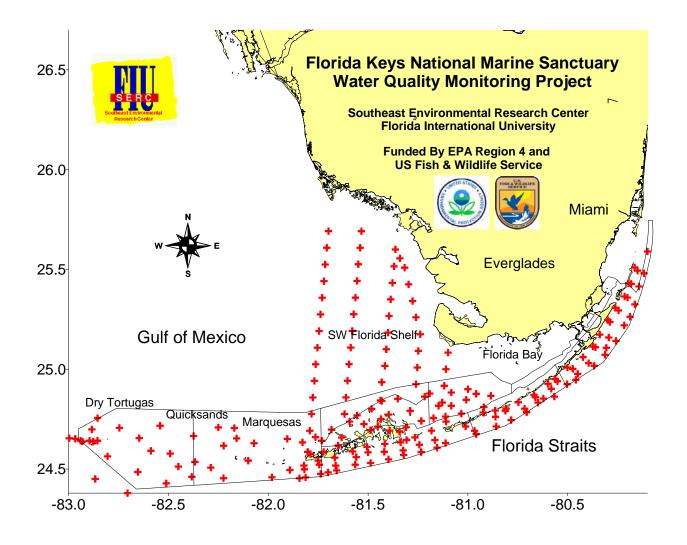
# 2010 ANNUAL REPORT OF THE WATER QUALITY MONITORING PROJECT FOR THE WATER QUALITY PROTECTION PROGRAM OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY



Joseph N. Boyer, Ph.D. and Henry O. Briceño, Ph.D.

Southeast Environmental Research Center OE-148, Florida International University Miami, FL 33199 <u>http://serc.fiu.edu/wqmnetwork/</u> This page is intentionally left blank

# 2010 ANNUAL REPORT OF THE WATER QUALITY MONITORING PROJECT FOR THE WATER QUALITY PROTECTION PROGRAM OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY

Principal Investigators Joseph N. Boyer, Ph.D. and Henry O. Briceño, Ph.D.

Southeast Environmental Research Center OE-148, Florida International University Miami, FL 33199 <u>http://serc.fiu.edu/wqmnetwork/</u>

US EPA Agreement #X7-96410604-6

This is Technical Report #536 of the Southeast Environmental Research Center, Florida International University. This page is intentionally left blank

# 2010 ANNUAL REPORT OF THE WATER QUALITY MONITORING PROJECT FOR THE WATER QUALITY PROTECTION PROGRAM OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY

Joseph N. Boyer, Ph.D. and Henry O. Briceño, Ph.D. Southeast Environmental Research Center OE-148, Florida International University Miami, FL 33199

Funded by the Environmental Protection Agency (X7-96410604-6) with contributions from US Fish & Wildlife Service

#### **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. 2010 and includes data from 62 quarterly sampling events at 155 stations within the FKNMS and SW Florida Shelf, including the Dry Tortugas National Park.

Field parameters measured at each station include salinity (practical salinity scale), temperature ( $^{\circ}$ C), dissolved oxygen (DO, mg | $^{-1}$ ), turbidity (NTU), relative fluorescence, and light attenuation (K<sub>d</sub>, m $^{-1}$ ). Water quality variables include the dissolved nutrients nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), dissolved inorganic nitrogen (DIN), and soluble reactive phosphate (SRP). Total unfiltered concentrations include those of nitrogen (TN), organic nitrogen (TON), organic carbon (TOC), phosphorus (TP), silicate (SiO<sub>2</sub>) and chlorophyll *a* (CHLA, µg | $^{-1}$ ).

The EPA developed Strategic Targets for the Water Quality Monitoring Project which state that beginning in 2008 through 2011, they shall 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 (K<sub>d</sub>, 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 2010.

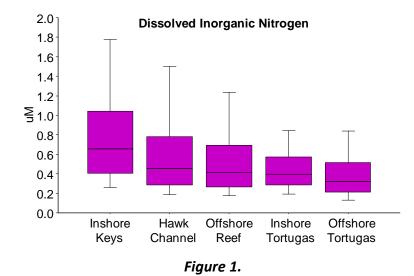
### Table 1: EPA WQPP WQ Targets from 1995-2005 Baseline

Targets for reef sites include chlorophyll *a* less than or equal to 0.35 micro grams/l and vertical attenuation coefficient for downward irradiance ( $K_d$ , i.e., light attenuation) less than or equal to 0.20 per meter. Targets for all sites in FKNMS include dissolved inorganic nitrogen (DIN) less than or equal to 0.75 micromolar and total phosphorus (TP) less than or equal to 0.25 micromolar. Compliances were calculated as percent of those achieving targets divided by total number of samples. Values in green are those years with % compliance greater than 1995-2005 baseline. Values in yellow are those years with % compliance less than 1995-2005 baseline.

	Reef S	tations	All Stations		
Year	CHLA ≤ 0.35 μg l <sup>-1</sup>	K <sub>d</sub> ≤ 0.20 m <sup>-1</sup>	DIN ≤ 0.75 μM (0.010 ppm)	TP ≤ 0.25 μM (0.0077 ppm)	
<mark>1995-05</mark>	1778 of 2367 (75.1%)	1042 of 1597 (65.2%)	7826 of 10254 (76.3%)	7810 of 10267 (76.1%)	
2006	196 of 225 (87.1%)	199 of 225 (88.4%)	<mark>432 of 990 (43.6%)</mark>	<mark>316 of 995 (31.8%)</mark>	
2007	198 of 226 (87.6%)	202 of 222 (91.0 %)	<mark>549 of 993 (55.3%)</mark>	<mark>635 of 972 (65.3%)</mark>	
2008	177 of 228 (77.6%)	181 of 218 (83.0%)	836 of 1,000 (83.6%)	<mark>697 of 1,004 (69.4%)</mark>	
2009	208 of 228 (91.2%)	189 of 219 (86.3%)	858 of 1,003 (85.5%)	869 of 1,004 (86.6%)	
2010	<mark>170 of 227 (74.9%)</mark>	176 of 206 (85.4%)	843 of 1000 (84.3%)	738 of 1,003 (73.6%)	

#### **EPA WQPP Water Quality Targets**

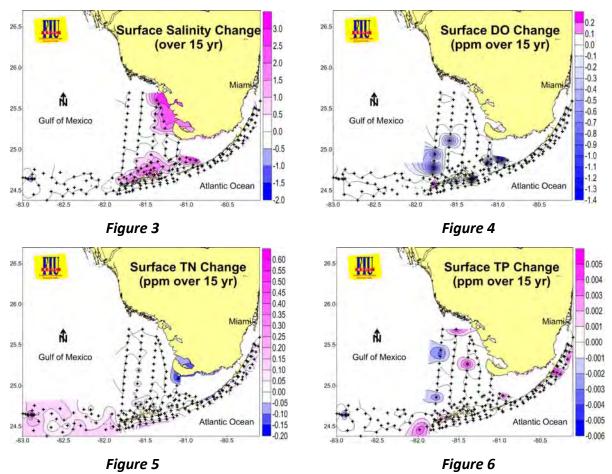
Several important results have been realized from this monitoring project. First, is documentation of elevated nitrate in the inshore waters of the Keys (Fig. 1). This result was evident from our first sampling event in 1995 and continues to be a characteristic of the ecosystem. Interestingly, this gradient 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.



Some variables showed noteworthy differences over the period of record (Fig 2). Since the 2005 hurricane season, water quality on the reef, especially DIN, have been elevated but have mostly returned to normal levels.

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 forcing. It is clear that trends observed inside the FKNMS are influenced by regional conditions outside the Sanctuary boundaries.

Trend analysis has shown that many variables have undergone significant changes in concentration over the 15 year period of record. Examples for salinity, DO, TN and TP are shown in Figures 3-6.



For 2010, in all regions of the FKNMS, water quality has returned to conditions prior to 2005 hurricane season (Fig. 7). Overall, TOC remains lower than the long term median mostly because it has been declining over the years. DO and light penetration were better than the norm.

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 (<u>http://serc.fiu.edu/wqmnetwork/</u>) where data and reports from the FKNMS is integrated with the other programs are available.

# **Table of Contents**

1.	Project Background	. 11
2.	Methods	. 14
2.1.	Field Sampling	. 14
2.2.	Laboratory Analysis	. 15
2.3.	Objective Classification Analysis	. 16
2.5.	Contour Maps	. 17
2.6.	Time Series Analysis	. 18
3.	Results	. 19
3.1.	Overall Water Quality of the FKNMS	. 19
3.2.	Objective Classification Analysis	. 21
3.3.	Contour Maps	. 25
3.4.	Time Series Analysis	. 28
4.	Overall Trends	. 41
4.1.	Strategic Targets	. 42
5.	Discussion	. 44
5.1.	Acknowledgments	. 71
6.	References	. 72
7.	Appendix 1	. 76

# 1. Project Background

The Florida Keys are an 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 original agreement 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.

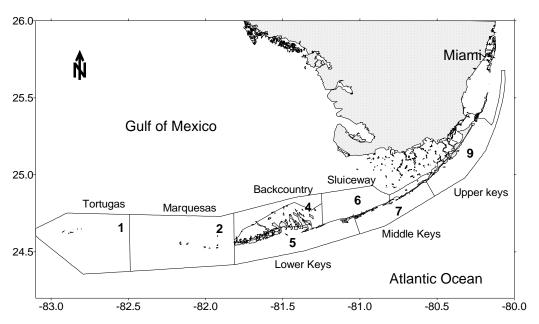


Figure 1. Map of FKNMS boundary including Segment numbers and common names.

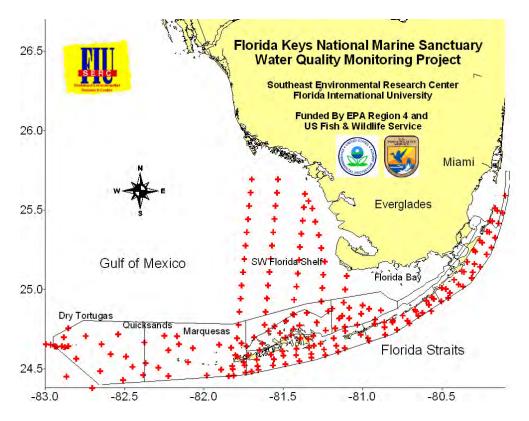
The waters of the FKNMS are characterized by complex water circulation patterns over both spatial and temporal scales with much of this variability due to seasonal influence in regional circulation regimes. The FKNMS is directly influenced by the Florida Current, the Gulf of Mexico Loop Current, inshore 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 (Gibson et al. 2008). 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 (Marguesas) includes the Marguesas 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 155 stations in the FKNMS, as well as SFWMD 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 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 and SW Florida Shelf.

## 2. Methods

#### 2.1. Field Sampling

The period of record of this study was from March 1995 to December 2010 which included 62 quarterly sampling events. For each event, field measurements and grab samples were collected from 155 fixed stations within the FKNMS boundary (Fig. 2). Depth profiles of temperature (°C), salinity (practical salinity scale), dissolved oxygen (DO, mg l<sup>-1</sup>), photosynthetically active radiation (PAR,  $\mu$ E m<sup>-2</sup> s<sup>-1</sup>), *in situ* chlorophyll *a* specific fluorescence (FSU), turbidity (NTU), depth as measured by pressure transducer (m), and density ( $\sigma_t$ , in kg m<sup>-3</sup>) 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<sub>d</sub>, m<sup>-1</sup>) 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<sup>-3</sup>), 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 every 0.5 m using a Li-Cor LI-1400 DataLogger equipped with a  $4\pi$  spherical sensor (LI-193SB). PAR data with depth was used to calculate K<sub>d</sub> 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 Niskin bottle (General Oceanics) except in the Backcountry, Sluiceway and SW Shelf 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/Shelf 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<sub>2</sub>), 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<sub>2</sub>-free air. TN was measured using an ANTEK 7000N Nitrogen Analyzer using O<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), and soluble reactive phosphorus (SRP) by flow injection analysis (Alpkem model RFA 300). Filters for CHLA content ( $\mu$ g l<sup>-1</sup>) 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 mg<sup>-1</sup> unless noted. All elemental ratios discussed were calculated on a molar basis. DO saturation in the water column (DO<sub>sat</sub> 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 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 hierarchical 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 (Briceno and Boyer 2010), 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 hierarchical cluster analysis algorithm with Ward distance calculations in order to aggregate stations into groups of similar water quality. The purpose of this analysis was to collapse the 155 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  $25^{th}$  and  $75^{th}$  percentiles (quartiles), and the ends of the whiskers are the  $5^{th}$  and  $95^{th}$  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 ( $<5^{th}$  and  $>95^{th}$  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.<u>Contour Maps</u>

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 Keys and Shelf data into contour maps of specific water quality variables (Surfer, Golden Software). We used kriging as the geostatistical algorithm because it is designed to minimize the error variance while at the same time maintaining point pattern continuity (Isaaks & Srivastava, 1989). Kriging is a general method of statistical interpolation that can be applied within any discipline to

sampled data from random fields that satisfy the appropriate mathematical assumptions. 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 to illustrate any temporal trends that might have occurred. Temporal trends were quantified by simple regression with significance set at P<0.10.

# 3. Results

#### 3.1. Overall Water Quality of the FKNMS

Summary statistics for all water quality variables from all 62 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 26.61 °C and salinity of 36.46; oxygen saturation of the water column (DO<sub>sat</sub>) was relatively high at 95.8%. On this coarse scale, the FKNMS exhibited very good water quality with median NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TP, and SiO<sub>2</sub> concentrations of 0.001, 0.003, 0.006, and 0.009 mg l<sup>-1</sup>, respectively. NH<sub>4</sub><sup>+</sup> 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 0.173 mg l<sup>-1</sup>). SRP concentrations were very low (median 0.001 mg l<sup>-1</sup>) and comprised only 6% of the TP pool. CHLA concentrations were also low overall, 0.24 µg l<sup>-1</sup>, but ranged from 0.01 to 7.38 µg l<sup>-1</sup>. TOC was 1. 763 mg l<sup>-1</sup>; a value higher than open ocean levels but consistent with coastal areas.

Median turbidity was low (0.67 NTU) as reflected in a low  $K_d$  (0.128 m<sup>-1</sup>). Overall, 27% 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 = 62.1) 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 2010 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 <sub>3</sub>	Surface	0.001	0.000	0.025	716
(mg l⁻¹)	Bottom	0.001	0.000	0.106	372
NO <sub>2</sub>	Surface	0.000	0.000	0.006	721
(mg l⁻¹)	Bottom	0.000	0.000	0.002	382
$NH_4^+$	Surface	0.003	0.000	0.098	722
(mg l <sup>-1</sup> )	Bottom	0.002	0.000	0.012	381
TN	Surface	0.173	0.036	0.584	722
(mg l <sup>-1</sup> )	Bottom	0.159	0.019	0.948	382
DIN	Surface	0.005	0.001	0.100	722
(mg l <sup>-1</sup> )	Bottom	0.004	0.000	0.115	379
TON	Surface	0.166	0.027	0.581	722
(mg l <sup>-1</sup> )	Bottom	0.155	0.013	0.946	379
ТР	Surface	0.006	0.001	0.038	722
(mg l <sup>-1</sup> )	Bottom	0.005	0.001	0.020	380
SRP	Surface	0.001	0.000	0.048	722
(mg l⁻¹)	Bottom	0.001	0.000	0.011	381
CHLA (mg l⁻¹)	Surface	0.240	0.011	7.383	722
тос	Surface	1.376	0.915	5.984	722
(mg l⁻¹)	Bottom	1.168	0.837	2.933	381
SiO <sub>2</sub>	Surface	0.009	0.000	2.758	722
(mg l⁻¹)	Bottom	0.006	0.000	0.605	381
Turbidity	Surface	0.672	0.032	23.893	706
(NTU)	Bottom	0.814	0.010	23.895	584
Salinity	Surface	36.46	34.08	41.90	686
	Bottom	36.47	34.23	39.92	683
Temperature	Surface	29.61	10.51	37.60	686
(°C)	Bottom	29.43	14.66	37.60	683
DO	Surface	6.22	4.74	9.58	686
(mg l <sup>-1</sup> )	Bottom	6.24	4.56	9.29	683
<b>K</b> <sub>d</sub> (m <sup>-1</sup> )		0.128	0.000	3.516	645
рН	Surface	7.940	6.160	8.220	105
TN:TP	Surface	62.111	15.976	345.300	722
DO Saturation	Surface	95.794	73.077	135.430	686
(%)	Bottom	96.185	70.132	134.928	683

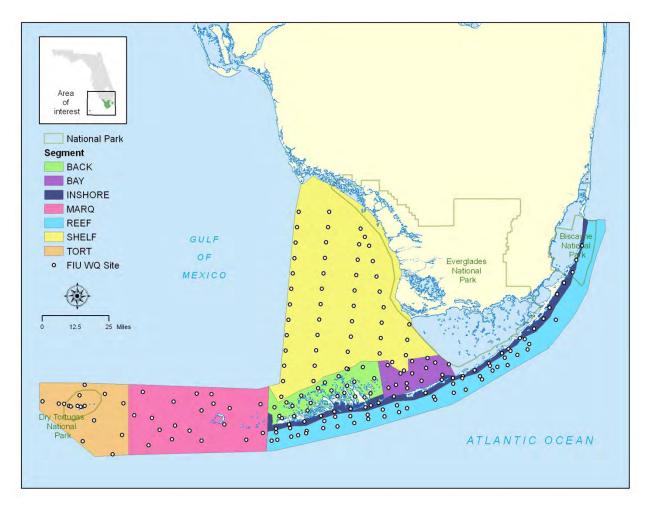
Variable	Depth	Median	Min.	Max.	n
I <sub>o</sub> (%)	Bottom	27.035	0.046	100.000	604
$\Delta \sigma_t$		0.005	-1.247	3.134	683
Si:DIN	Surface	0.909	0.007	289.371	721

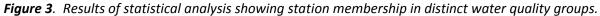
#### 3.2. Objective Classification Analysis

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. These five principal components accounted for 56.8% of the total variance of the original variables. PC1 had high factor loadings for NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, 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<sub>2</sub> 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.

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 hierarchical clustering algorithm used the mean and SD of the four factor scores of each station to classify all 155 sampling sites into 6 groups having robust correspondence in water quality (Fig. 3): Backcountry (BACK), western bayside Middle Keys (BAY), Inshore Keys (INSHORE), Marquesas (MARQ), Offshore Keys (Reef), and Tortugas (TORT). The SW Florida Shelf (SHELF) was assigned as a separate zone, making a total of 7 groups.





Although the differences among the 7 zones were subtle, they were statistically significant and allowed us to say that the overall nutrient gradient, from highest to lowest concentrations, was BACK>BAY>SHELF>INSHORE>MARQUESAS>REEF>TORT (Table 3).

The BACK zone was composed primarily stations located inside and north of the Lower Keys (Fig. 3). This group was highest in nutrients, especially  $NO_3^-$ ,  $NH_4^+$ , TN, and TP, as well as TOC (Fig. 4). In the shallow BACK sites we expect that either nutrient transport from the SW Shelf

and/or benthic flux of nutrients might be more important than anthropogenic loading. The BACK also had highest salinity and DO, relative to other regions.

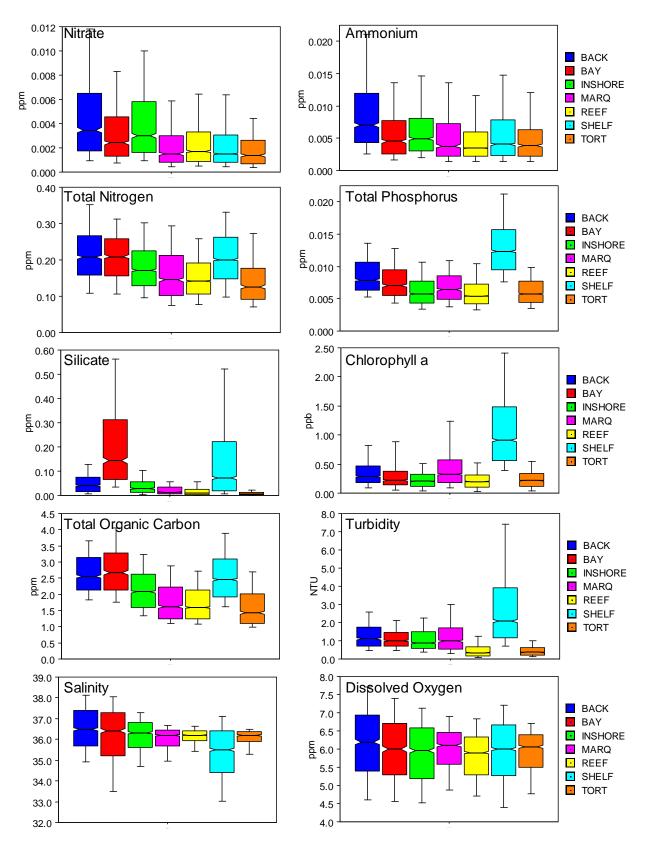
The BAY (Sluiceway) included sites most influenced by Florida Bay and water moving south from the SW Shelf. It was highest in SiO<sub>2</sub>, high in TN, TP, and TOC, but was relatively low in inorganic nutrients and CHLA. BAY sites had greatest range in salinity than the other areas.

The SHELF was composed of 49 stations located north of the jurisdictional boundary of the FKNMS. The SHELF is influenced by both Everglades freshwater discharge and by southward transport of coastal Gulf of Mexico waters. Therefore, SHELF waters greatly influence the FKNMS via advection of nutrients through the Middle and Lower Keys. The SHELF has highest TP, CHLA, and turbidity, high TN, SiO<sub>2</sub>, and lowest salinity of any other region.

The water quality of INSHORE, MARQ, REEF, and TORT zones was most similar to each other. The INSHORE and REEF zones may be interpreted as representing an onshore-offshore nutrient gradient. The INSHORE zone included the innermost sites of the Keys, which are shallow, closest to any possible anthropogenic nutrient sources, and typically more turbid than REEF zone from beach wave resuspension. These sites were slightly elevated in DIN, TN, and TOC relative to the REEF sites. The INSHORE zone had comparable TP and CHLA as in the REEF and TORT zones. No significant inshore-offshore gradient was observed for TP or CHLA.

The MARQ zone was made up of sites between Key West and Rebecca Shoals. This is an area of relatively shallow water which separates the SW Shelf from the Atlantic Ocean. The MARQ zone had higher TP, CHLA, and turbidity than TORT and REEF zones but was comparable in N.

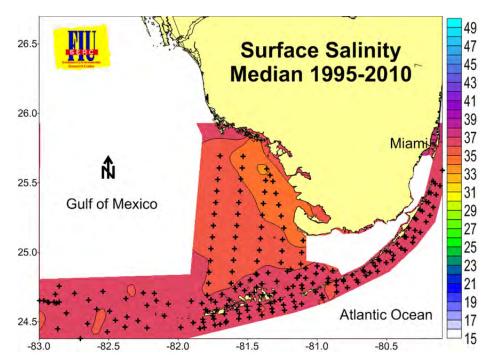
The REEF zone was made up of all Hawk Channel and reef tract sites of the mainland Keys. This zone had very low nutrients, TP, CHLA, and turbidity. The TORT zone was composed of all sites west of Rebecca Shoal, including those in Dry Tortugas National Park. The distinction between the REEF and TORT zones was driven by the slightly higher TN and TOC concentrations and lower TP found in the REEF zone.



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

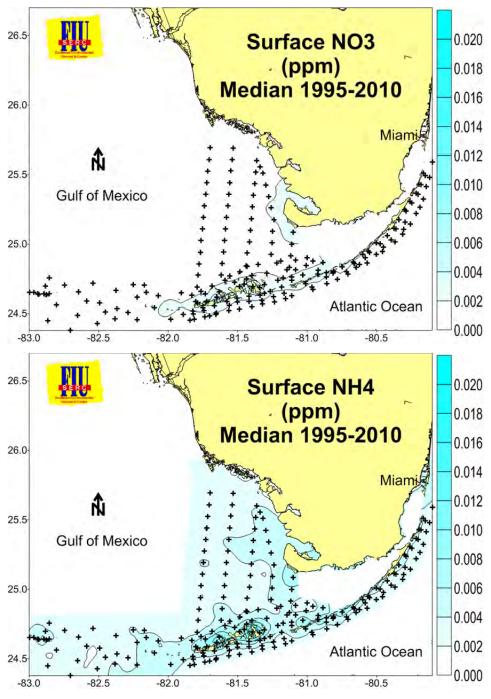
#### 3.3. Contour Maps

All contour maps of combined data from EPA and SFWMD projects are archived on the website <a href="http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm">http://serc.fiu.edu/wqmnetwork/CONTOUR%20MAPS/ContourMaps.htm</a> and are updated quarterly. An example of such (Fig. 5) shows the median 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.



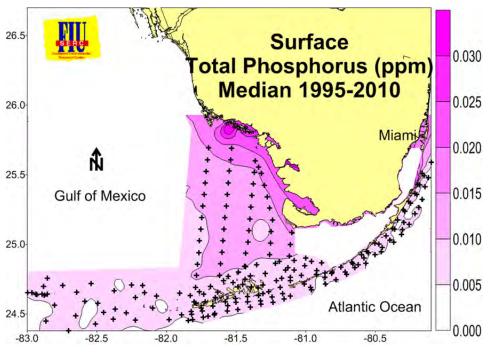
*Figure 5.* Median salinity field for the region showing freshwater inputs and marine influence.

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.

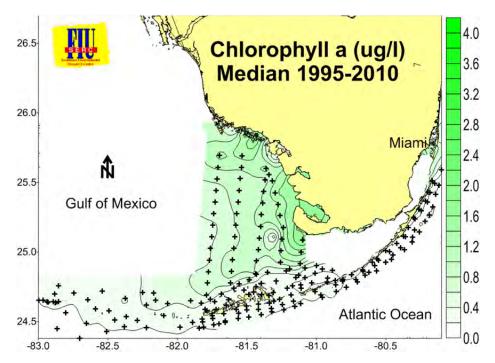


*Figure 6.* Median nitrate and ammonium in the region.

In contrast, TP 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 median total phosphorus in the region.



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

#### 3.4. Time Series Analysis

We must always keep in mind that trend analysis is limited to the window of observation; trends change with continued data collection. In addition, water quality in the Keys is largely externally-driven and may fluctuate according to climactic or disturbance events of longer periodicity. Trends may even reverse during a period of record. Examples of this are shown in Figures 9-11, where trends can be seen to be 1) monotonic, 2) episodically driven, and 3) reversing.

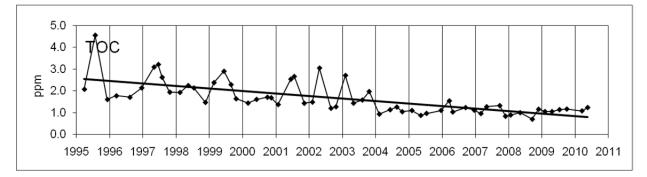
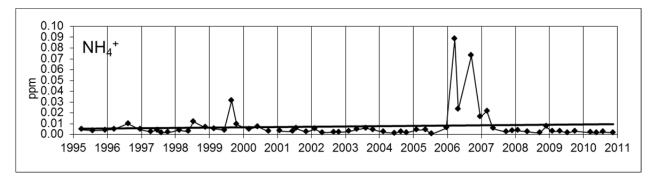


Figure 9. Monotonic trend in TOC at Carysfort Reef.



**Figure 10.** Episodically driven trend in  $NH_4^+$  at The Elbow.

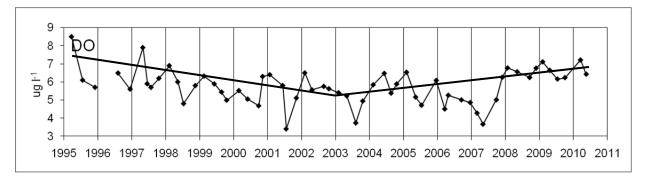


Figure 11. Reversing trend in DO at Carysfort Reef.

Least squares regressions for each water quality variable were calculated for the 15 year period of record. Only slopes having significant trends (p < 0.01) in ppm yr<sup>-1</sup>, or as noted were reported; non-significant trends were coded as slope = 0. Some of the slopes are very small, but to get an idea of total change over the period of record, the annual slopes were multiplied by 15 and plotted as contour maps of Total Change for 15 year period (Fig. 12-22).

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. That said, significant increases and decreases in some water quality variables has occurred. 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.

 $NO_3^-+NO_2^-$  ( $NO_x^-$ ) has generally remained the same or declined slightly over the region (Fig. 12). Declines were greatest in surface waters of the Backcountry and inshore of Middle Keys. Interestingly, the sites off Elliot Key – Triumph Reef, Old Rhodes Key, and White Bank exhibited increases in bottom  $NO_x^-$ .

 $NH_4^+$  has also generally remained the same in most surface waters of the FKNMS except for the Atlantic side of the Marquesas and Tortugas where it increased by 0.005-0.02 ppm (Fig. 13). There was no change in  $NH_4^+$  in bottom waters except for a few inshore sites in the Middle Keys where it decreased and increases at the same sites in the Upper Keys where  $NO_x^-$  was also seen to increase.

Surface TN increased slightly (0.05-0.10 ppm, total) in the Tortugas/Marquesas and at many offshore reef sites throughout the FKNMS (Fig. 14). This trend did not hold for bottom TN as only increases were observed in Tortugas region. Significant increases in TN (up to 0.5 ppm) were observed in the Fort Jefferson area of the Dry Tortugas National Park.

TP concentrations were relatively constant throughout the FKNMS with a few notable exceptions (Fig. 15). TP increased at sites offshore of the Upper Keys and along one inshoreoffshore transect Rattlesnake Key - White Bank - The Elbow. The same trend was seen in bottom waters as well as at Mosquito Bank. Contrary to TN, TP decreased significantly in Fort Jefferson area of the Dry Tortugas National Park. Overall CHLA concentrations declined or stayed the same throughout the FKNMS (Fig 16) with largest decreases in the west Marquesas. CHLA increased in the Sluiceway around SW Florida Bay and in station along the northern edge of the SW Shelf. These increases were driven by phytoplankton blooms from outside the FKNMS.

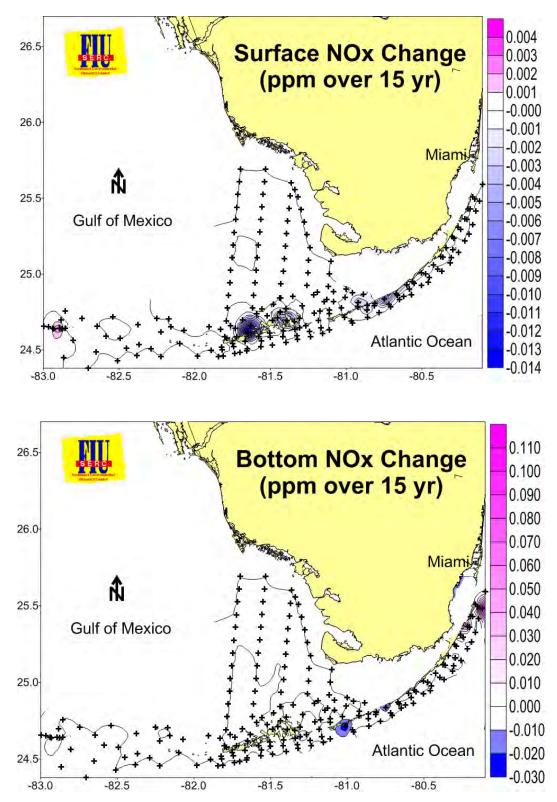
Light extinction ( $K_d$ ) declined at most sites (Fig. 17), which is a good thing as it means that there was an increase in light penetration to the benthos over time.  $K_d$  increased greatly on the SW Shelf adjacent to Everglades freshwater outputs from mangrove rivers. We believe the output of colored dissolved organic matter (CDOM) from mangrove forest accounts for this change.

With the exception of a few areas, DO did not change over the region in both surface and bottom waters (Fig. 18). Significant declines in surface and bottom DO were observed in NE Sluiceway – adjacent to Florida Bay, Spanish Harbor Keys, and Long Beach area. Some areas adjacent to Florida Bay experienced decreases up to 1.5 ppm for the period of record. This is problematic as DO is an important requirement for animal life.

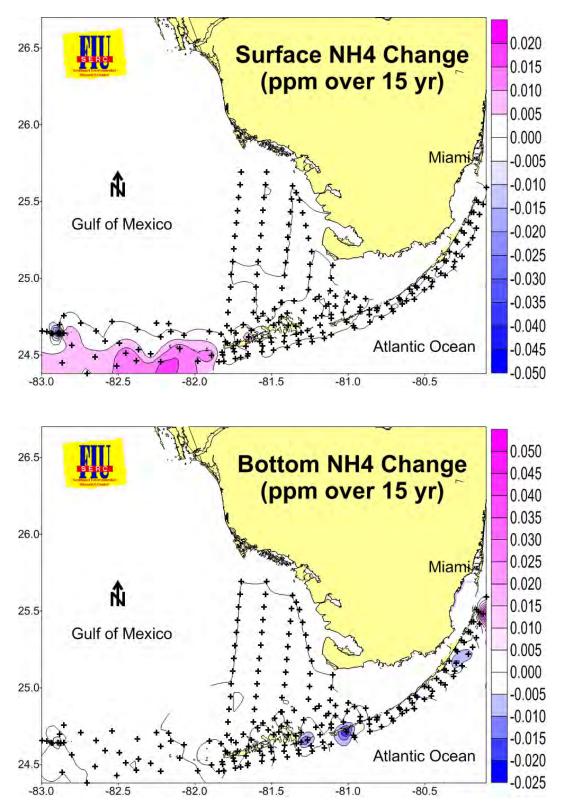
SiO<sub>2</sub> changed very little. Increases were observed in NE Sluiceway adjacent to Florida Bay, while increases occurred at Mosquito Bank and Molasses Reef Channel (Fig. 19).

Changes in water turbidity did not always correspond with K<sub>d</sub>, indicating that CDOM probably has more impact on the light field than does fine particulate seston (Fig. 20). In western Florida Bay, turbidity decreased with declines in light penetration. This points out the fact that turbidity is not the only optical property affecting light penetration. The strong decline in surface TOC over the FKNMS and SW Shelf may help explain this contradiction (Fig 21). In most areas, TOC has declined 1-2 ppm over the period of record. The decrease in color associated with this DOm is another important component of light penetration.

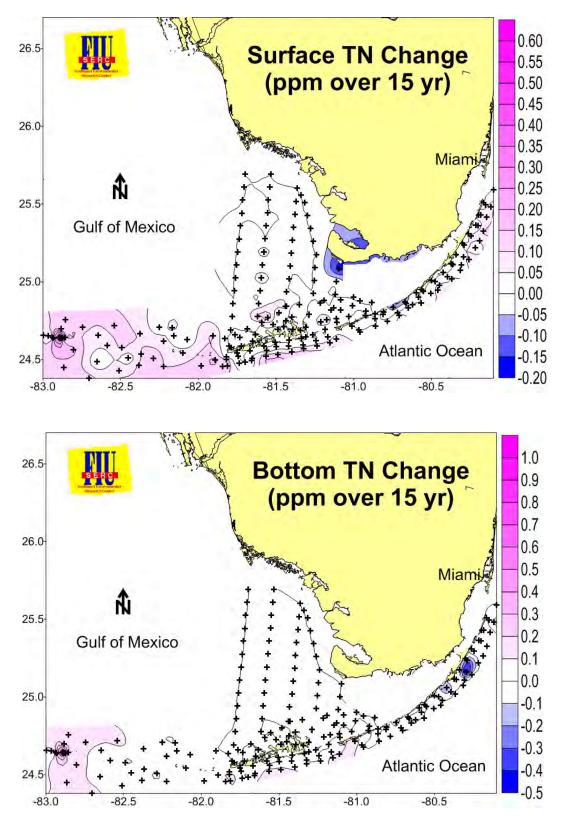
Finally, salinity on the Oceanside of the FKNMS has ton changed. However salinity in both surface and bottom waters of the of the gulfside areas - Backcountry, Sluiceway, and SW Shelf has increased dramatically (Fig. 22). We attribute these increases to climactic cycles and Everglades water management.



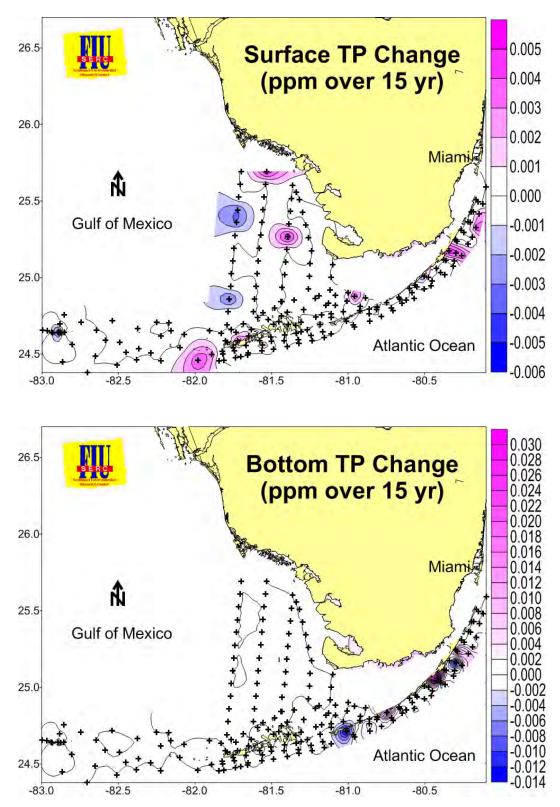
**Figure 12.** Total change in  $NO_3^++NO_2^-$  in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



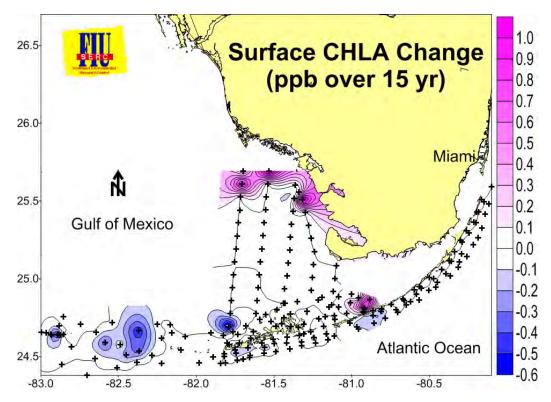
**Figure 13.** Total change in  $NH_4^+$  in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



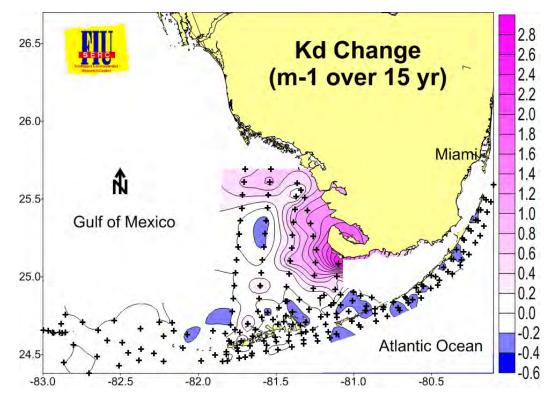
*Figure 14.* Total change in TN in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



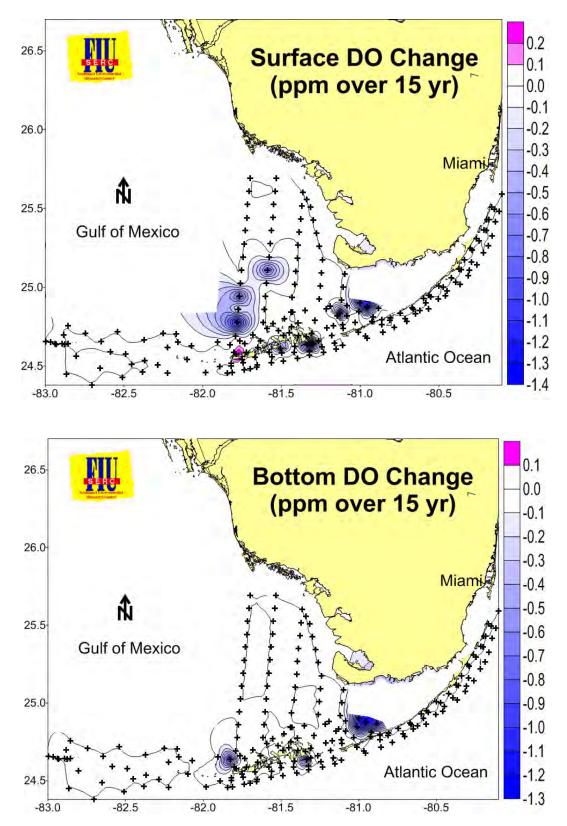
*Figure 15.* Total change in TP in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



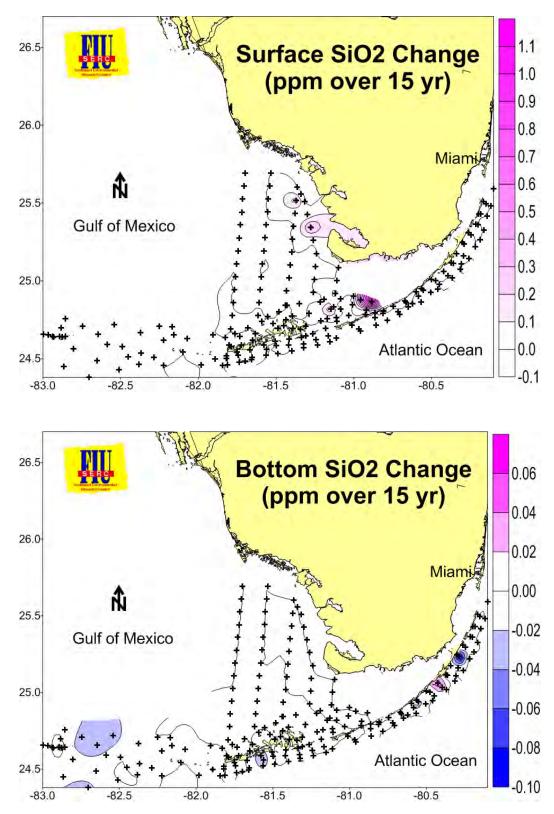
**Figure 16.** Total change in CHLA in surface waters for 15 year period calculated from significant trends (p<0.10).



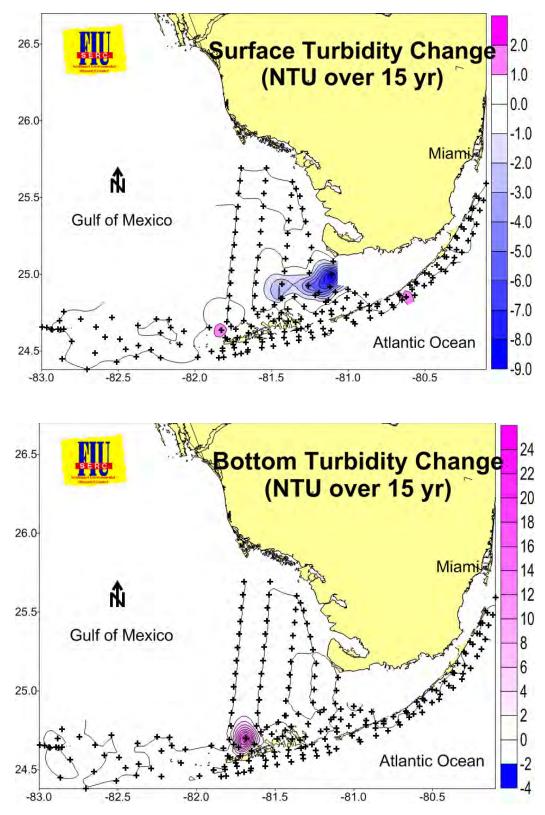
*Figure 17.* Total change in  $K_d$  for 15 year period calculated from significant trends (p<0.10).



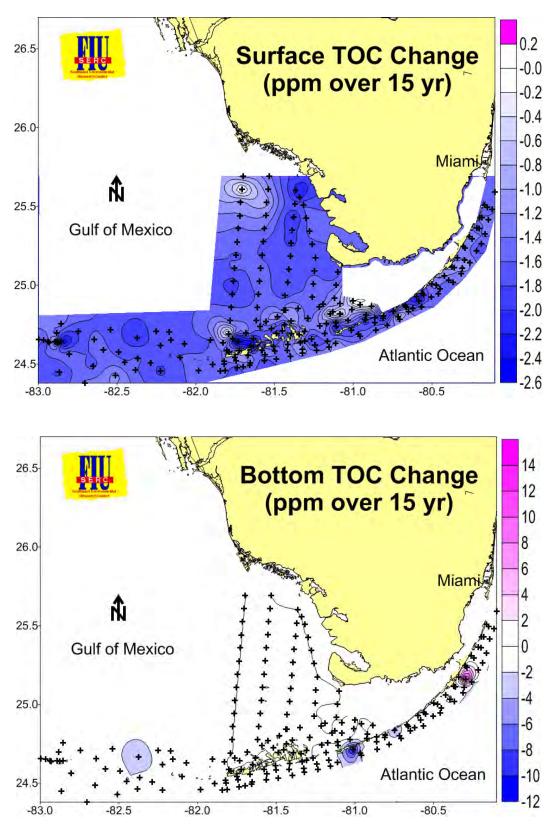
*Figure 18.* Total change in DO in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



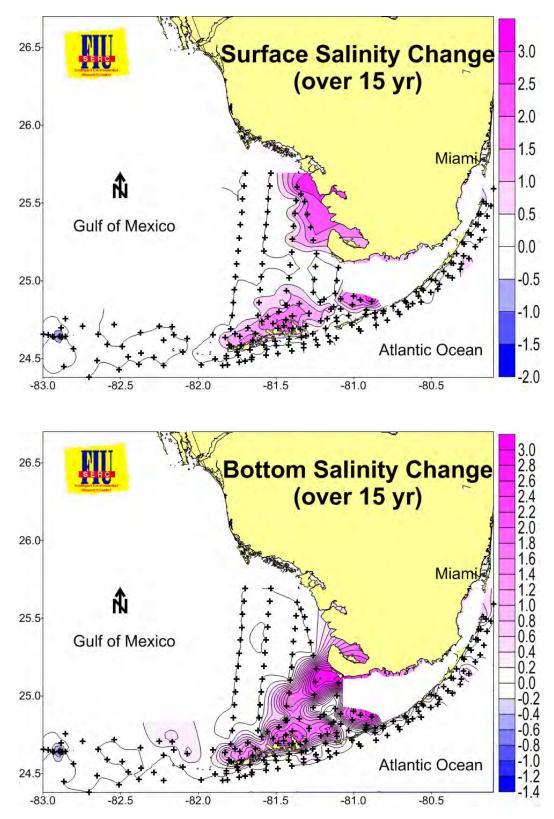
**Figure 19.** Total change in SiO<sub>2</sub> in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



*Figure 20.* Total change in Turbidity in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



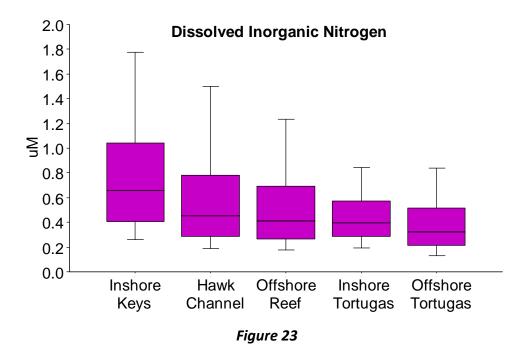
*Figure 21.* Total change in TOC in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).



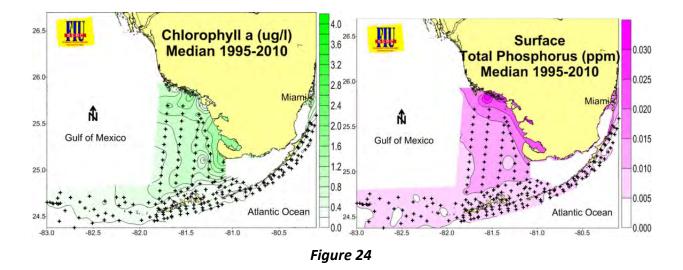
*Figure 22.* Total change in Salinity in surface and bottom waters for 15 year period calculated from significant trends (p<0.10).

## 4. 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 23). 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.



Second, highest CHLA concentrations are seen on the SW Florida Shelf with a strong gradient towards the Marquesas and Tortugas (Fig. 24). This is due to higher TP concentrations on the Shelf as a result of southerly advection of water along the coast.



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.

#### 4.1. Strategic Targets

The EPA developed Strategic Targets for the Water Quality Monitoring Project which state that beginning in 2008 through 2011, 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/I and the vertical attenuation coefficient for downward irradiance (K<sub>d</sub>, 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 3 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2010.

#### Table 3. EPA WQPP WQ Targets from 1995-2005 Baseline

Targets for reef sites include chlorophyll *a* less than or equal to 0.35 micro grams/l and vertical attenuation coefficient for downward irradiance ( $K_d$ , i.e., light attenuation) less than or equal to 0.20 per meter. Targets for all sites in FKNMS include dissolved inorganic nitrogen (DIN) less than or equal to 0.75 micromolar and total phosphorus (TP) less than or equal to 0.25 micromolar. Compliances were calculated as percent of those achieving targets divided by total number of samples. Values in green are those years with % compliance greater than 1995-2005 baseline. Values in yellow are those years with % compliance less than 1995-2005 baseline.

	Reef S	tations	All Stations		
			DIN ≤ 0.75 μM	TP ≤ 0.25 μM	
Year	CHLA ≤ 0.35 μg l <sup>-1</sup>	K <sub>d</sub> ≤ 0.20 m <sup>-1</sup>	(0.010 ppm)	(0.0077 ppm)	
<mark>1995-05</mark>	1778 of 2367 (75.1%)	1042 of 1597 (65.2%)	7826 of 10254 (76.3%)	7810 of 10267 (76.1%)	
2006	196 of 225 (87.1%)	199 of 225 (88.4%)	<mark>432 of 990 (43.6%)</mark>	<mark>316 of 995 (31.8%)</mark>	
2007	198 of 226 (87.6%)	202 of 222 (91.0 %)	<mark>549 of 993 (55.3%)</mark>	<mark>635 of 972 (65.3%)</mark>	
2008	177 of 228 (77.6%)	181 of 218 (83.0%)	836 of 1,000 (83.6%)	<mark>697 of 1,004 (69.4%)</mark>	
2009	208 of 228 (91.2%)	189 of 219 (86.3%)	858 of 1,003 (85.5%)	869 of 1,004 (86.6%)	
2010	<mark>170 of 227 (74.9%)</mark>	176 of 206 (85.4%)	843 of 1000 (84.3%)	<mark>738 of 1,003 (73.6%)</mark>	

#### **EPA WQPP Water Quality Targets**

## 5. Discussion

Water quality is a subjective measure of ecosystem well-being. Aside from the physicalchemical 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 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, 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, Gibson et al. 2008).

Spatial patterns of salinity in coastal South Florida show these major sources of freshwater to have more than just local impacts (Fig. 25). 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. The

opposite also holds true; hypersaline waters from Florida Bay may be transported through the Sluiceway to inshore sites in the Middle Keys.

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 usually 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. All these forces have large influence on other water quality variables, especially DO (Fig. 26). Lowest DO concentrations tend to develop inside the Backcountry during warmest months.

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.

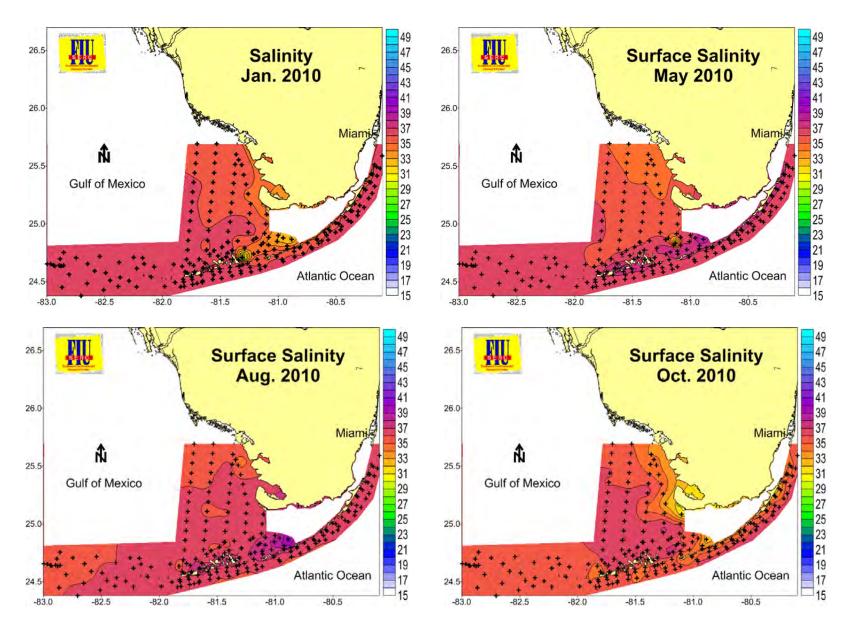
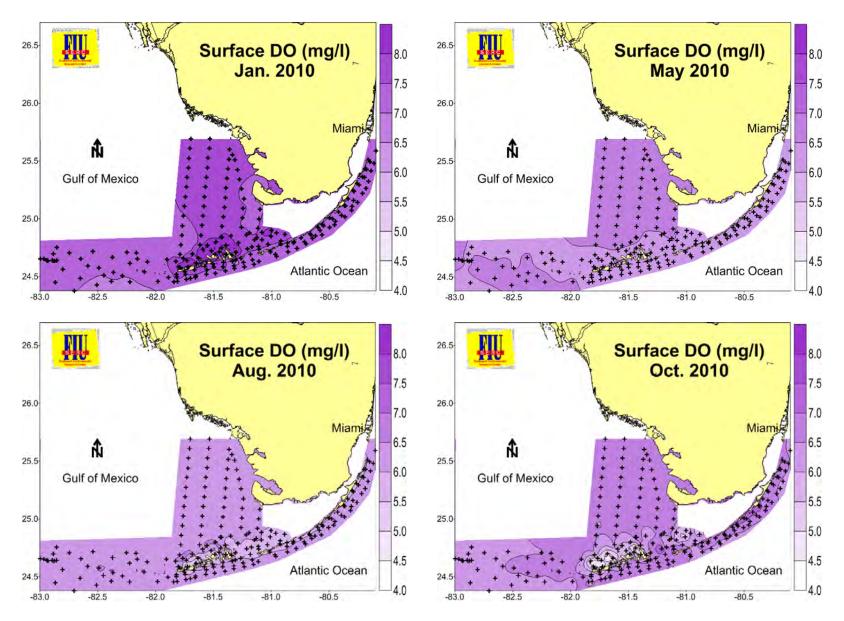


Figure 25. Surface salinity distributions across the region during 2010.



*Figure 26.* Surface dissolved oxygen distributions across the region during 2010.

Visualization of spatial patterns of NO<sub>3</sub><sup>-</sup> concentration over South Florida waters provide an extended view of source gradients over the region (Fig. 27). Biscayne Bay, Florida Bay, and the Shark River area of the west coast exhibited higher NO<sub>3</sub><sup>-</sup> concentrations relative to the FKNMS and Shelf (Caccia and Boyer 2005, Boyer and Briceño 2007). Elevated NO<sub>3</sub><sup>-</sup> 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). A large source of NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> concentrations are the result of N<sub>2</sub> fixation/nitrification within the mangroves (Pelegri and Twilley 1998) and not simple transport of agricultural N from northern Everglades.

The oceanside transects off the uninhabited Upper Keys (off Biscayne Bay) exhibited the lowest alongshore NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> relative to Hawk Channel and the reef tract which is also demonstrated in our analysis. Interestingly, NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> on the transect off uninhabited Loggerhead Key. We suggest this source of NO<sub>3</sub><sup>-</sup> in the Keys is the due to human shoreline development.

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.

The elevated DIN concentrations in the Backcountry are not easily explained. We think that the high concentrations found there are due to a combination of anthropogenic loading,

physical entrapment, and benthic N<sub>2</sub> 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<sub>2</sub> fixation may potentially be very important in the N budget of the Backcountry. Measured rates of N<sub>2</sub> fixation in a *Thalassia* bed in Biscayne Bay, having very similar physical and chemical conditions, were 540 µmol N m<sup>-2</sup> d<sup>-1</sup> (Capone and Taylor 1980). Without the plant community N demand, one day of N<sub>2</sub> fixation has the potential to generate a water column concentration of >0.014 ppm NH<sub>4</sub><sup>+</sup> (0.5 m deep). Much of this NH<sub>4</sub><sup>+</sup> is probably nitrified and may help account for the elevated NO<sub>3</sub><sup>-</sup> concentrations observed in this area as well. Clearly, N<sub>2</sub> 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.

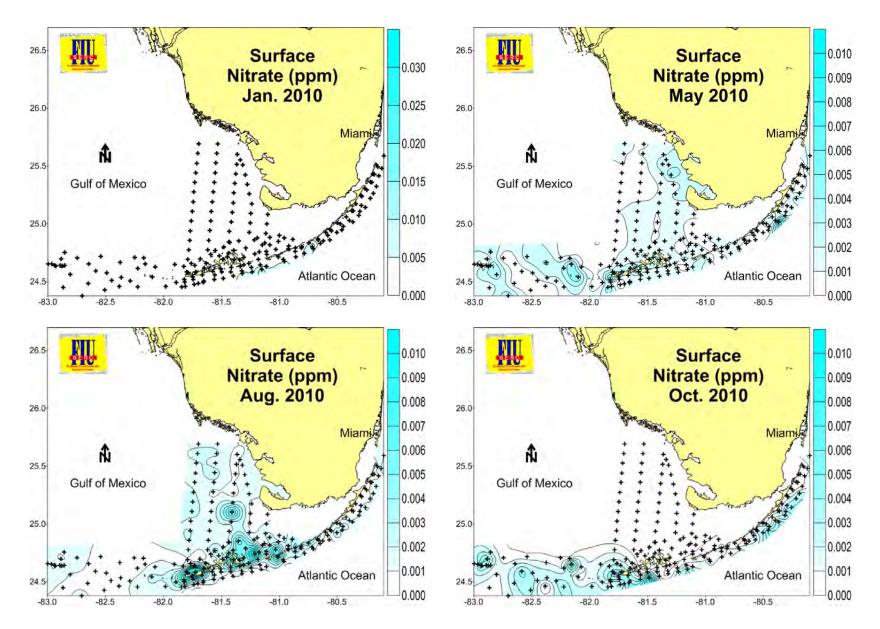


Figure 27. Surface nitrate distributions across the region during 2010.

Interestingly, in many cases for 2010 and other years, NO<sub>3</sub><sup>-</sup> was highest in the bottom waters on the offshore reef tract (Fig. 28). We attribute this to regular "upwelling" (actually internal tidal bores) of deep water onto the reef tract (Leichter et al. 2003). It is a regular and persistent phenomenon which may deliver high nutrient waters to the offshore reef tract independent of any anthropogenic source. In 2010, NO<sub>3</sub><sup>-</sup> concentrations were as high as 0.169 ppm at Fish Haven.

In many situations, independent water masses may be distinguished by difference in density (sigma-*t*,  $\sigma_t$ ) between surface and bottom ( $\Delta\sigma_t$ , Fig. 29). Since density is driven more by salinity than temperature, we do not always observe differences in  $\sigma_t$  between surface and bottom during upwelling events. However, decreased temperature of bottom waters ( $\Delta$ T, Fig. 30) from intrusion of deeper oceanic waters is clearly an indicator of increased NO<sub>3</sub><sup>-</sup> (Fig. 28). These upwelling events also affect other nutrient species such as NH<sub>4</sub><sup>+</sup>, TP, and SRP in these bottom waters as well.

In 2010, the NW area of the Tortugas segment experienced the strongest stratification event seen in years. This event was driven by salinity as well as temperature as  $\Delta \sigma_t$  values were strongly positive (Fig. 29). No anomalous increase of bottom nutrients was observed.

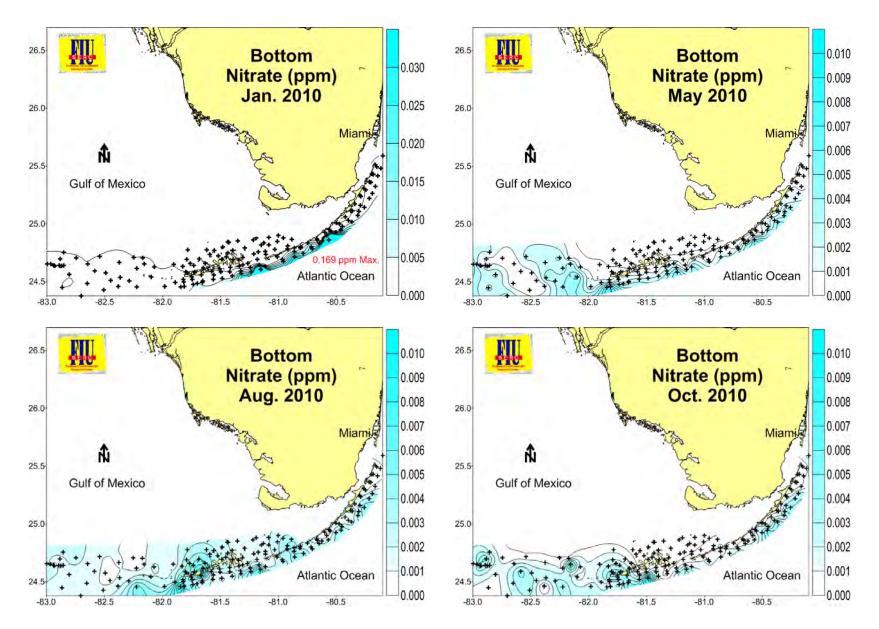
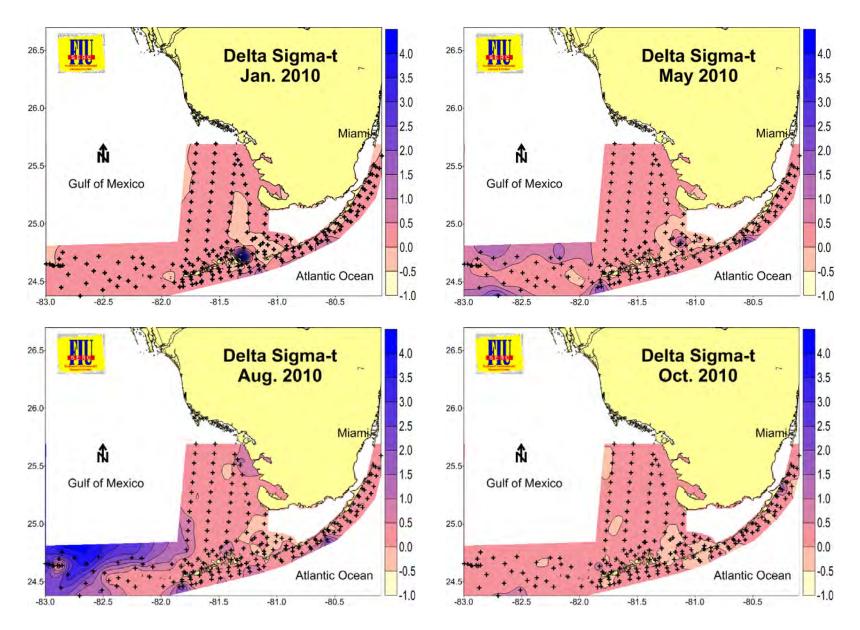


Figure 28. Bottom nitrate distributions across the region during 2010.



*Figure 29.* Surface and bottom density differences ( $\Delta \sigma_t$ ) across the region during 2010.

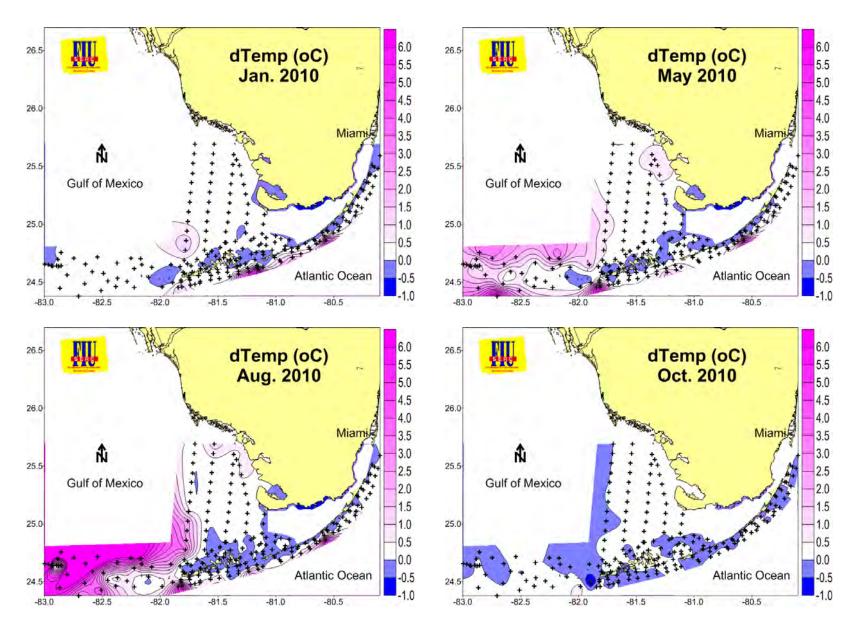
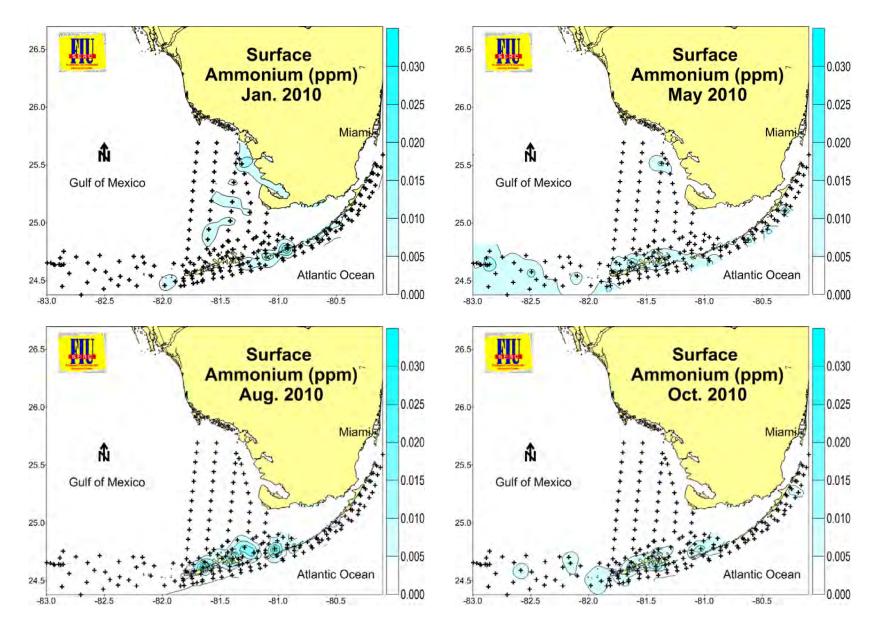


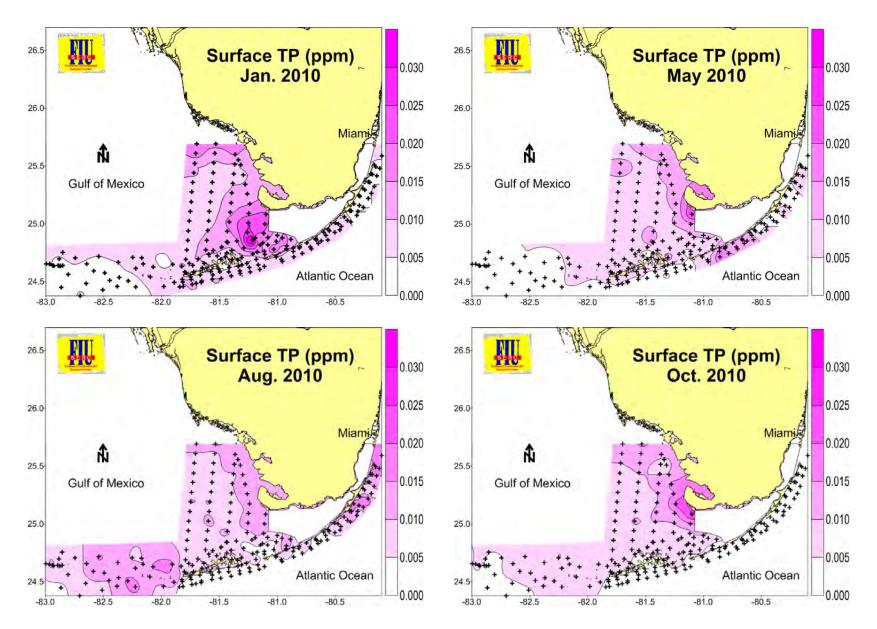
Figure 30. Surface and bottom temperature differences across the region during 2010.

 $NH_4^+$  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. 31).  $NH_4^+$ 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. Typically, there is 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 31.* Surface ammonium distribution across the region during 2010.

Spatial patterns in TP in South Florida coastal waters were strongly driven by the west coast sources (Fig. 32). A gradient in TP extended from the inshore waters of Whitewater Bay - Ten Thousand Islands mangrove complex out onto the Shelf and Tortugas. Gradients also extended from western Florida Bay to the Middle/Lower Keys. The spatial distribution of TP on the Shelf is driven by freshwater inputs from mangrove rivers and transport of Gulf of Mexico waters through the region. No significant evidence of a groundwater source exists (Corbett et al. 2000). However, there is evidence of a significant terrestrial source of TP to Biscayne Bay (Caccia and Boyer 2007), which may impact inshore waters of Upper Keys.



*Figure 32.* Distributions of surface total phosphorus across the region during 2010.

Concentrations of TOC (Fig. 33) and TON (Fig. 34) 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. This gradient weas 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 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).

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.

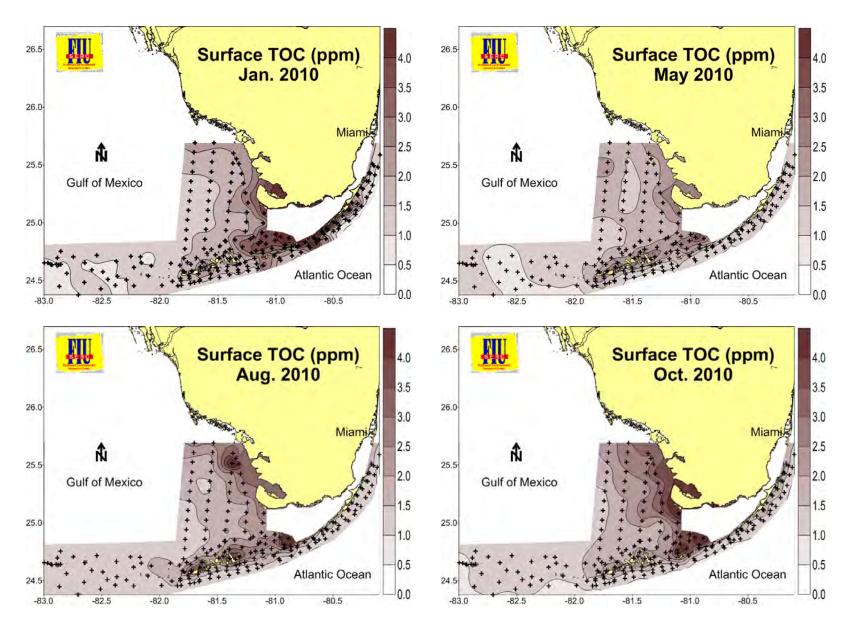
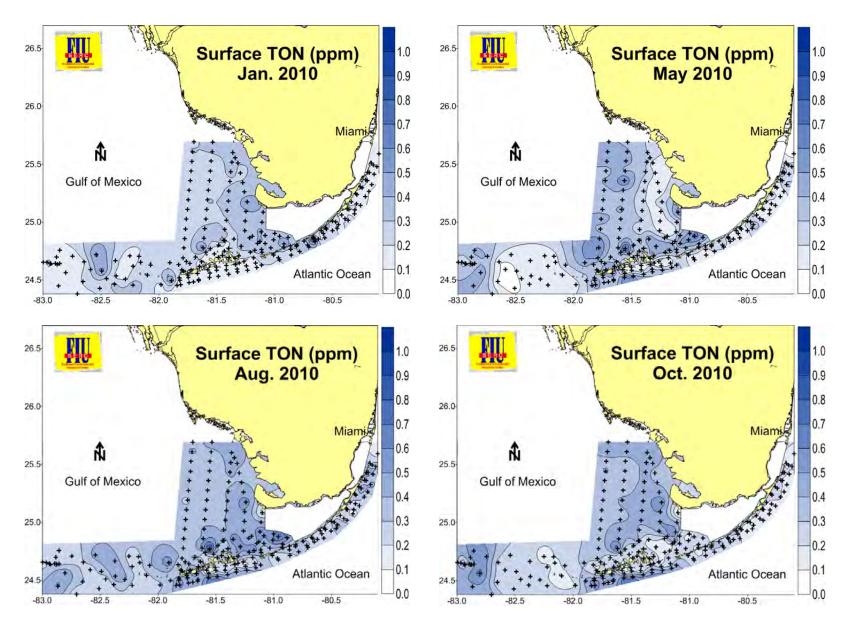


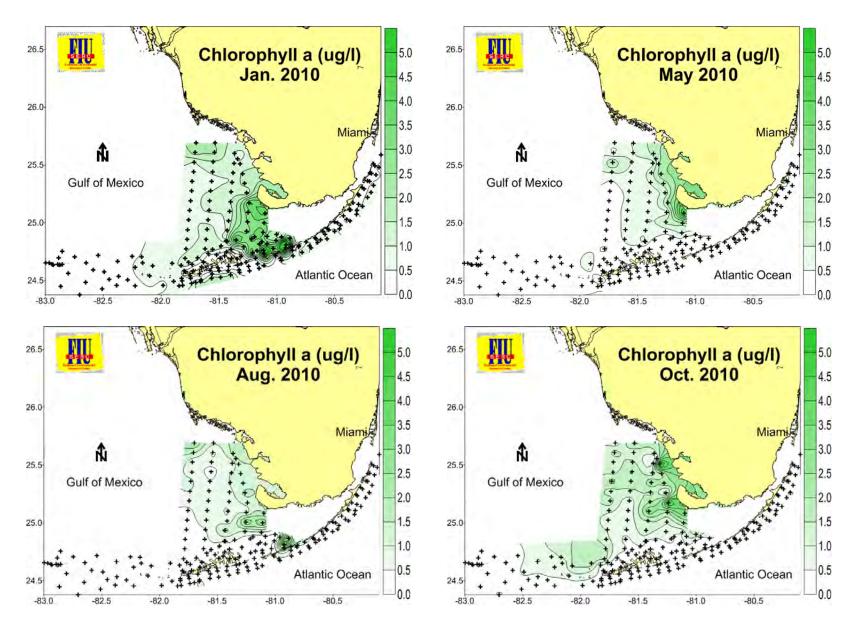
Figure 33. Distributions of surface total organic carbon across the region during 2010.



*Figure 34.* Distributions of surface total organic nitrogen across the region during 2010.

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 the Shelf, NW Florida Bay, and the Ten Thousand Islands exhibited high levels of CHLA relative to the FKNMS (Fig. 35). It is interesting that CHLA concentrations on the Shelf are higher in the Marquesas ( $0.36 \ \mu g \ l^{-1}$ ) 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  $\mu g \ l^{-1}$ 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.

The oceanside transects in the Upper Keys exhibited the lowest overall CHLA concentrations of any area 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.



*Figure 35.* Distributions of surface chlorophyll a across the region during 2010.

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 36). 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.

Large scale observations of turbidity clearly show patterns of onshore-offshore gradients which extend out onto the Shelf to the Marquesas (Stumpf et al. 1999). Strong turbidity gradients were observed on the Shelf but reef tract levels were remarkably low regardless of inshore levels. Elevated inshore turbidity is most probably due to the shallow water column being easily resuspended by wind and wave action. Light extinction (K<sub>d</sub>) was highest alongshore and improved with distance from land. This trend was expected as light extinction is related to water turbidity (Fig 37). However, in Keys waters, CDOM is a more prominent driver of light penetration.

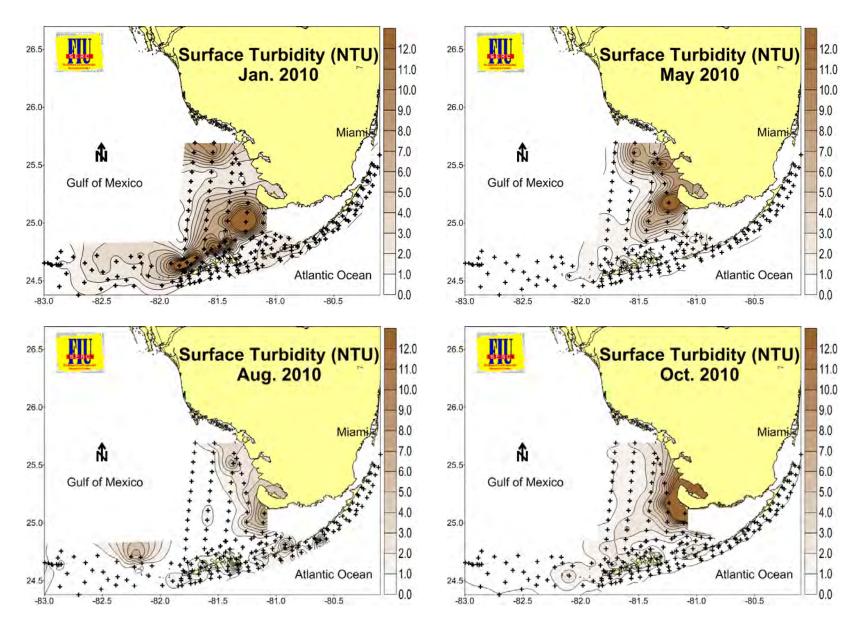


Figure 36. Distributions of surface turbidity across the region during 2010.

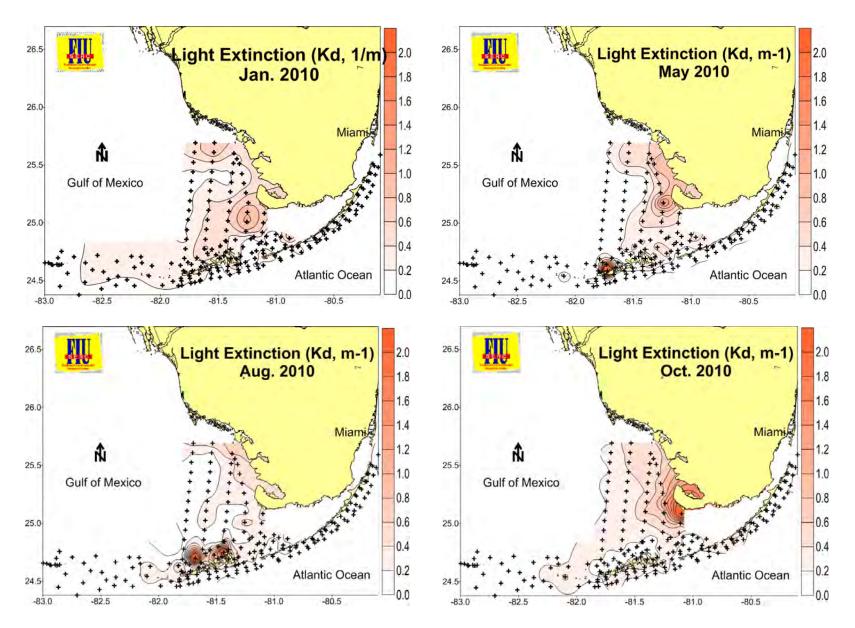
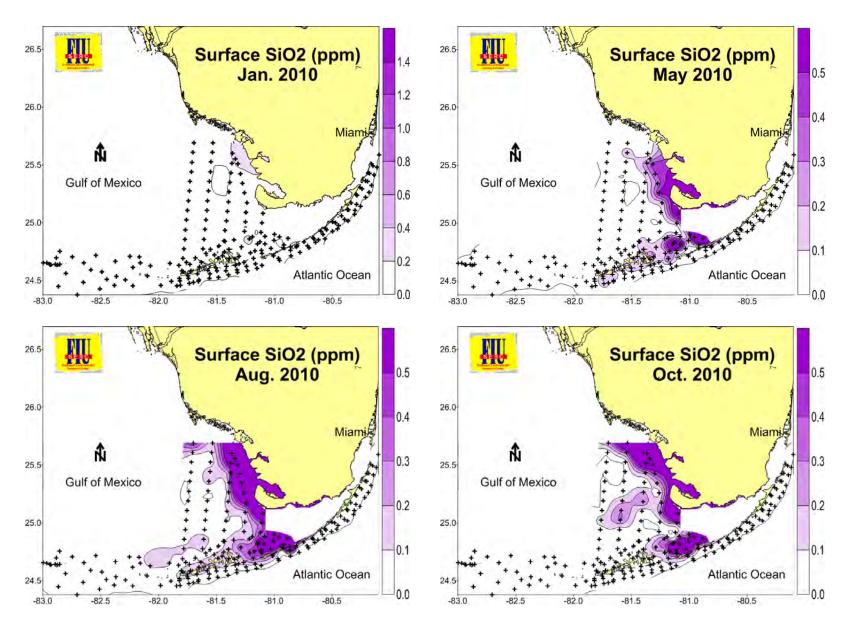


Figure 37. Distributions of Light extinction across the region during 2010.

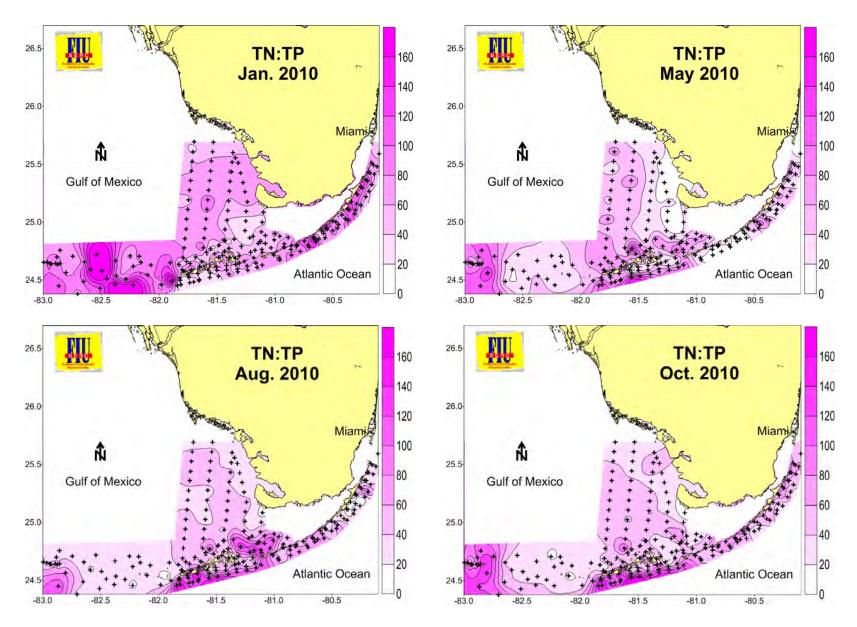
Surface SiO<sub>2</sub> concentrations exhibited a pattern similar to salinity (Fig. 38). The source of SiO<sub>2</sub> in this geologic area of carbonate rock and sediments is from siliceous periphyton (diatoms) growing in the Shark River Slough, Taylor Slough, and C-111 basin watersheds. Unlike the Mississippi River plume with CHLA concentrations of 76  $\mu$ g l<sup>-1</sup> (Nelson and Dortch 1996), phytoplankton biomass on the Shelf (1-2  $\mu$ g l<sup>-1</sup> CHLA) was not sufficient to account for the depletion of SiO<sub>2</sub> in this area. Therefore, SiO<sub>2</sub> concentrations on the Shelf are depleted mostly by mixing (although we no longer have data from the Shelf), allowing SiO<sub>2</sub> to be used as a semi-conservative tracer of freshwater in this system (Ryther et al. 1967; Moore et al. 1986).

In the Lower and Middle Keys, it is clear that the source of SiO<sub>2</sub> to the nearshore Atlantic waters is through the Sluiceway and Backcountry (Fig. 38). SiO<sub>2</sub> 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<sub>2</sub> 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.

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 (Fig. 39). 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.



*Figure 38.* Distributions of surface silicate across the region during 2010.



*Figure 39.* Distributions of surface TN:TP ratio across the region during 2010.

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 (<u>http://serc.fiu.edu/wqmnetwork/</u>) where data and reports 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) are available.

## 5.1.Acknowledgments

We thank all the field and laboratory technicians involved with this project, especially Jeff Absten, Antuanet Cuello, Pat Given, Ruth Justiniano, Mark Kershaw, Lyndi Kirkman, Pete Lorenzo, Grisel Menendez, Bill Pomenti, Dania Sancho, Sandro Stumpf, and Milagros Timeraos. Special thanks to Captain Dave Ward of the R/V Magic II for professional support of the monitoring program. This project was possible due to continued funding by the US-EPA (Agreement # X7-96410604-6) and US Fish & Wildlife Service. This is Technical Report #T-536 of the Southeast Environmental Research Center at Florida International University.

## 6. 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. 2006. Shifting N and P limitation along a north-south gradient of mangrove estuaries in South Florida. <u>Hydrobiologia</u> 269: 167-177.
- BOYER, J. N. AND H. O. BRICEÑO. 2007. FY2006 Annual Report of the South Florida Coastal Water Quality Monitoring Network. SFWMD/SERC Cooperative Agreement #4600000352. SERC Tech. Rep. T-351. <u>2006 CWQMN.pdf</u>
- 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).
   <u>Estuaries</u> 20: 743-758.
- BOYER, J. N., J. W. FOURQUREAN, AND R. D. JONES. 1999. Seasonal and long-term trends in water quality of Florida Bay (1989-1997). <u>Estuaries</u> 22:417-430.
- 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.
- BOYER, J. N., AND R. D. JONES. 2002. A view from the bridge: External and internal forces affecting the ambient water quality of the Florida Keys National Marine Sanctuary, p. 609-628. *In* J.
  W. Porter and K. G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press.
- BOYER, J. N., P. STERLING, AND R. D. JONES. 2000. Maximizing information from a water quality monitoring network through visualization techniques. <u>Estuarine, Coastal and Shelf Science</u> 50: 39-48.
- BRICEÑO, H. O., AND J. N. BOYER. 2010. Climactic controls on nutrients and phytoplankton biomass in a sub-tropical estuary, Florida Bay, USA. <u>Estuaries and Coasts</u> 33: 541–553.
- CACCIA, V. G., AND J. N. BOYER. 2005. Spatial patterning of water quality in Biscayne Bay, Florida as a function of land use and water management. <u>Marine Pollution Bulletin</u> 50: 1416-1429.
- CACCIA, V. G., AND J. N. BOYER. 2007. A nutrient loading budget for Biscayne Bay, Florida. <u>Marine</u> <u>Pollution Bulletin</u> 54: 994–1008.

- 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.
- CHRISTIAN, R. R., J. N. BOYER, D. W. STANLEY, AND W. M. RIZZO. 1991. Multi-year distribution patterns of nutrients in the Neuse River Estuary, North Carolina. <u>Marine Ecology Progress Series</u> 71:259-274.
- CORBETT, D. R., K. DILLON, W. BURNETT, AND J. CHANTON. 2000. Estimating the groundwater contribution into Florida Bay via natural tracers <sup>222</sup>Rn and CH<sub>4</sub>. <u>Limnology and</u> <u>Oceanography</u> 45:1546-1557.
- 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., M.D. DURAKO, M.O. HALL AND L.N. HEFTY. 2002. Seagrass distribution in south
  Florida: a multi-agency coordinated monitoring program, p. 497-522. *In* J. W. Porter and K.
  G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An
  Ecosystem Sourcebook. CRC Press.
- 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. <u>Estuarine, Coastal and Shelf Science</u> 36:295-314.
- GIBSON, P. J., J. N. BOYER, AND N. P. SMITH. 2008. Nutrient Mass Flux between Florida Bay and the Florida Keys National Marine Sanctuary. <u>Estuaries and Coasts</u> 31: 21–32.
- HIRSCH, R. M., R. B. ALEXANDER, AND R. A. SMITH. 1991. Selection of methods for the detection and estimation of trends in water quality. <u>Water Resources Research</u> 27:803-813.
- ISAAKS, E. H., AND R. M. SRIVASTAVA. 1989. An Introduction to Applied Geostatistics. Oxford Press, 561 pp.
- KLEIN, C. J., AND S. P. ORLANDO JR. 1994. A spatial framework for water-quality management in the Florida Keys National Marine Sanctuary. <u>Bulletin of Marine Science</u> 54: 1036-1044.
- LAPOINTE, B. E., AND M. W. CLARK. 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida Keys. <u>Estuaries</u> 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. <u>Estuaries</u> 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. <u>Bulletin of Marine Science</u> 54: 621-646.
- LEE, T. N., E. WILLIAMS, E. JOHNS, D. WILSON, AND N. P. SMITH. 2002. Transport processes linking South Florida ecosystems, p. 309-342. *In* J. W. Porter and K. G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press.
- 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. <u>Limnology and Oceanography</u> 41: 1490-1501.
- LEICHTER, J. J., AND S. L. MILLER. 1999. Predicting high-frequency upwelling: Spatial and temporal patterns of temperature anomalies on a Florida coral reef. <u>Continental Shelf Research</u> 19: 911-928.
- LEICHTER, J. J., H. L. STEWART, AND S. L. MILLER. 2003. Episodic nutrient transport to Florida coral reefs. <u>Limnology and Oceanography</u> 48:1394-1407.
- MOORE, W. S., J. L. SARMIENTO, AND R. M. KEY. 1986. Tracing the Amazon component of surface Atlantic water using <sup>228</sup>Ra, salinity, and silica. <u>Journal of Geophysical Research</u> 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. <u>Marine Ecology</u> <u>Progress Series</u> 136: 163-178.
- NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION. 1995. Florida Keys National Marine Sanctuary Draft Management Plan/Environmental Impact Statement.
- OVERLAND, J. E. AND R. W. PREISENDORFER. 1982. A significance test for principal components applied to cyclone climatology. <u>Monthly Weather Review</u> 110:1-4.
- PITTS, P. A. 1997. An investigation of tidal and nontidal current patterns in Western Hawk Channel, Florida Keys. <u>Continental Shelf Research</u> 17: 1679-1687.
- REDFIELD, A. C. 1958. The biological control of chemical factors in the environment. <u>American</u> <u>Scientist</u> 46: 205-222.

- 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. <u>Estuaries</u> 22: 398-416.
- 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. <u>Journal of</u> Marine Research 25: 69-83.
- Sмітн, N. P. 1994. Long-term Gulf-to-Atlantic transport through tidal channels in the Florida Keys. <u>Bulletin of Marine Science</u> 54: 602-609.
- SOLÓRZANO, L., AND J. H. SHARP. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnology and Oceanography 25:754-758.
- STUMPF, R. P., M. L. FRAYER, M. J. DURAKO, AND J. C. BROCK. 1999. Variations in water clarity and bottom albedo in Florida Bay from 1985-1997. <u>Estuaries</u> 22: 431-444.
- SZMANT, A. M., AND A. FORRESTER. 1996. Water column and sediment nitrogen and phosphorus distribution patterns in the Florida Keys, USA. <u>Coral Reefs</u> 15: 21-41.

# 7. Appendix 1

Table 3.	Statistical summary of water quality in zones for the period of record. Data are
summariz	zed 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 <sub>3</sub>	2	0.09	0.00	1.33	82
(ppm)	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 <sub>3</sub>	2				
(ppm)	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 <sub>2</sub> <sup>-</sup>	2	0.06	0.00	0.25	82
(ppm)	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 <sub>2</sub>	2				
(ppm)	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
(ppm)	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				
(ppm)	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
(ppm)	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				
(ppm)	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
(ppm)	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

Bottom					n
BULLUIII	1	11.32	2.21	42.78	43
TON	2				
(ppm)	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
(ppm)	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				
(ppm)	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
(ppm)	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				
(ppm)	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	0.32	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
тос	2	231.33	135.31	505.54	82
(ppm)	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
тос	2				
(ppm)	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
Surface	1	1.53	0.00	89.00	557
SiO <sub>2</sub>	2	4.74	0.00	55.16	78
(ppm)	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 <sub>2</sub>	2				
(ppm)	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

_	Variable	Cluster	Median	Min.	Max.	n
	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
	Bottom	1	36.13	28.77	39.66	585
	Salinity	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	1	26.71	17.32	36.10	586
	Temperature	2	26.94	17.49	32.65	82
	(°C)	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

Variable	Cluster	Median	Min.	Max.	n
Bottom	1	26.78	17.32	33.40	585
Temperature	2	26.90	17.49	32.36	81
(°C)	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	1	6.20	0.91	11.30	586
DO	2	5.88	4.23	8.11	82
(mg l <sup>-1</sup> )	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	1	6.20	2.70	11.40	585
DO	2	5.97	4.31	8.10	81
(mg l⁻¹)	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
K <sub>d</sub>	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 <sub>sat</sub>	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

Variable	Cluster	Median	Min.	Max.	n
Bottom	1	91.48	41.56	166.85	585
DO <sub>sat</sub>	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
$\Delta \delta_t$	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