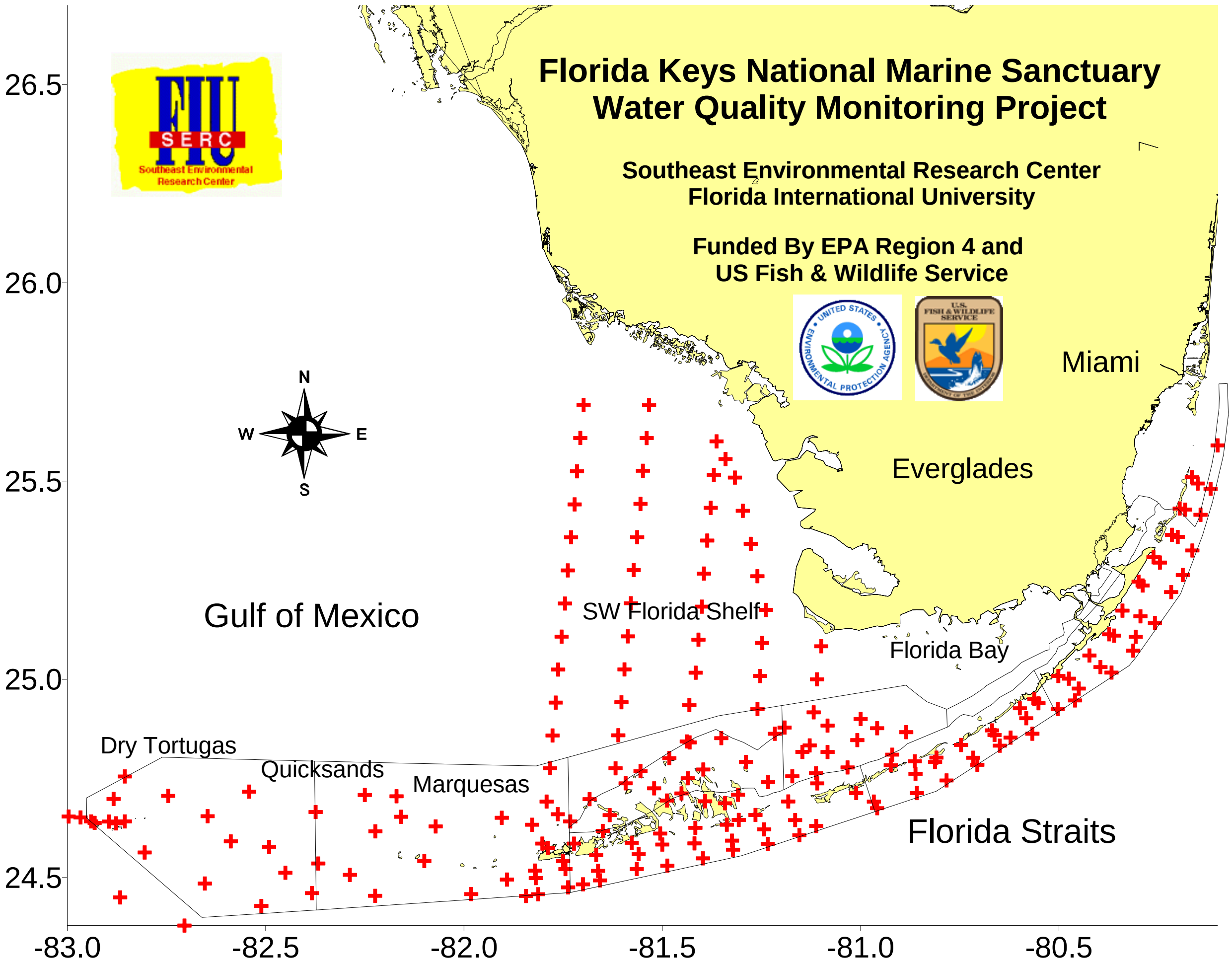
2011 ANNUAL REPORT
OF THE WATER QUALITY MONITORING PROJECT
FOR THE WATER QUALITY PROTECTION PROGRAM
OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY

Executive Summary



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US EPA Agreement #X7-95469410

This is Technical Report #592 of the Southeast Environmental Research Center,

Florida International University.

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Funded by the Environmental Protection Agency Agreement #X7-95469410
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. 2011 and includes data from 66 quarterly sampling events within the FKNMS and SW Florida Shelf, including the Dry Tortugas National Park. Due to budget cuts only 110 stations have been monitored since Nov. 2011 (205 in the past), excluding the SW Florida Shelf and 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 (Kd, m^{-1}). Water quality variables include the dissolved nutrients nitrate ($NO3^-$), nitrite ($NO2^-$), ammonium ($NH4^+$), 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 (SiO2) and chlorophyll *a* (CHLA, µg l^{-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 0.35 micrograms/l and the vertical attenuation coefficient for downward irradiance (Kd, i.e., light attenuation) should be less than or equal to 0.20 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 0.25 micromolar. Table 1 shows the number of sites and percentage of total sites complying with these Strategic Targets for 2011.

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

EPA WQPP Water Quality Targets

	Reef Stations		All Stations (except Shelf)	
Year	**CHLA ≤ 0.35 ug l^{-1}**	**Kd ≤ 0.20 m^{-1}**	**DIN ≤ 0.75 µM (≤ 0.010 ppm)**	**TP ≤ 0.25 µM (≤ 0.0077 ppm)**
1995-05	1,778 of 2,367 (75.1%)	1,042 of 1,597 (65.2%)	7,826 of 10,254 (76.3%)	7,810 of 10,267 (76.1%)
2006	196 of 225 (87.1%)	199 of 225 (88.4%)	432 of 990 (43.6%)	316 of 995 (31.8%)
2007	198 of 226 (87.6%)	202 of 222 (91.0%)	549 of 993 (55.3%)	635 of 972 (65.3%)
2008	177 of 228 (77.6%)	181 of 218 (83.0%)	836 of 1,000 (83.6%)	697 of 1,004 (69.4%)
2009	208 of 228 (91.2%)	189 of 219 (86.3%)	858 of 1,003 (85.5%)	869 0f 1,004 (86.6%)
2010	170 of 227 (74.9%)	176 of 206 (85.4%)	843 of 1,000 (84.3%)	738 of 1,003 (73.6%)
2011	162 of 229 (70.7%)	150 of 207 (72,5%)	738 of 922 (80.0%)	844 of 923 (91.4%)

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 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.

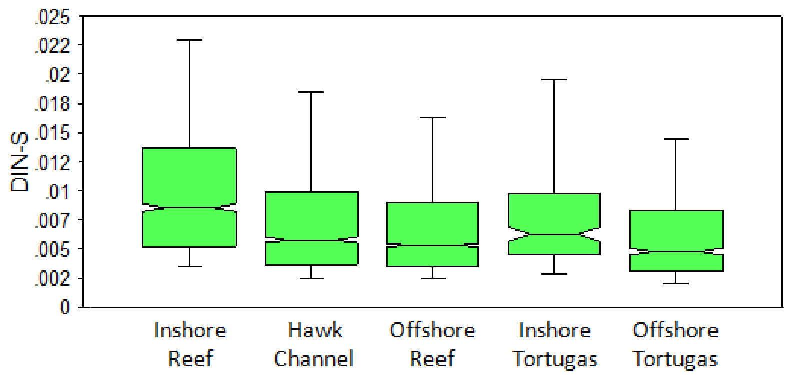

Figure 1.*Box-and-whisker plot*

Some variables showed noteworthy differences over the period of record. This brings up another important point; when looking at what are perceived to be local patterns, 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 climatologic 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 16 year period of record. The overall net tendencies are shown in Fig 2 for TN, DIN, CHLa, Salinity, Turbidity and Kd. TN has increased along the whole archipelago; DIN increased preferentially towards the Marquesas, Dry Tortugas and the Seven Mile Bridge; CHLa has increased in the northern Shelf area and in the Seven Mile Bridge area; Salinity increases characterize the Backcountry and the northwestern Shelf; Turbidity has declined in the Backcountry-south Shelf area; and water transparency , as expressed by Kd has deteriorated in the Shelf while slightly improving along the Keys. Total Organic Carbon has consistently declined in all stations the last 16 years (not shown).

The large scale of this monitoring program has allowed us, until now, 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 been 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 and reports from the FKNMS are available.

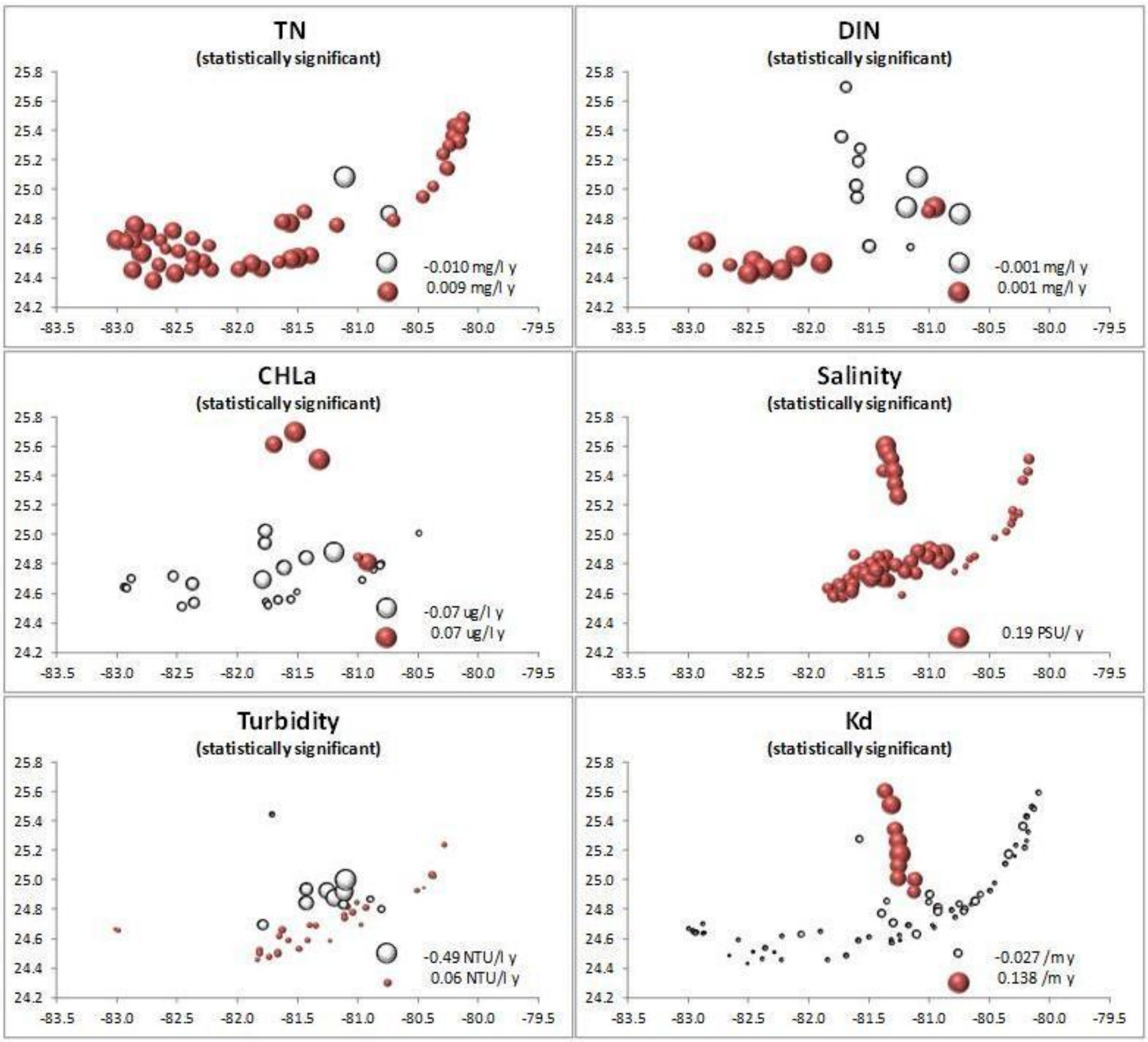

Figure 2: Statistically significant water quality trends. Red bubbles indicate stations with increasing trends and white ones indicate declining tendencies

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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. 3). 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.

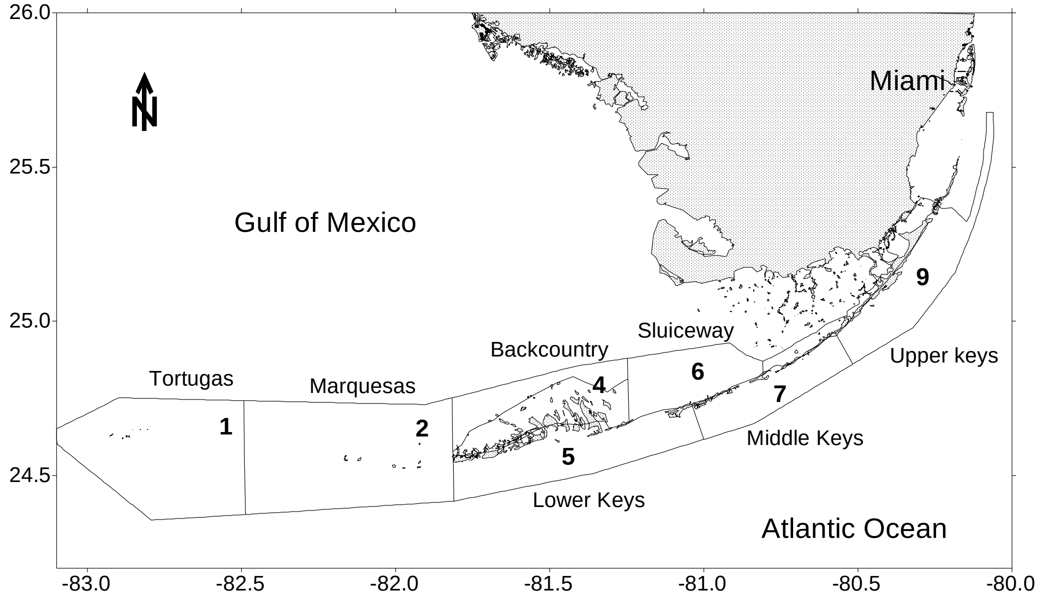

***Figure 3**. Map of FKNMS boundary including Segment numbers and common names.*

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. 3). Station locations were developed using a stratified random design along onshore/offshore transects in Segment 5, 7, and 9 or within EPA-Environmental Monitoring and Assessment Program (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 DTNP boundary, but later, due to budget constraints sampling in the DRTO region was halted since July 2011. Segment 2 (Marquesas) includes the Marquesas Keys and a shallow sandy area between the Marquesas and Tortugas called the Quicksands. Segments 2 (Marquesas) and 4 (Backcountry) are both influenced by water moving south along the SW Shelf. Segment 4 contains the shallow, hard-bottomed waters on the gulfside of the Lower Keys. Segment 6 (Sluiceways) can be considered as part of western Florida Bay. This area is 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.

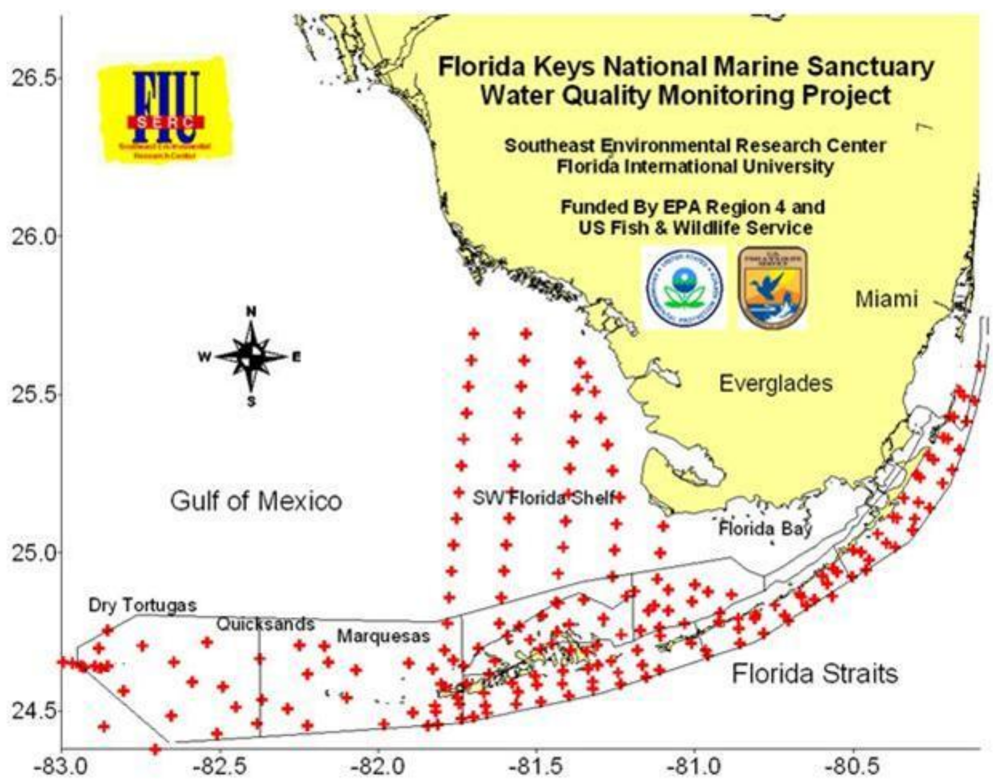

Figure 4. *The SERC Water Quality Monitoring Network showing the distribution of fixed sampling stations (+) within the FKNMS and SW Florida Shelf.*

2. Methods

2.1. Field Sampling

The period of record of this study was from March 1995 to December 2011 which included 66 quarterly sampling events. For each event field measurements and grab samples were collected from over 200 fixed stations within the FKNMS boundary (Fig. 4; Table 2), except for surveys 50 to 56 (Oct 2007-May 2009) when 48 Shelf stations were dropped. Starting in November 2011 there was a new reduction in the program and only 110 sites were sampled, including ten new stations located close to shore. Depth profiles of temperature (°C), salinity (practical salinity scale), dissolved oxygen (DO, mg l^{-1}), photosynthetically active radiation (PAR, $\mu E\ m^{-2}\ s^{-1}$), *in situ* chlorophyll *a* specific fluorescence (FSU), turbidity (NTU), 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.

Table 2: *Changes in monitoring coverage along the period of record*

Surveys	Stations	From	To
1 to 9	200	Mar-95	Aug-97
10 to 49	204	Oct-97	Sep-07
50 to 56	156	Oct-07	May-09
57 to 65	205	Jul-09	Jul-11
66	111	Nov-11	Dec-11

In the Backcountry area (Segment 4, Fig. 3) where it is too shallow to use a CTD, surface salinity and temperature were measured using a combination salinity-conductivitytemperature-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 4π spherical sensor (LI-193SB). PAR data with depth was 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 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_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 (μg 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. Analytical detection limits for year 2011 are shown in Table 3. It is important to point-out that these methodologies and especially the very low detection limits guarantee analytical quality in FIU/SERC facilities which are not achieved by any other laboratory in the State of Florida.

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^{-1} 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).

***Table 3**: FIU's Water Quality Lab Method detection limits for year 2011*

Analysis	SOP	Method Name	MDL (umoles/L)	PQL (umoles/L)	MDL (mg/L)	PQL (mg/L)
		modification of	SW	SW	SW	SW
N+N	SERC-004	EPA353.2	0.18	0.96	0.0025	0.0134
NO2-N	SERC-004	EPA353.2	0.04	0.16	0.0006	0.0022
NH4-N	SERC-004	EPA350.1	0.30	1.00	0.0042	0.0140
SRP	SERC-004	EPA365.1	0.06	0.40	0.0019	0.0124
TP	SERC-008	EPA365.1	0.60	0.10	0.0186	0.0031
TP- soil	SERC-008	EPA365.1	0.42	3.87	0.0130	0.1200
Si	SERC-005	EPA370.1	0.08	1.00	0.0022	0.0280
TOC	SERC-007	EPA415.1	4.17	20.83	0.05	0.25
TN - ANTEK 9000	SERC-006	ASTM D5176	5.71	17.86	0.08	0.25
Chl-a		SM10200H	0.10		0.10	

PQL values are established equal to the lowest calibration standard of each analysis.
Any reported value below PQL (S1) will be flagged and considered real but uncertain, as per LOQ definition
SOP= Standard Operating Procedure
MDL= Method Detection Limit
PQL= Practical Quantitation Limit
SW= Seawater

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; Briceño and Boyer 2010), Biscayne Bay (Briceño and Boyer 2010), and the Ten Thousand Islands (Boyer 2006; Briceño and Boyer 2011). 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 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 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

Temporal trends were quantified by simple regression with significance set at $P<0.10$. This approach simply evaluates the statistical significance of slope of secular trend, and is very responsive to changes at the extremes of the POR. Given that statistical significance is an arbitrary selection, bubble-diagrams were constructed to identify changes along the POR for all slopes disregarding their significance, and also for significant slopes only. The former display “tendencies” and the later identify trends. When these diagrams are shown side-by-side, they illustrate where changes are perhaps beginning to occur (tendencies) and where those changes have been consolidated (trend) for the parameter under consideration.

3. Results

3.1. Overall Water Quality of the FKNMS

Summary statistics for all water quality variables during 2011 and for 1995-2010 are shown in Table 3 for comparison purposes, as median, minimum, maximum, and number of samples (Table 1). Overall, the region was warm and euhaline with a median temperature of 25.88 °C and salinity of 36.17; oxygen saturation of the water column (DO_{sat}) was relatively high at 97.4%. On this coarse scale, the FKNMS exhibited very good water quality with median NO_3^-, NH_4^+, TP, and SiO_2 concentrations of 0.001, 0.004, 0.005 and 0.025 mg l^{-1}, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (~66%). However, DIN comprised a small fraction (4%) of the TN pool with TON making up the bulk (median 0.16 mg l^{-1}). SRP concentrations were very low (median 0.001 mg l^{-1}) and comprised only 12% of the TP pool. CHLA concentrations were also low overall, 0.32 µg l^{-1}, but ranged from 0.02 to 4.46 µg l^{-1}. TOC was 1. 76 mg l^{-1}; a value higher than open ocean levels but consistent with coastal areas. Median turbidity was low (0.70 NTU) as reflected in a low K_d (0.205 m^{-1}). Overall, 25% of incident light (I_o) reached the bottom. Molar ratios of TN to TP suggested a general P limitation of the water column (median TN:TP = 68.0) but this must be tempered by the fact that much of the TN is not bioavailable. Finally, median molar ratio DIN:SRP was 11.5, slightly below Redfield ratio (16) and suggesting slight DIN limitation (Redfield, 19.

Figure 5 shows percent change between 2011 and previous years (1995-2010) for all variables. Largest increases correspond to density difference between surface and bottom waters (46% DSIGT), followed by SiO2-B (34%), SRP-B (31%), SRP-S (26%), DIN:TP (26%), TN:TP (21%), NH4-B (18%) and Kd (17%). On the other extreme, the largest declines are those of NO3-S (-54%), DIN:SRP (-50%), TP-S (-43%), TURB-S (-21%), %Io (-21%), TP-B (-21%), NOx-S (-21%) and TOC-S (-15%). So, in general, there is improvement in WQ

***Table 4**. Summary statistics for each water quality variable in the FKNMS for the 2010 period of record. Data are summarized as median, minimum value, maximum value, and number of samples (Count).*

Variable	Depth	2011 Count	2011 Minimum	2011 Maximum	2011 Median	1995-2010 Median
NOX	surface	725	0.0001	0.0335	0.0016	0.0019
(mg l^{-1})	bottom	501	0.0001	0.0200	0.0015	0.0018
NO3	surface	701	0.0000	0.0276	0.0010	0.0015
(mg l^{-1})	bottom	474	0.0000	0.0188	0.0010	0.0014
NO2	surface	724	0.0001	0.0058	0.0005	0.0006
(mg l^{-1})	bottom	501	0.0000	0.0041	0.0005	0.0005
NH4	surface	724	0.0001	0.0699	0.0044	0.0041
(mg l^{-1})	bottom	501	0.0003	0.0334	0.0041	0.0034
TN	surface	726	0.05	0.79	0.16	0.1740
(mg l^{-1})	bottom	501	0.06	0.92	0.15	0.1425
DIN	surface	725	0.0008	0.1033	0.0062	0.0066
(mg l^{-1})	bottom	501	0.0006	0.0408	0.0059	0.0055
TON	surface	726	0.0482	0.7815	0.1534	0.1642
(mg l^{-1})	bottom	501	0.0242	0.9160	0.1417	0.1347
TP	surface	726	0.0014	0.0548	0.0049	0.0070
(mg l^{-1})	bottom	501	0.0017	0.0520	0.0047	0.0056
SRP	surface	716	0.0000	0.0467	0.0013	0.0009
(mg l^{-1})	bottom	492	0.0000	0.0474	0.0012	0.0009
TOC	surface	684	0.00	9.76	1.76	2.01
(mg l^{-1})	bottom	432	0.86	6.90	1.61	1.55
SiO2	surface	725	0.0001	2.6102	0.0246	0.0237
(mg l^{-1})	bottom	501	0.0001	2.1230	0.0180	0.0119
TURB	surface	715	0.0000	17.1213	0.7000	0.8500
(NTU)	bottom	524	0.0000	30.0000	0.5650	0.6250
SAL	surface	723	28.94	39.78	36.17	36.20
(PSU)	bottom	684	29.14	39.79	36.27	36.24
TEMP	surface	723	16.52	33.74	25.88	27.10
(^{o}C)	bottom	684	13.39	33.67	25.82	26.76
DO	surface	674	5.72	11.02	6.67	6.05
(mg l^{-1})	bottom	635	5.52	9.38	6.69	6.04
SAT	surface	613	0.00	171.28	97.41	90.41
%	bottom	602	0.00	144.83	97.53	90.02
CHLA (μ l^{-1})	surface	726	0.02	4.46	0.32	0.30
Kd (m^{-1})	column	665	0.0002	3.9906	0.2053	0.1713
pH	surface	31	7.82	8.40	8.16	7.88
TN:TP	surface	615	5.40	568.40	68.01	53.46
N:P	surface	605	0.35	280.72	11.54	17.27
DIN:TP	surface	615	0.28	49.67	2.81	2.07
%Io	surface	708	0.00	100.00	24.86	30.17
DSIGT	surface	602	-0.67	2.85	0.03	0.01
Si:DIN	surface	614	0.01	211.64	1.90	1.66

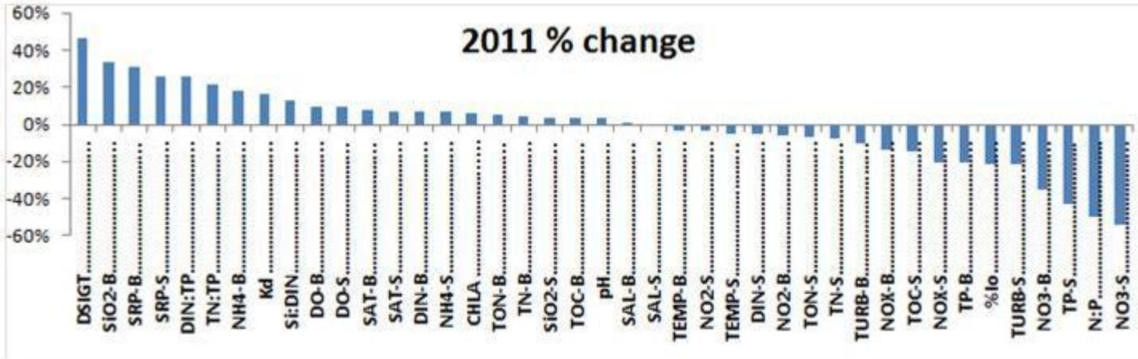

Figure 5: *Percentage change of 2011 water quality as compared to 1995-2010*

3.2. Objective Classification Analysis

Principal Component Analysis (PCA) and Hierarchical Cluster analysis were performed in tandem in 2010 to classify and to group the Sanctuary waters as a function of their biogeochemical composition (Boyer and Briceño 2011 FKNMS REPORT). PCA identified five components accounting for 56.8% of the total variance of the original variables. The hierarchical clustering algorithm used the mean, SD, median and median absolute deviation of the five factor scores of each station to classify all 155 sampling sites into 6 groups having robust correspondence in water quality (Fig. 6): 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. Further subdivision of the INSHORE segment into 3 classes (Lower, Middle and Upper Keys) and the SHELF also into 3 classes has been proposed by Briceño et al (2011 EPA Report and Paper).

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 approximately BACK>BAY>SHELF>=INSHORE>=MARQUESAS>REEF>TORT

The BACK zone (23 stations) was highest in nutrients, especially NO_3^-, NH_4^+ and TN, and second in TP, as well as TOC (Fig. 7). 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.

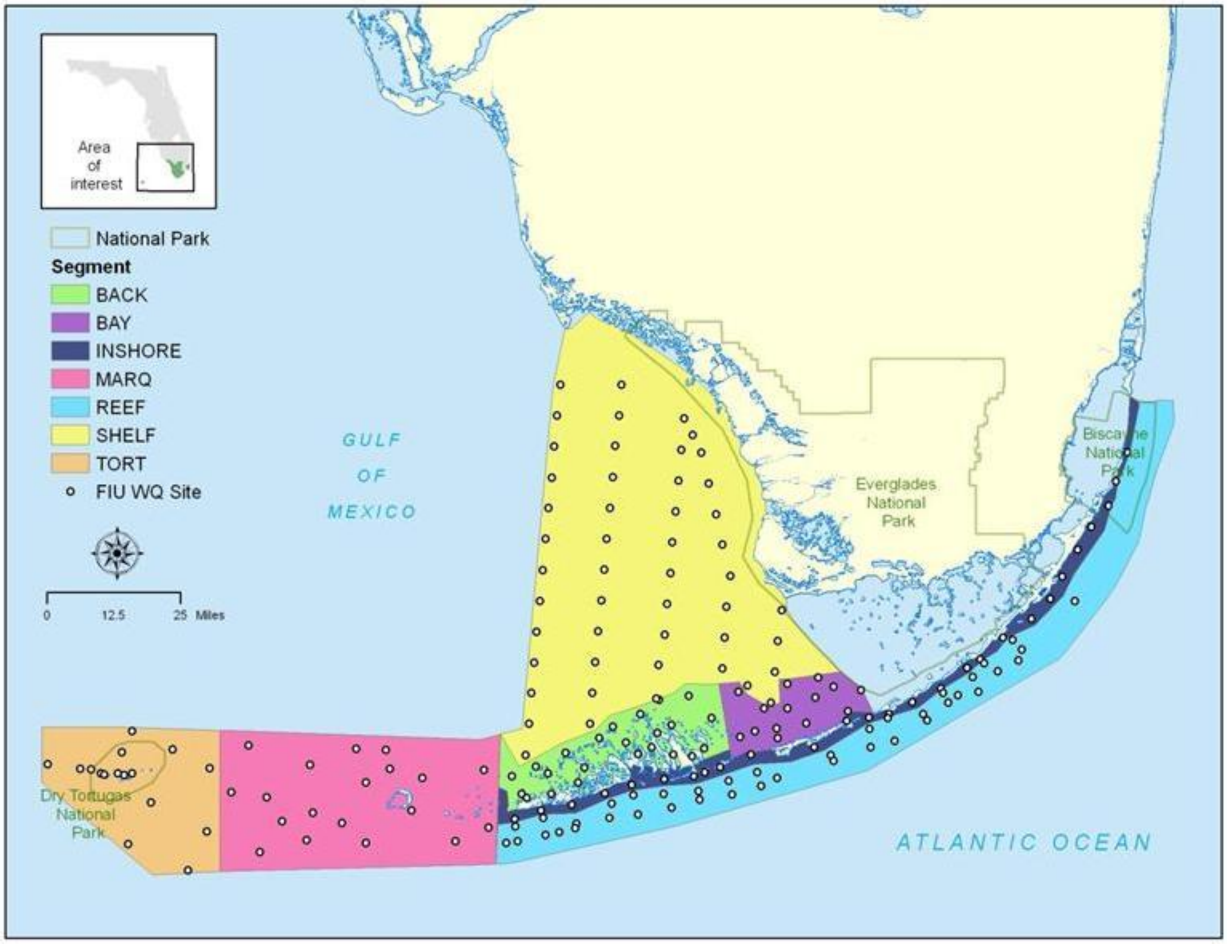

Figure 6. *Results of statistical analysis showing station membership in distinct water quality groups.*

The BAY (Sluiceway; 15 stations) included sites most influenced by Florida Bay and water moving south from the SW Shelf. It was highest in SiO_2, 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, TN and turbidity, high SiO_2, and lowest salinity of any other region.

The water quality of MARQ, REEF, and TORT zones was most similar to each other and characterized by the lowest nutrient concentrations. 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.

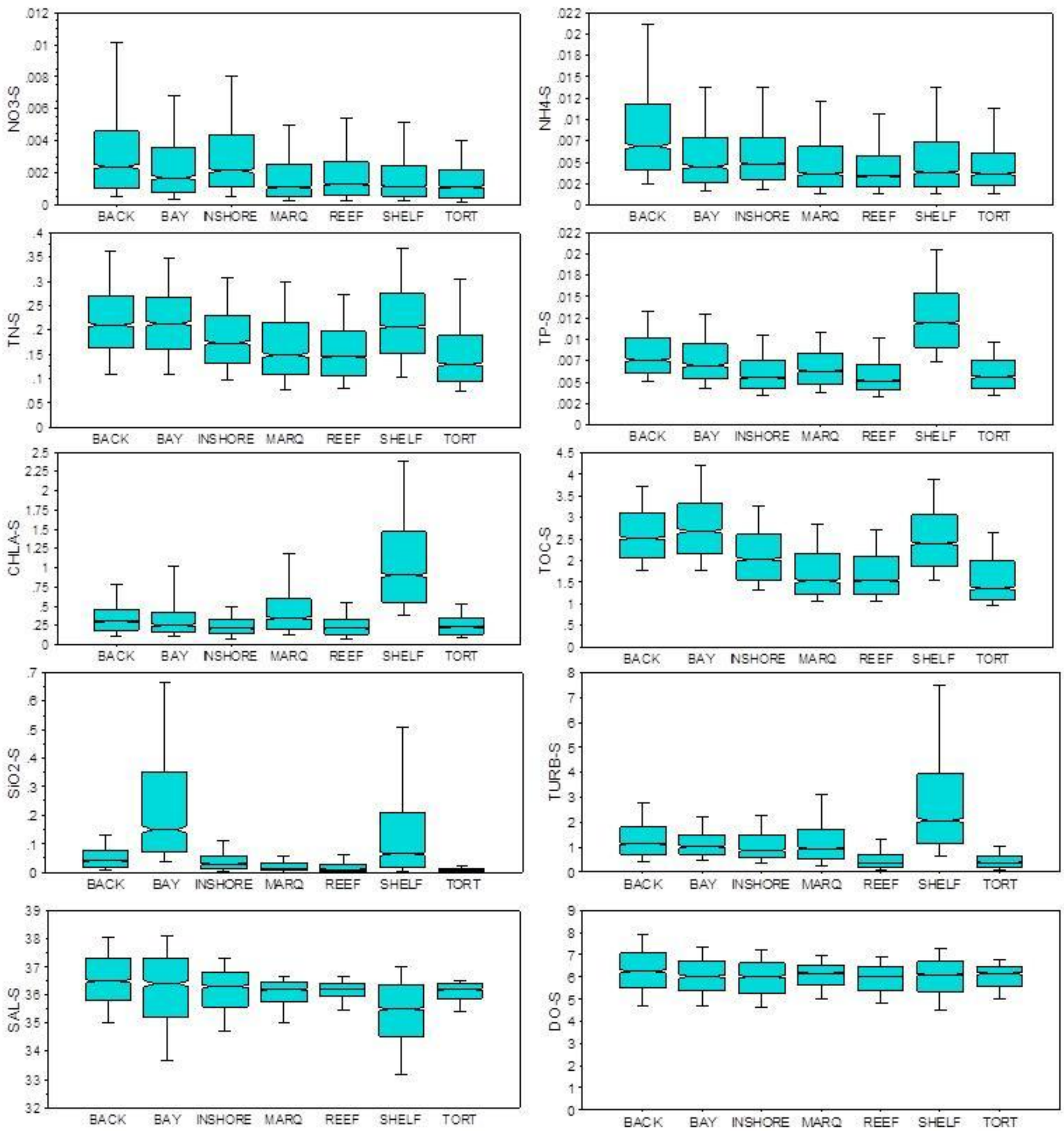

Figure 7: *Box-and-whisker plots showing median and distribution of NO_3^-, NH_4^+,TN, TP, CHLA, TOC, SiO_2, turbidity, DO, and salinity as stratified by water quality cluster. Notches in the box that do not overlap with another are considered significantly different.*

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. Incorporation of ten new stations (#500 to #509) since November 2011 will better define the proposed gradient from inshore to reef.

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. TORT sites within the Dry Tortugas National Park were dropped since November 2011.

3.3. Contour Maps

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 periodically. An example of such maps shows the median distribution of salinity across the region (Fig. 8). 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.

The usual distribution of dissolved NO_3^- is very different from that for salinity (Fig. 9). This implies that there are other factors responsible for its distribution, such a phytoplankton and seagrass uptake as well as N_2 fixation and benthic remineralization.

In contrast, TP distribution is the opposite of salinity patterns (Fig. 10). This implies that the source of P on the Shelf is preferentially 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. 10 and 11). Contour plots for all remaining variables are shown in Appendix 1

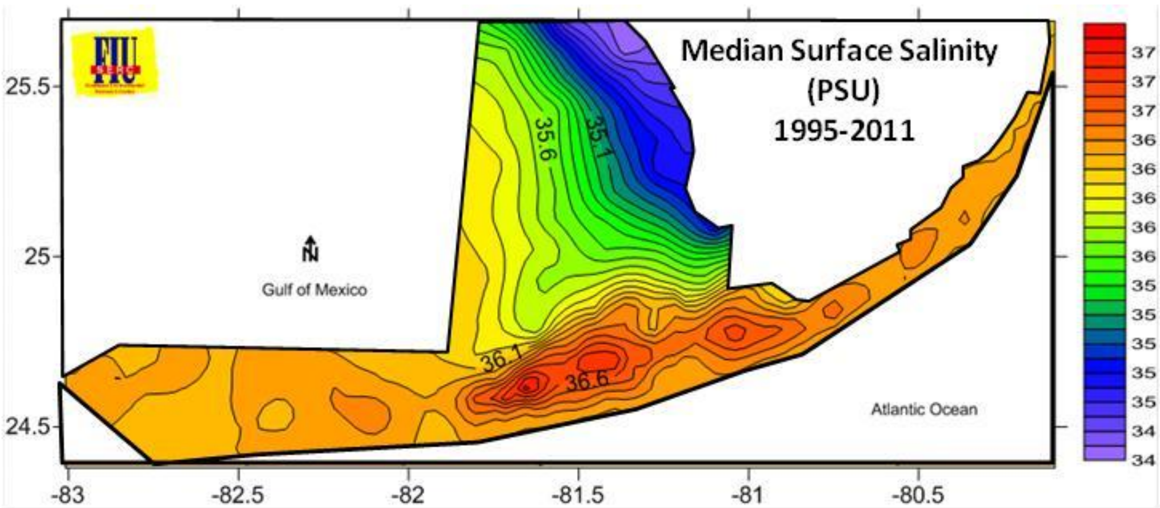

***Figure 8**. Median salinity field for the region showing freshwater inputs from the Everglades, marine influence and higher salinities in shallow waters of the Backcountry (evaporation?).*

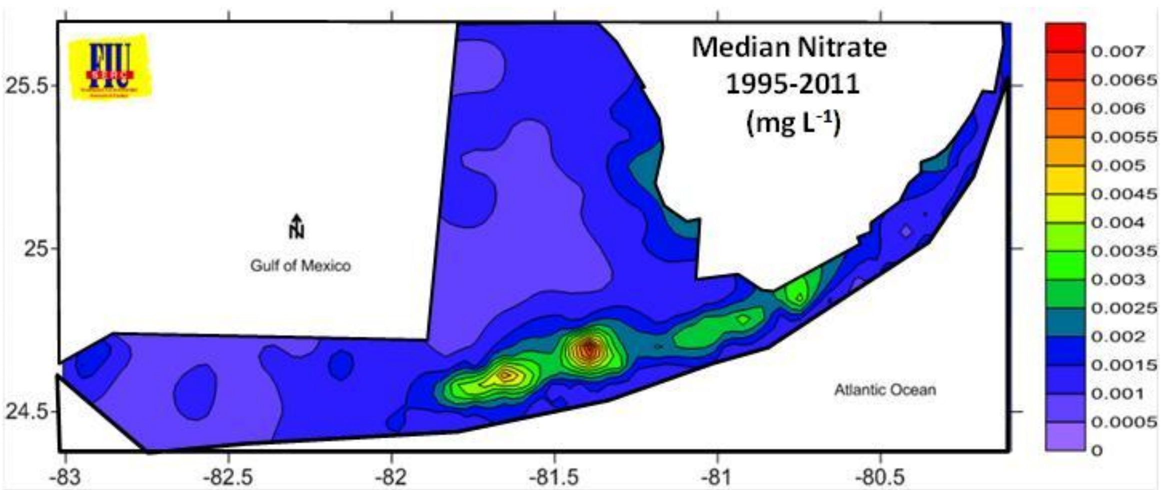

***Figure 9**. Median nitrate concentration for the Florida Keys-Shelf Region*

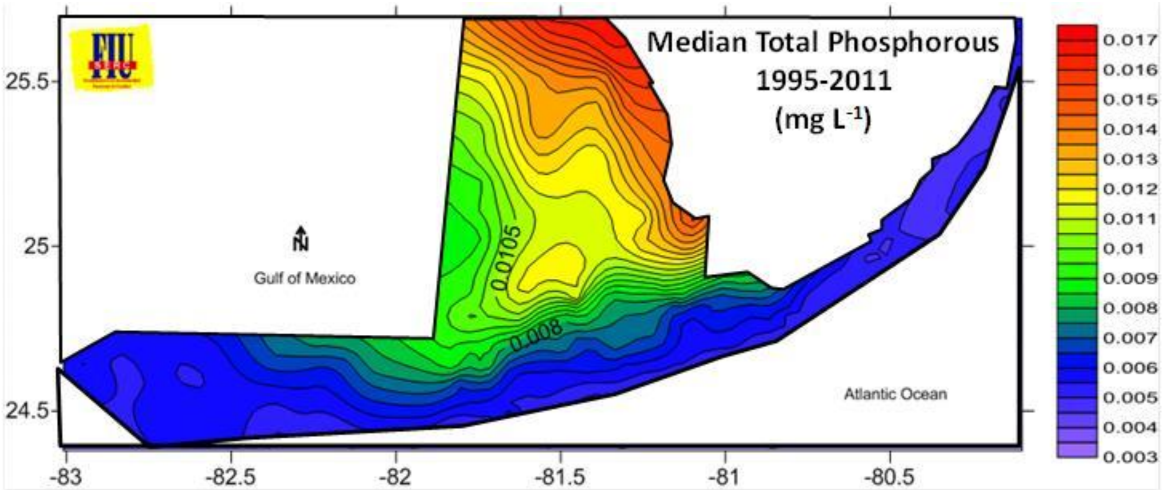

Figure 10: *Distribution of median total phosphorus in the region.*

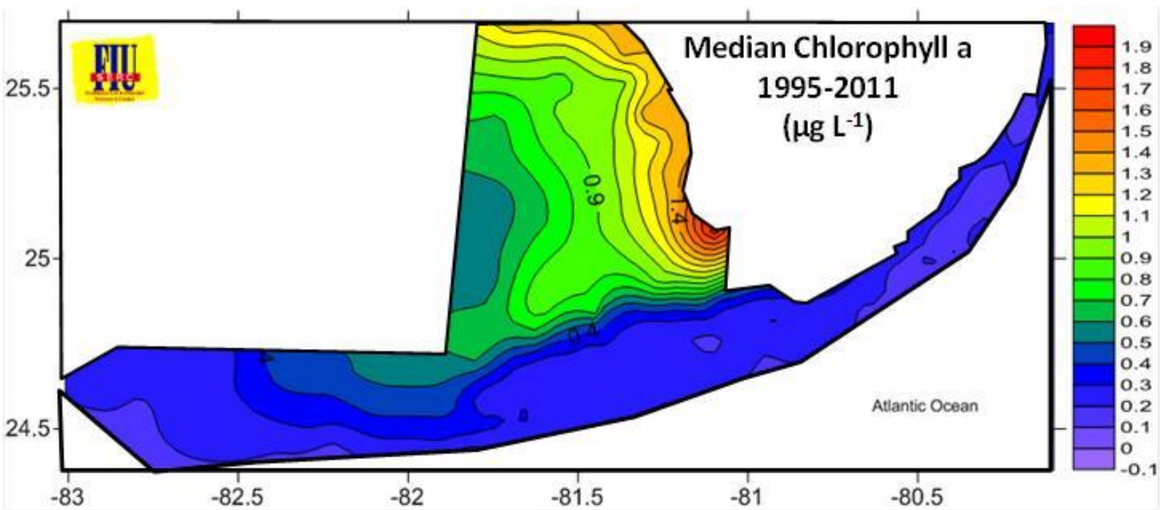

Figure 11*. Median chlorophyll a in the region showing the similarity to TP distribution.*

3.4. Time-Series Analysis

After 16 years of monitoring water quality in the Keys we came to the conclusion that water quality is largely externally-driven and most fluctuations are modulated by climatic or disturbance events of varied periodicity, and by ocean circulation. 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). Anthropogenic impacts on water quality are difficult to assess as we move away from islands and urban centers and into waters influenced by oceanic processes. This complex dependence may cause tendencies to fluctuate and even reverse during a period of record. The importance of climate on South Florida coastal resources and especially water quality of the Florida Keys and Bay has been widely discussed and recognized in the literature (Johns and Lee 2011; Briceño and Boyer 2010; Gibson et al 2008; FOCC 2009) and

Slope of least squares linear regressions for each water quality variable were calculated for the 16-year period of record to explore secular trend. Only slopes having significant trends at probability $p < 0.01$, were considered significant. Slopes whose probabilities were larger than 0.1 were considered to indicate just a “tendency”, and as such are reported here. Under this approach, not only trends but tendencies may be valuable as an early warning indicator of potential problems and issues with water quality. Most of the slopes, significant or not, are in fact very small, but to get an idea of total change over the period of record, all are displayed in bubble-diagrams for the 16 year period (Fig. 12-22). In these diagrams the bubble’s diameter is proportional to the magnitude of the plotted variable.

Clearly, there have been large changes in the FKNMS water quality over time, but the only sustained monotonic trends that have been observed are a region-wide decline in TOC, an increase in TN and a surface temperature increase in SHELF waters. That said, significant increases and declines in some water quality variables have 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 hydrology and climate forcing. Contour maps and bubble-charts highlight these relationships very effectively.

NO_3^-+NO_2^- (NO_x^-) in surface waters had a general tendency to remain the same or to decline slightly overall (Fig. 12) with significant trends only as declines in waters of the westernmost Backcountry and inshore of Lower and Middle Keys. Tendency of bottom NO_x^- was also declining, especially in Tortugas, with a couple of exceptions. No cluster of bottom stations with significant NO_x^- trend was observed.

Surface NH_4^+ general tendency was to decline in SHELF and increase elsewhere along the Keys, especially in the Atlantic side of the Marquesas and Tortugas (Fig. 13), the Backcountry, and less so at INSHORE and REEF. Significant increases exist for the Marquesas and Tortugas as well as significant declines in scattered sites in SHELF. Tendency in NH_4^+ in bottom waters was to decline, and the trend was also to decline in scattered sites in TORT, mid MARQ, LK and MK.

Surface TN tendency was to increase region-wide, except in some locations in BACK and eastern SHELF areas, where it tended to decline. Significant TN trends increased in the Tortugas/Marquesas and at several offshore reef sites throughout the FKNMS (Fig. 14). Bottom TN tendency was to increase especially in TORT, MARQ and REEF offshore LK and UK. Tendency and trend for bottom TN are very similar to those of surface TN. Significant bottom trends are all increases in Tortugas, western Marquesas, the reef track offshore the Lower Keys, and an isolated cluster at the extreme northeast (Fig 14).

TP concentrations were relatively constant throughout the FKNMS (small bubble-size in Fig 15) with slight increases at sites INSHORE and REEF, and small declines in SHELF sites. Significant declines were mostly along the western border of SHELF. The same tendency was seen in bottom waters of the Sanctuary, but without significant trend.

Surface DO tendencies (Fig 16) show a contrast between declining in Shelf and Sluiceways sites and increases from Marquesas to Upper Keys, but significant trends are restricted to a few sites in the Backcountry, Lower and Upper Keys. Bottom DO tendencies on the contrary are of increases except for some localities in the Sluiceways. Bottom DO trends occurred as increases in the Lower Keys and western Shelf, and declines in the Sluiceways. These significant declines in surface and bottom DO in NE Sluiceways – adjacent to Florida Bay, Spanish Harbor Keys, and Long Beach areas were also reported in 2010. This is problematic as DO is an important requirement for animal life.

Surface SiO_2 changed very little, with increases observed in NE Sluiceways adjacent to Florida Bay. Bottom SiO_2 also remained unchanged except for the increase at the same locality in the Sluiceways as observed in surface samples (Fig. 17). Turbidity changes in surface waters are primarily declines in the Shelf southeastern extreme, facing Florida Bay. Turbidity did not correspond with K_d, indicating that CDOM probably has more impact on the light field than does fine particulate seston (Fig. 18). Turbidity in bottom samples tends to increase and develops a strong and significant increasing trend in Lower Keys waters.

TOC displays a robust regional declining trend in practically all stations (Fig 19). This TOC decline, observed over the FKNMS and SW Shelf, may help explain why Turbidity and Kd are unrelated. 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.

Salinity in surface waters of the Backcountry, Sluiceways and northeastern SHELF has increased dramatically (Fig. 20), with little change elsewhere. The loci of major change are those where, first, evaporation plays an important role to increase salinity in shallow waters, namely the Backcountry; and second, where contrasting water masses, Everglades' fresh and Shelf marine waters meet, and are subjected to both, sea-level rise and/or Everglades's water management. Conceptually, thse sites should be the one where changes are more discernible. Bottom salinities follow similar tendency and trend patterns as those of surface samples.

Light extinction (K_d) tendency was to decline at most sites INSHORE and on the reef track (Fig. 21), suggesting that there was an increase in light penetration to the benthos over time. K_d increased greatly and significantly on the eastern 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.

Overall CHLA tendency was to display a strong gradient from increases on the northern SHELF to declines on its southern portions. Additionally, it declined in MARQ and stayed about the same throughout the REEF, INSHORE and TORT (Fig 22). CHLA also increased in the Sluiceway around SW Florida Bay, but these increases were driven by wind blown or advected phytoplankton blooms from outside the FKNMS.

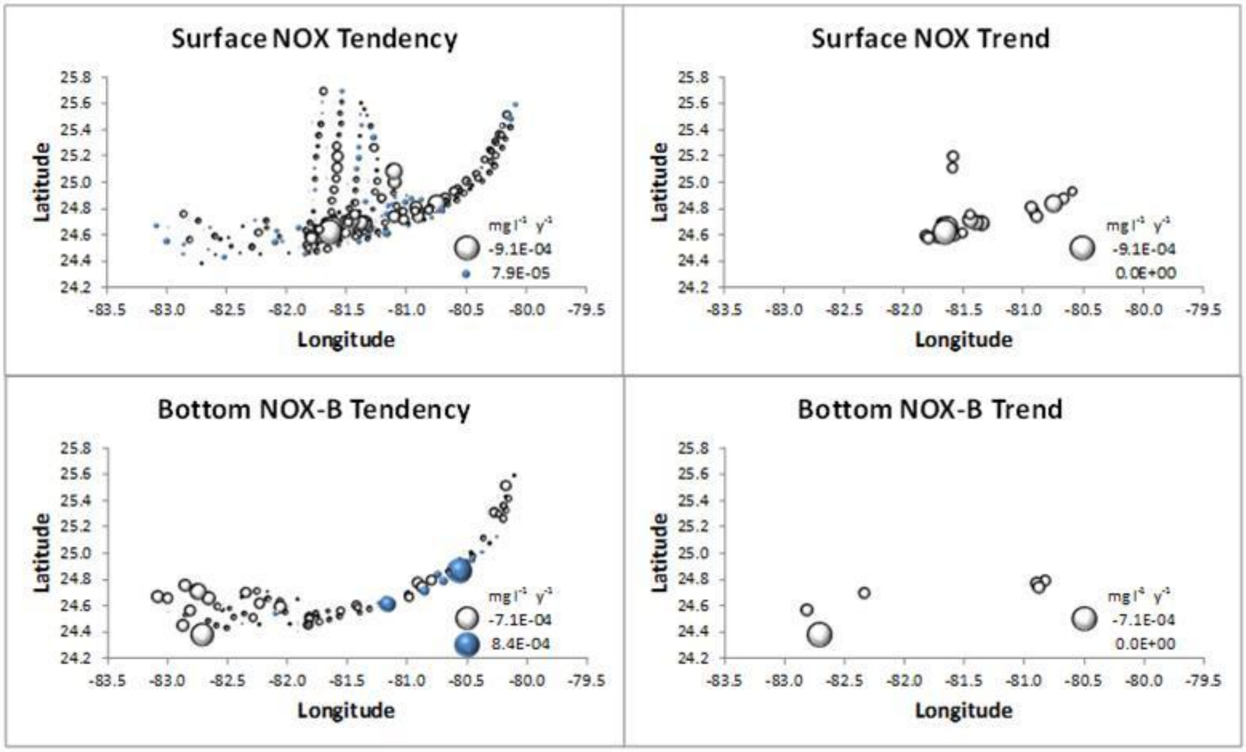

Figure 12. *Tendency and trend in* $NO_3^-+NO_2^-$ (NO_x^-) *in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

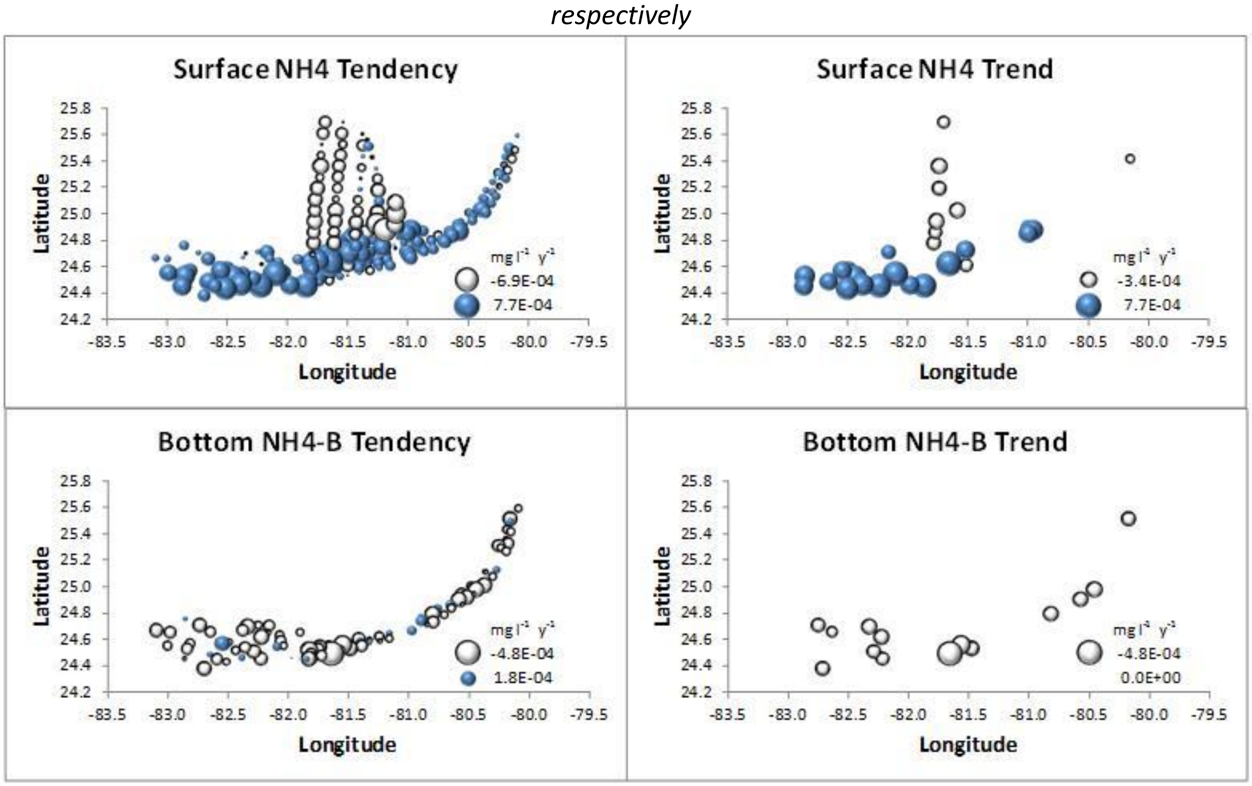

Figure 13. *Tendency and trend in* NH_4^+ *in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

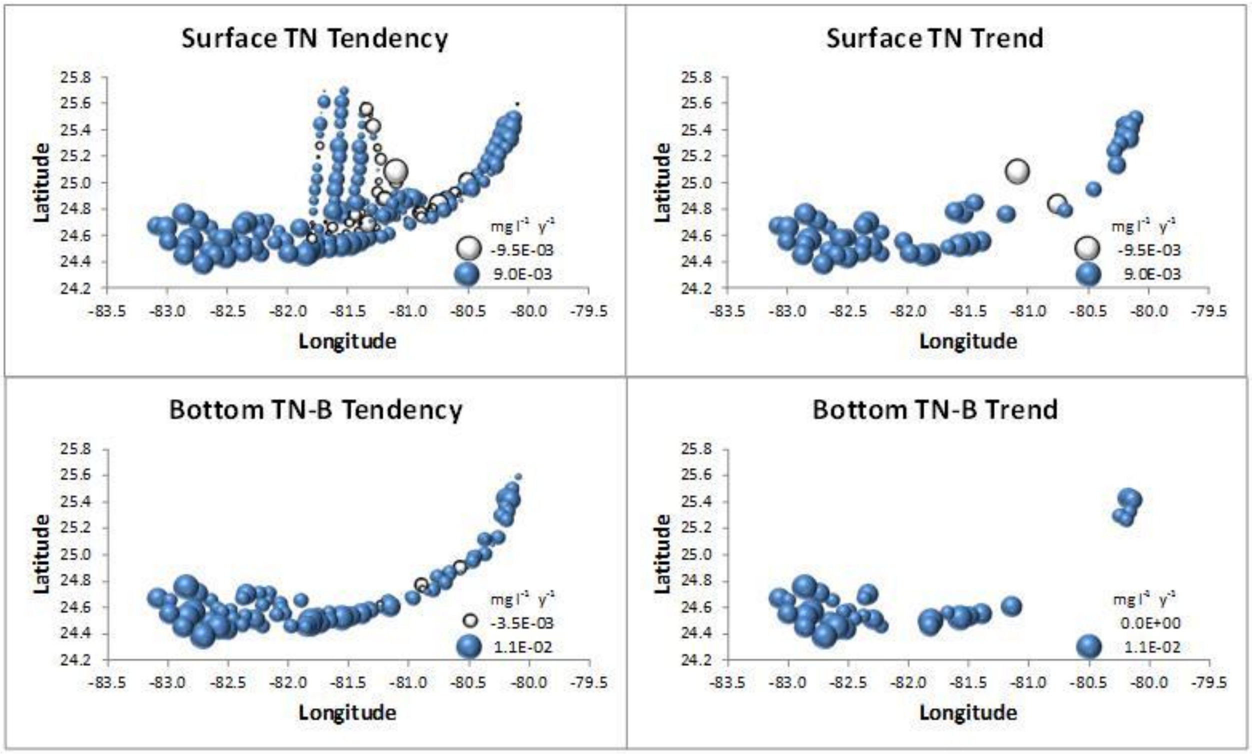

Figure 14. *Tendency and trend in TN in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

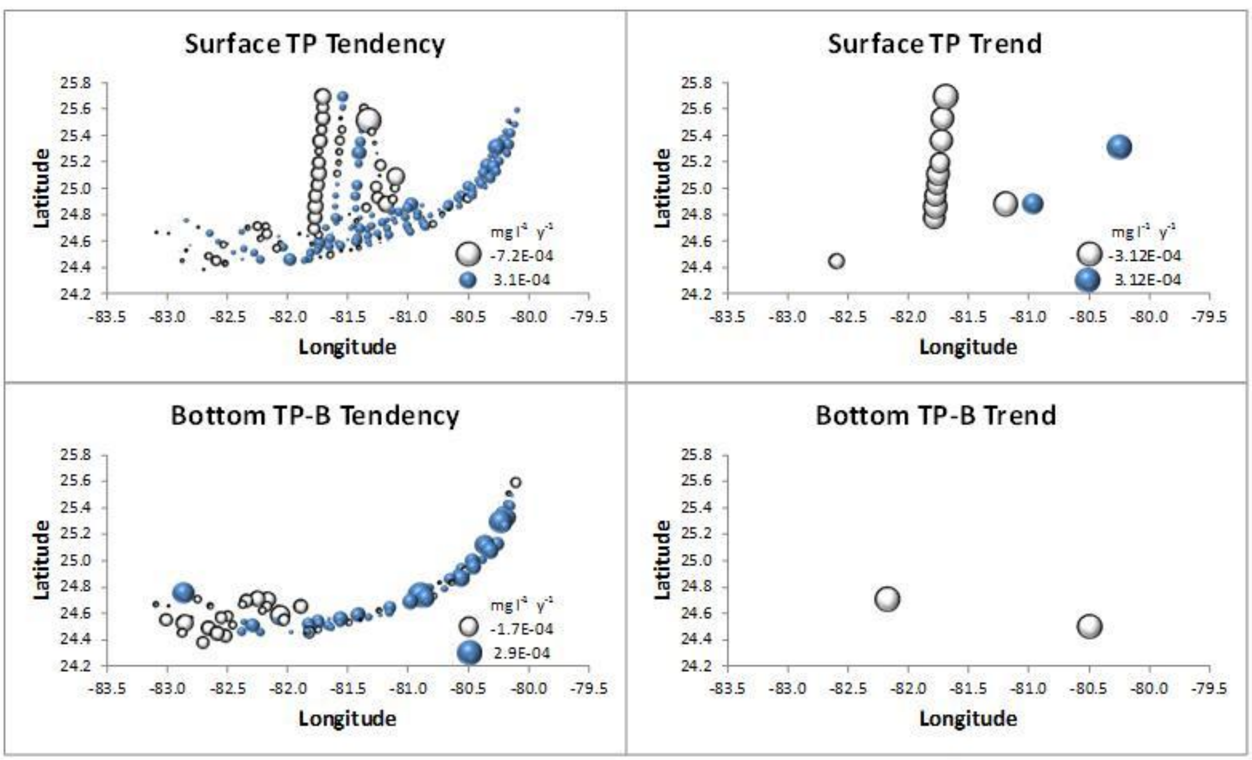

Figure 15. *Tendency and trend in TP in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

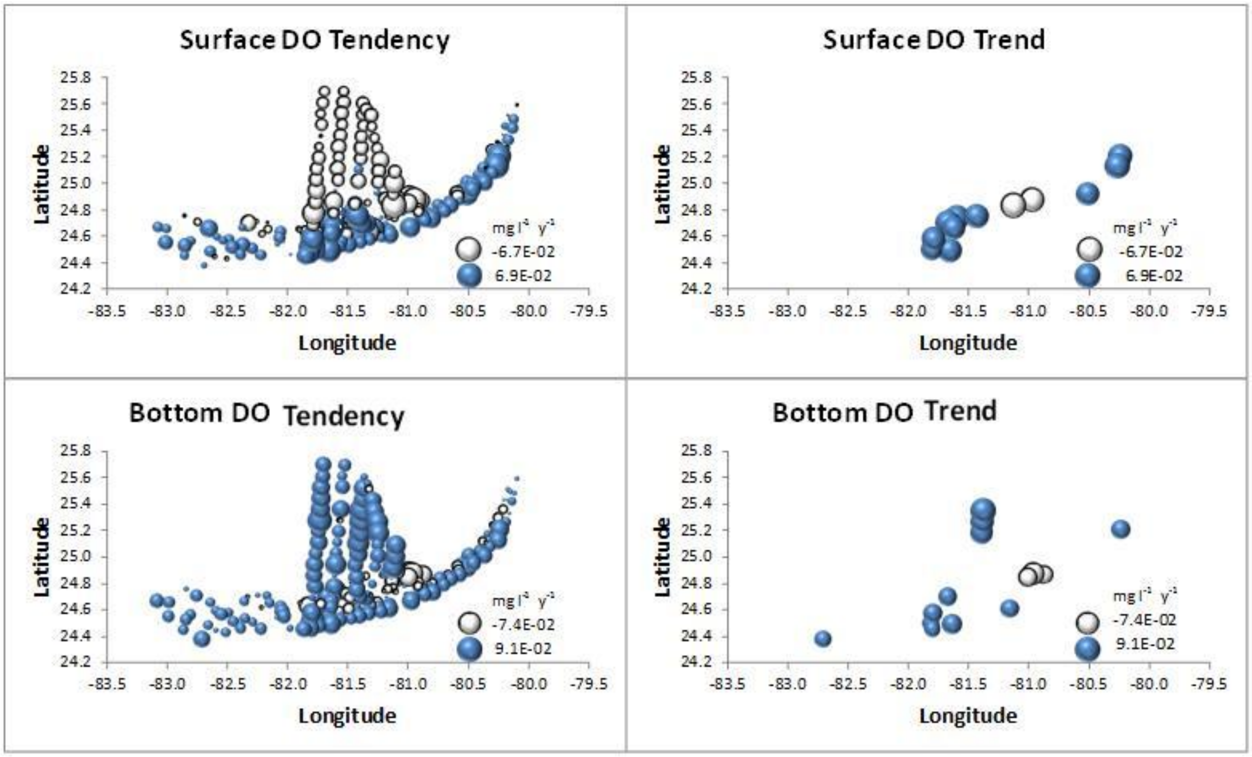

Figure 16. *Tendency and trend in DO in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

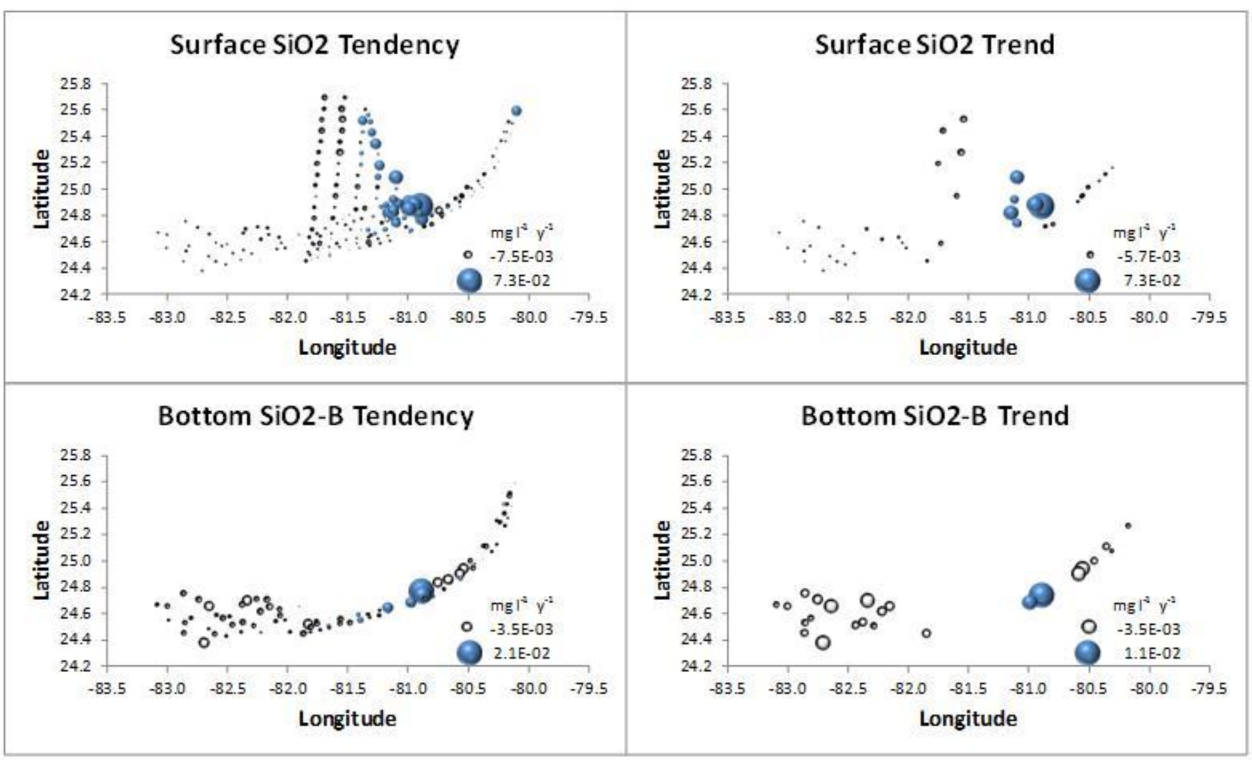

Figure 17. *Tendency and trend in SiO_2 in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively.*

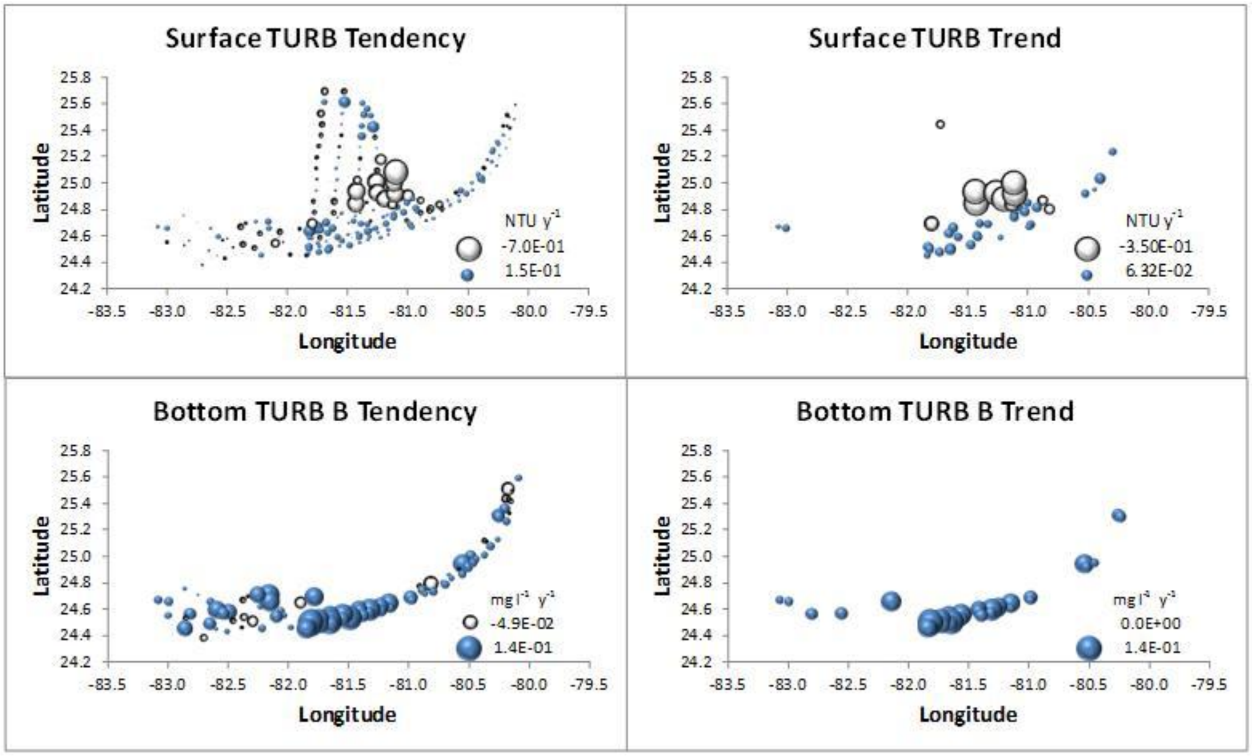

Figure 18. *Tendency and trend in Turbidity in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively.*

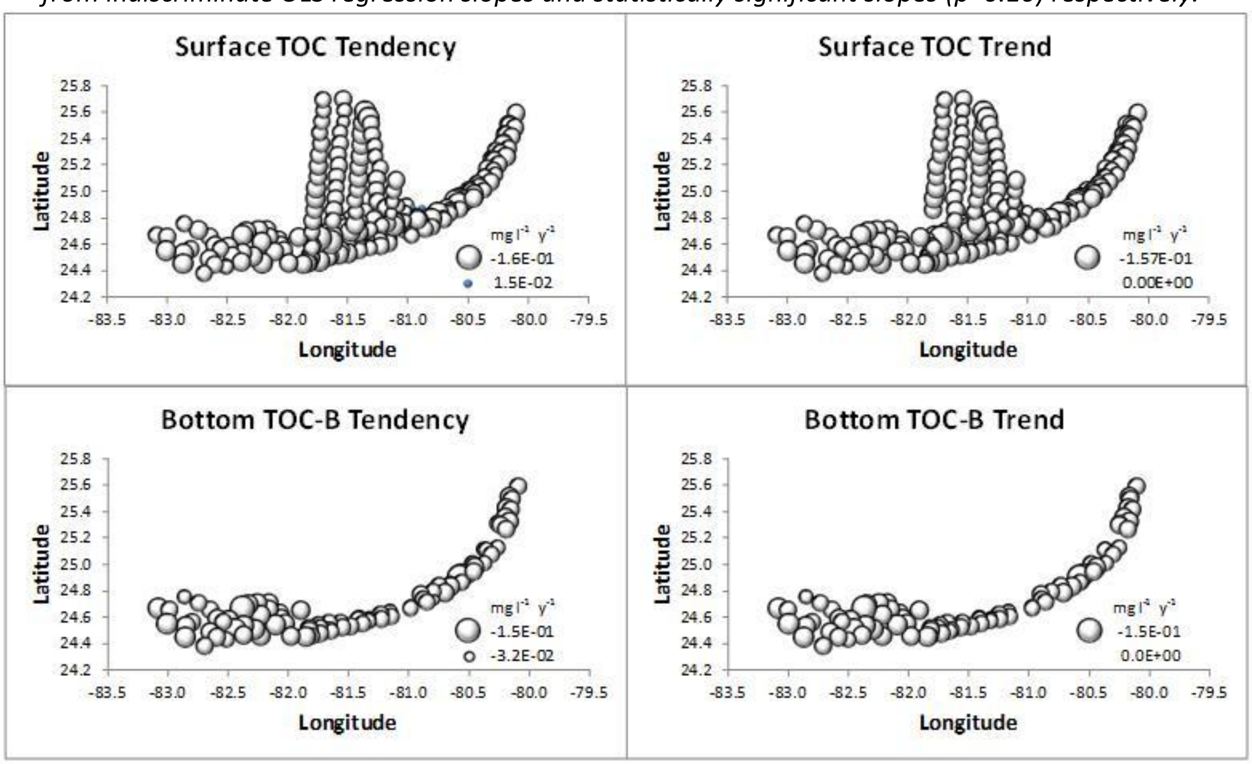

Figure 19. *Tendency and trend in TOC in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively.*

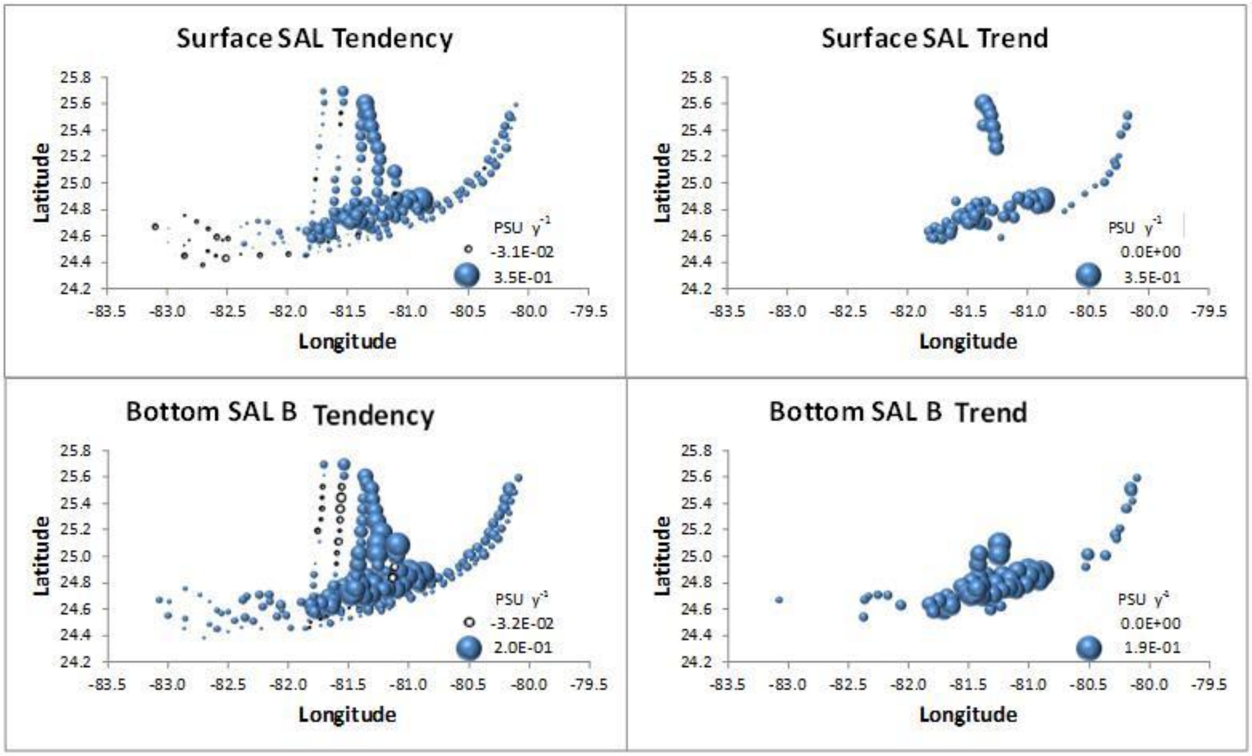

Figure 20. *Tendency and trend in Salinity in surface and bottom waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively.*

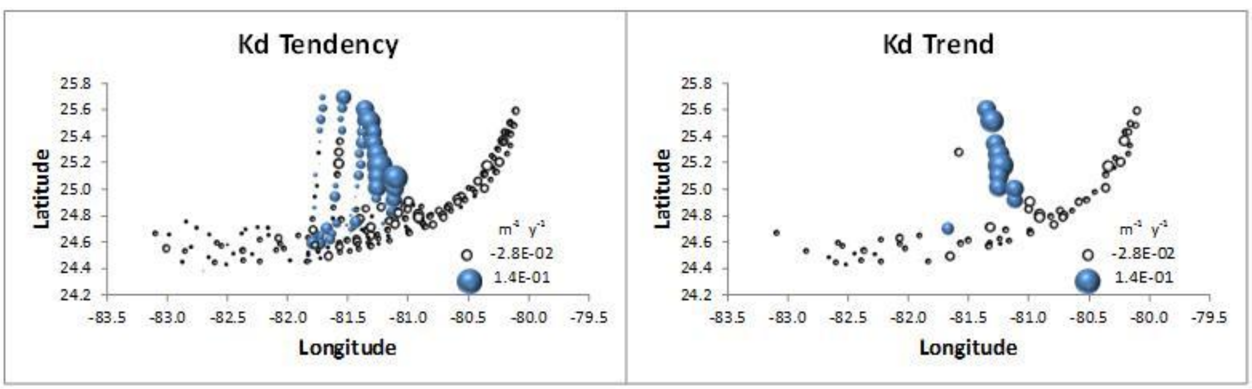

Figure 21. *Tendency and trend in K_d in waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

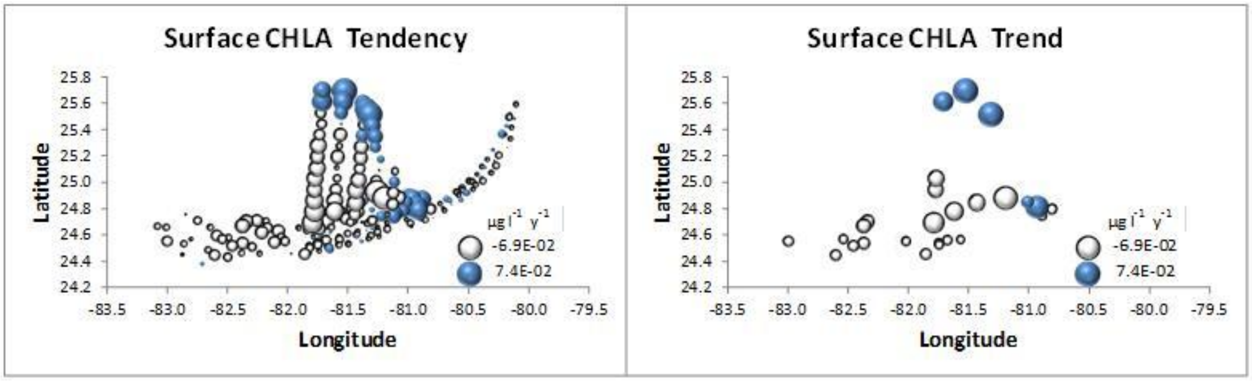

Figure 22. *Tendency and trend in CHLa in waters for 16 year period calculated from indiscriminate OLS regression slopes and statistically significant slopes (p<0.10) respectively*

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.

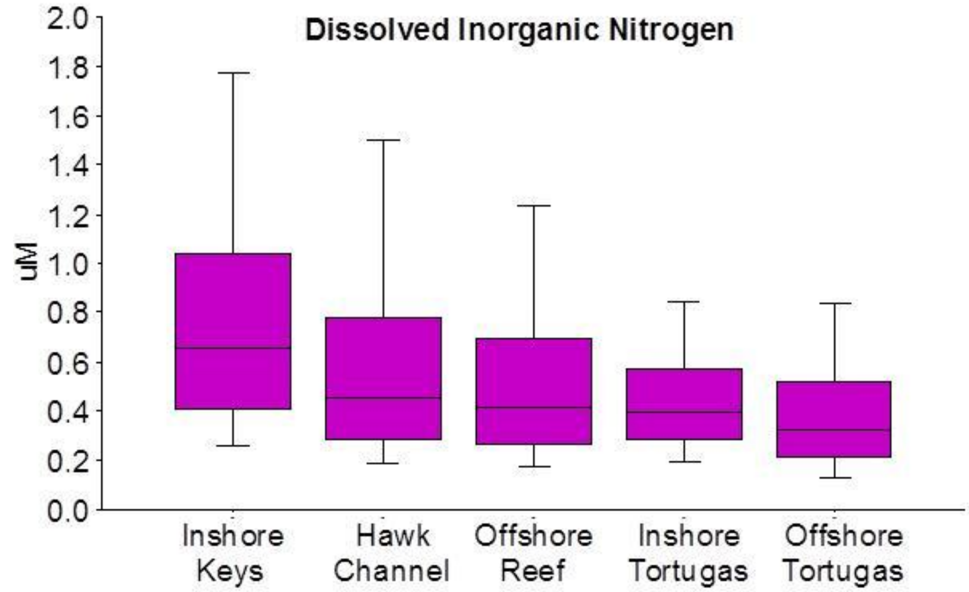

Figure 23

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.

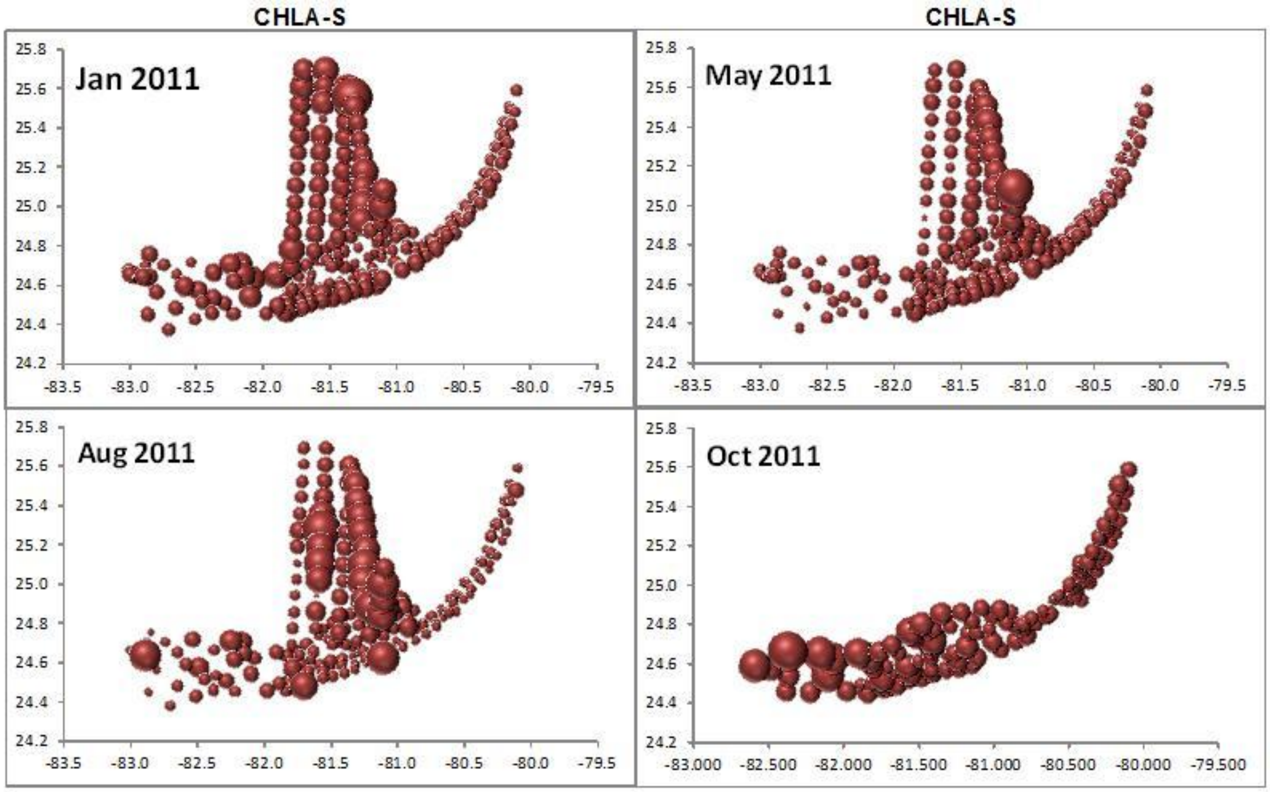

Figure 24. *Regional distribution of Chlorophyll a concentrations (µg l^{-1}) during 2011. Median values are 0.38, 0,31, 0.32 and 0.21 µ l^{-1} CHLa for Jan, May, Aug and Oct 2011 respectively*

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/l and the vertical attenuation coefficient for downward irradiance (K_d, 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 Baseline and for 2006 to 2011.

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

EPA WQPP Water Quality Targets

	Reef Stations		All Stations (except Shelf)	
Year	**CHLA ≤ 0.35 ug l^{-1}**	**Kd ≤ 0.20 m^{-1}**	**DIN ≤ 0.75 µM (≤ 0.010 ppm)**	**TP ≤ 0.25 µM (≤ 0.0077 ppm)**
1995-05	1,778 of 2,367 (75.1%)	1,042 of 1,597 (65.2%)	7,826 of 10,254 (76.3%)	7,810 of 10,267 (76.1%)
2006	196 of 225 (87.1%)	199 of 225 (88.4%)	432 of 990 (43.6%)	316 of 995 (31.8%)
2007	198 of 226 (87.6%)	202 of 222 (91.0%)	549 of 993 (55.3%)	635 of 972 (65.3%)
2008	177 of 228 (77.6%)	181 of 218 (83.0%)	836 of 1,000 (83.6%)	697 of 1,004 (69.4%)
2009	208 of 228 (91.2%)	189 of 219 (86.3%)	858 of 1,003 (85.5%)	869 0f 1,004 (86.6%)
2010	170 of 227 (74.9%)	176 of 206 (85.4%)	843 of 1,000 (84.3%)	738 of 1,003 (73.6%)
2011	162 of 229 (70.7%)	150 of 207 (72,5%)	738 of 922 (80.0%)	844 of 923 (91.4%)

5. 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, Gibson et al. 2008).

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 salinity (Fig 25). 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.

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.

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.

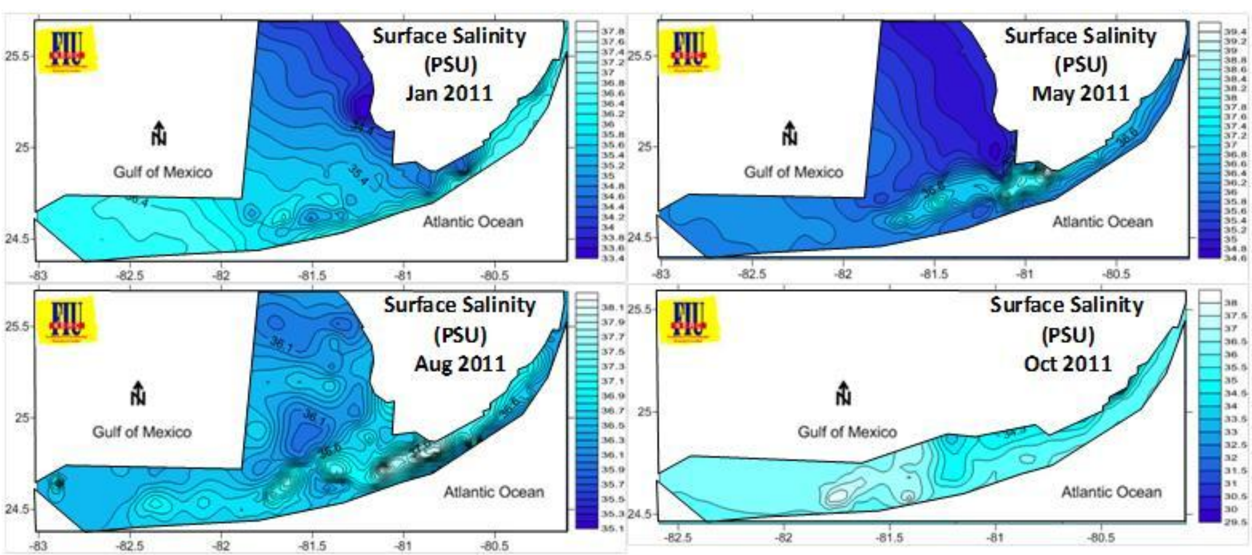

Figure 25: *Surface salinity patterns during 2011*

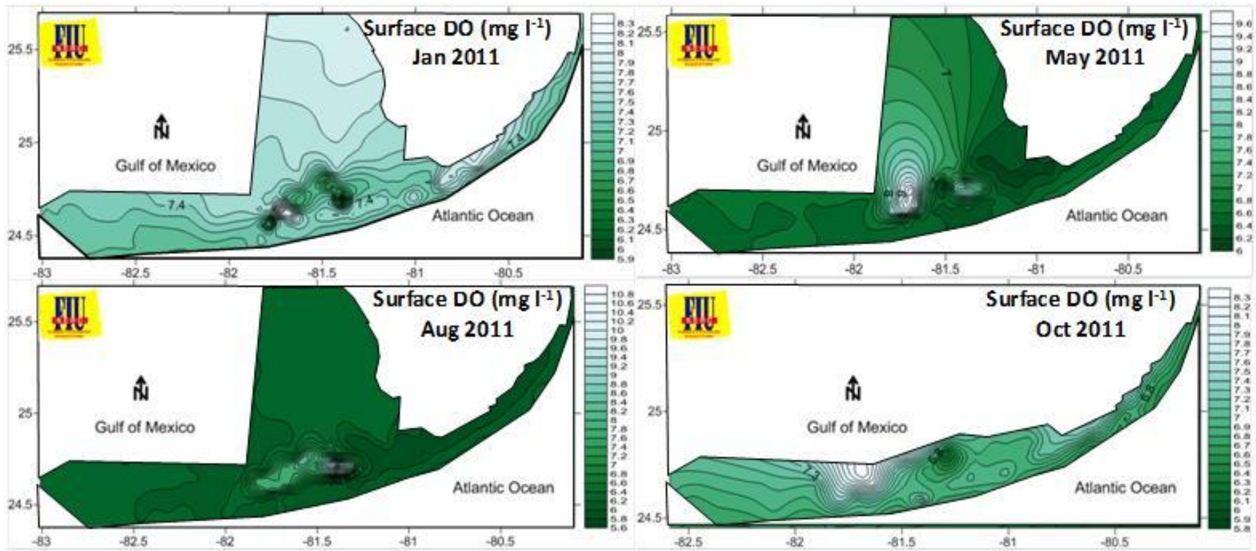

Figure 26: Surface dissolved oxygen (DO) distribution in the region during year 2011

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_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 >0.014 ppm 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 exported as DIN to the FKNMS in general.

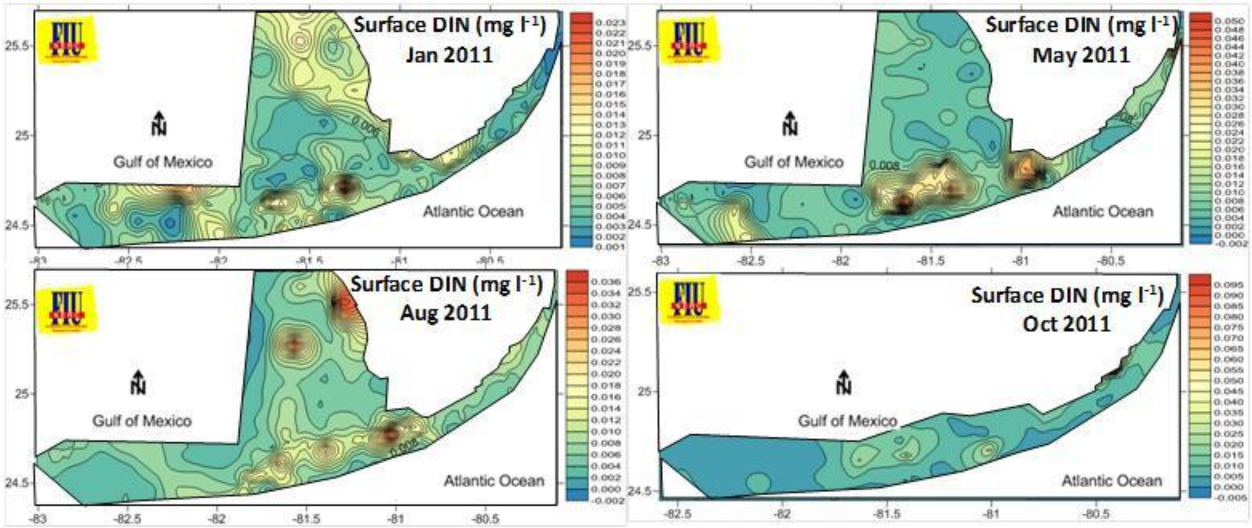

Figure 26: Surface dissolved inorganic nitrogen(DIN) distribution in the region during year 2011

Interestingly, in some instances NO_3^- was highest in the bottom waters on the offshore reef tract. 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 many situations, independent water masses may be distinguished by difference in density (sigma-*t*, σ_t) between surface and bottom. Since density is driven more by salinity than temperature, we do not always observe differences in σ_t between surface and bottom during upwelling events. However, decreased temperature of bottom waters from intrusion of deeper oceanic waters may be an indicator of increased upwelling-driven changes. These upwelling events may also affect nutrient species such as NH_4^+, 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 and no anomalous increase of bottom nutrients was observed. Again in Aug 2011 $\Delta\sigma_t$ increased significantly (Fig. 29).

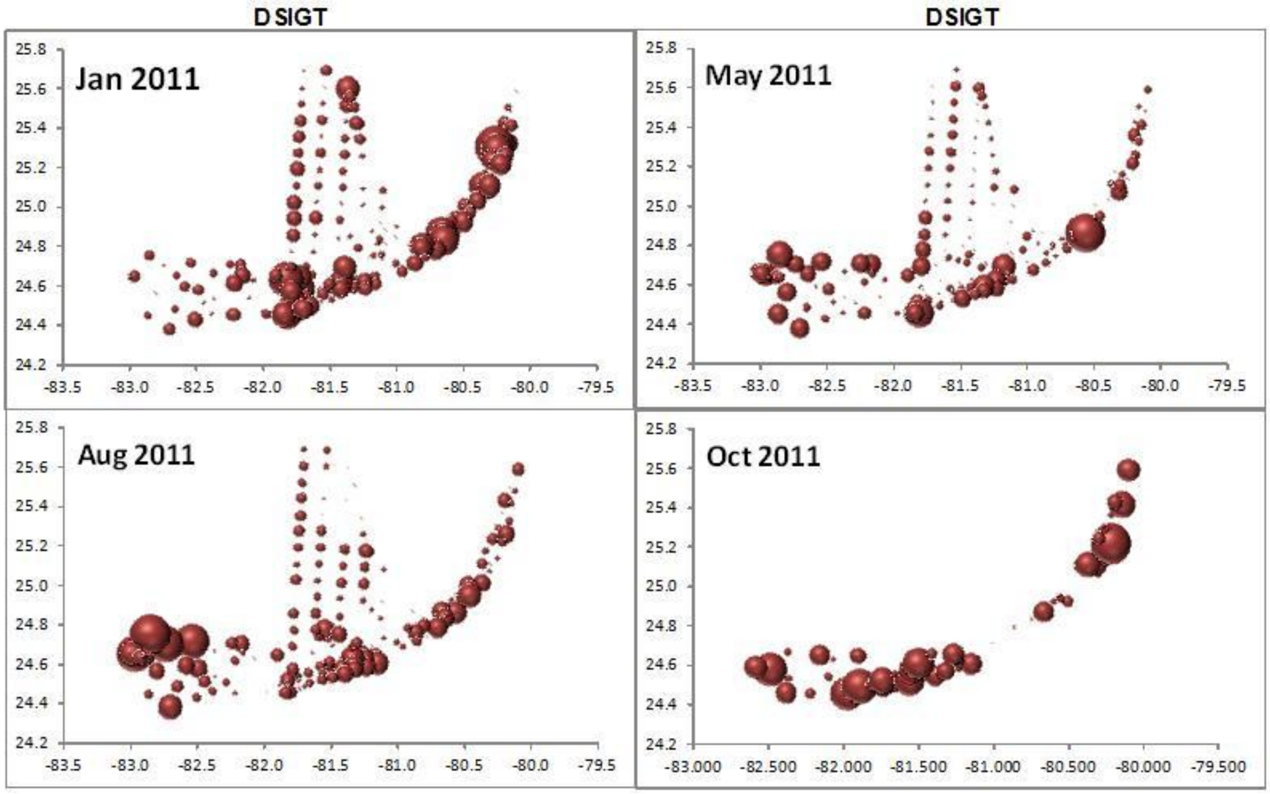

Figure 29*. Surface and bottom density differences ($\Delta\sigma_t$) across the region during 2010*

NH_4^+ concentrations were distributed with highest levels in Shelf facing the Ten Thousand Islands, and the Backcountry (Fig. 30). NH_4^+ shows 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.

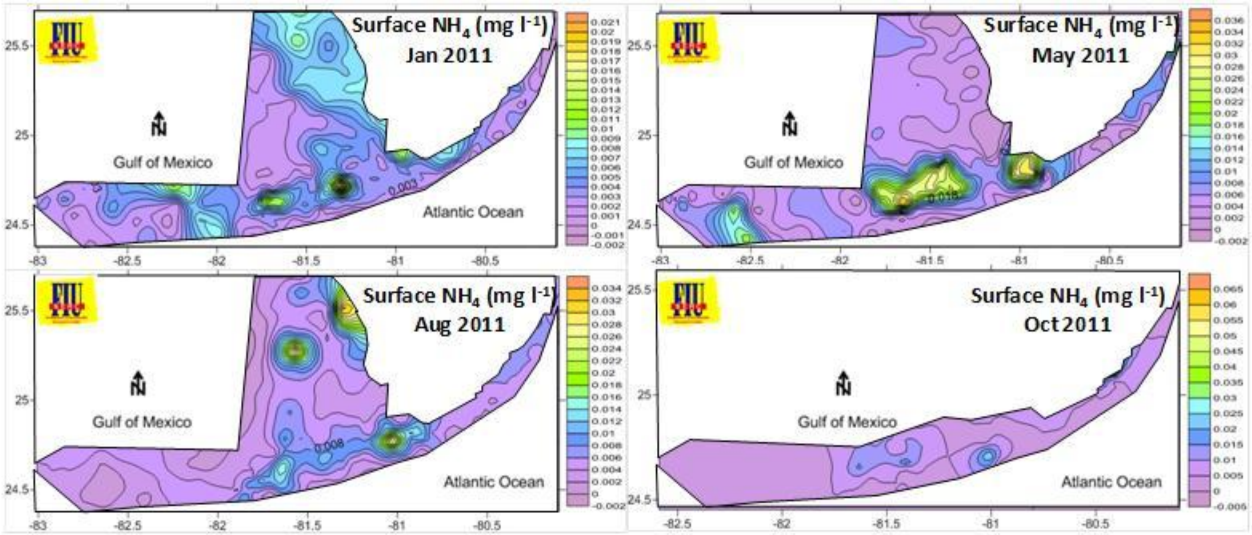

Figure 30. *Surface ammonium (*NH_4^+*) distribution in the region during year 2011*

Spatial patterns in TP in South Florida coastal waters were strongly driven by the west coast sources (Fig. 31). 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.

Concentrations of TOC (Fig. 32) and TON (not shown) are remarkably similar in pattern of distribution across the South Florida coastal hydroscape. The decreasing gradient from west coast to Tortugas was very similar to that of TP. This gradient was 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).

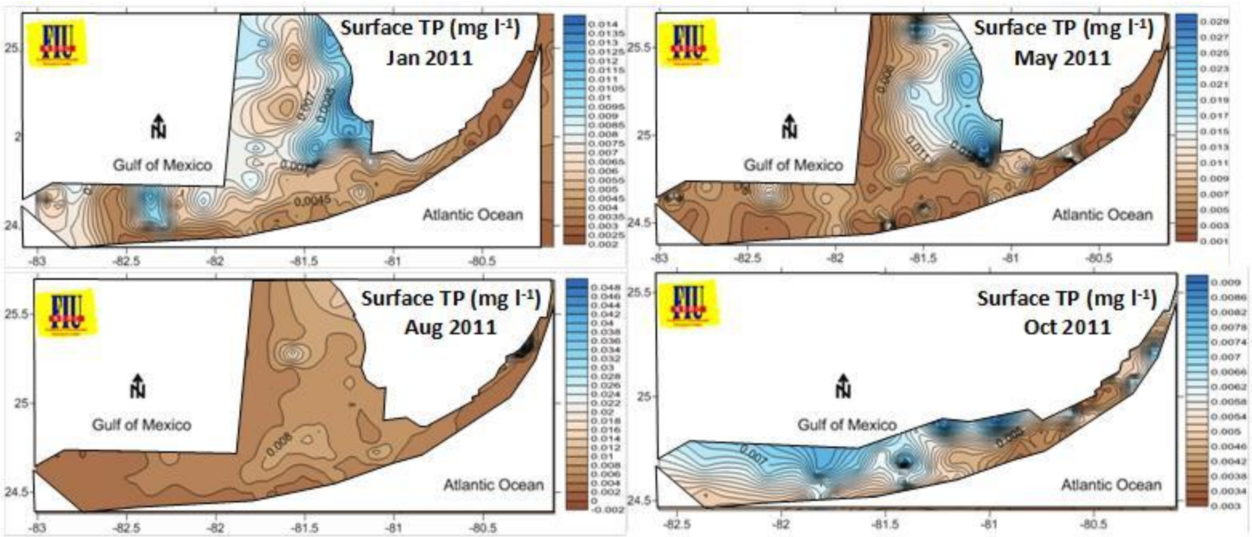

Figure 31. *Surface Total Phosphorous (*TP) *distribution in the region during year 2011*

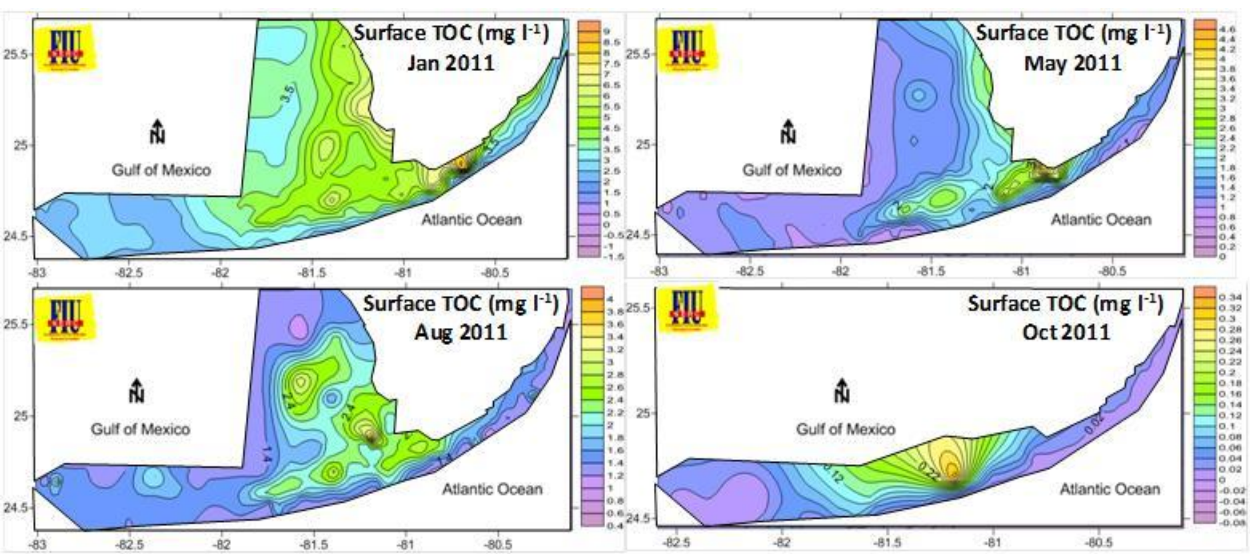

Figure 32. *Surface Total Organic Carbon (*TOC) *distribution in the region during year 2011*

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 imply 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 the Shelf, NW Florida Bay, and the Ten Thousand Islands exhibited high levels of CHLA relative to the FKNMS (Fig. 33). 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.

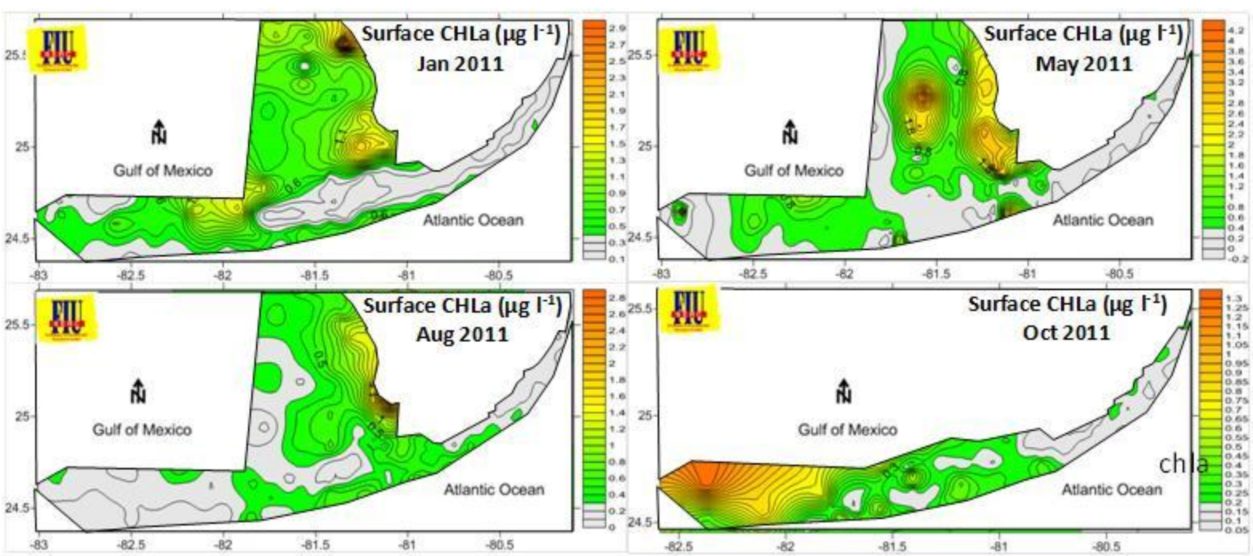

Figure 33. *Surface Total Organic Carbon (*TOC) *distribution in the region during year 2011*

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.

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 34). 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.

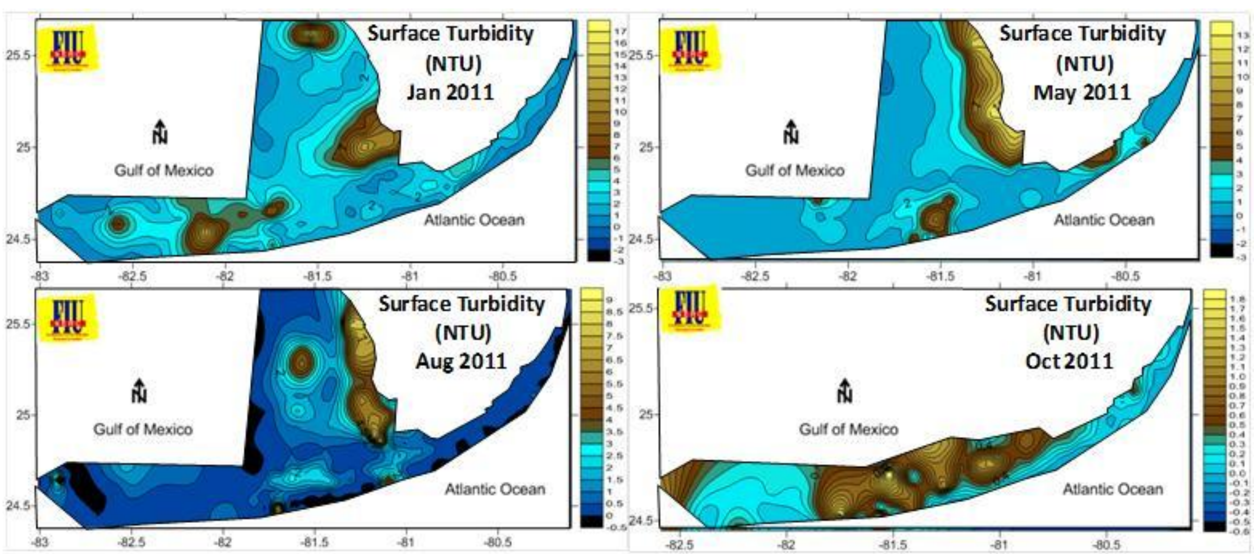

Figure 34. *Surface Turbidity distribution in the region during year 2011*

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_d) was highest alongshore and improved with distance from land. This trend was expected as light extinction is related to water turbidity (Fig 35). However, in Keys waters, CDOM is a more prominent driver of light penetration.

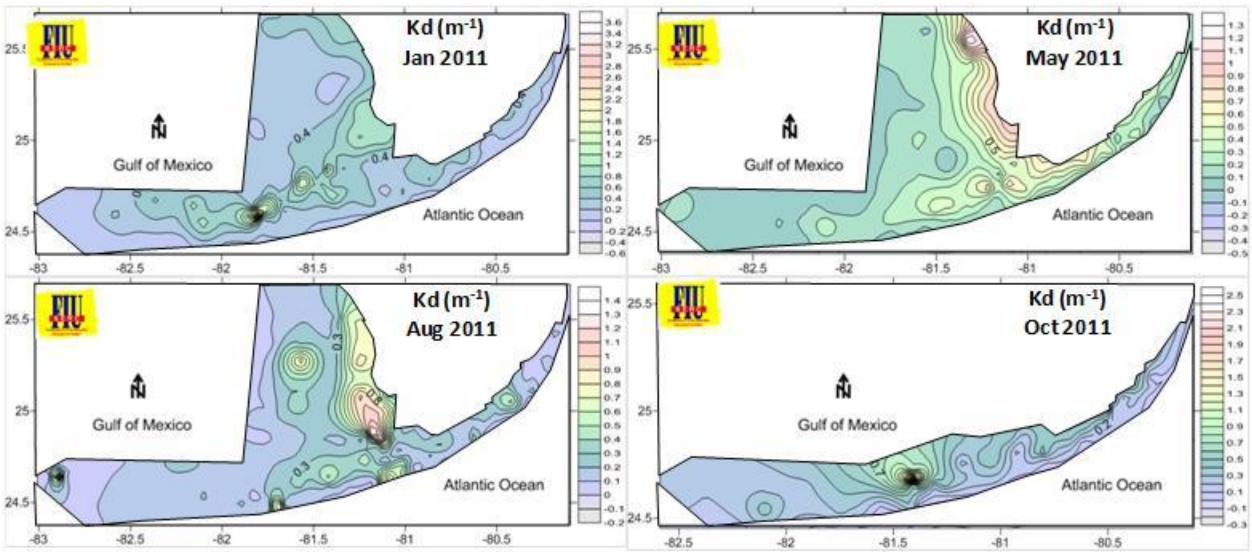

Figure 35. *Light extinction (Kd) distribution in the region during year 2011*

Surface SiO_2 concentrations exhibited a pattern (Fig. 36) suggesting that the source of SiO_2 in this geologic area of carbonate rock and sediments is from siliceous periphyton (diatoms) growing in the western Florida Bay. 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 are depleted mostly by mixing (although we no longer have data from the Shelf), allowing SiO_2 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_2 to the nearshore Atlantic waters is through the Sluiceway and Backcountry (Fig. 36). 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.

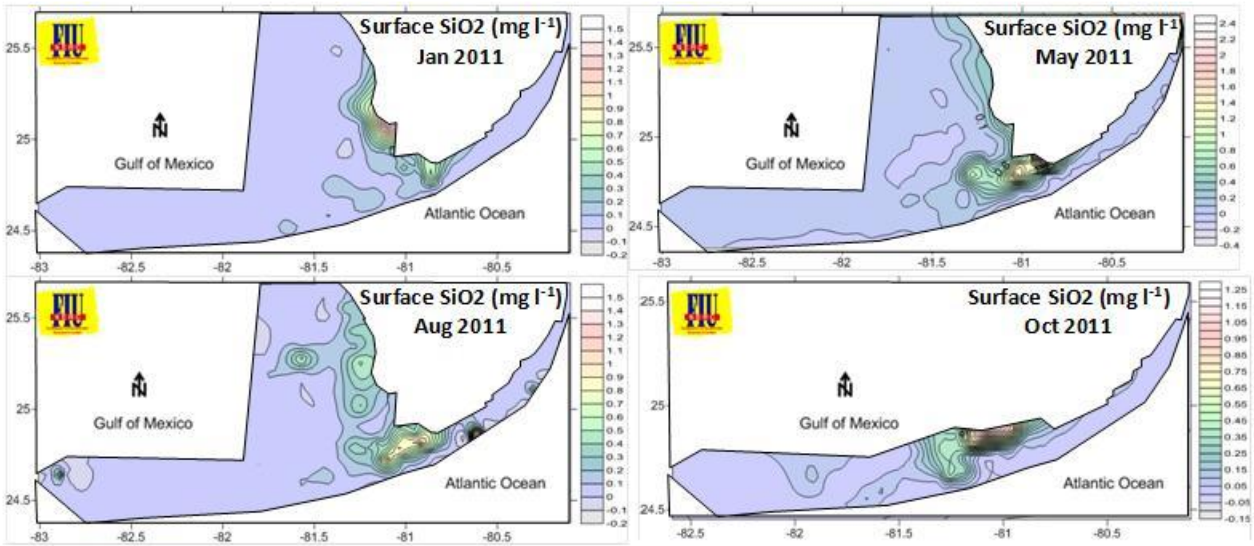

Figure 36. *Surface Silica (*SiO_2*) distribution in the region during year 2011*

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.

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 climate forcing. 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 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, 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-592 of the Southeast Environmental Research Center at Florida International University.

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APPENDIX 2	Regression Slopes	5 pages