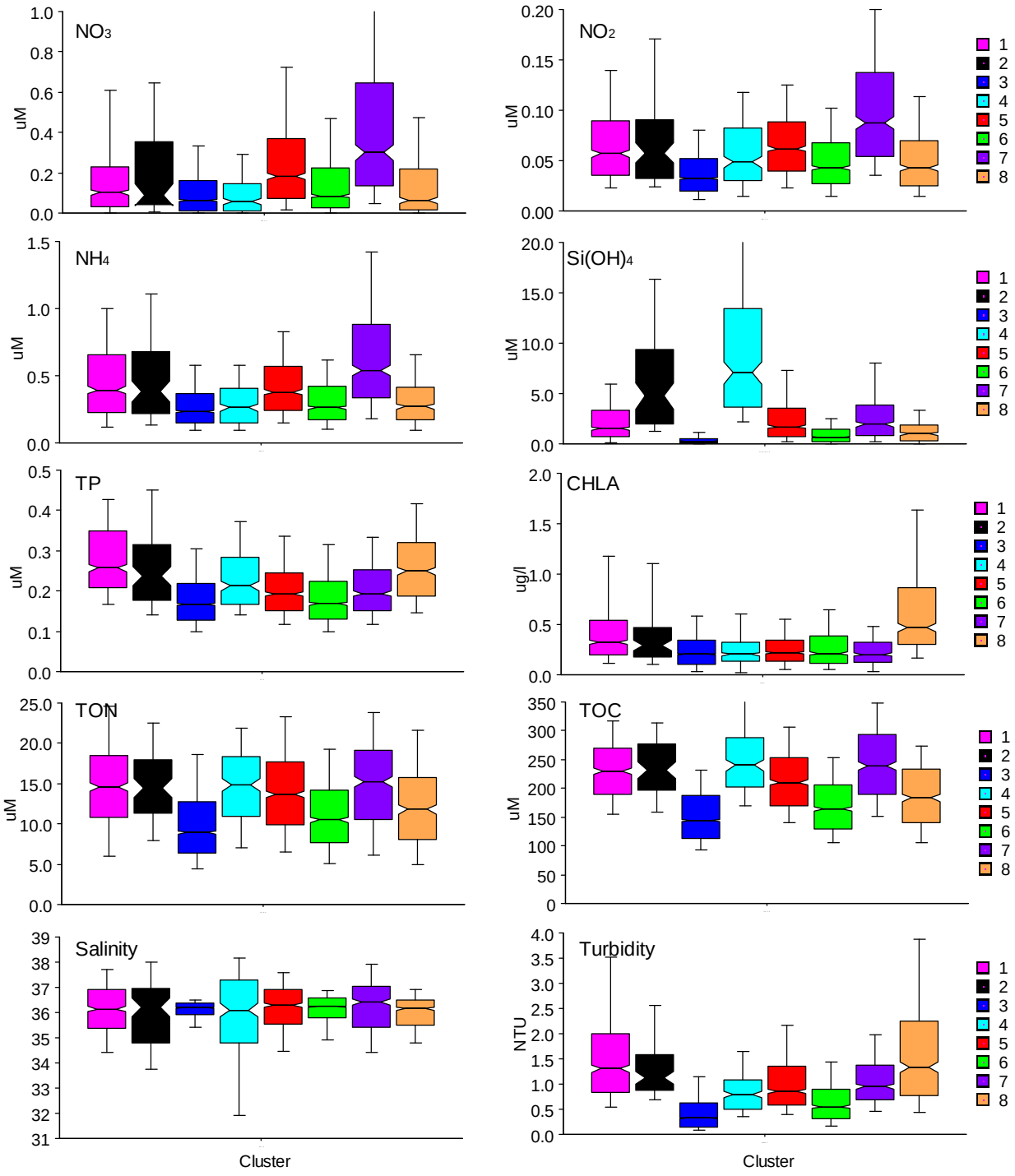

Figure 4. *Box-and-whisker plots showing median and distribution of NO_3^-, NO_2^-, NH_4^+, SiO_2, TP, CHLA, TON, TOC, salinity, and turbidity stratified by water quality cluster. Notches in the box that do not overlap with another are considered significantly different.*

3.3. Contour Maps

All contour maps of combined data from EPA and SFWMD projects are archived on the website http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm and are updated quarterly. An example of such (Fig. 5) shows the distribution of salinity across the region. Both freshwater sources and marine influences are visible using this approach. The major freshwater sources to the region are the Shark River/Slough system on the SW coast and the Taylor Slough/C-111 Basin in eastern Florida Bay. Southerly currents along the SW coast and Shelf moves water through the Keys passes and may impact the reef tract.

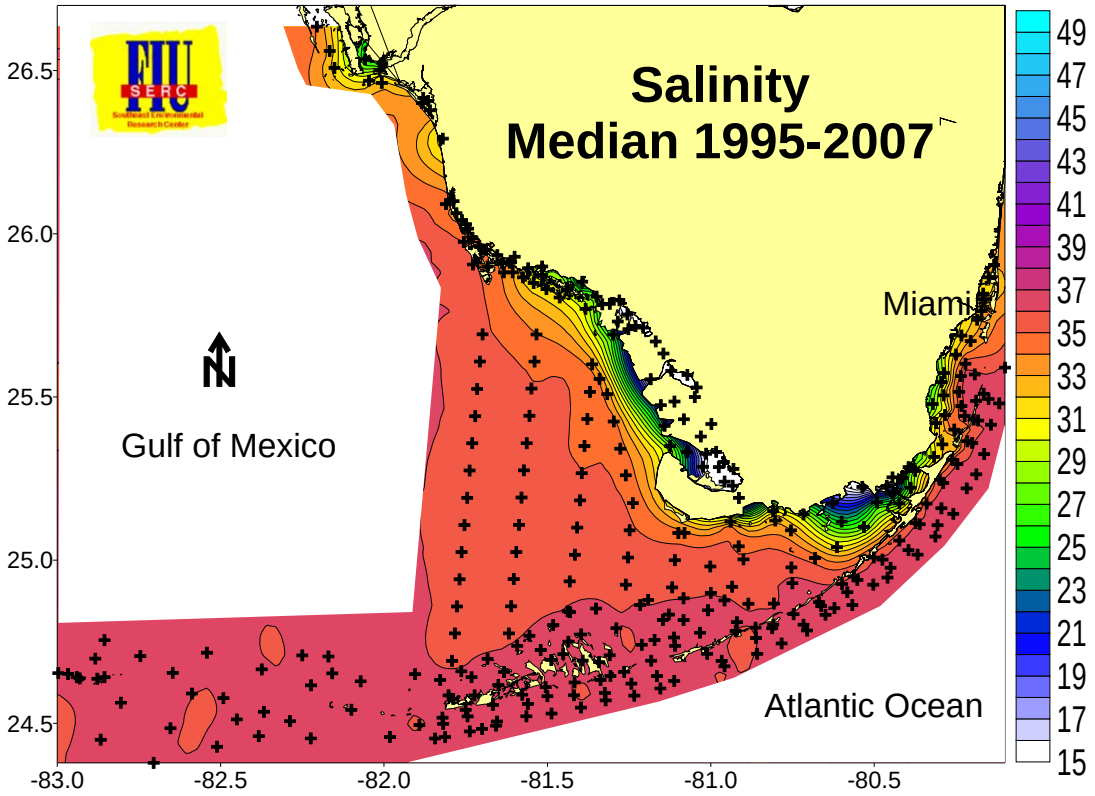

Figure 5. *Example of contour map of median salinity field for the region showing freshwater inputs and marine influence.*

The usual distribution of dissolved NO_3^- and NH_4^+ are very different than that for salinity (Fig. 6). This implies that there are other factors responsible for their distributions, such a phytoplankton and seagrass uptake as well as N_2 fixation and benthic remineralization.

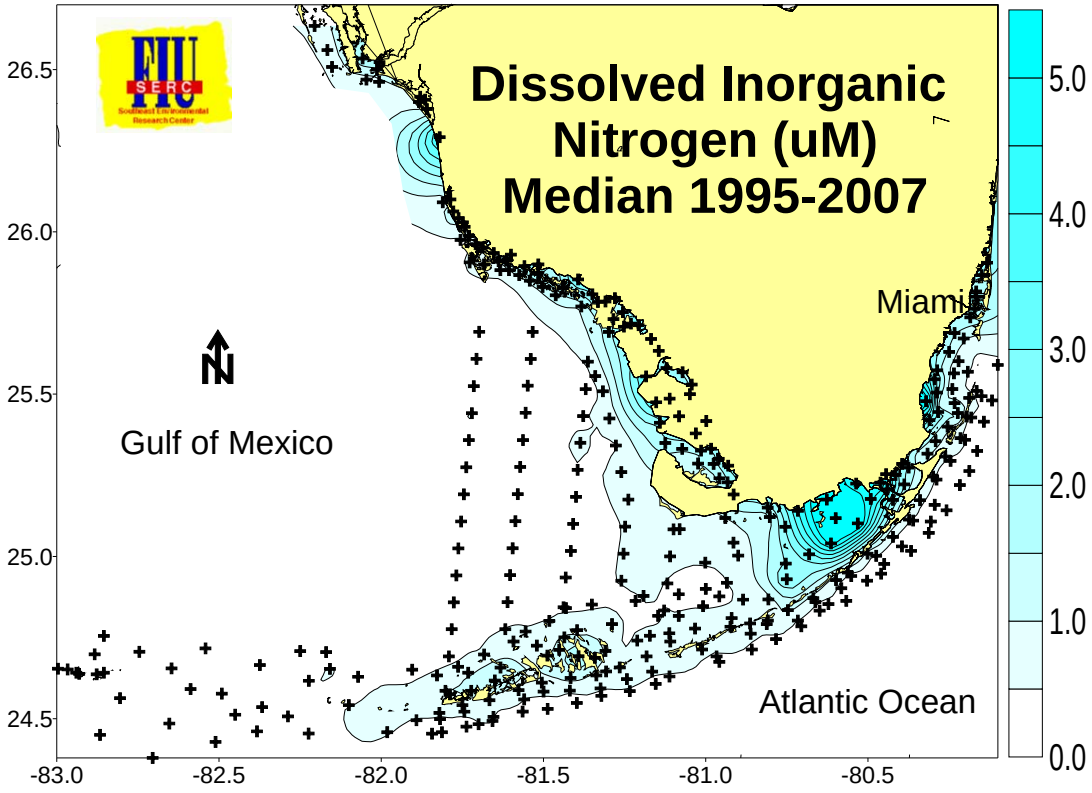

Figure 6. *Example of contour map of dissolved inorganic N (nitrate, nitrite, and ammonium) in the region.*

In contrast, total phosphorus distributions often are very similar to salinity patterns, but only on the west coast (Fig. 7). This implies that the source of P on the Shelf is partially terrestrial and partly from southward transport of coastal waters from above Cape Romano. It is important to note that the CHLA concentrations are tightly coupled to TP availability (Fig. 8).

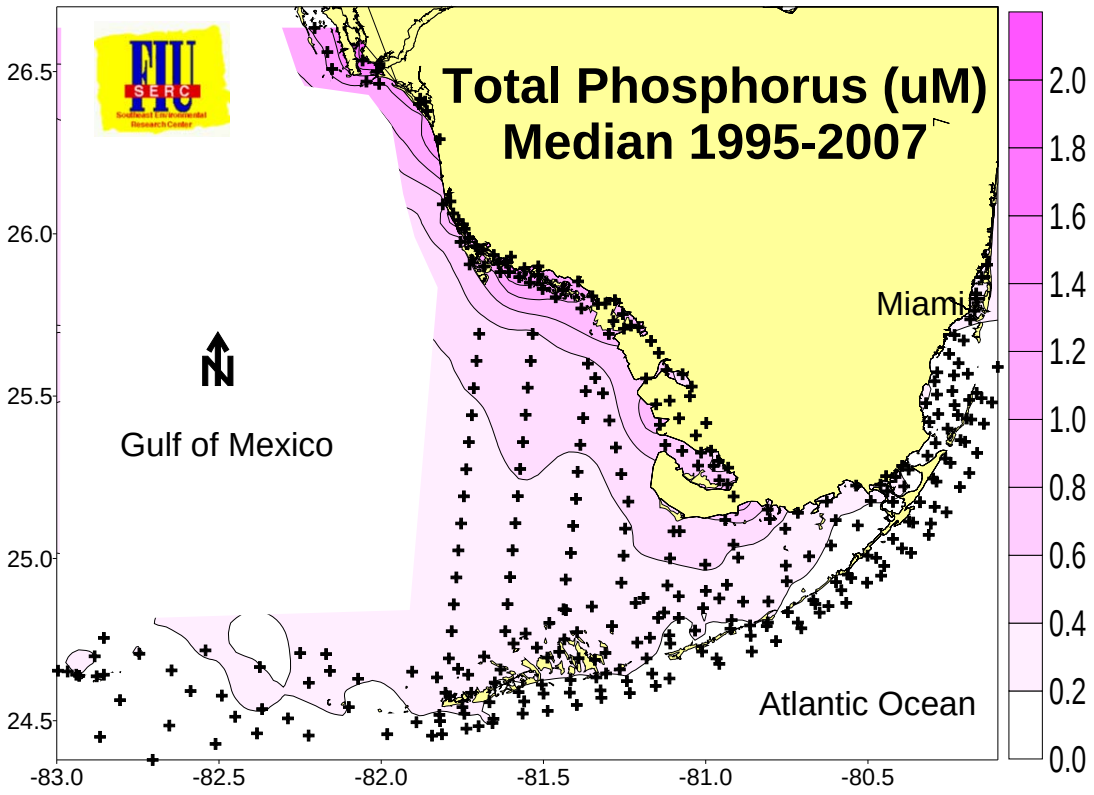

Figure 7. *Distribution of total phosphorus in the region.*

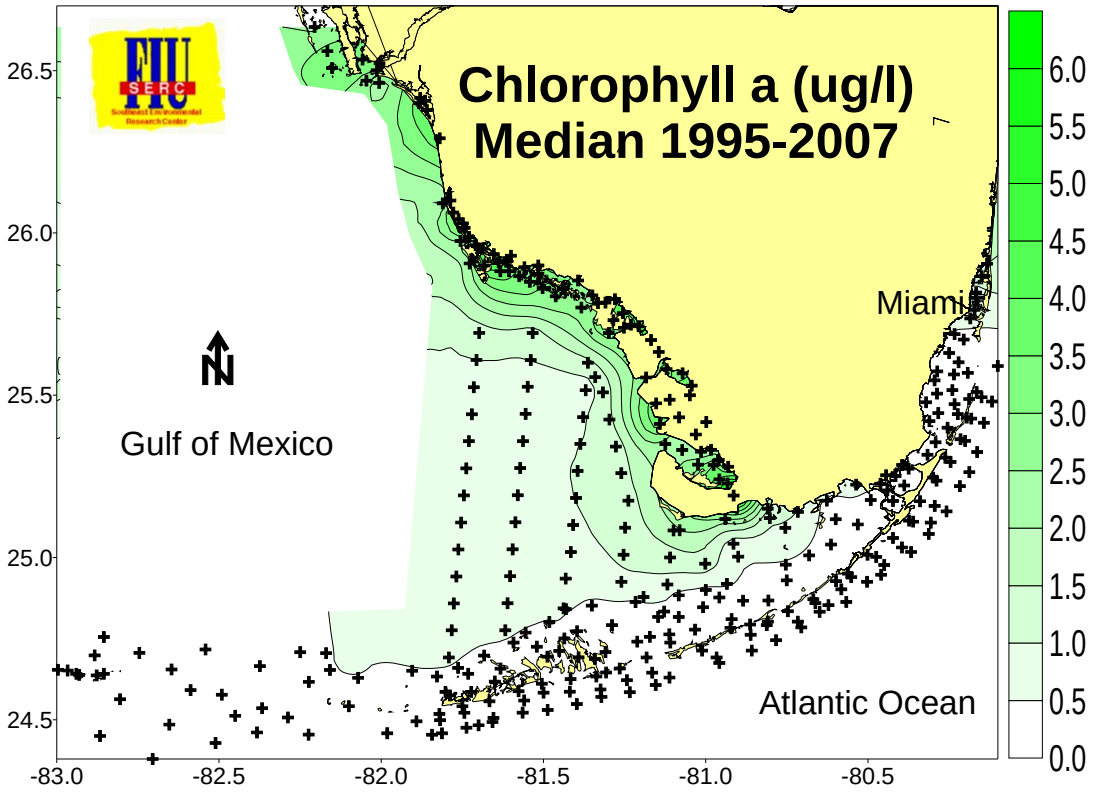

Figure 8. *Distribution of chlorophyll a in the region showing the similarity to TP distribution.*

3.4. Time Series Analysis

In previous report we have observed significant increasing trends in TP, NO_3^-, and decreasing TON. We ascribed these trends as being driven primarily by large scale circulation patterns. Since then, there have been trend reversals in some nutrient concentrations. Figures 9-14 show temporal trends in the median and range of the data (box-and-whisker plots) for each spatial cluster and water quality variable by quarterly sampling event.

The outer reef tract/Tortugas sites (**Cluster 3**, Fig 9a&b) and North Marquesas/North Backcountry (**Cluster 8**, Fig 14a&b) showed declines in salinity during the past few years and increases in stratification of the water column ($\Delta\sigma_t$). This lower salinity layer also had higher concentrations of NO_3^-, NH_4^+, TP and turbidity with concomitant decrease in DO_{sat}. Interestingly, CHLA was not affected by these changes. By the last quarter of sampling, most of these parameters had returned to earlier levels. TOC continues to show long term declines in concentration.

Cluster 6, the inshore Upper Keys/Hawk Channel Lower Keys, mirrored the patterns seen in **Cluster 3** except that some of the concentrations were higher for the nearshore sites (Fig. 10a&b). In some cases, like NO_3^-, the signal was more damped. **Cluster 5**, the inshore Middle and Lower Keys/Sluiceway, mirrored the patterns seen in other clusters as well however, no evidence of water column stratification was observed because of the shallowness of the sites (Fig 11a&b). Both the Bayside Middle Keys/Inside Backcountry/Inshore Long & Lower Keys (**Cluster 7**, Fig 12a&b) and Backcountry/North Sluiceway (**Cluster 1**, Fig 13a&b) showed elevated NH_4^+ and TP with lower DO_{sat} but we saw no evidence of salinity differences.

This brings up an important point that, when looking at what are perceived to be local trends, we find that they may occur across the whole region at more subtle levels. This spatial autocorrelation in water quality is an inherent property of interconnected systems such as coastal and estuarine ecosystems which are driven by hydrological and climatological forcing.

Clearly, there have been large changes in the FKNMS water quality over time, but the only sustained monotonic trend that has been observed is a decline in TOC. We must always keep in mind that trend analysis is limited to the window of observation; trends may change with additional data collection.

Cluster 3 – Reef Tract/Tortugas

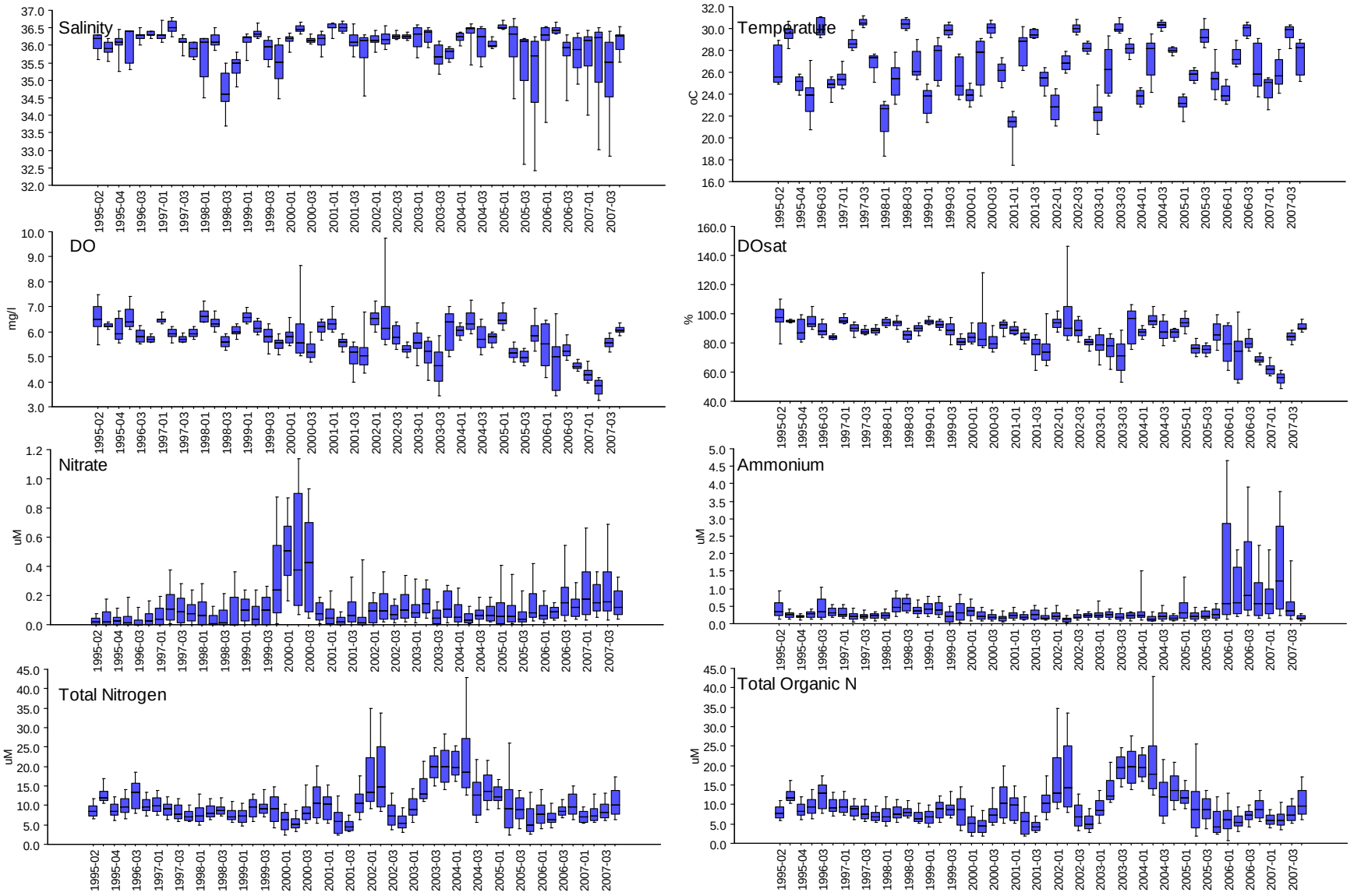

Figure 9a.

Cluster 3 – Reef Tract/Tortugas

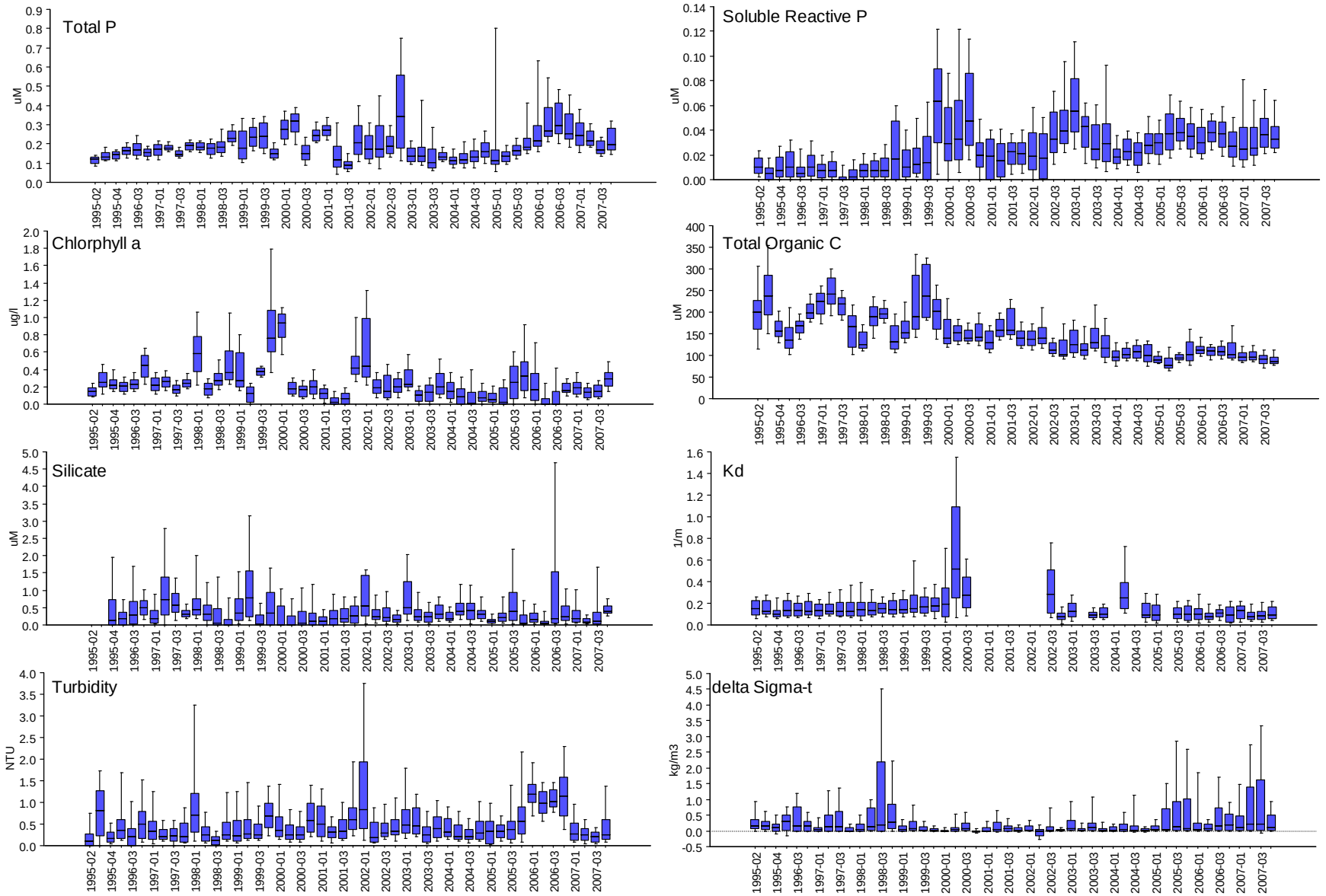

Figure 9b.

Cluster 6 – Inshore Upper Keys/Hawk Channel Lower Keys

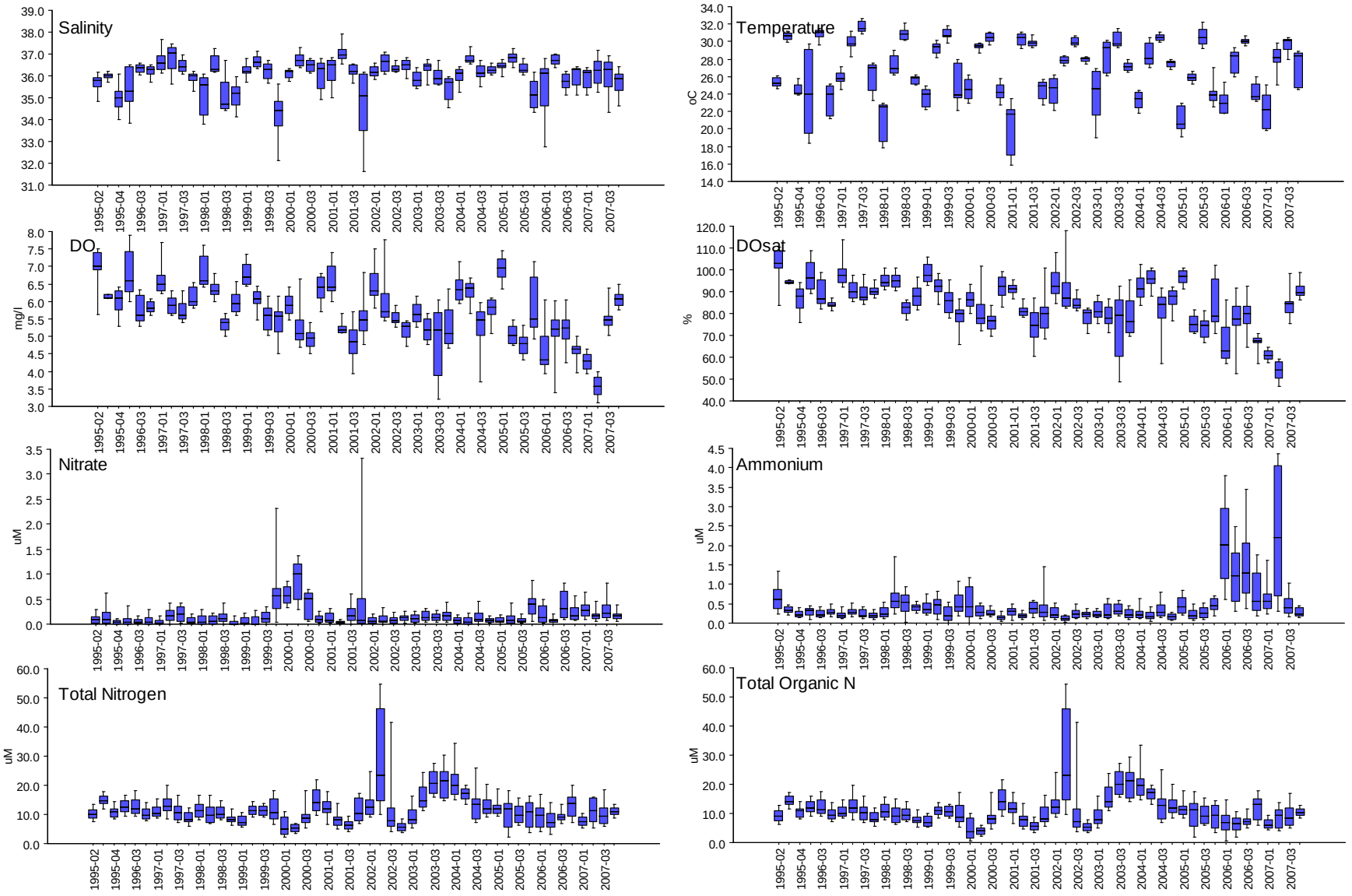

Figure 10a.

Cluster 6 – Inshore Upper Keys/Hawk Channel Lower Keys

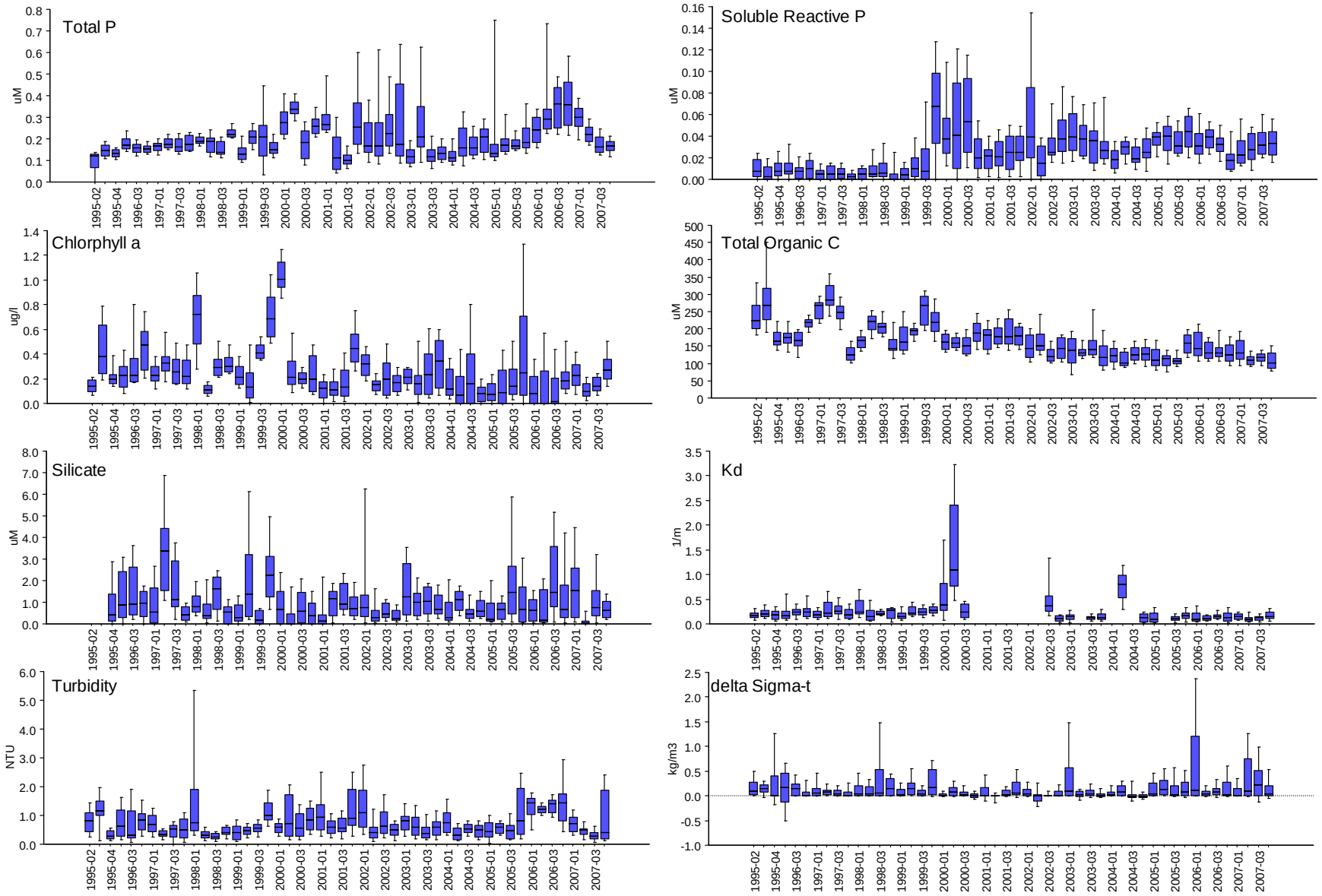

Figure 10b

Cluster 5 – Inshore Middle and Lower Keys/Sluiceway

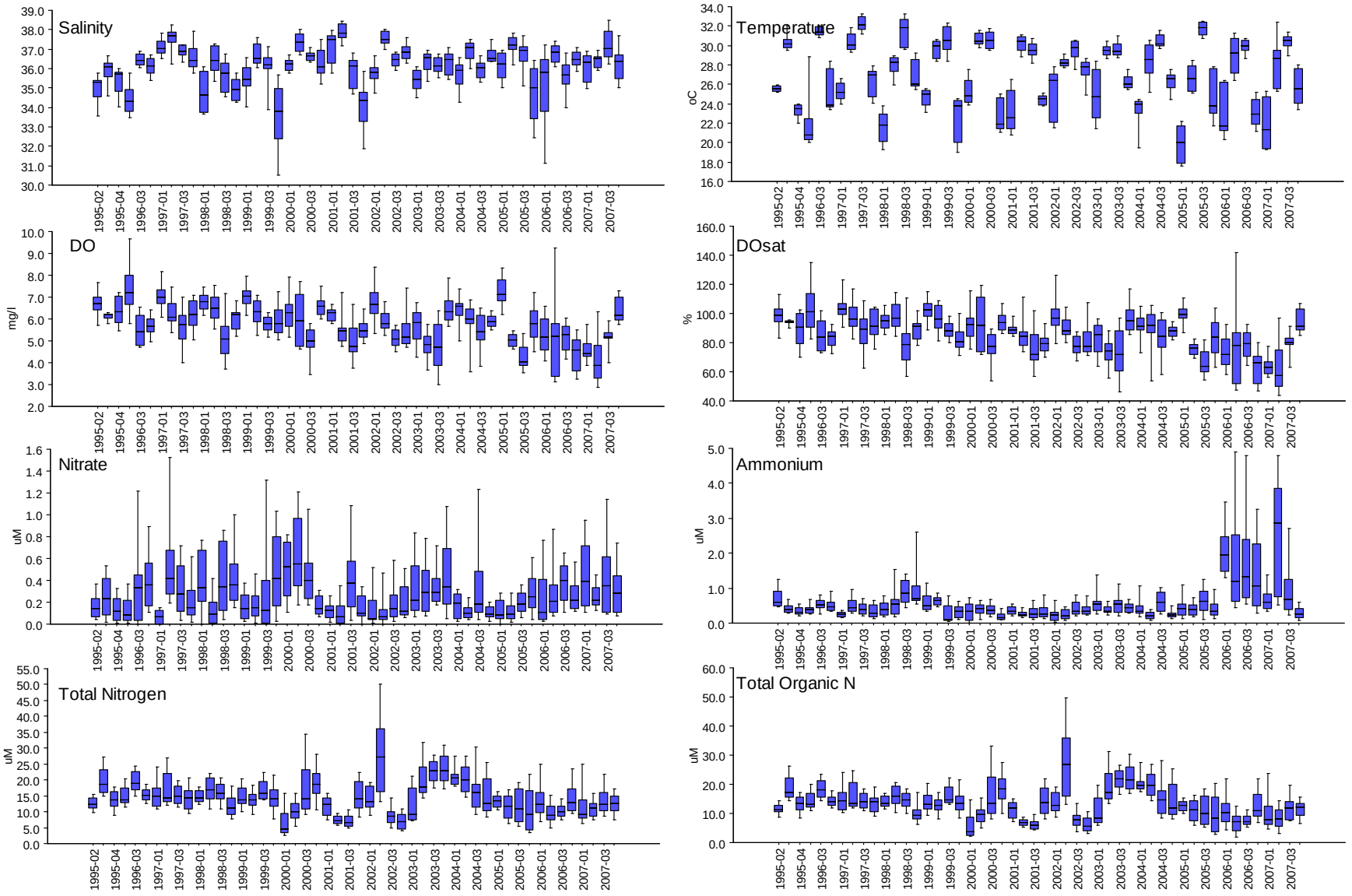

Figure 11a

Cluster 5 – Inshore Middle and Lower Keys/Sluiceway

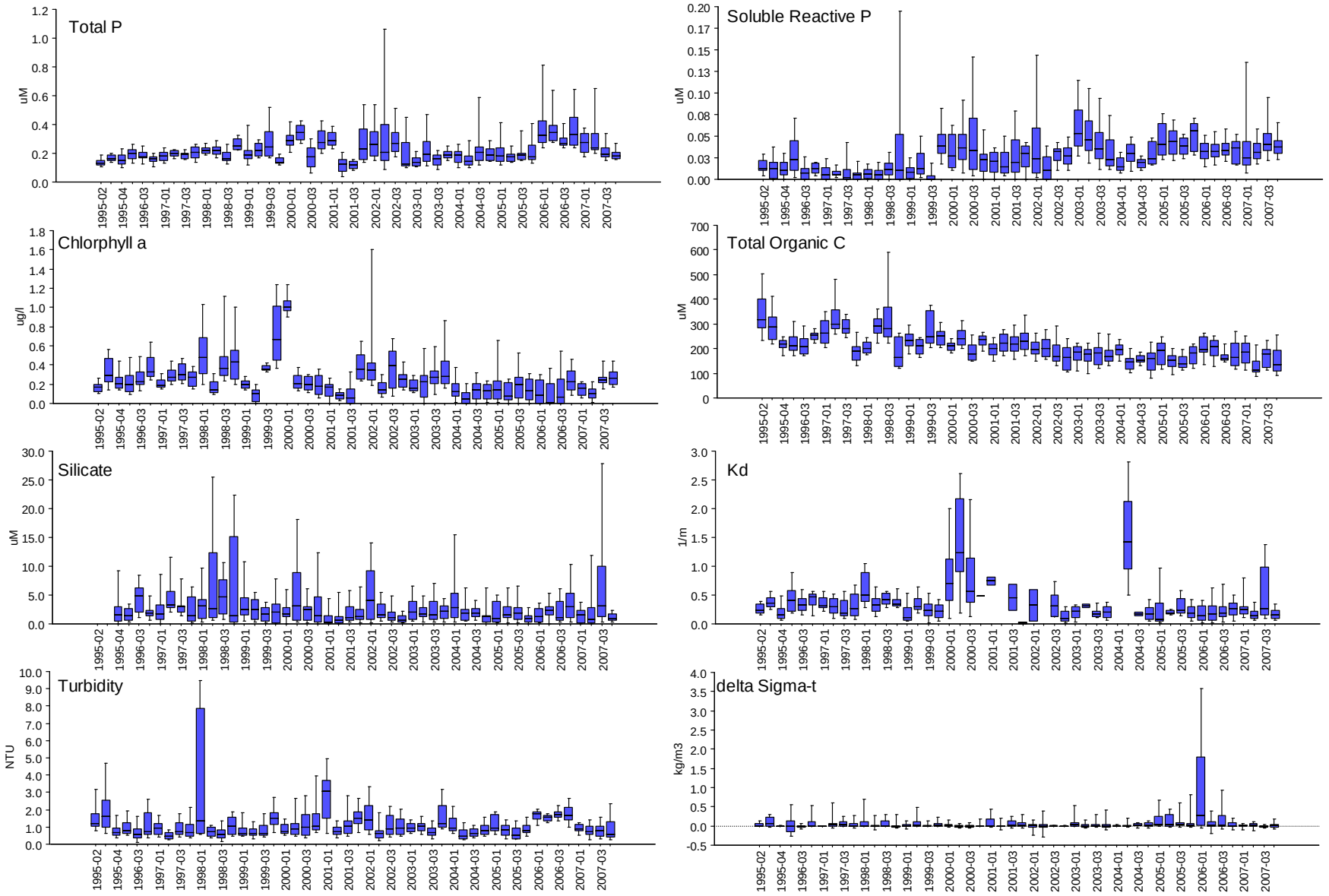

Figure 11b

Cluster 7 – Bayside Middle Keys/Inside Backcountry/Inshore Long & Lower Matecumbe

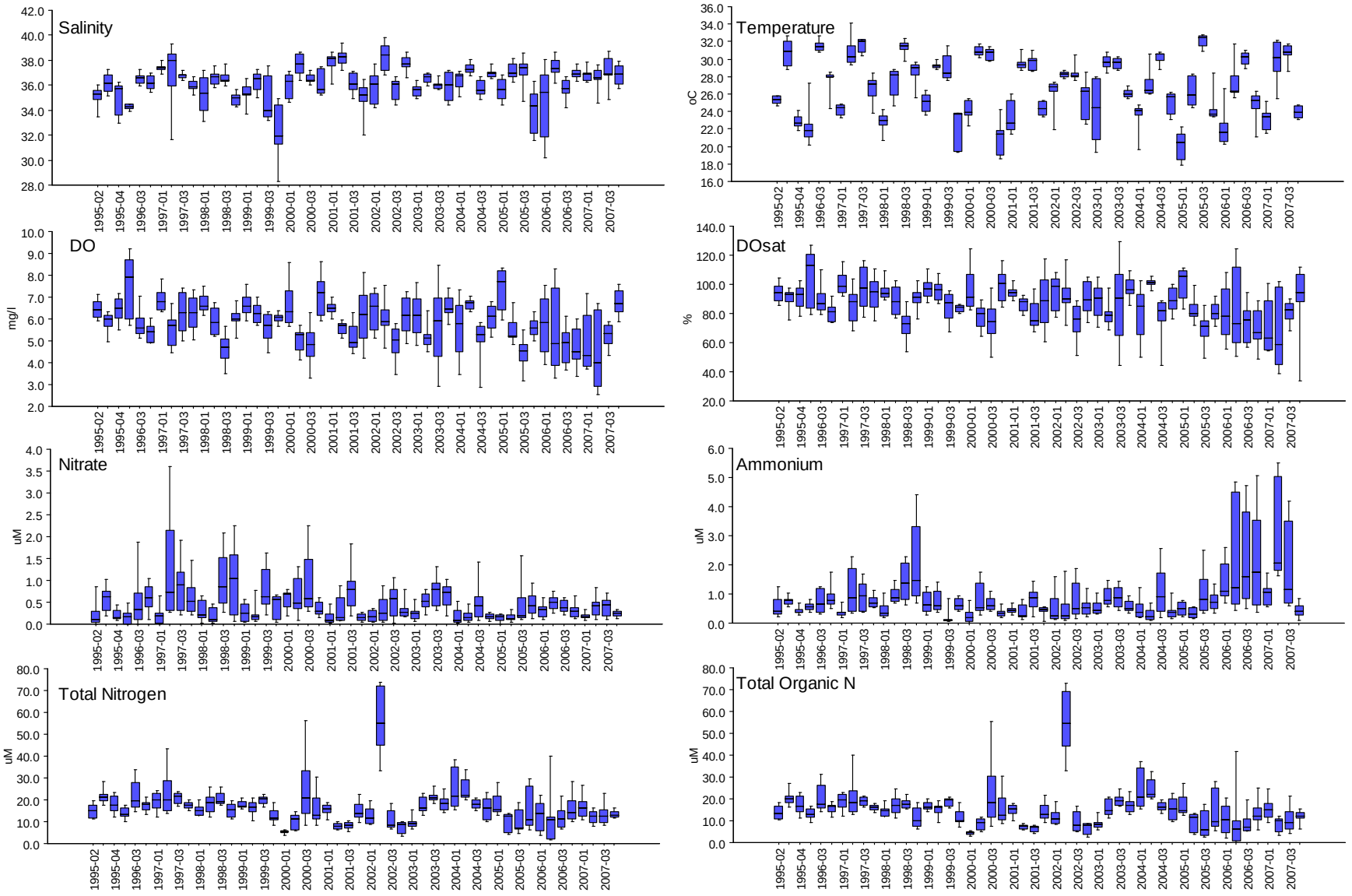

Figure 12a.

Cluster 7 – Bayside Middle Keys/Inside Backcountry/Inshore Long & Lower Matecumbe

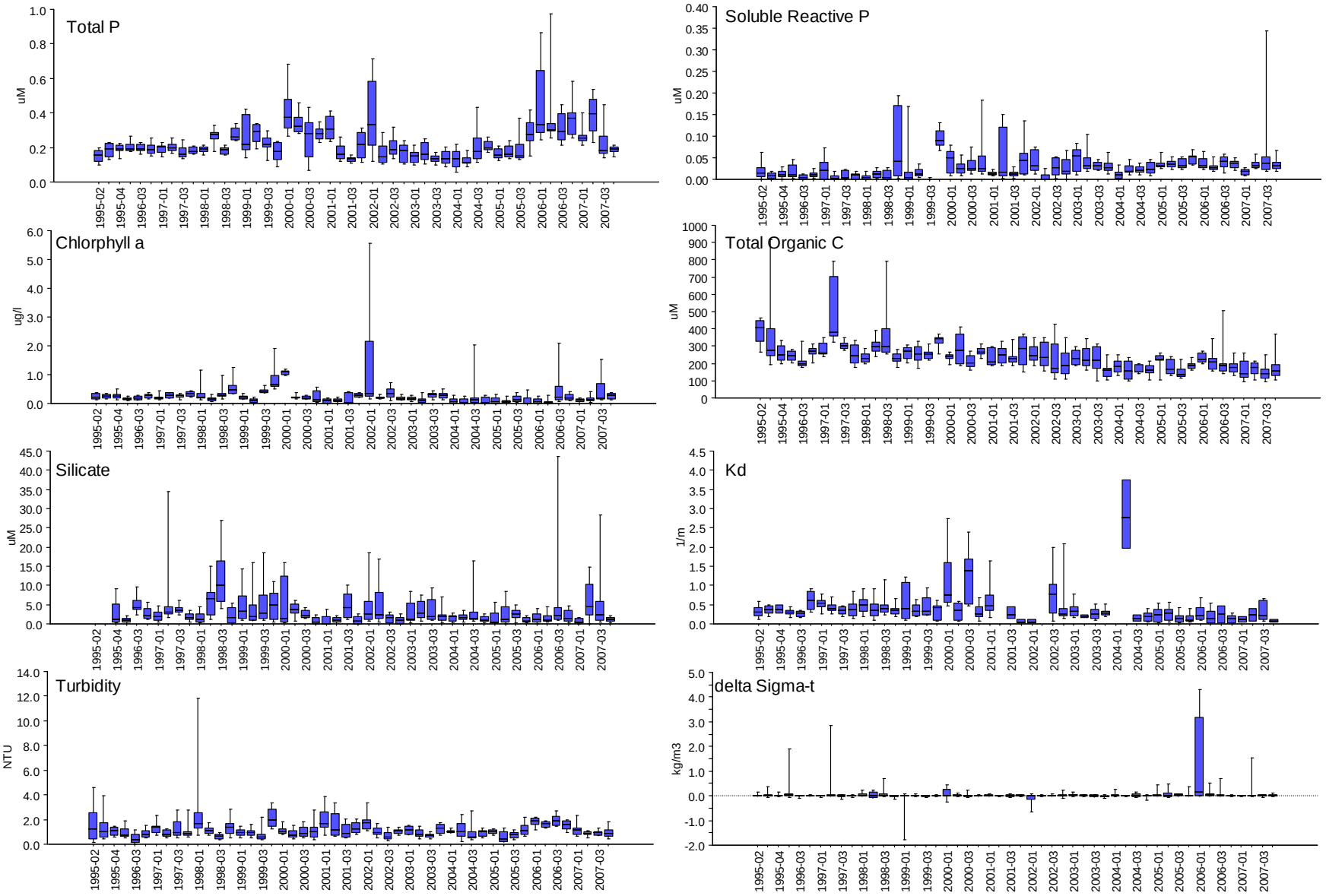

Figure 12b.

Cluster 1 – Backcountry/North Sluiceway

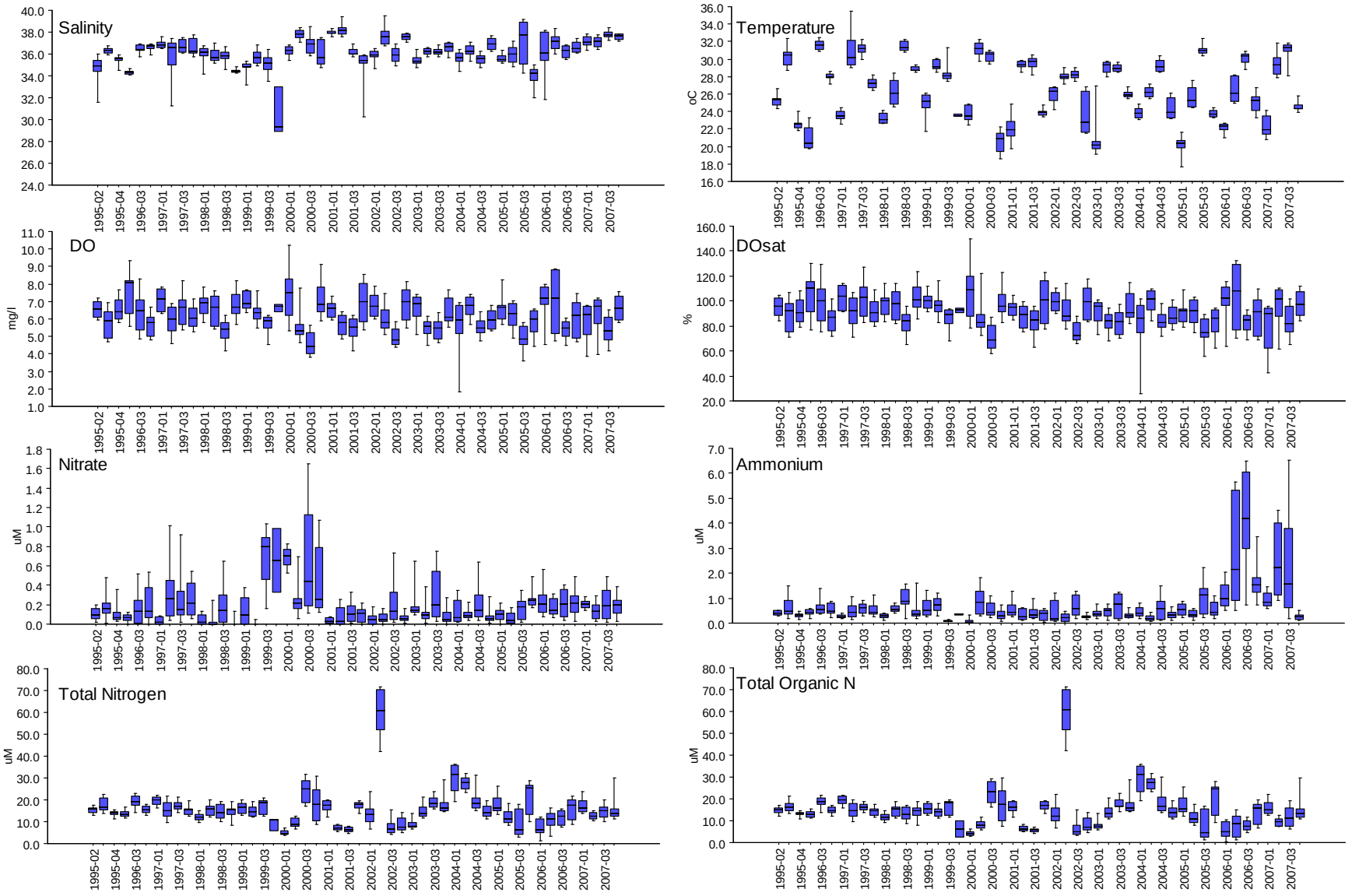

Figure 13a.

Cluster 1 – Backcountry/North Sluiceway

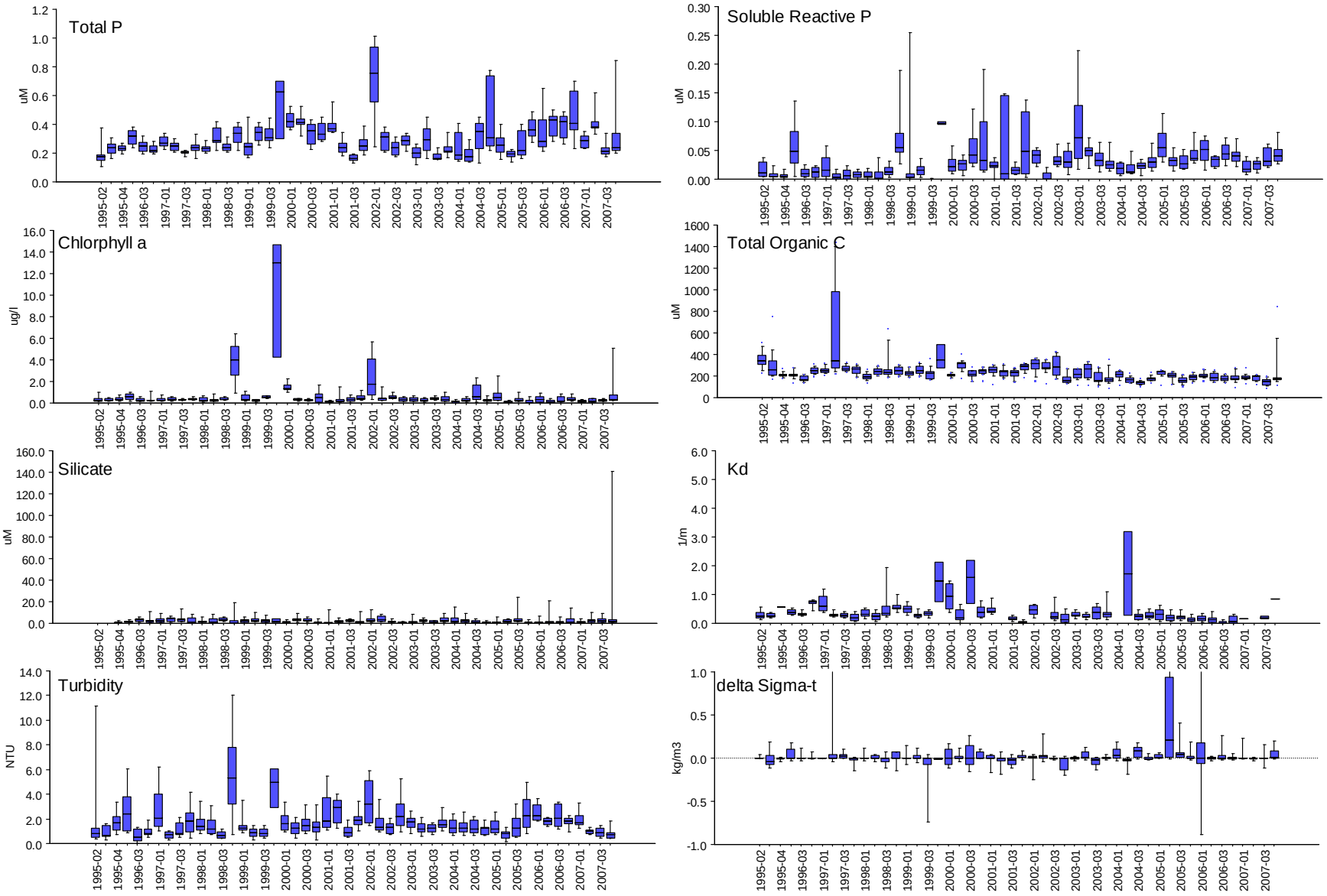

Figure 13b.

Cluster 8– North Marquesas/North Backcountry

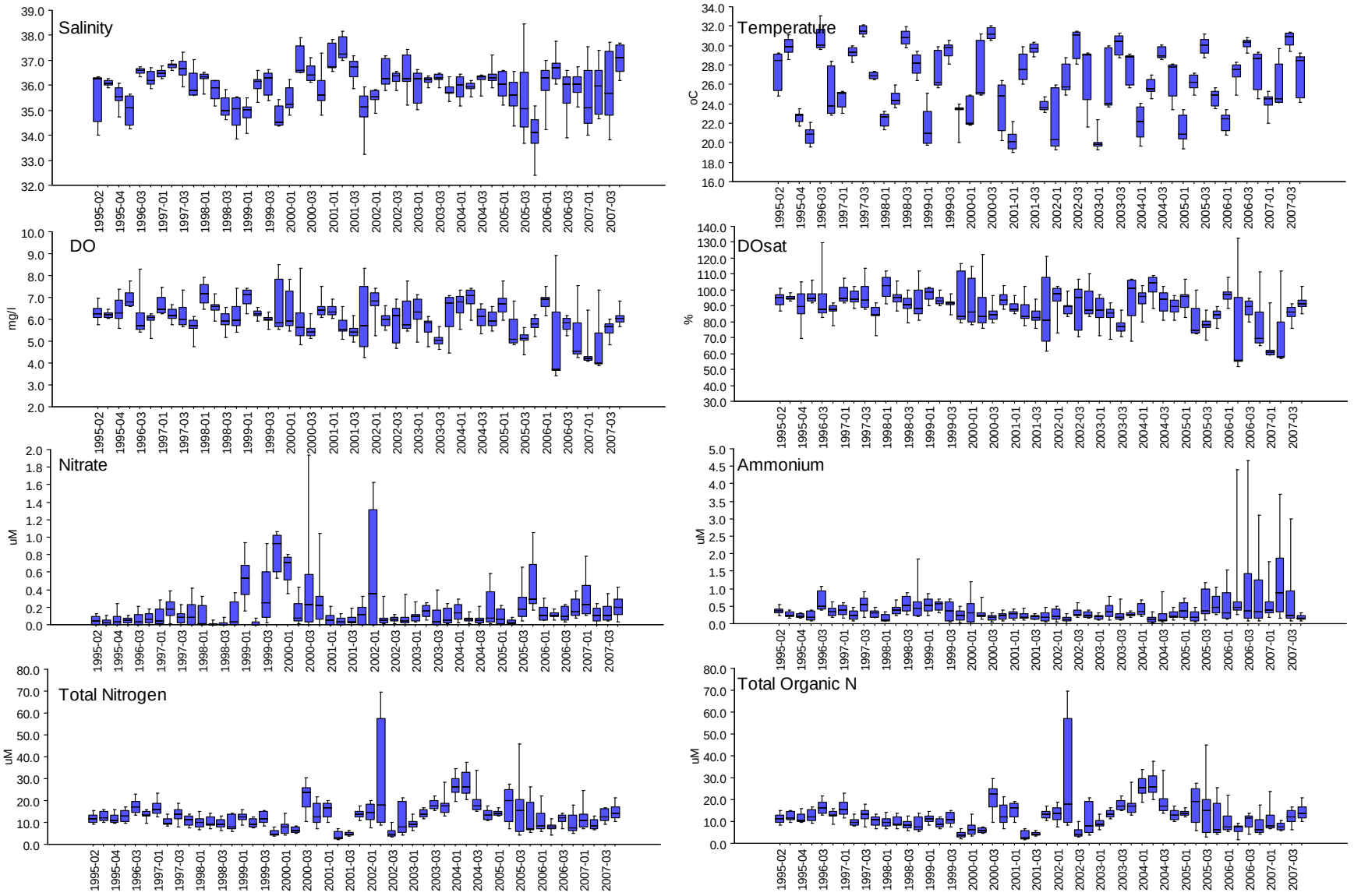

Figure 14a.

Cluster 8– North Marquesas/North Backcountry

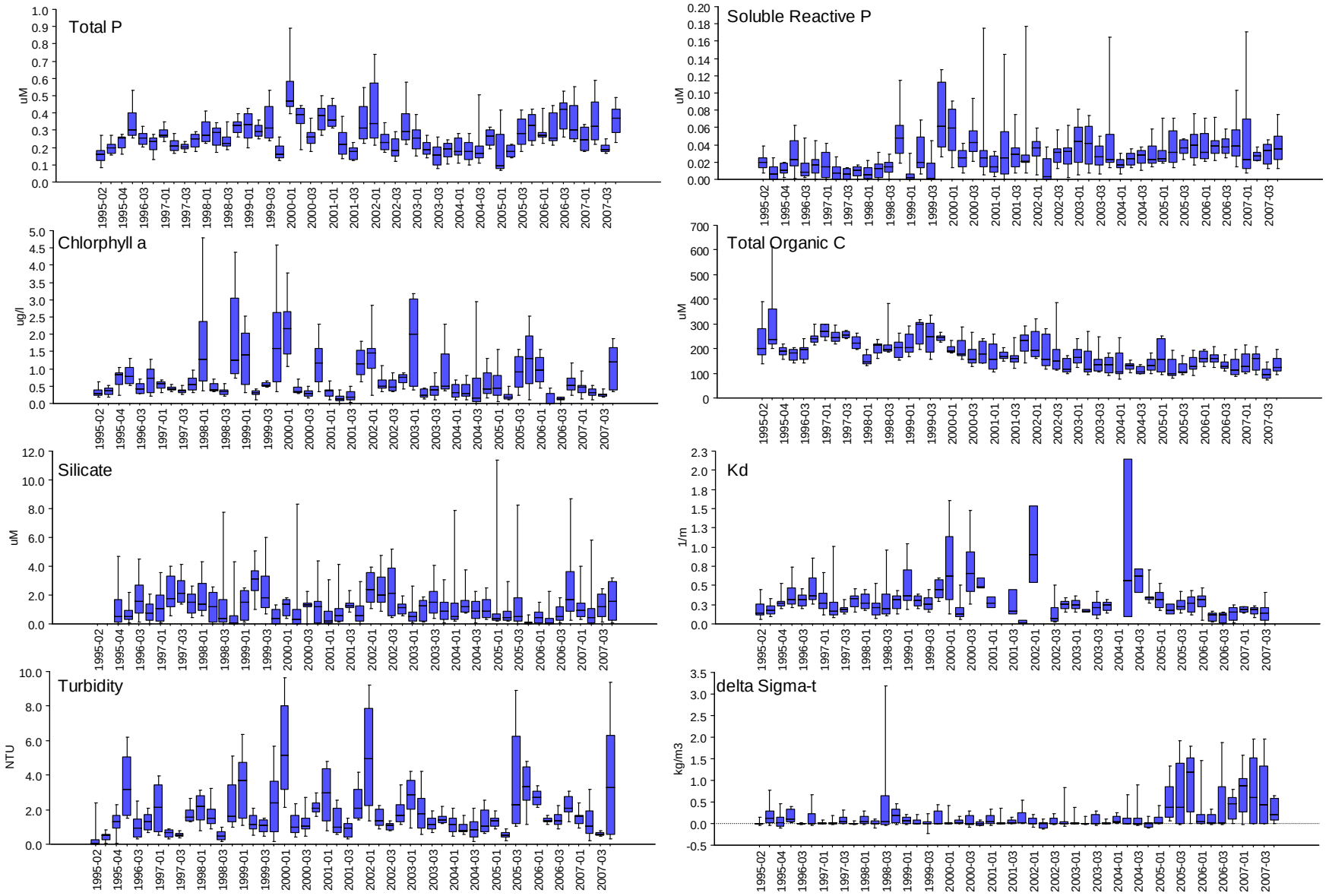

Figure 14b.

4. State of FKNMS Water Quality for 2007

Total precipitation for 2007 was 150.3 cm y^{r-1} making it equal to the median value year since 1991. Nevertheless, July and August were above their respective medians by about 11 cm. Hurricanes were not an issue during this year.

In the Reef Tract/Tortugas (**Cluster 3**), DIN (mostly as NH_4^+) was elevated relative to the long term median (Fig. 15). TOC and TON were lower than the long term median mostly because they have been declining over the years. TP, CHLA, salinity, and temperature showed little if any difference. DO in the first two quarters was significantly lower than the long term median while turbidity was lower for the whole year.

The Inshore Upper Keys/Hawk Channel Lower Keys sites (**Cluster 6**) experienced similar conditions as the Reef Tract/Tortugas (Fig. 16). DIN was higher than normal. TON, TOC, DO and turbidity were lower than usual. Moving to the Inshore Middle and Lower Keys/Sluiceway (**Cluster 5**), we observed similar patterns in water quality as for the other areas with the exception that turbidity was relatively unchanged (Fig. 17). For the Bayside Middle Keys/Inside Backcountry/Inside Long & Lower Matecumbe sites (**Cluster 7**), TP was elevated for the second quarter while salinity was elevated for the last quarter (Fig. 18). Overall, the same tends as above were observed here as well. Similar trends were observed in the Backcountry/North Sluiceway sites (**Cluster 1**) and the North Marquesas/North Backcountry (**Cluster 8**), but the Backcountry/North Sluiceway showed significantly elevated salinity for the whole year.

Cluster 3 – Reef Tract/Tortugas

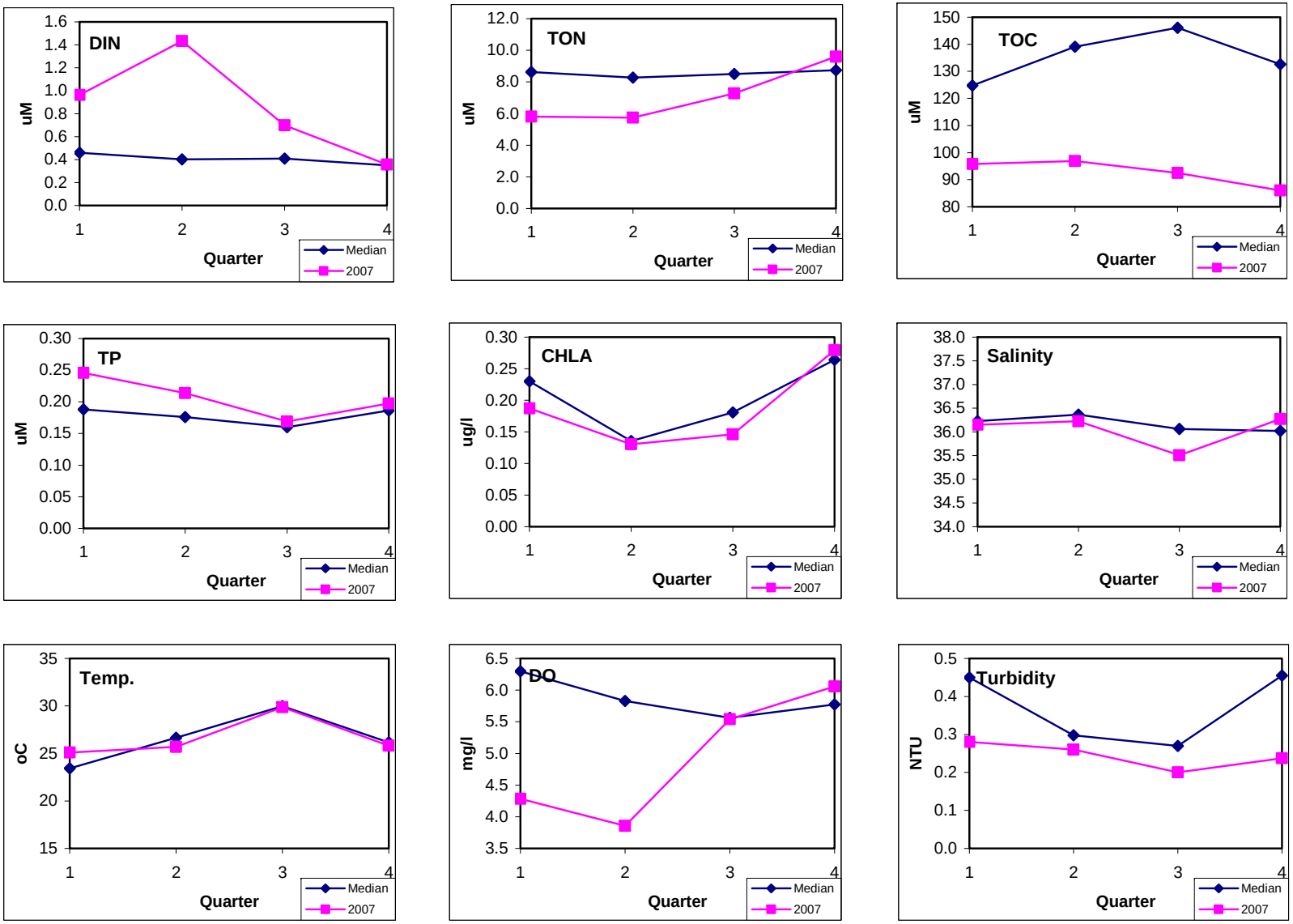

Figure 15. *Comparison of long-term median with 2006 data.*

Cluster 6 – Inshore Upper Keys/Hawk Channel Lower Keys

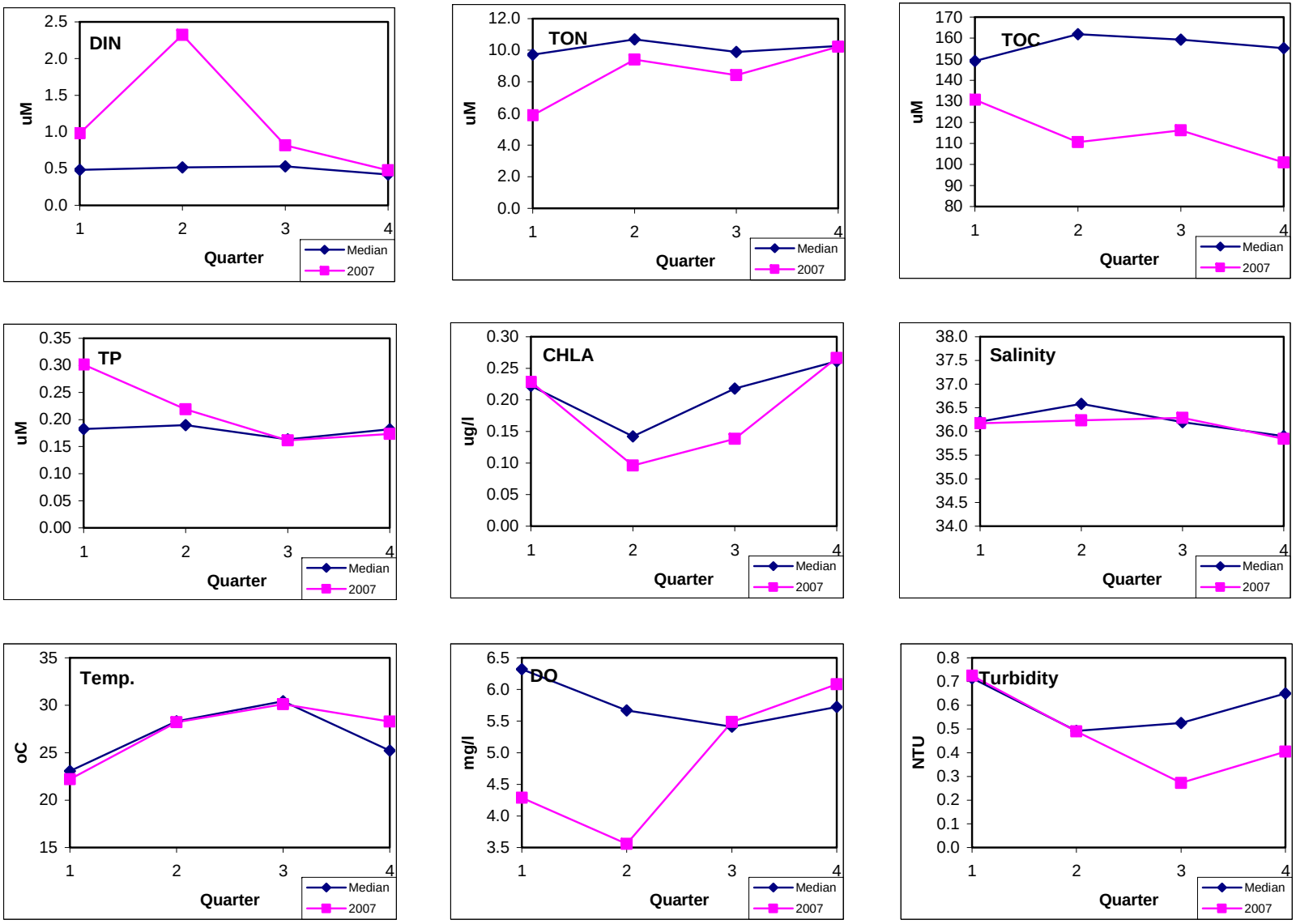

Figure 16. *Comparison of long-term median with 2006 data.*

Cluster 5 – Inshore Middle and Lower Keys/Sluiceway

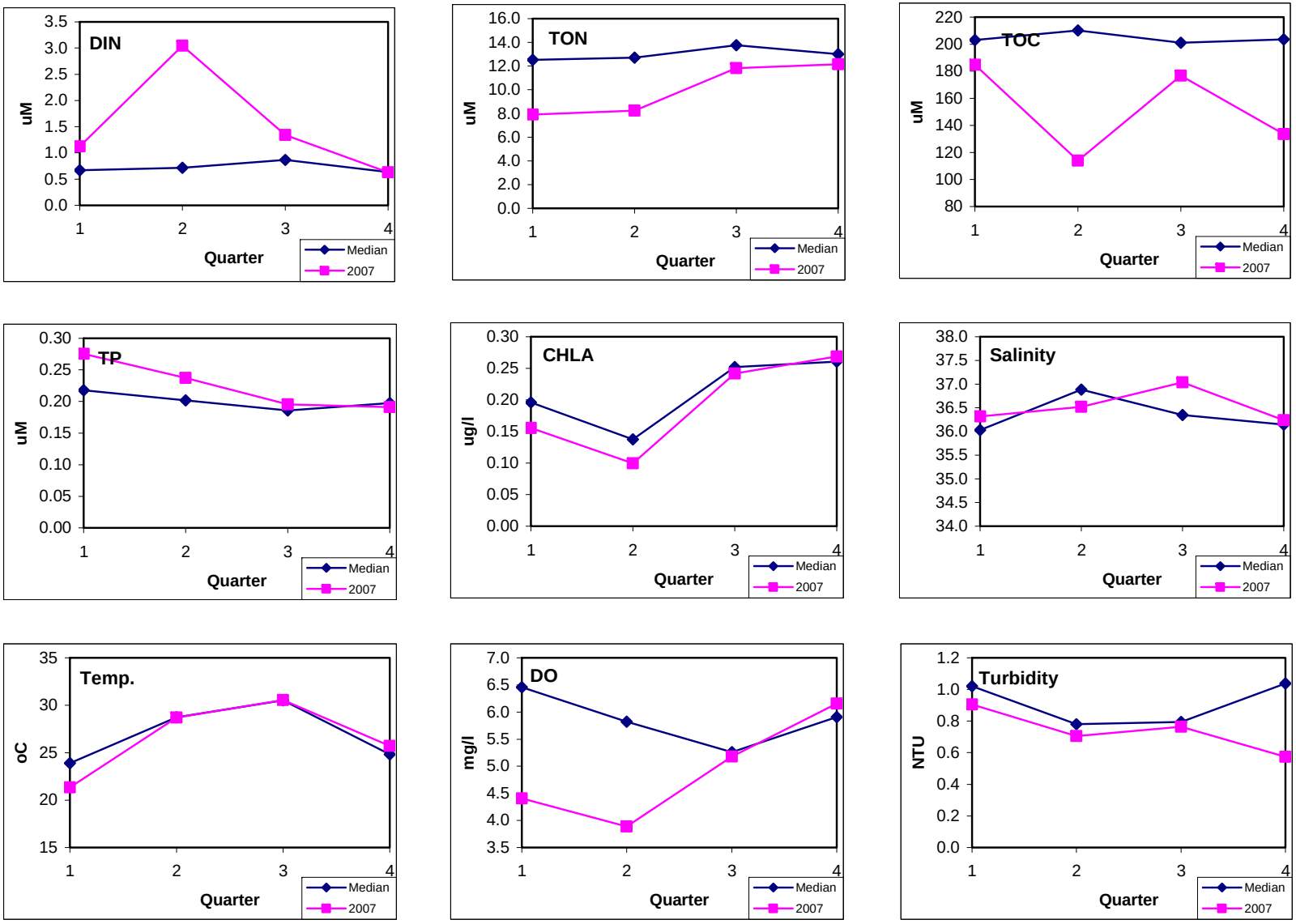

Figure 17. *Comparison of long-term median with 2006 data.*

Cluster 7 – Bayside Middle Keys/Inside Backcountry/Inshore Long & Lower Matecumbe

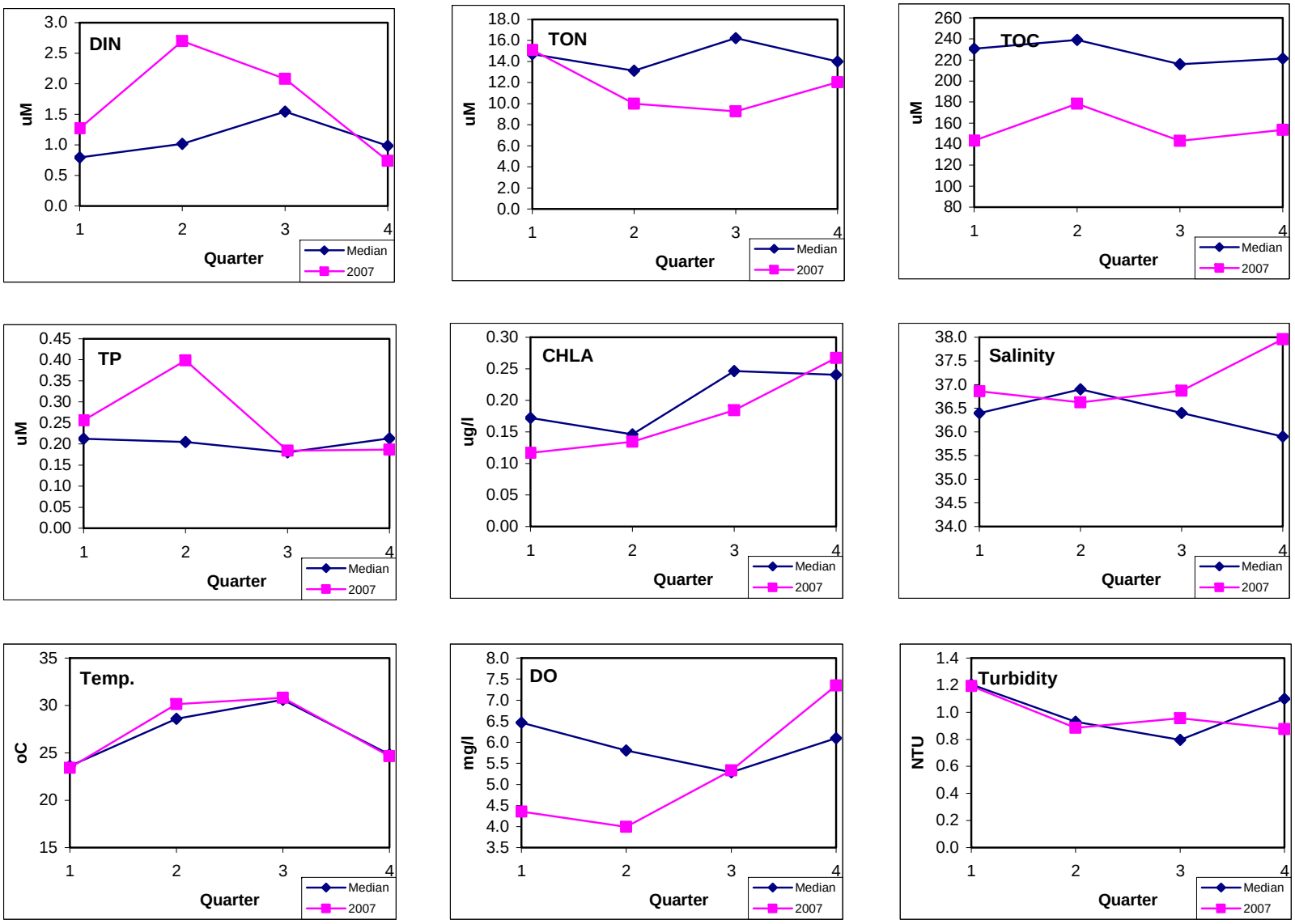

Figure 18. *Comparison of long-term median with 2006 data.*

Cluster 1 – Backcountry/North Sluiceway

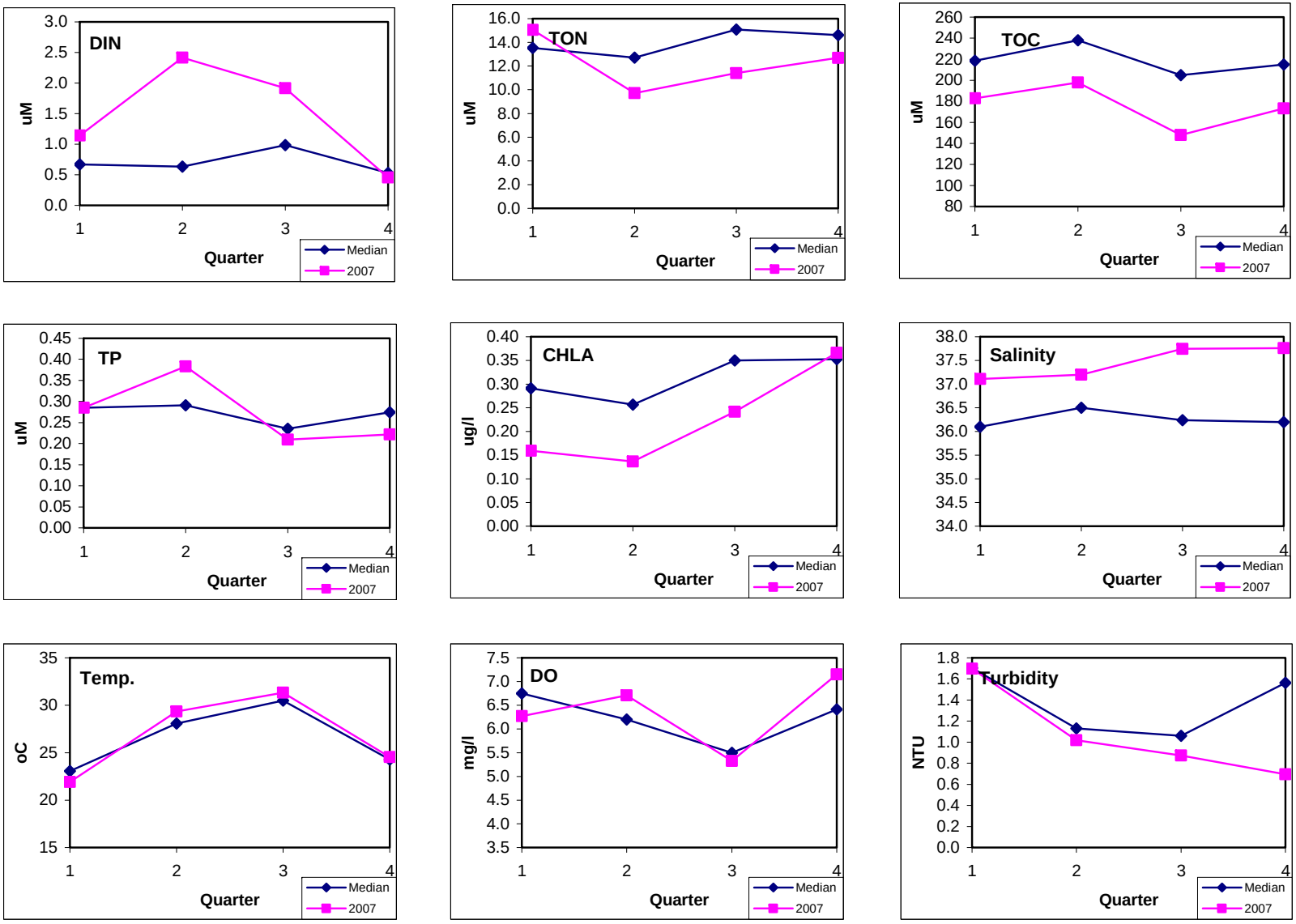

Figure 19. *Comparison of long-term median with 2006 data.*

Cluster 8– North Marquesas/North Backcountry

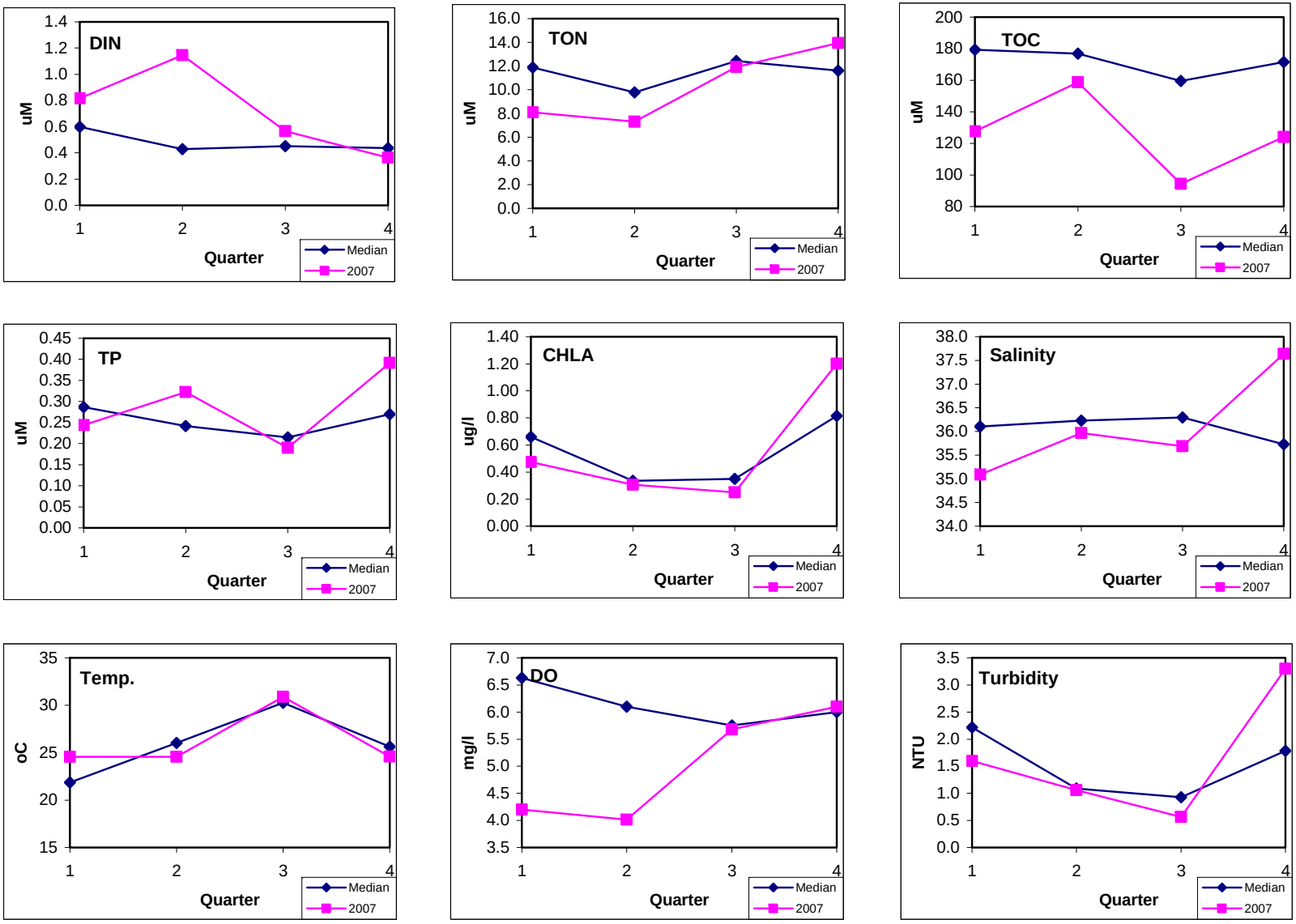

Figure 20. *Comparison of long-term median with 2006 data.*

5. Overall Trends

Several important results have been realized from this monitoring project. First, is documentation of elevated nitrate in the inshore waters of the Keys (Fig 21). This result was evident from out first sampling event in 1995 and continues to be a characteristic of the ecosystem. Interestingly, this gradient was not observed in a comparison transect from the Tortugas (no human impact). This type of distribution implies an inshore source which is diluted by low nutrient Atlantic Ocean waters. Presence of a similar gradient in TOC and decreased variability in salinity from land to reef also support this concept. There were no trends in either TP or CHLA with distance from land.

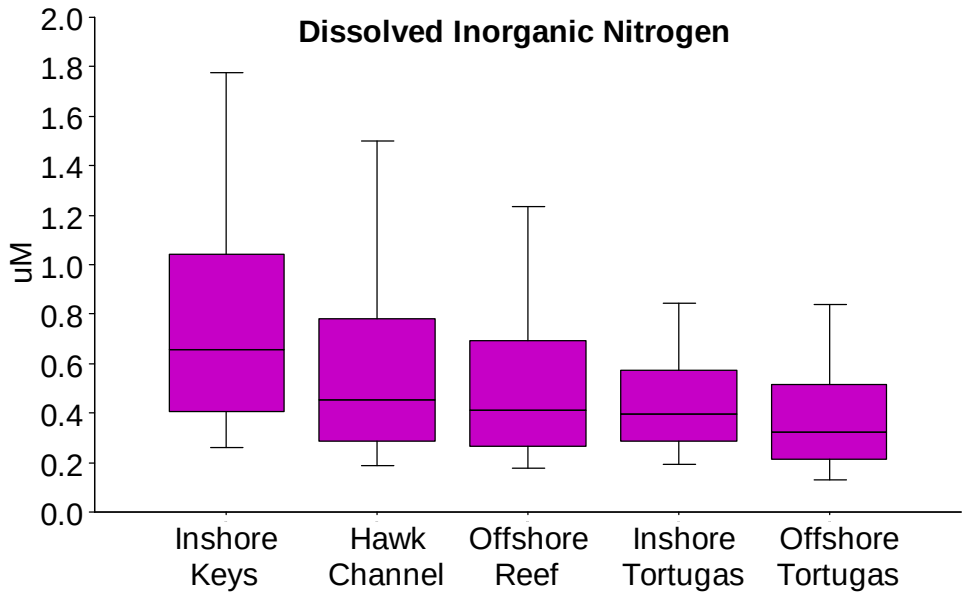

Figure 21

Second, highest CHLA concentrations are seen on the SW Florida Shelf with a strong gradient towards the Marquesas and Tortugas (Fig. 22). This is due to higher TP concentrations on the Shelf as a result of southerly advection of water along the coast.

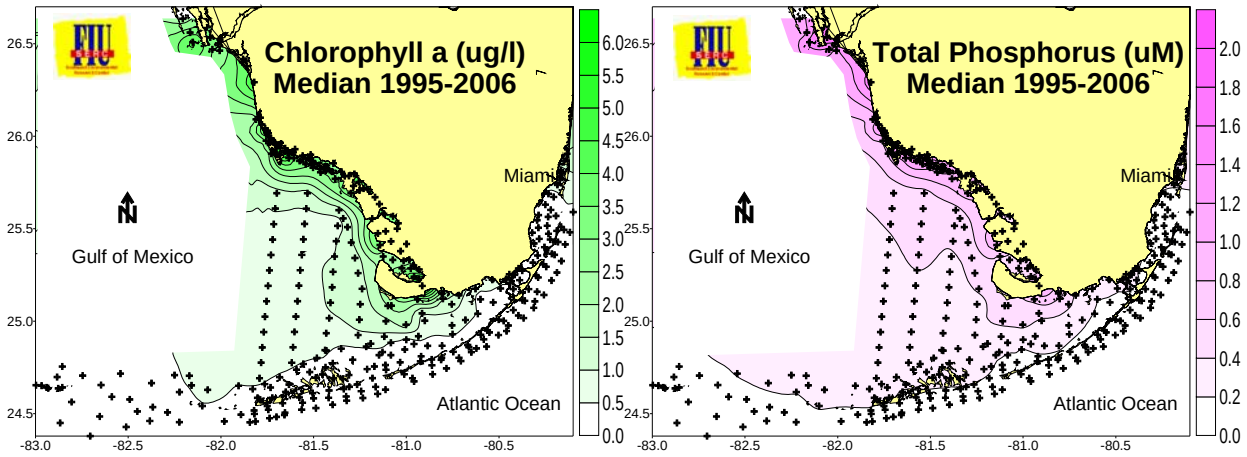

Figure 22

Clearly, there have been large changes in the FKNMS water quality over time, and some sustained monotonic trends have been observed, however, we must always keep in mind that trend analysis is limited to the window of observation. Trends may change, or even reverse, with additional data collection. This brings up another important point; when looking at what are perceived to be local trends, we find that they seem to occur across the whole region but at more damped amplitudes. This spatial autocorrelation in water quality is an inherent property of highly interconnected systems such as coastal and estuarine ecosystems driven by similar hydrological and climatological forcings. It is clear that trends observed inside the FKNMS are influenced by regional conditions outside the Sanctuary boundaries.

6. Discussion

Water quality is a subjective measure of ecosystem well being. Aside from the physical-chemical composition of the water there is also a human perceptual element which varies according to our intents for use (Kruczyinski and McManus 2002). 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. Most of the important anthropogenic inputs are regulated and most likely controlled by management activities, however, recent studies have shown that nutrients from shallow sewage injection wells may be leaking into nearshore surface waters (Corbett et al. 1999). 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 (Boyer and Jones 2002).

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 along-shore 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, Lee et al. 2002) 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. 3 and http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm). In Biscayne Bay, freshwater is released through the canal system operated by the South Florida Water Management District; the impact is clearly seen to affect northern Key Largo by causing episodic depressions in salinity at alongshore sites. Freshwater entering NE Florida Bay via overland flow from Taylor Slough and C-111 basin 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. 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 to impact the Shelf waters. 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 affect 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 as an increase in the range and variability of salinity rather than as a large depression in salinity.

In addition to surface currents there is evidence that internal tidal bores regularly impact the Key Largo reef tract (Leichter et al. 1996; Leichter and Miller 1999). 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 sub-thermocline water. According to $\Delta\sigma_t$, 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.

Surface SiO_2 concentrations exhibited a pattern similar to salinity. The source of SiO_2 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 CHLA concentrations of 76 $\mu g\ l^{-1}$ (Nelson and Dortch 1996), phytoplankton biomass on the Shelf (1-2 $\mu g\ l^{-1}$ CHLA) was not sufficient to account for the depletion of SiO_2 in this area. Therefore, SiO_2 concentrations on the Shelf were depleted mostly by mixing, allowing SiO_2 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 SiO_2 input to southern Biscayne Bay (Caccia and Boyer 2005), 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 SiO_2 to the nearshore Atlantic waters is through the Sluiceway and Backcountry (Fig. 19). SiO_2 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. There is an interesting peak in SiO_2 concentration in an area of the Sluiceway, which is densely covered with the seagrass, *Syringodium* (Fourqurean et al. 2002). We are unsure as to the source but postulate that it may be due to benthic flux.

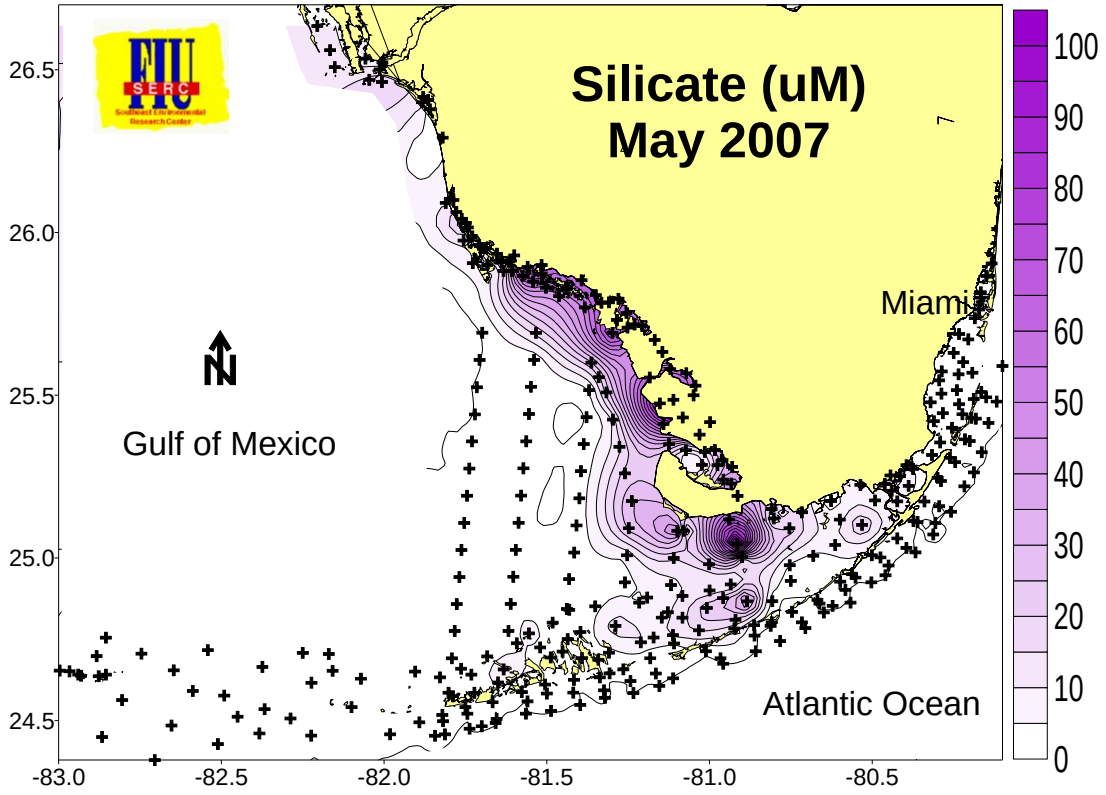

Figure 19. *Example of silicate distributions across the region during spring 2007.*

Visualization of spatial patterns of NO_3^- concentration over South Florida waters provide an extended view of source gradients over the region (see website). Biscayne Bay, Florida Bay, and the Shark River area of the west coast exhibited higher NO_3^- concentrations relative to the FKNMS and Shelf (Caccia and Boyer 2005, Boyer and Briceño 2007). 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 et al. 1997, Caccia and Boyer 2007). 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). We speculate that in both cases, elevated NO_3^- concentrations are the result of N_2 fixation/nitrification within the mangroves (Pelegri and Twilley 1998). The oceanside transects off the uninhabited Upper Keys (off Biscayne Bay in Seg. 9) exhibited the

lowest alongshore NO_3^- 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. 20). 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. We suggest this source of NO_3^- in the Keys is the due to human shoreline development.

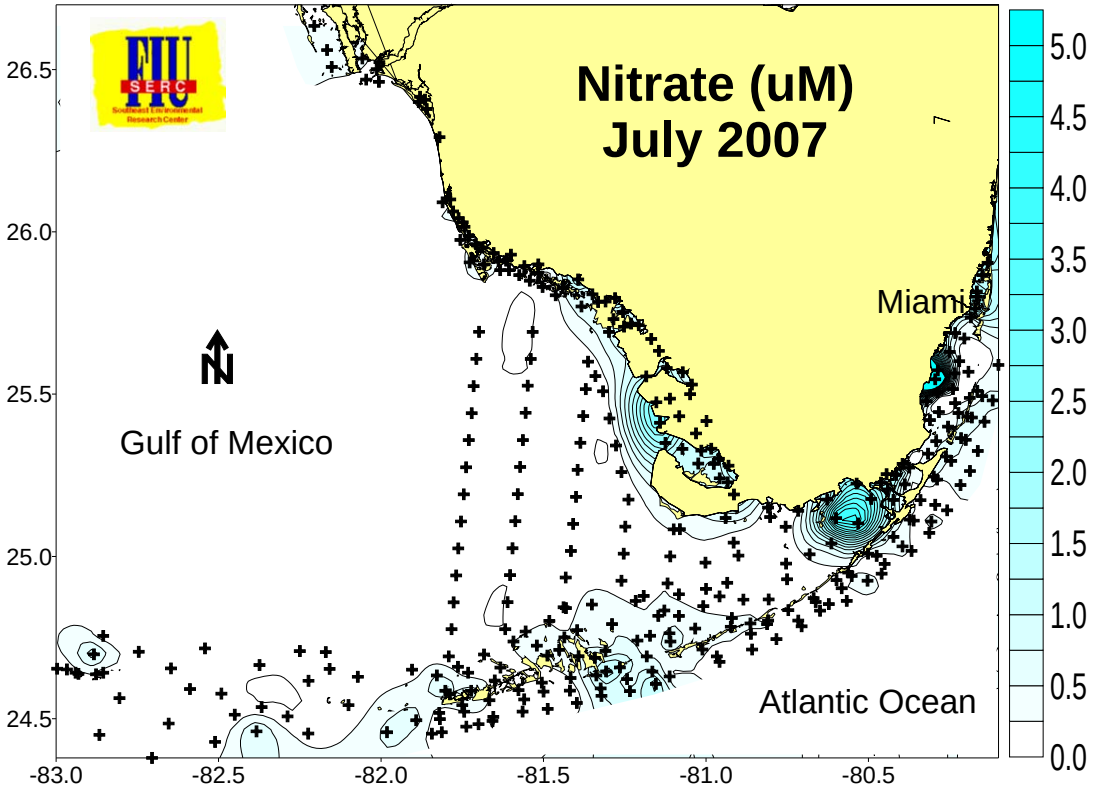

Figure 20. *Example of nitrate distributions across the region during summer 2007.*

Figure 20 also shows that a distinct intensification of NO_3^- occurs in the Backcountry region. Part of this increase may due to 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 also exhibits high NO_3^- which is uninhabited by man, which 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 locally elevated salinity values. Another possibility is a contribution of benthic N_2 fixation/nitrification in this very shallow area.

NH_4^+ concentrations were distributed in a similar manner as NO_3^- with highest levels occurring in Florida Bay, the Ten Thousand Islands, and the Backcountry (Fig. 21). 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 offshore implies an onshore N source which is diluted with distance from land by low nutrient Atlantic Ocean waters.

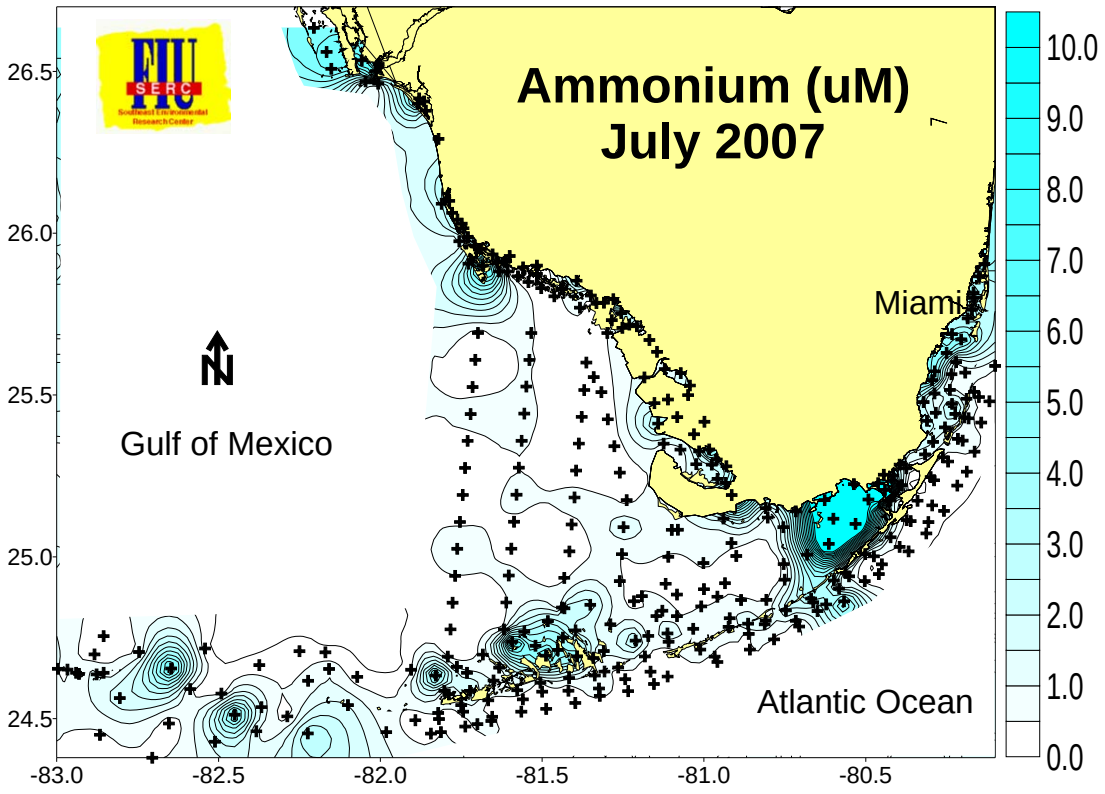

Figure 21. *Example of ammonium distributions across the region during summer 2007.*

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 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 sources (Fig. 22). A small gradient in TP extended from the inshore waters of Whitewater Bay - Ten Thousand Islands mangrove complex out onto the Shelf and Tortugas. A weak gradient also extended from north central Florida Bay to the Middle Keys. It has been postulated that groundwater may be a source of TP in this region, however, what evidence exists does not indicate a significant subterranean source (Corbett et al. 2000). However, there is evidence of a significant terrestrial source of TP to Biscayne Bay (Caccia and Boyer 2007).

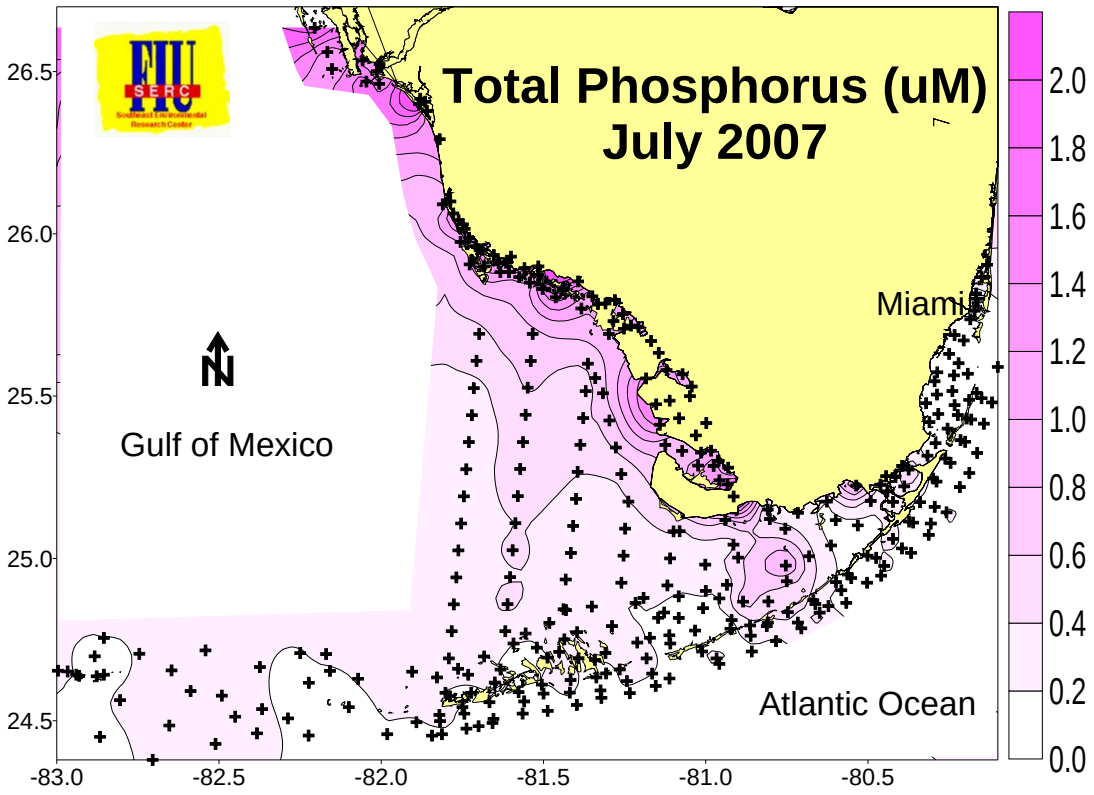

Figure 22*. Example of total phosphorus distributions across the region during summer 2007.*

In the Keys, there was evidence of elevated TP in alongshore stations of the Middle and Lower Keys but the differences were very small. 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); most is organic P. 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 (Appendix). 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 organic P. It is unlikely that the source of TP 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 TP 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 (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 (Meeder et al. 1997).

Concentrations of TOC (Fig. 23) and TON (Appendix) 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 also observed in Biscayne Bay. Both these gradients were most probably 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, Boyer et al. 1997).

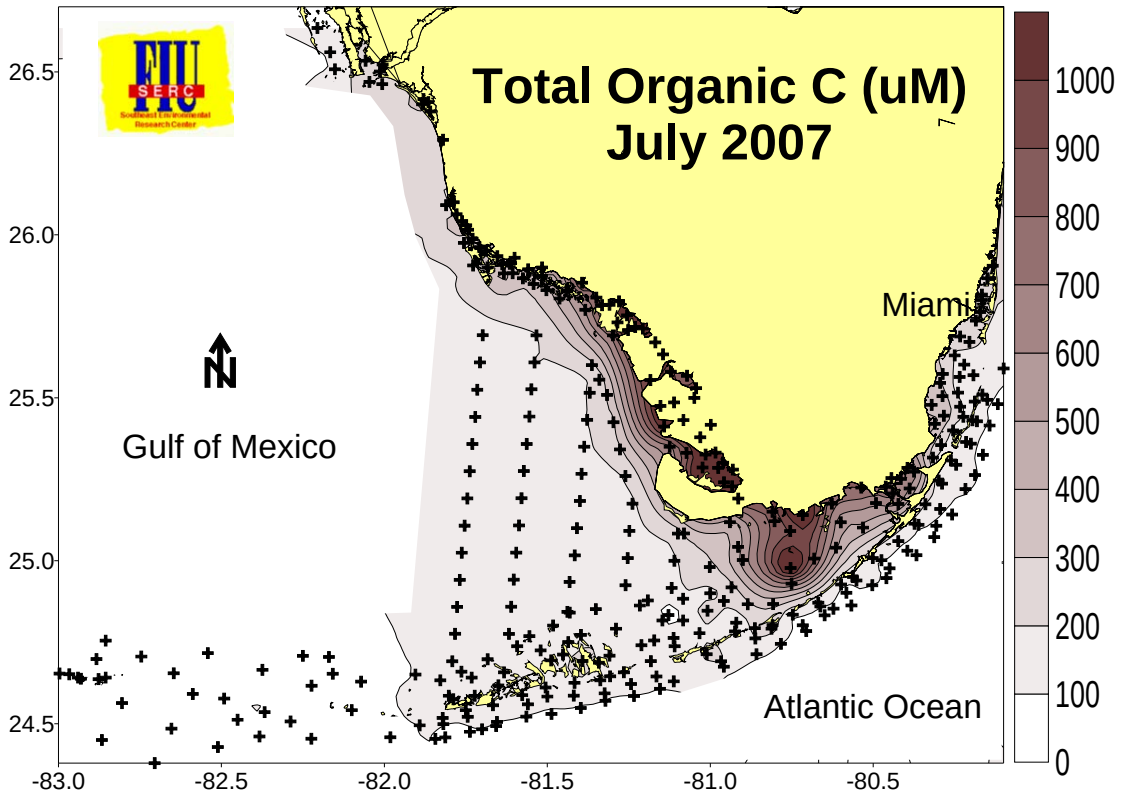

Figure 23*. Example of total organic carbon distributions across the region during summer 2007.*

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. Strong offshore gradients in TOC and TON existed for all mainland Keys segments 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 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 CHLA concentrations showed that NW Florida Bay, Whitewater Bay, and the Ten Thousand Islands exhibited high levels of CHLA relative to Biscayne Bay, Shelf, and FKNMS (Fig. 24). The highest CHLA concentrations were found in west coast mangrove estuaries (up to 45 $\mu g\ l^{-1}$ in Alligator Bay, TTI). CHLA is also routinely higher (~2 $\mu g\ l^{-1}$) in NW Florida Bay along the channel

connecting the Shelf to Flamingo. It is interesting that CHLA concentrations are higher in the Marquesas (0.36 µg l^{-1}) than in other areas of the FKNMS. 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 historically rich Tortugas shrimping grounds. A CHLA concentration of 2 µg l^{-1} in the water column of a reef tract might be considered an indication of eutrophication. Conversely, a similar CHLA level in the Quicksands indicates a productive ecosystem which feeds a valuable shrimp fishery.

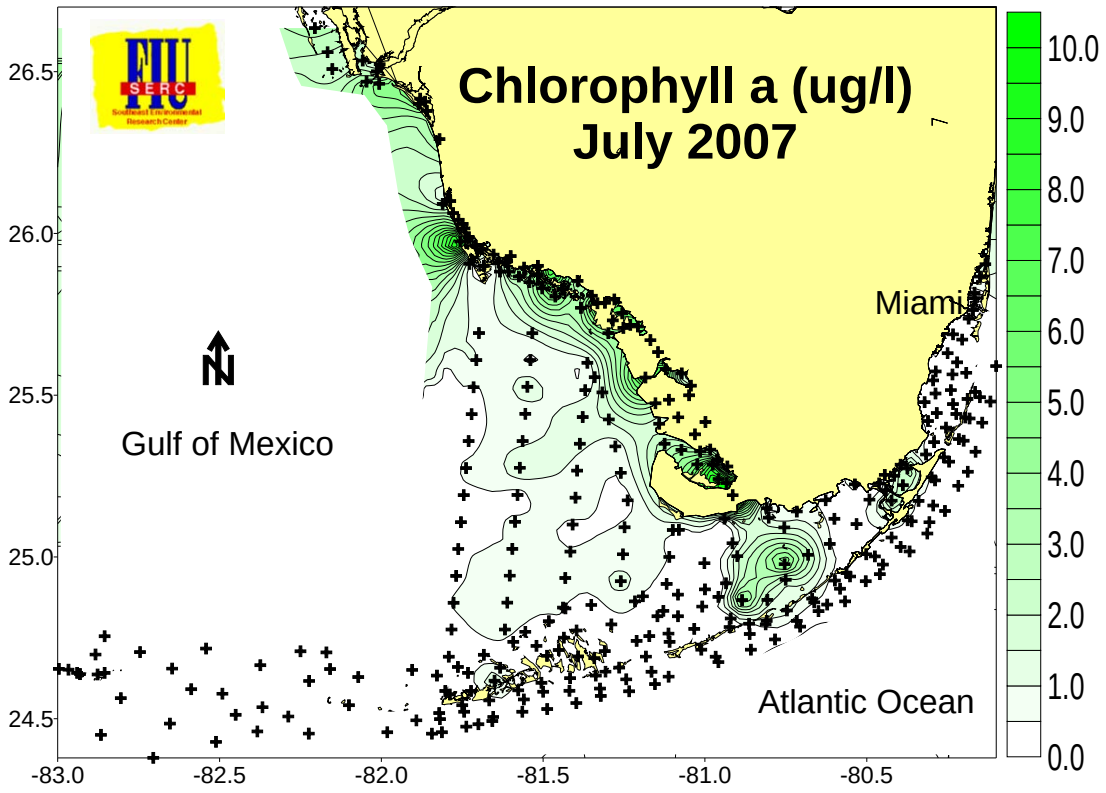

Figure 24. *Example of chlorophyll a distributions across the region during summer 2007.*

The oceanside transects in the Upper Keys exhibited the lowest overall CHLA concentrations of any zone in the FKNMS. Transects off the Middle and Lower Keys showed that a drop in CHLA occurred at reef tract sites; there was no linear decline with distance from shore. Interestingly, CHLA concentrations in the Tortugas transect showed a similar pattern as the mainland Keys. Inshore and Hawk Channel CHLA concentrations among Middle Keys, Lower

Keys and Tortugas sites were not significantly different. As inshore CHLA concentrations in the Tortugas were similar to those in the Middle and Lower Keys, we see no evidence of persistent phytoplankton bloom transport from Florida Bay.

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 25). The fine grained, low density carbonate sediments in this area are easily resuspended, rapidly transported, and have high light scattering potential. Sustained high turbidity of the water column indirectly affects benthic community structure by decreasing light penetration, promoting seagrass extinction.

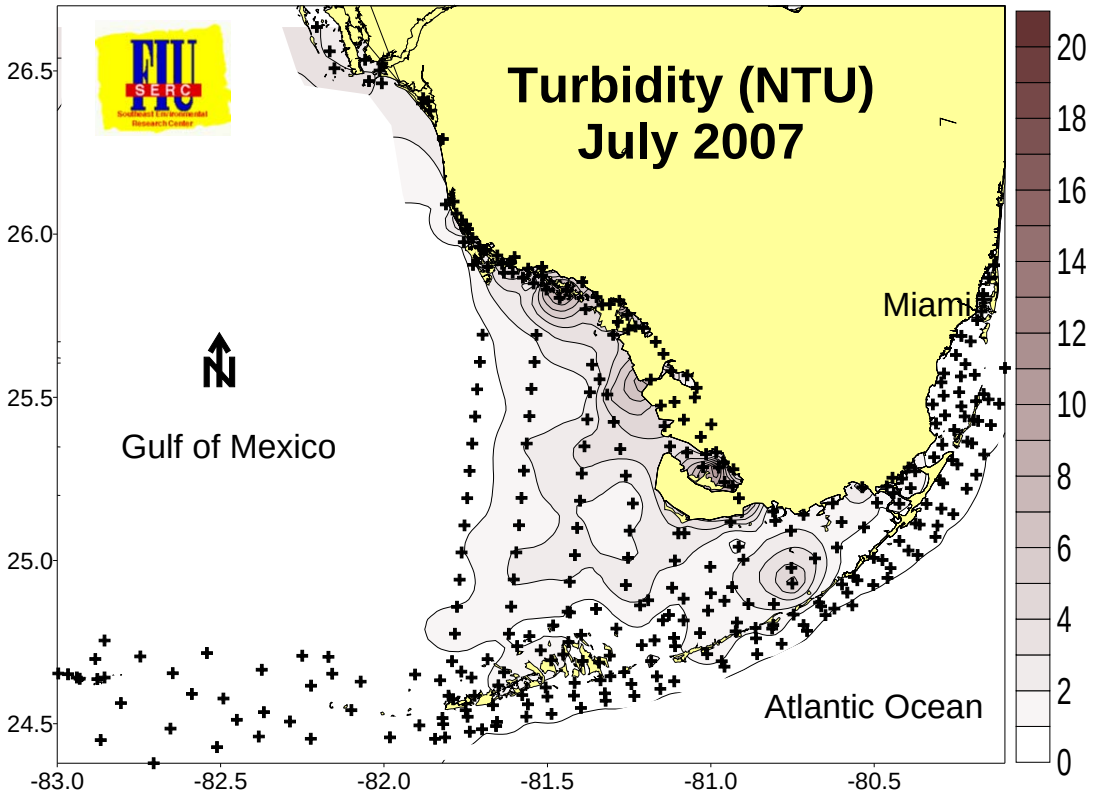

Figure 25. *Example of turbidity distributions across the region during summer 2007.*

Large scale observations of turbidity clearly show patterns of onshore-offshore gradients which extend out onto the Shelf to the Marquesas (Appendix; Stumpf et al. 1999). In the last ten years, turbidities in Florida Bay have increased dramatically in the NE and central regions (Boyer et al. 1999, Boyer and Briceño 2007) 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 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. Light extinction (K_d) was highest alongshore and improved with distance from land. This trend was expected as light extinction is directly related to water turbidity.

Using the TN:TP ratio has been used as a relatively simple method of estimating potential nutrient limitation status of phytoplankton (Redfield 1967). Most of the South Florida hydroscape has TN:TP values >> 16:1, indicating the potential for phytoplankton to be limited by P at these sites. However, most of the TN is not available to phytoplankton while much of the TP is labile. Therefore, using the TN:TP ratio overestimates potential P limitation and should be recognized as such (Fig. 26).

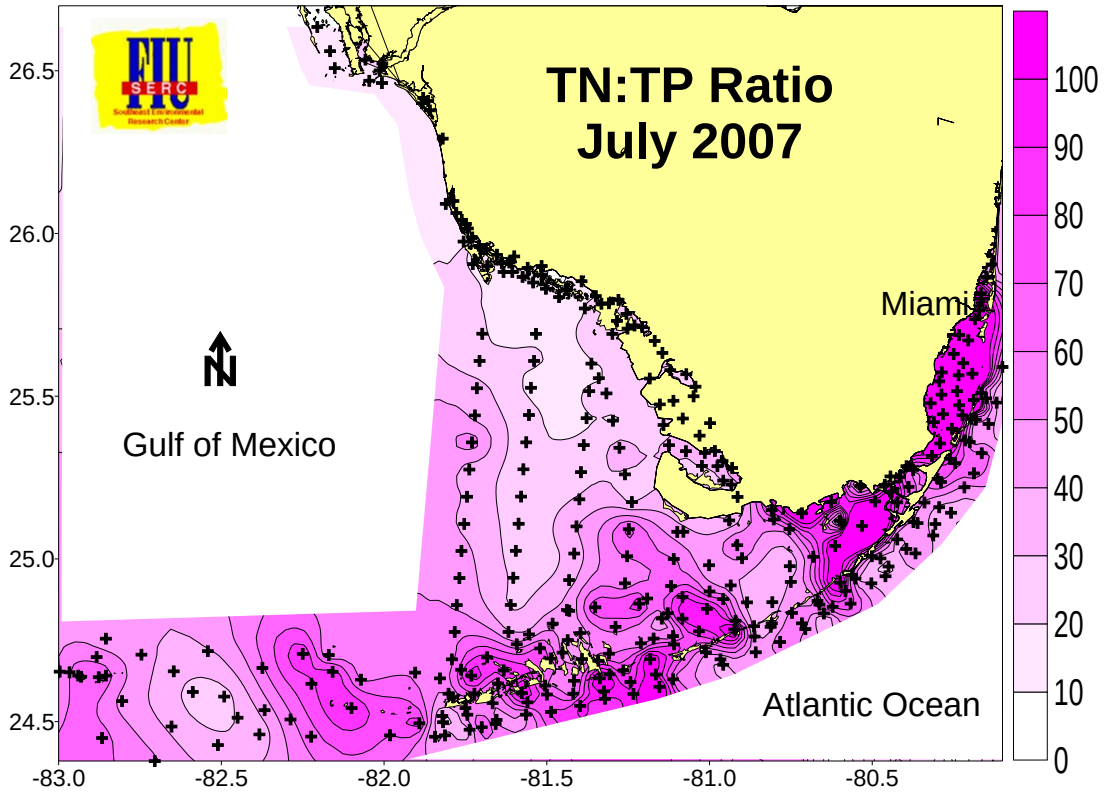

***Figure 26**. Example of DIN:TP ratio distribution across the region during summer 2006.*

The bulk of Florida Bay and both southern and northern Biscayne Bay were severely P limited, mostly as a result of high DIN concentrations. Most of the FKNMS is routinely P limited using this metric. Interestingly, the Shelf and Tortugas area was the least P limited of all zones and exhibited a significant regression between SRP and CHLA. 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 2006). 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).

This brings up an important point that, when looking at what are perceived to be local trends, we find that they seem to occur across the whole region but at more damped amplitudes. This spatial autocorrelation in water quality is an inherent property of highly interconnected systems such as coastal and estuarine ecosystems driven by similar hydrological and climatological forcings. Clearly, there have been large changes in the FKNMS water quality over time, and some sustained monotonic trends have been observed, however, we must always keep in mind that trend analysis is limited to the window of observation. Trends may change, or even reverse, with additional data collection.

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.

We continue to maintain a website (http://serc.fiu.edu/wqmnetwork/) where data from the FKNMS is integrated with the other parts of the SERC water quality network (Florida Bay, Whitewater Bay, Biscayne Bay, Ten Thousand Islands, and SW Florida Shelf) and displayed as downloadable contour maps, time series graphs, and interpretive reports.

One note of importance is that the South Florida Water Management District cancelled all funding for monitoring of the SW Florida Shelf effective Oct.1, 2007. We thank the FKNMS Sanctuary Advisory Committee and EPA for their letter of support

6.1.Acknowledgments

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8. Appendices

8.1. Appendix 1

Color contour maps of water quality variables by sampling event may be viewed and downloaded at http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm. These maps encompass all 354 stations of the SERC Water Quality Monitoring Network which includes the FKNMS, Biscayne Bay, Florida Bay, Whitewater Bay, Ten Thousand Islands, and Southwest Florida Shelf. The data was collected over a period of a month so care should be taken in interpreting these maps as they are not truly synoptic.

8.2.Appendix 2

Table 3. Statistical summary of water quality in zones for the period of record. Data are summarized as median, minimum (Min.), maximum value (Max.), and number of samples (*n*).

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	0.10	0.00	3.04	586
NO_3^-	2	0.09	0.00	1.33	82
(μM)	3	0.06	0.00	2.30	2506
	4	0.06	0.00	0.81	209
	5	0.18	0.00	2.11	821
	6	0.09	0.00	5.90	1221
	7	0.30	0.00	4.42	459
	8	0.06	0.00	2.11	501
Bottom	1	0.04	0.00	1.33	43
NO_3^-	2				
(μM)	3	0.08	0.00	4.46	2351
	4				
	5	0.12	0.00	1.17	136
	6	0.09	0.00	5.01	1017
	7	0.06	0.01	0.39	3
	8	0.07	0.00	1.94	334
Surface	1	0.06	0.00	0.45	586
NO_2^-	2	0.06	0.00	0.25	82
(μM)	3	0.03	0.00	0.71	2513
	4	0.05	0.00	0.35	209
	5	0.06	0.00	0.25	823
	6	0.04	0.00	0.42	1222
	7	0.09	0.00	0.40	459
	8	0.04	0.00	0.37	500
Bottom	1	0.04	0.01	0.20	43
NO_2^-	2				
(μM)	3	0.04	0.00	1.73	2356
	4				
	5	0.06	0.00	0.25	137
	6	0.05	0.00	0.36	1017
	7	0.06	0.04	0.10	4
	8	0.05	0.00	0.32	334

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	0.39	0.00	4.97	585
NH_4^+	2	0.38	0.07	10.32	82
(μM)	3	0.24	0.00	2.73	2513
	4	0.27	0.00	3.17	209
	5	0.38	0.00	4.03	823
	6	0.27	0.00	5.03	1221
	7	0.54	0.00	4.62	459
	8	0.27	0.00	2.21	499
Bottom	1	0.27	0.00	0.95	43
NH_4^+	2				
(μM)	3	0.24	0.00	2.90	2352
	4				
	5	0.33	0.03	2.49	137
	6	0.27	0.00	3.88	1016
	7	0.44	0.30	0.64	4
	8	0.28	0.00	1.91	334
Surface	1	15.37	2.46	71.94	587
TN	2	15.52	3.90	63.44	82
(μM)	3	9.42	1.00	67.85	2510
	4	15.40	3.14	69.95	209
	5	14.41	0.92	86.60	821
	6	11.10	0.73	213.21	1217
	7	16.27	2.37	73.72	460
	8	12.48	2.18	70.17	501
Bottom	1	11.88	2.47	43.09	43
TN	2				
(μM)	3	9.04	0.88	56.87	2343
	4				
	5	13.88	2.61	52.83	132
	6	11.04	0.96	153.75	1002
	7	17.78	15.53	21.80	3
	8	11.26	2.30	95.88	334
Surface	1	14.61	0.98	71.65	585
TON	2	14.51	3.41	62.91	82
(μM)	3	8.95	0.00	67.72	2500
	4	14.82	2.89	69.19	209
	5	13.70	0.51	85.88	816
	6	10.50	0.39	212.89	1213
	7	15.22	1.32	73.23	459
	8	11.79	1.55	70.00	499

Variable	Cluster	Median	Min.	Max.	*n*
Bottom	1	11.32	2.21	42.78	43
TON	2				
(μM)	3	8.47	0.00	56.54	2324
	4				
	5	13.22	2.27	52.67	132
	6	10.44	0.00	153.43	996
	7	15.91	15.14	16.68	2
	8	10.60	1.90	95.77	333
Surface	1	0.26	0.07	1.09	585
TP	2	0.24	0.10	0.83	82
(μM)	3	0.17	0.00	1.22	2513
	4	0.21	0.05	0.50	209
	5	0.19	0.02	1.39	825
	6	0.17	0.00	1.78	1223
	7	0.19	0.03	0.84	460
	8	0.25	0.05	1.35	499
Bottom	1	0.21	0.08	0.45	42
TP	2				
(μM)	3	0.17	0.00	1.50	2350
	4				
	5	0.17	0.02	0.77	132
	6	0.17	0.00	1.02	1011
	7	0.18	0.14	0.39	3
	8	0.23	0.05	0.67	333
Surface	1	0.02	0.00	0.30	586
SRP	2	0.02	0.00	0.22	82
(μM)	3	0.02	0.00	0.23	2502
	4	0.02	0.00	0.26	209
	5	0.02	0.00	0.56	820
	6	0.02	0.00	0.21	1221
	7	0.02	0.00	0.20	459
	8	0.02	0.00	0.20	500
Bottom	1	0.02	0.00	0.17	43
SRP	2				
(μM)	3	0.02	0.00	0.39	2347
	4				
	5	0.02	0.00	0.15	137
	6	0.02	0.00	0.36	1013
	7	0.01	0.01	0.11	5
	8	0.02	0.00	0.16	334

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	0.09	0.01	5.62	583
APA	2	0.09	0.02	0.55	82
(μM hr^{-1})	3	0.04	0.01	0.79	2395
	4	0.08	0.01	0.52	209
	5	0.07	0.01	2.52	819
	6	0.06	0.00	0.50	1211
	7	0.09	0.02	1.43	460
	8	0.06	0.02	3.03	471
Bottom	1	0.05	0.02	0.46	39
APA	2				
(μM hr^{-1})	3	0.04	0.00	0.44	2233
	4				
	5	0.07	0.00	0.49	135
	6	0.06	0.01	0.50	1010
	7	0.05	0.05	0.05	2
	8	0.05	0.02	0.34	305
Surface	1	0.32	0.00	15.24	587
Chl *a*	2	0.30	0.00	4.95	82
(μg l^{-1})	3	0.21	0.00	3.12	2510
	4	0.20	0.00	7.35	208
	5	0.22	0.00	2.79	825
	6	0.21	0.00	2.02	1223
	7	0.20	0.00	6.20	459
	8	0.47	0.00	6.81	501
Surface	1	230.01	88.54	1435.42	586
TOC	2	231.33	135.31	505.54	82
(μM)	3	144.17	18.38	1054.79	2511
	4	239.85	132.00	702.50	209
	5	210.02	28.81	670.25	823
	6	164.52	22.79	805.31	1217
	7	238.38	84.98	1653.54	459
	8	183.65	68.85	950.44	501
Bottom	1	178.54	88.11	446.04	43
TOC	2				
(μM)	3	142.75	0.00	883.10	2343
	4				
	5	206.17	78.56	392.63	136
	6	162.54	21.69	2135.83	1007
	7	225.90	147.40	281.73	3
	8	161.79	75.83	847.71	335

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	1.53	0.00	89.00	557
SiO_2	2	4.74	0.00	55.16	78
(μM)	3	0.26	0.00	17.90	2391
	4	7.07	0.30	88.53	199
	5	1.71	0.00	127.11	784
	6	0.67	0.00	18.95	1167
	7	1.93	0.00	37.36	436
	8	0.99	0.00	22.43	477
Bottom	1	1.05	0.00	3.93	40
SiO_2	2				
(μM)	3	0.30	0.00	17.89	2236
	4				
	5	1.60	0.00	30.20	130
	6	0.77	0.00	18.35	966
	7	0.32	0.30	0.34	2
	8	0.96	0.00	9.71	318
Surface	1	1.31	0.00	37.00	581
Turbidity	2	1.13	0.20	5.55	82
(NTU)	3	0.33	0.00	10.14	2486
	4	0.79	0.00	7.70	208
	5	0.86	0.00	16.20	821
	6	0.55	0.00	8.80	1221
	7	0.95	0.00	17.35	458
	8	1.33	0.00	11.84	493
Bottom	1	1.67	0.00	9.10	52
Turbidity	2				
(NTU)	3	0.36	0.00	11.18	2329
	4				
	5	0.77	0.00	16.90	156
	6	0.56	0.00	7.95	1020
	7	0.72	0.00	4.89	12
	8	1.58	0.00	15.96	331
Surface	1	36.14	28.79	39.64	585
Salinity	2	36.22	29.59	40.30	82
	3	36.19	26.70	37.80	2488
	4	36.10	27.69	40.90	208
	5	36.30	29.51	40.00	798
	6	36.24	28.02	38.50	1200
	7	36.40	27.95	40.39	452
	8	36.15	30.33	39.06	493

Variable	Cluster	Median	Min.	Max.	*n*
Bottom Salinity	1	36.13	28.77	39.66	585
	2	36.21	29.62	40.20	81
	3	36.20	32.63	37.80	2478
	4	36.07	27.69	40.90	208
	5	36.39	29.52	40.00	792
	6	36.28	30.48	38.50	1192
	7	36.40	27.99	40.37	449
	8	36.18	30.41	39.14	490
Surface Temperature (^{o}C)	1	26.71	17.32	36.10	586
	2	26.94	17.49	32.65	82
	3	26.89	16.30	32.20	2489
	4	27.64	17.69	34.56	208
	5	27.62	15.10	39.60	799
	6	27.42	15.40	33.00	1203
	7	27.57	17.78	35.00	452
	8	26.10	17.75	34.50	494
Bottom Temperature (^{o}C)	1	26.78	17.32	33.40	585
	2	26.90	17.49	32.36	81
	3	26.20	16.30	32.00	2479
	4	27.66	17.69	32.99	208
	5	27.67	15.10	33.40	795
	6	27.22	15.40	32.60	1194
	7	27.58	17.78	36.80	449
	8	25.95	17.68	34.50	491
Surface DO (mg l^{-1})	1	6.20	0.91	11.30	586
	2	5.88	4.23	8.11	82
	3	5.90	0.08	13.53	2467
	4	6.13	1.60	10.50	208
	5	5.97	0.64	10.80	793
	6	5.80	1.48	14.53	1197
	7	5.96	1.67	9.70	452
	8	6.14	2.26	10.80	493
Bottom DO (mg l^{-1})	1	6.20	2.70	11.40	585
	2	5.97	4.31	8.10	81
	3	5.90	1.35	13.90	2441
	4	6.20	4.30	10.60	208
	5	6.00	2.78	10.30	791
	6	5.90	3.19	9.80	1185
	7	5.99	2.10	9.80	449
	8	6.20	3.00	10.90	489

Variable	Cluster	Median	Min.	Max.	*n*
K_d	1	0.31	0.00	3.18	454
(m^{-1})	2	0.30	0.01	3.72	52
	3	0.13	0.00	2.75	1740
	4	0.36	0.01	3.27	109
	5	0.30	0.01	3.14	499
	6	0.20	0.00	3.41	833
	7	0.33	0.01	4.08	315
	8	0.27	0.01	3.31	361
Surface	1	91.60	12.92	165.46	586
DO_{sat}	2	89.29	63.88	118.95	82
(%)	3	87.92	1.23	191.57	2467
	4	92.87	23.03	148.20	208
	5	88.53	9.74	153.34	793
	6	86.89	22.70	226.21	1196
	7	89.22	25.82	134.81	452
	8	90.90	31.23	169.87	493
Bottom	1	91.48	41.56	166.85	585
DO_{sat}	2	90.23	65.37	125.13	81
(%)	3	87.65	19.29	207.01	2440
	4	94.27	65.20	149.62	208
	5	89.26	42.89	152.24	791
	6	87.70	46.74	144.02	1184
	7	89.75	32.44	132.00	449
	8	91.23	41.17	171.44	489
$\Delta\sigma_t$	1	0.00	-1.50	6.53	584
(kg m^{-3})	2	0.00	-0.22	0.37	81
	3	0.04	-3.19	6.64	2467
	4	0.00	-0.37	1.96	208
	5	0.00	-1.44	5.66	788
	6	0.03	-3.05	6.00	1188
	7	0.00	-4.42	4.36	449
	8	0.01	-0.74	3.74	491