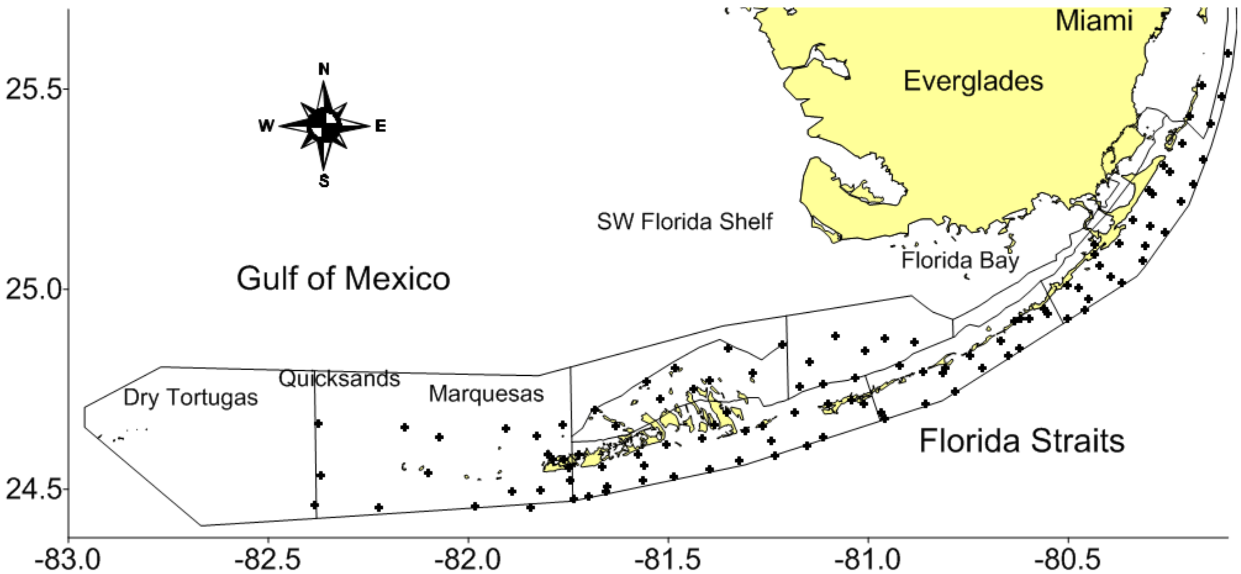
2012 ANNUAL REPORT
OF THE WATER QUALITY MONITORING PROJECT
FOR THE WATER QUALITY PROTECTION PROGRAM
OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY



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Funded by the Environmental Protection Agency (X7-95469410-2)

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 – Sep. 2012 and includes data from 69 quarterly sampling at 155 sampling sites events within the FKNMS, including the Dry Tortugas National Park (DRTO). This annual report reflects funding cutbacks resulting in reduction of spatial sampling to 112 sites, none within DRTO.

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

The EPA developed Strategic Targets for the Water Quality Monitoring Project (SP-47) which state that beginning in 2008 through 2012, 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_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 1 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2012.

We must recognize that the reduction of sampling sites in western FKNMS (less human-impacted sites) and the increase in inshore sites (heavily human-impacted sites) has introduced a bias to the dataset which results in a reporting problem, perhaps requiring a revision of SP-47 to correct this deviation.

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	
Year	CHLA ≤ 0.35 µg l^{-1}	K_d ≤ 0.20 m^{-1}	DIN ≤ 0.75 µM (0.010 ppm)	TP ≤ 0.25 µM (0.0077 ppm)
1995-05	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%)	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 of 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	146 of 215 (67.9%)	156 of 213 (73.2%)	432of 569 (75.9%)	507 of 569 (89.1%)
2012	142 of 168 (84.5%)	135 of 168 (80.4%)	268 of 447 (60.0%)	368 of 447 (82.3%)

Several important results have been realized from this monitoring project. First is the documentation of elevated nutrient concentrations (DIN, TP and SiO2) in waters close to shore along the Keys, and corresponding responses from the system, such as higher phytoplankton biomass (CHLA), turbidity and light attenuation (K_d), as well as lower oxygenation (DO) and lower salinities of the water column (Figure 1). These changes, associated to human impact, have become more obvious in a new series of ten stations (# 500 to #509) located very close to shore and sampled since November 2011 (SHORE; Fig 1).

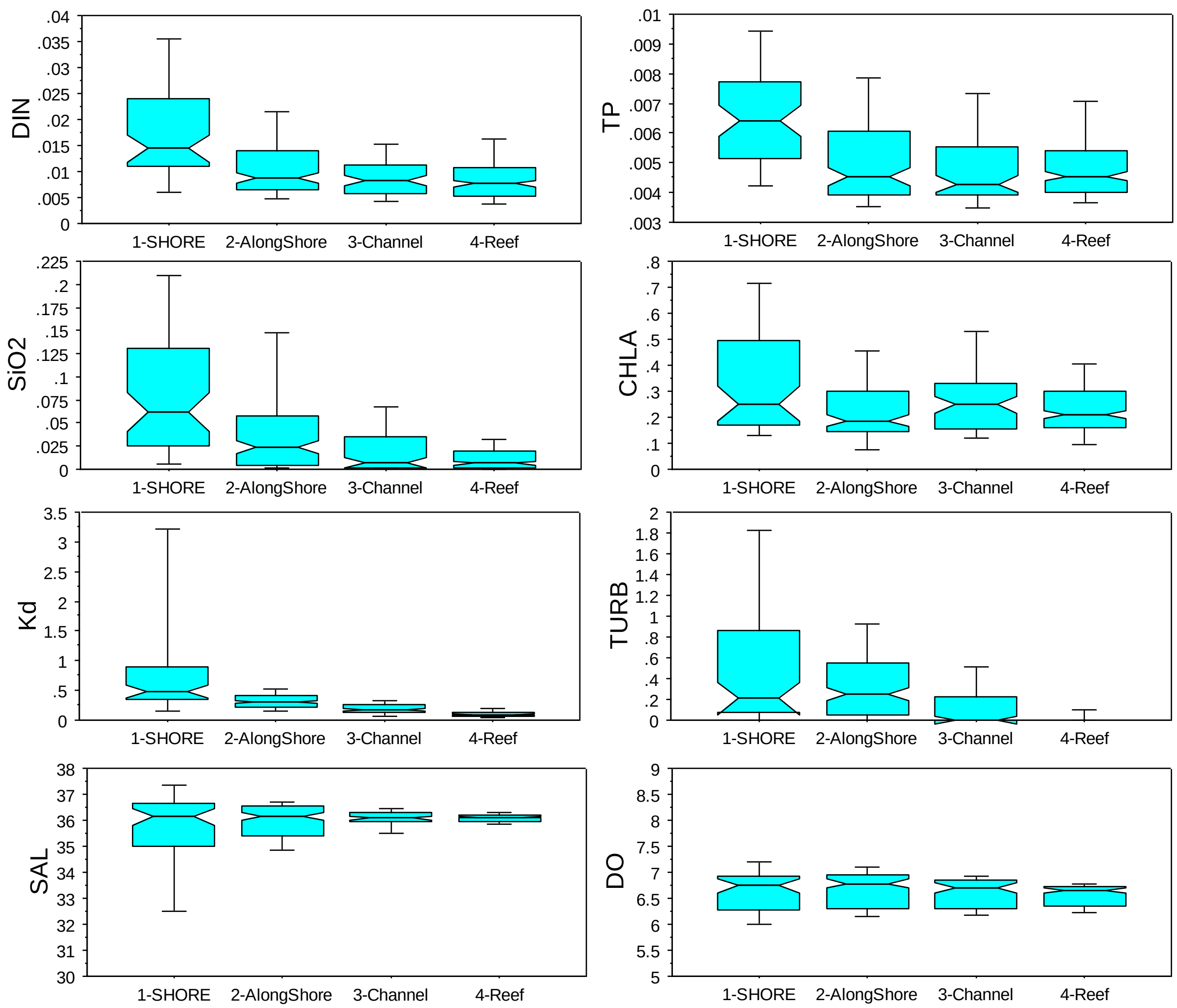

Figure 1. *Nutrient and response changes along transect from shore sites (~100 m) to reef-track*

This trend, especially for DIN was evident from our first sampling event in 1995 and was not observed in a comparison transect from the Tortugas (no human impact). This pattern suggests a land-bound, freshwater end-member as the main nutrient source. The slight increase in TP in reef samples may indicate a contribution from ocean upwelling as well. In summary, this type of distribution would imply a relatively nutrient-rich land source which is diluted by low nutrient Atlantic Ocean waters.

This raises 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. The incorporation of new stations very close to shore, where human impact is more evident, opens a new window to our scope, one which will contribute to unravel the dynamics of human-ecosystem interactions in the Sanctuary.

Trend analysis has shown that many variables have undergone significant changes in concentration over the 18 year period of record. Examples are shown in Figures 3-6.

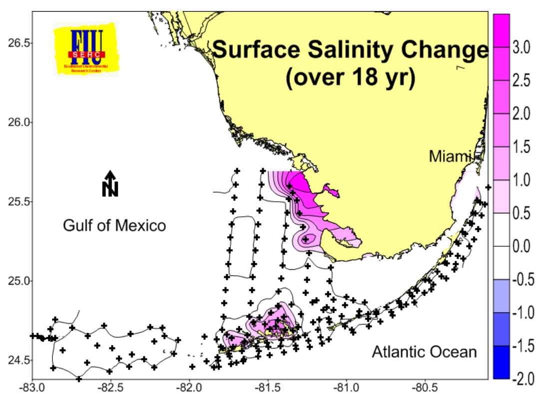

Figure 3

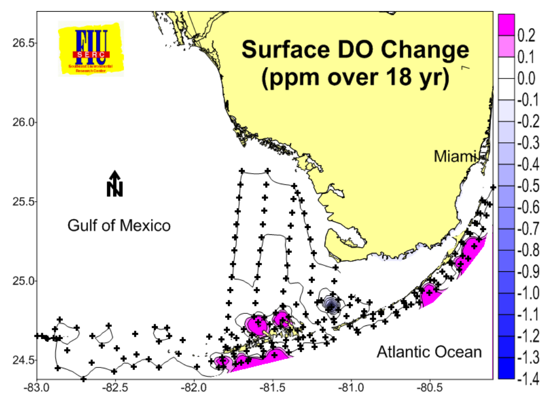

Figure 4

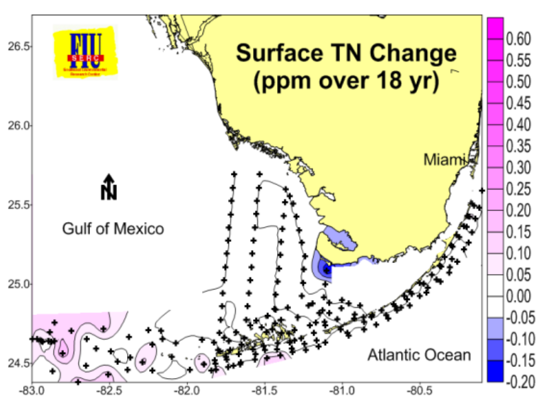

Figure 5

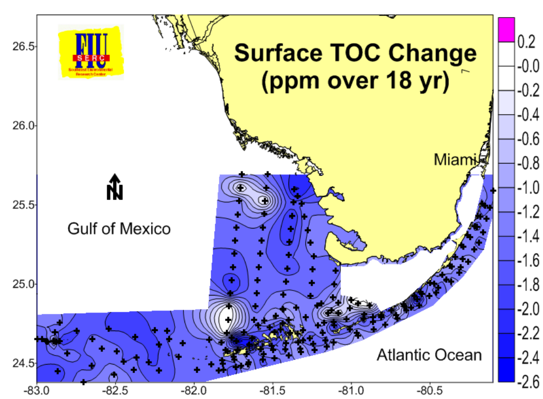

Figure 6

For 2012, in all regions of the FKNMS, water quality was generally very good with little change year to year. Overall, TOC was lower than the long term median mostly because it has been consistently declining over the years. We are not sure why this is happening, but expect it is tied to a larger, regional decline. 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. We recently characterized and spatially subdivided South Florida's coastal and estuarine waters (Briceño et al. 2010, 2013), including the FKNMS which rendered seven biogeochemically distinct water bodies whose spatial distribution are closely linked to geomorphology, circulation, benthic community pattern, and to water management (Fig. 7). This segmentation has been adopted with minor changes by federal (EPA) and state (FDEP) environmental agencies to derive numeric nutrient criteria. This confirms that 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 integrated with other available programs.

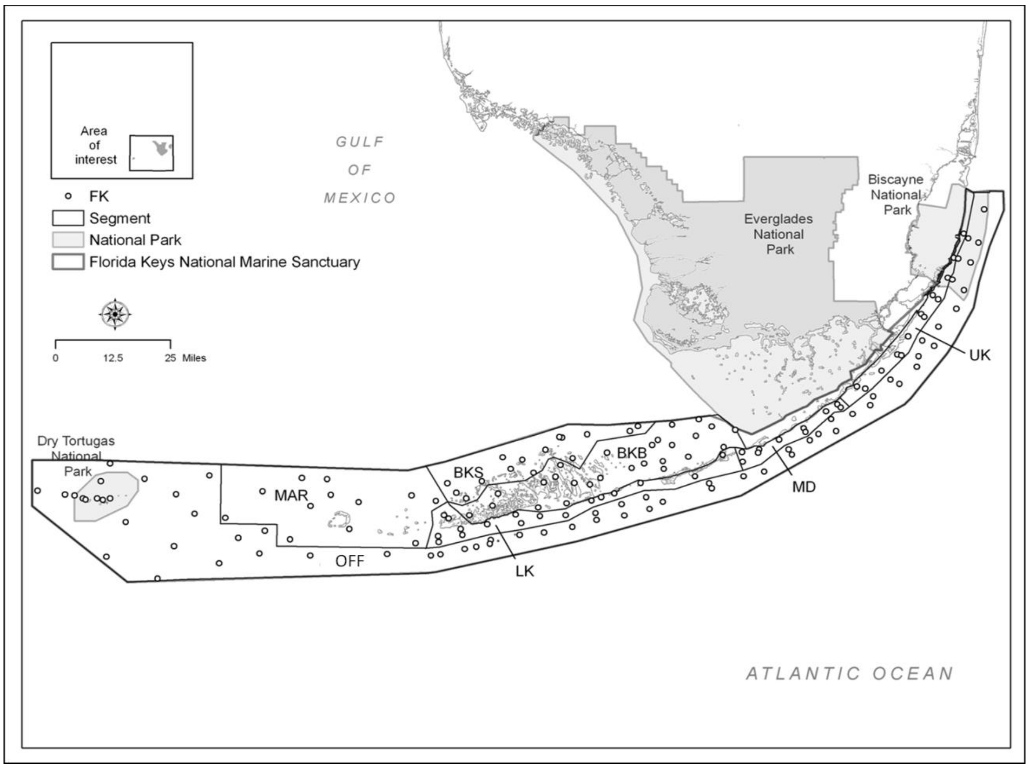

Figure 7: *Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys*

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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. 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.

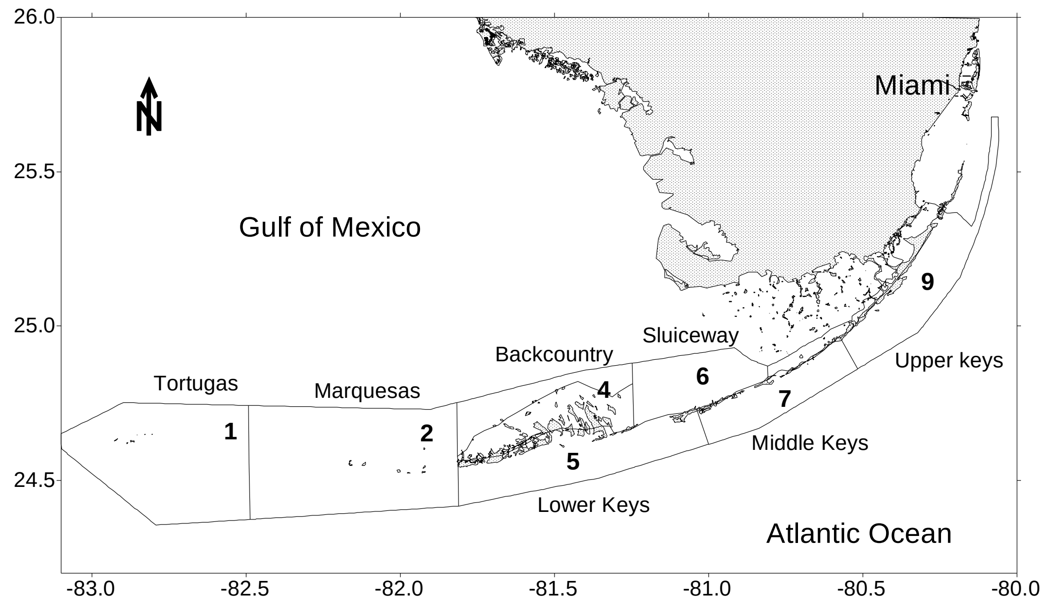

Figure 1: *Map of original FKNMS boundary including collapsed segment numbers and common names. Modified after Klein and Orlando (1994)*

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 sub-areas which was collapsed to 7 for routine sampling (Fig. 1). Station locations were developed using a stratified random design along onshore/offshore transects in sub-areas 5, 7, and 9 or within EMAP grid cells in sub-areas 1, 2, 4, and 6.

Sub-area 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. Sub-area 2 (Marquesas) includes the Marquesas Keys and a shallow sandy area between the Marquesas and Tortugas called the Quicksands. Sub-area 4 (Backcountry) contains the shallow, hard-bottomed waters on the gulfside of the Lower Keys. Sub-areas 2 and 4 are both influenced by water moving south along the SW Shelf. Sub-area 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). Sub-areas 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.

Although the original quarterly sampling of 155 stations has been cut back to 112 (Fig. 2), it still provides a unique opportunity to explore the spatial component of water quality variability in the FKNMS, but eliminates the possibility of linking the Sanctuary's water quality to external sources of variability.

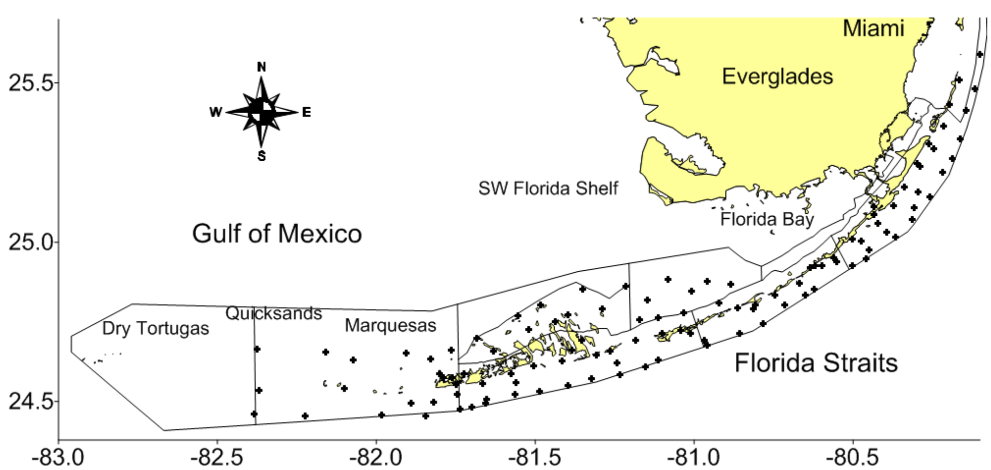

***Figure 2**. The SERC Water Quality Monitoring Network showing the current distribution of fixed sampling stations within the FKNMS.*

2. Methods

2.1.Field Sampling

The period of record of this study was from March 1995 to September 2012 which included 70 quarterly sampling events. For this year, field measurements and grab samples were collected from 112 fixed stations within the FKNMS boundary (Fig. 2). Depth profiles of temperature (°C), salinity (practical salinity scale), dissolved oxygen (DO, mg l^{-1}), photosynthetically active radiation (PAR, µE m^{-2} s^{-1}), 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.

In the Backcountry area (Sub-area 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 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 and Sluiceway where surface water was collected directly into sample bottles. Duplicate, unfiltered water samples were dispensed into 3x sample rinsed 120 ml HDPE bottles for analysis of total constituents. Duplicate water samples for dissolved nutrients were dispensed into 3x sample rinsed 150 ml syringes which were then filtered by hand through 25 mm glass fiber filters

(Whatman GF/F) into 3x sample rinsed 60 ml HDPE bottles. The resulting wet filters, used for chlorophyll *a* (CHLA) analysis, were placed in 1.8 ml plastic centrifuge tubes to which 1.5 ml of 90% acetone/water was added (Strickland and Parsons 1972).

All samples were kept on ice in the dark during transport to the laboratory. During overnight stays in the Lower Keys sampling, filtrates and filters (not total samples) were frozen until further analysis.

2.2. Laboratory Analysis

Samples were analyzed for ammonium (NH_4^+), nitrate+nitrite (NO_x^-), nitrite (NO_2^-), total nitrogen (TN), soluble reactive phosphorus (SRP), total phosphorus (TP), total organic carbon (TOC), silicate (SiO_2), chlorophyll *a* (CHLA, $\mu g\ l^{-1}$), and turbidity (NTU) using standard laboratory methods. Dissolved nutrients were defined using Whatman GF/F filters with a nominal pore size of 0.8 µm. A 60 ml sample was collected from a Niskin bottle using a syringe and filtered through a 25 mm Whatman GF/F filter. The filtrate was collected in a 60 ml high density polyethylene (HDPE) bottle and the filter stored in a vial with 90% acetone for extraction of CHLA. An additional 120 ml sample was collected directly from the Niskin bottle for analysis of TN, TP, and turbidity.

NH_4^+ was analyzed by the indophenol method (Koroleff 1983). NO_2^- was analyzed using the diazo method and NO_x^- was measured as nitrite after cadmium reduction (Grassoff 1983a,b). The ascorbic acid/molybdate method was used to determine SRP (Murphy and Riley 1962). High temperature combustion and high temperature digestion were used to measure TN (Frankovich and Jones 1998; Walsh 1989) and TP (Solórzano and Sharp 1980), respectively. TOC was determined using the high temperature combustion method of Sugimura and Suzuki (1988). Silicate was measured using the heteropoly blue method (APHA 1995). Samples were analyzed for CHLA content by spectrofluorometry of acetone extracts (Yentsch and Menzel 1963). Protocols are presented in EPA (1993) and elsewhere as 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). Some parameters were not measured directly but calculated by difference. Nitrate (NO_3^-) was calculated as NO_X^--NO_2^-;

total dissolved inorganic nitrogen (DIN) as $NO_X^- + NH_4^+$., and total organic nitrogen (TON) as TN - DIN. All variables are reported in ppm (mg l^{-1}) unless otherwise noted.

In accordance with EPA policy, the FKNMS water quality monitoring program adhered to existing rules and regulations governing QA and QC procedures as described in EPA guidance documents. The FIU-SERC Nutrient Laboratory maintained NELAP certification during this project.

2.3. Stratification/Classification Analysis

The spatial framework for FKNMS water quality management was proposed on the basis of geographical variation of regional circulation patterns (Klein and Orlando, 1994). This framework has been the leading guideline since 1995. Nevertheless, with all the water quality data collected the last 18 years it is possible to refine the segmentation of the Sanctuary to better follow water biogeochemistry. Hence, sampling 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 which uses factor analysis followed by hierarchical clustering algorithm to classify sites as to their overall water quality. This approach has been very useful in understanding the drivers influencing nutrient biogeochemistry in Florida Bay (Boyer et al. 1997; Briceño and Boyer 2010), Biscayne Bay (Caccia and Boyer 2005), and the Ten Thousand Islands (Boyer 2006). More recently, Briceño et al. (2013) used the same methodology to subdivide South Florida's coastal and estuarine waters including the segmentation of the FKNMS presented here.

The present Factor Analysis does not include species with more that 12% non-detects (determinations which fell below the method detection limit), among them, SiO2=13%; NO2=20%; NH4=24%; NOx=39%; SRP=42%; and NO3=52%. In the past, non-detects were replaced by the Method Detection Limit (MDL; EPA-Region 2, 1997), but recent work by Helsel (2005) have demonstrated the unsuitability of this replacement practice.

Selected data were first standardized as Z-scores prior to analysis to reduce artifacts of differences in magnitude among variables. Factor analysis (MINITAB 16®) was used to define statistically significant composite variables (factors) from the original data (Overland and Preisendorfer 1982). The factor solution was rotated (using VARIMAX; Kaiser 1958) in order to facilitate the interpretation of the factors, and the factor scores were saved for each data record. Mean, SD, median and median absolute deviation of the factor scores for each station, over the 1995-2009 period of record, were then used as independent variables in a hierarchical cluster analysis algorithm (Ward linkage with Euclidean distances; MINITAB 16®), 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 (Surfer, Golden Software) of specific water quality variables until 2011, when monitoring of the Shelf was dropped. 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 of the Ordinary Linear Regression slope set at $p<0.10$.

3. Results

3.1. Overall Water Quality of the FKNMS

Summary statistics for all water quality variables from FY2012 sampling events are shown as number of samples (*n*), minimum, maximum, and median (Table 2). Overall, the region remains warm and euhaline with a median temperature of 25.45 °C and salinity of 36.08; dissolved oxygen saturation of the water column (DO_{sat}) was relatively high at 98.2%. On this coarse scale, the FKNMS exhibited very good water quality with median NO_3^-, NH_4^+, TP, and SiO_2 concentrations of 0.0011, 0.0062, 0.0052, and 0.0243 mg l^{-1}, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (~70%). However, DIN comprised a small fraction (4%) of the TN pool with TON making up the bulk (median 0.1361 mg l^{-1}). SRP concentrations were very low (median 0.0012 mg l^{-1}) and comprised only 6% of the TP pool. CHLA concentrations were also low overall, 0.20 µg l^{-1}, but ranged from 0.01 to 12.29 µg l^{-1}. TOC was 1. 476 mg l^{-1}; a value higher than open ocean levels but consistent with coastal areas.

Median turbidity was very low (0.09 NTU) as reflected in a low K_d (0.200 m^{-1}). Overall, 36.9% 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 = 63.5) but this must be tempered by the fact that much of the TN may not be bioavailable (DIN:TP = 3.4).

***Table 2**. Summary statistics for each water quality variable in the FKNMS for the FY2012 period of record. Data are summarized as number of samples (n), minimum value (Min.), maximum value (Max.), and Median.*

	Dept	*n*	Min.	Max	Median
NO_3^-	Surface	435	0.00002	0.02355	0.00106
(mg l^{-1})	Bottom	273	0.00008	0.03315	0.00119
NO_2^-	Surface	445	0.00005	0.00236	0.00042
(mg l^{-1})	Bottom	280	0.00002	0.00256	0.0003
NH_4^+	Surface	447	0.00088	0.05687	0.00703
(mg l^{-1})	Bottom	280	0.00083	0.06974	0.00564
TN	Surface	447	0.04837	0.66594	0.13818
(mg l^{-1})	Bottom	280	0.04893	0.93333	0.10885
DIN	Surface	447	0.00117	0.06441	0.00873
(mg l^{-1})	Bottom	280	0.00177	0.07123	0.0074
TON	Surface	447	0.03978	0.64239	0.12914
(mg l^{-1})	Bottom	280	0.03241	0.92244	0.10019
TP	Surface	447	0.0026	0.03011	0.00531
(mg l^{-1})	Bottom	280	0.00265	0.02701	0.00457
SRP	Surface	447	0.00014	0.01788	0.00088
(mg l^{-1})	Bottom	280	0.00008	0.00861	0.00093
CHLA (ug l^{-1})	Surface	444	0.0119	12.2895	0.2148
TOC	Surface	447	0.92012	5.823	1.4955
(mg l^{-1})	Bottom	280	0.8925	6.9285	1.212
SiO_2	Surface	447	0.00006	1.55093	0.0199
(mg l^{-1})	Bottom	280	0.00012	0.76747	0.00605
Turbidity	Surface	446	0	31.00	0.015
(NTU)	Bottom	283	0	6.30	0.000
Salinity	Surface	447	26.28	37.87	36.09
(mg l^{-1})	Bottom	445	27.21	37.92	36.12
Temperature	Surface	447	20.74	32.61	26.25
(^oC)	Bottom	445	20.74	32.61	25.94
DO	Surface	447	3.13	8.87	6.52
(mg l^{-1})	Bottom	445	3.29	8.88	6.56
K_d m^{-1}	Surface	424	0.00058	16.9305	0.20873
TN:TP	Surface	447	15.98591	247.1488	59.35129
DIN:TP	Surface	447	0.4386	25.42134	3.64442
DO Saturation	Surface	447	44.66796	127.7343	97.44605
(%)	Bottom	445	47.04051	126.0667	97.5782
I_o (%)	Bottom	424	4.25E-10	99.71244	37.73734
$\Delta\sigma_t$		445	-0.51793	1.09245	0.01344
Si:DIN	Surface	447	0.00495	60.36662	1.04415

3.2. Objective Classification Analysis

Our basin segmentation was accomplished following the objective analysis procedure of Boyer et al. (1997) to group sampling stations, combining factor analysis and hierarchical clustering methods in tandem. Factor analysis identified four composite variables (hereafter called FAC1, FAC2 etc.) that passed the rule N for significance at $p<0.05$ (Overland and Preisendorfer 1982) indicating four separate modes of variation in the data (Table 3). These four factors accounted for 66% of the total variance of the original variables. FAC1 had high factor loadings for TP, CHLA, and turbidity and was designated as the "Phytoplankton" factor. The covariance of TP with CHLA implies that, in many areas, phytoplankton biomass may be limited by P availability. This is contrary to much of the literature on the subject which usually ascribes N as being the limiting factor for phytoplankton production in coastal oceans. Temperature and DO were inversely related and dominated FAC2. TN and TOC controlled FAC3, the "organic" factor, suggesting that most TN is in the organic form. Finally, FAC4 was mostly a function of salinity ("marine" factor).

Table 3: *Factor Loadings. Eight variables rendered 4 Factors accounting for 66% of total variance*

Variable	FAC1	FAC2	FAC3	FAC4
TN	0.026	-0.013	0.715	0.257
TP	0.749	0.06	-0.087	0.305
CHLa	0.677	-7.24E-05	0.172	-0.251
TOC	0.206	0.193	0.751	-0.159
Turbidity	0.683	-0.159	0.169	-0.075
Salinity	0.001	0.123	0.083	0.893
DO	-0.04	-0.795	0.071	0.028
Temperature	-0.15	0.785	0.279	0.219

Next was the clustering of sampling stations. In order to account for both, magnitude and variability in the clustering procedure, we used parametric (mean and SD) and non-parametric (median and median absolute deviation) of retained factor scores, at each station, as input into hierarchical clustering routines (Ward linkage with Euclidean distances; MINITAB 16®). The hierarchical clustering algorithm classified all original 155 FKNMS sampling sites into 7 classes having robust correspondence in water quality. We recognized that it is difficult to draw a border line separating segments within a continuous and non-static water body, where any contact is probably transitional. Once the class was defined and its spatial grouping was ascertained, segment boundaries were generated by multiple approaches based on geomorphology, bathymetry, circulation patterns (Klein & Orlando, 1994), and best professional judgment. The final FKNMS segmentation was as follows: Offshore (OFF); Marquesas (MAR); Backcountry (BKC), Back Shelf (BKS), Lower Keys (LK), Middle Keys (MK), and Upper Keys (UK) (Fig. 3).

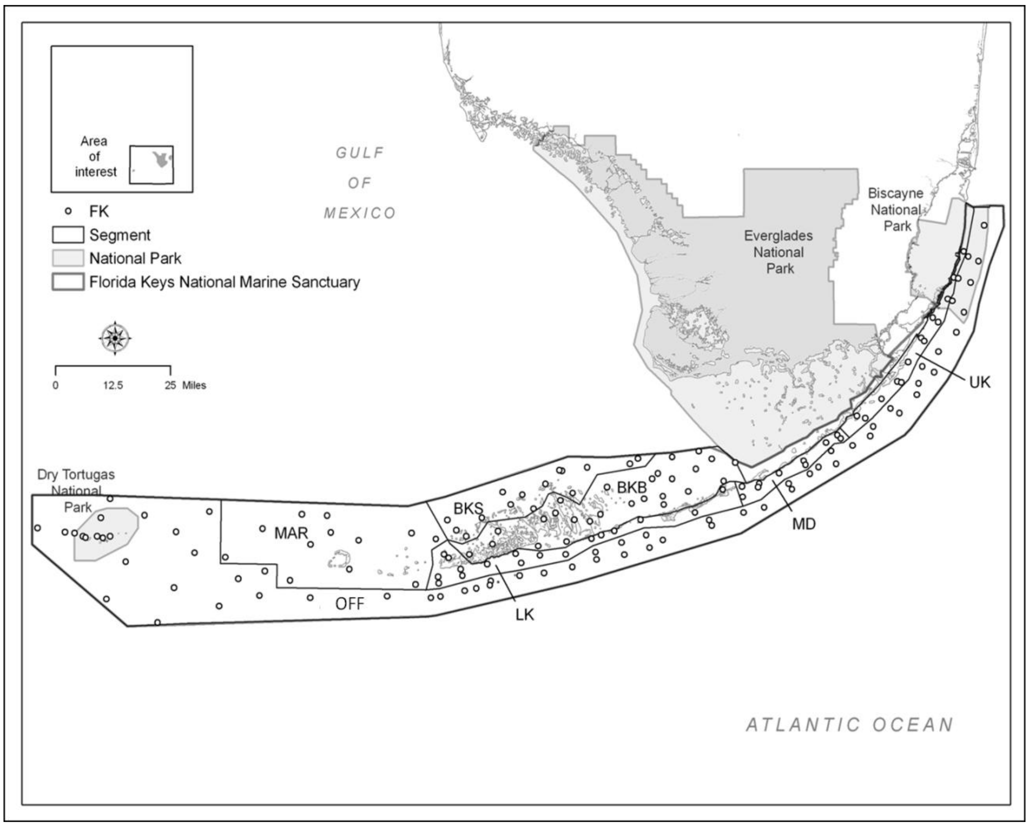

Figure 3: *Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys*

The recently implemented stations close to shore were not used for this classification. In their short life-span they have displayed a common tendency to be nutrient-enriched and at the lower salinity extreme, as compared to the rest of the sites. Hence, we have grouped these ten stations as an additional class (SHORE), not for mapping purposes at this time, but for comparison and exploration of human impacts on water quality.

Most differences among segments were rather subtle, BKB, BKS and SHORE are the most nutrient-enriched segments while the UK and OFF were at the less-enriched extreme. The BKB zone was composed primarily of stations located inside and north of the Lower Keys and extending to the Sluice area (Fig. 4). This class was highest in nutrients, especially TN, TON, TOC, SiO_2, TP, TOC and DIN, leading to high CHLA and turbidity. In the shallow BKB sites we expect that either nutrient transport from the SW Shelf and south Florida Bay and/or benthic flux of nutrients might be more important than anthropogenic loading. The BKB also had highest salinity and DO, relative to other regions. The BKS is located to the north of BKB and includes sites most influenced by water moving south from the SW Florida Shelf and exchange with BKB waters. It was highest in TP and relatively high in TN, TON, SRP, SiO_2, TOC, DO, turbidity and salinity.

The MAR zone was made up of sites between Key West and Rebecca Shoals. This is an area of relatively shallow water with complex circulation pattern which separates the SW Shelf from the Atlantic Ocean. The water quality of MAR is very low in TOC and relatively low in all N species and SiO_2, but displays relatively high TP and SRP, and the highest values and the largest range of variability in CHLA and turbidity, perhaps linked to shallow waters and sediment re-suspension.

There is a general nutrient gradient from higher levels at LK to MK to the UK, the less enriched one. Additionally, these three segments, closer to the islands, have higher nutrient levels than those offshore (OFF), underscoring the impact on water quality from the Keys and the strong control exerted by the Loop and Florida currents. The LK, MK and UP included the innermost sites of the Keys, which are shallow, closest to any possible anthropogenic nutrient sources, and typically more turbid than reef zones (OFF) from beach wave re-suspension. These sites were slightly elevated in DIN, TN, TON, SiO_2 and TOC relative to the OFF sites.

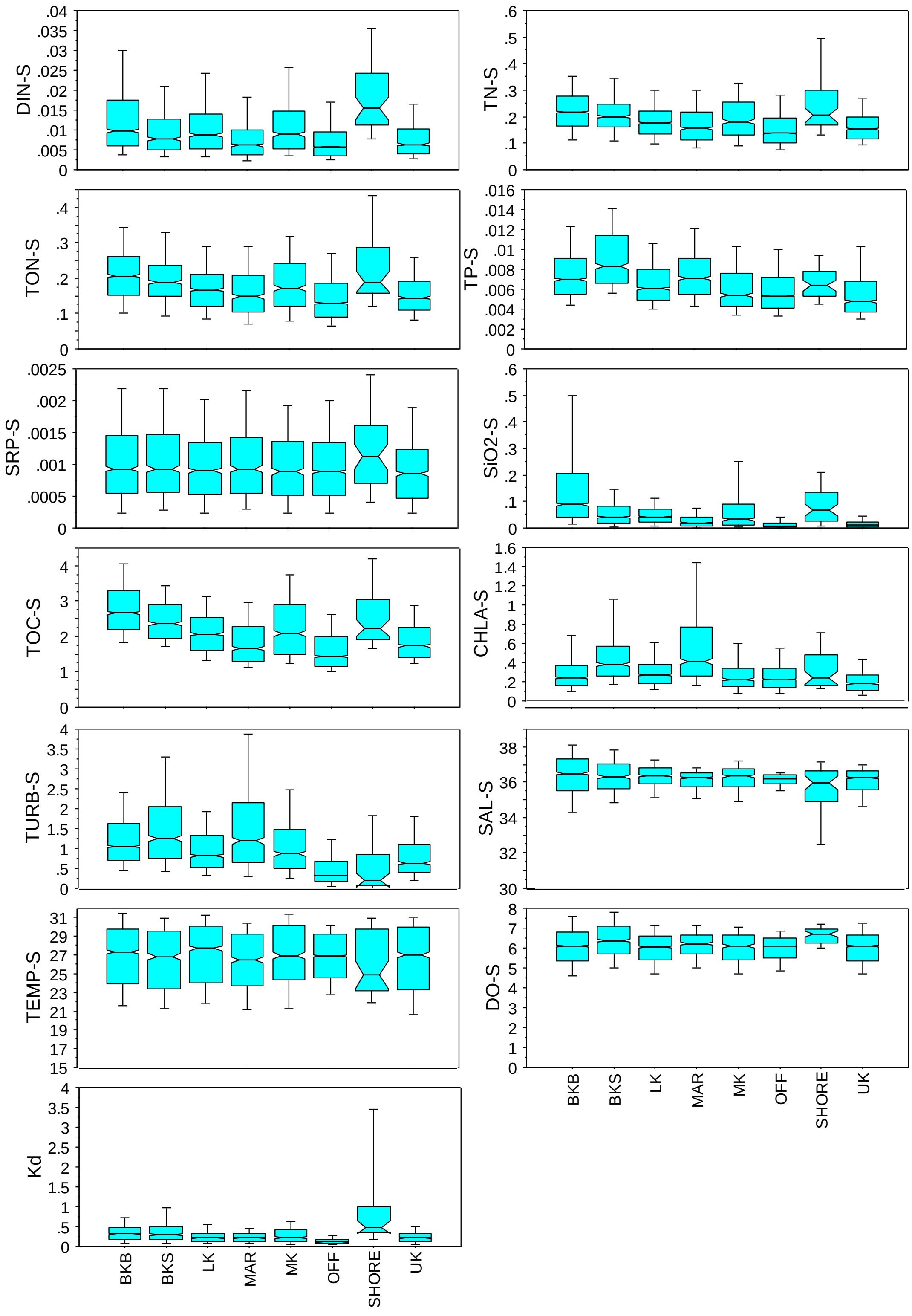

***Figure 4**. Box-and-whisker plots of surface (S) samples showing median and distribution of DIN, TN, TON, TP, SRP, SiO_2, TOC and CHLA, TOC, turbidity, salinity, temperature, DO and Kd as stratified by water quality cluster. Notches in the box that do not overlap with another are considered significantly different.*

The OFF zone was made up of all Hawk Channel and reef tract sites of the mainland Keys and all sites west of Rebecca Shoal, including those in Dry Tortugas National Park. This zone had very low nutrients, TP, CHLA, and turbidity.

3.3. Historical Conditions

All contour maps of are produced 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.

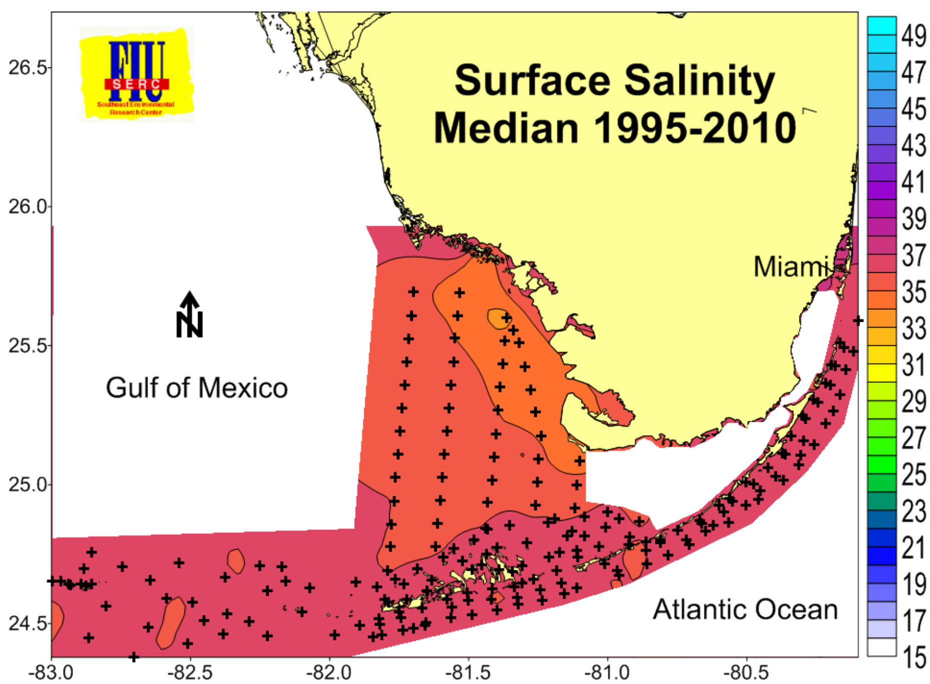

Figure 5*. Median salinity field for the region showing freshwater inputs and marine influence.*

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.

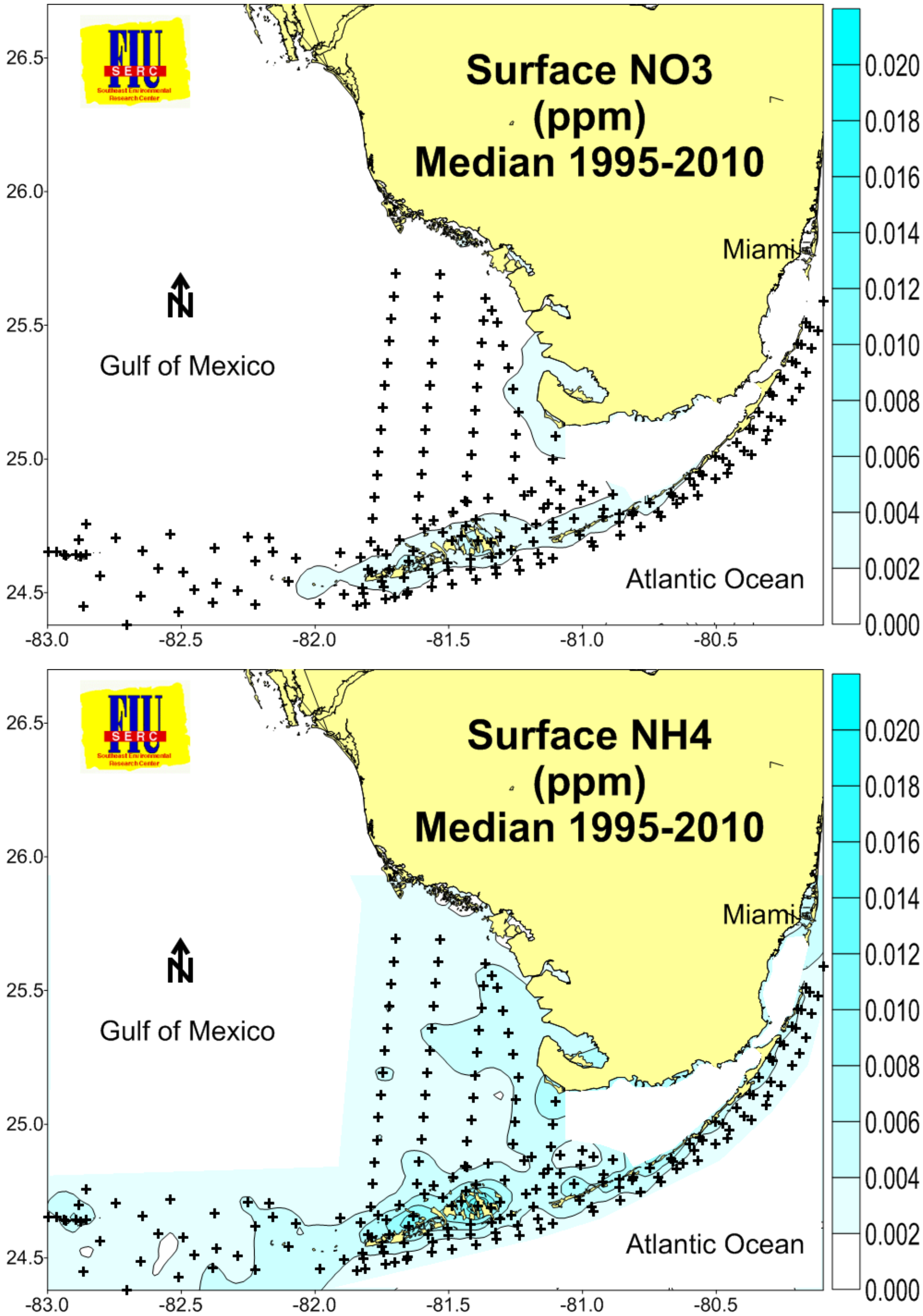

***Figure 6**. Median nitrate and ammonium in the region.*

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).

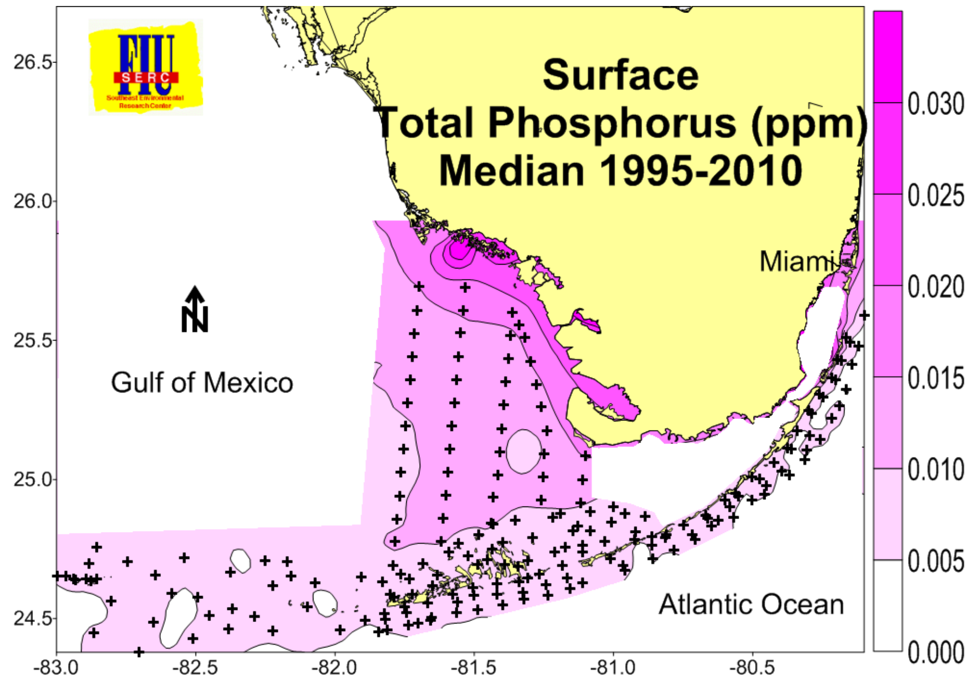

Figure 7. *Distribution of median total phosphorus in the region.*

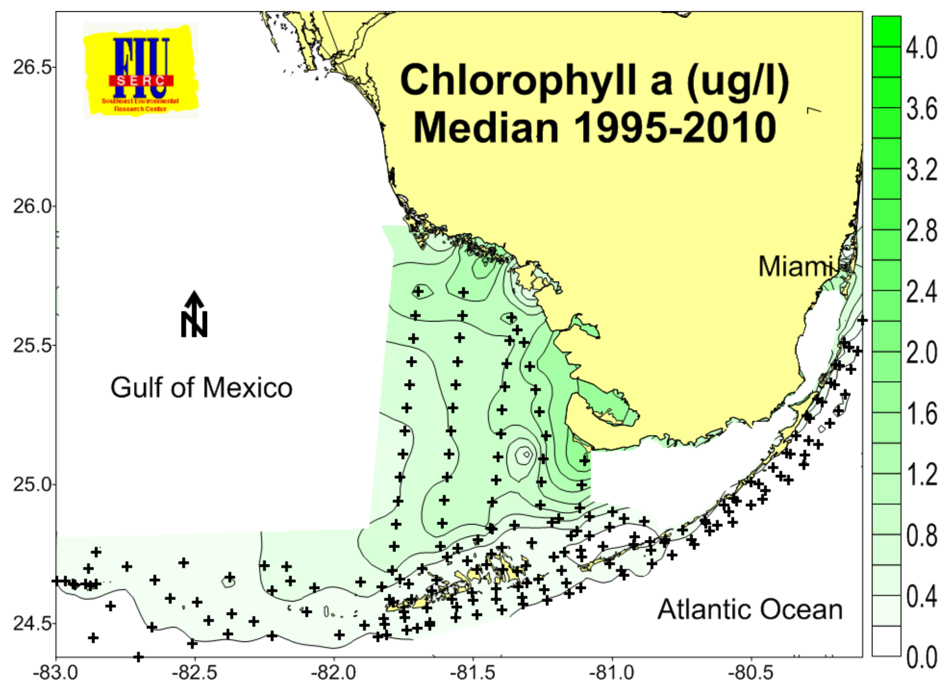

Figure 8. *Median chlorophyll a in the region showing the similarity to TP distribution.*

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 climatic 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.

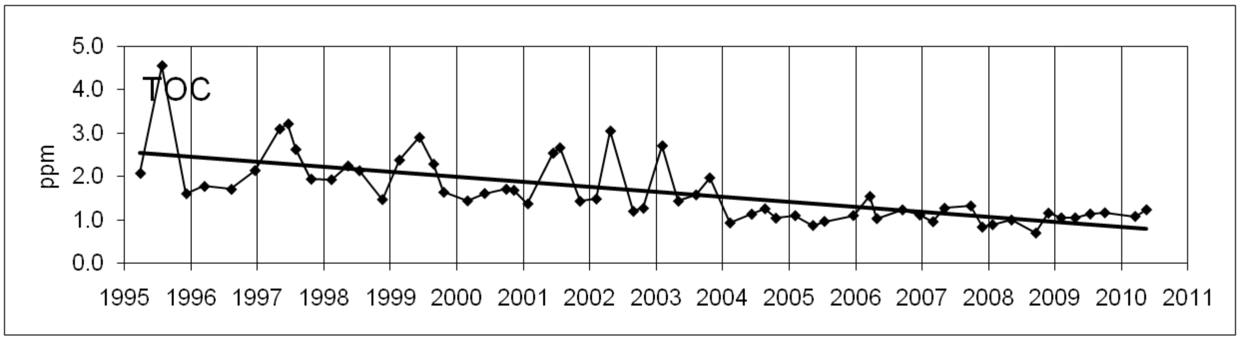

Figure 9. *Monotonic trend in TOC at Carysfort Reef.*

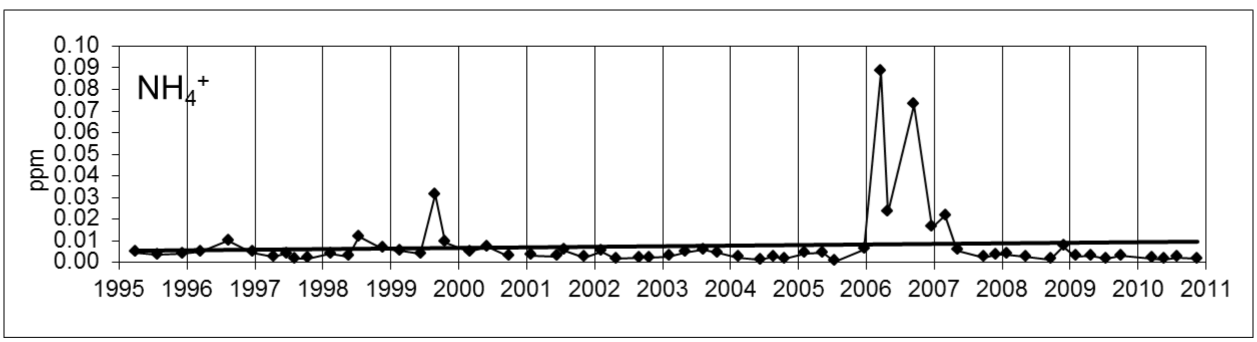

Figure 10. *Episodically (hurricane) driven pattern in NH_4^+ at The Elbow.*

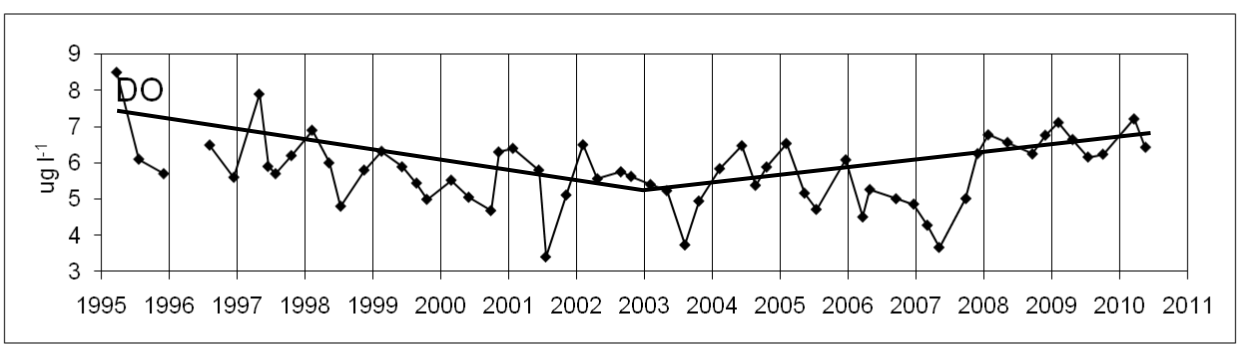

Figure 11. *Reversing trend in DO at Carysfort Reef.*

Least squares regressions for each water quality variable were calculated for the 18 year period of record. Only slopes having significant trends ($p < 0.1$) in ppm yr^{-1}, 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 18 and plotted as contour maps of Total Change for 18 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. 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 0.005-0.015 ppm (Fig. 13). Surface TN increased slightly (0.15-0.20 ppm, total) in the Tortugas/Marquesas and at a few offshore reef sites south of the Lower Keys (Fig. 14). Significant declines in TN (up to -0.15 ppm) were observed in the easternmost Shelf, south of Cape Sable. TP concentrations were relatively constant throughout the FKNMS with a few notable exceptions (Fig. 15). TP decreased significantly in the westernmost transects of the Shelf, due north of Key West.

Overall CHLA concentrations declined or stayed the same throughout the FKNMS (Fig 16) with largest decreases in the west Marquesas. Light extinction (K_d) stayed the same at most sites (Fig. 17) with a few scattered declines along the reef-track, 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 east Shelf adjacent to the Ten Thousand Islands-Whitewater Bay freshwater outputs from mangrove rivers. We believe the output of colored dissolved organic matter (CDOM) from mangrove forest accounts for this change. Also, some increases were observed in the Backcountry north of Key West.

Significant declines in surface DO (up to -1.5 ppm) were observed in only one restricted area in NE Sluiceway – adjacent to Florida Bay, Spanish Harbor Keys, and Long Beach area (Fig. 18). Some areas adjacent to Florida Bay experienced decreases up to 0.8 ppm for the period of record. This is problematic as DO is an important requirement for animal life. SiO_2 changed very little. Increases were observed in NE Sluiceway adjacent to Florida Bay (Fig. 19).

Changes in water turbidity did not correspond with K_d, indicating that other factors (CDOM?) probably have more impact on the light field than does fine particulate seston (Fig. 20). Most significant turbidity declines occur in western Florida Bay-southeastern Shelf. In most areas, TOC has declined over the period of record (Fig. 21). There were strong declines in surface TOC over the SW Shelf and the FKNMS, especially in the Backcountry and the Middle Keys (Fig 21). This decline in TOC is favorable given that TOC declines correspond with declines in CDOM (an important driver of light penetration) and water color.

Finally, salinity on the Backcountry and offshore Ten Thousand Islands-Whitewater Bay on the easternmost Shelf have increased substantially (up to 3.21) in the last 18 years (Fig. 22). We attribute these increases to climatic cycles, Everglades water management, and perhaps sea-level-rise. Although we do not have a definitive explanation, it is important to notice that those significant increases in salinity coincidentally occur where K_d has also increased significantly (Fig. 17). Perhaps sea-level-rise and/or wind-driven waves have caused sea water to advance shoreward and to re-suspend bottom sediments.

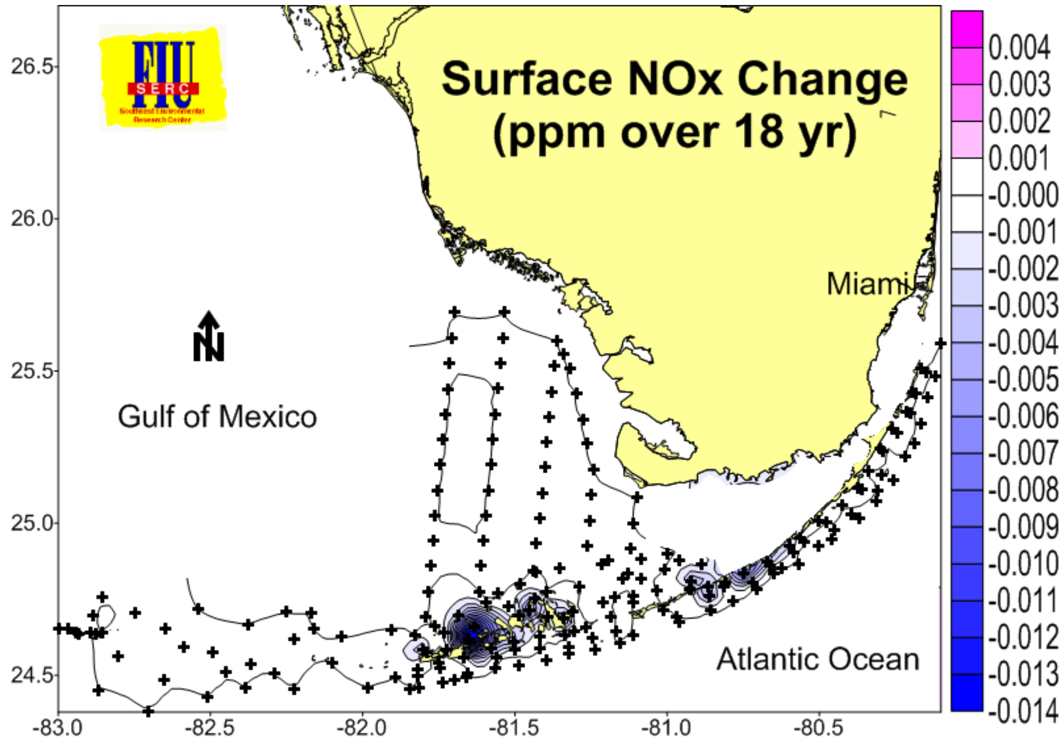

Figure 12. *Total change in* NO_3^-+NO_2^- *in surface waters for 18 year period calculated from significant trends (p<0.10).*

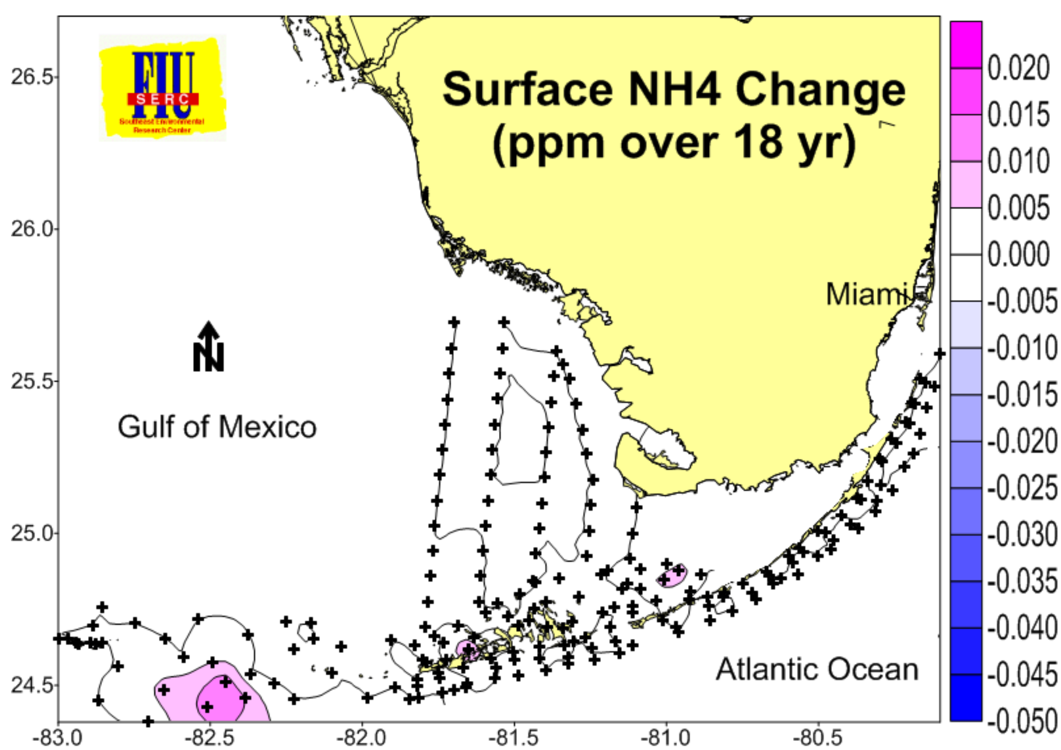

Figure 13. *Total change in* NH_4^+ *in surface waters for 18 year period calculated from significant trends (p<0.10).*

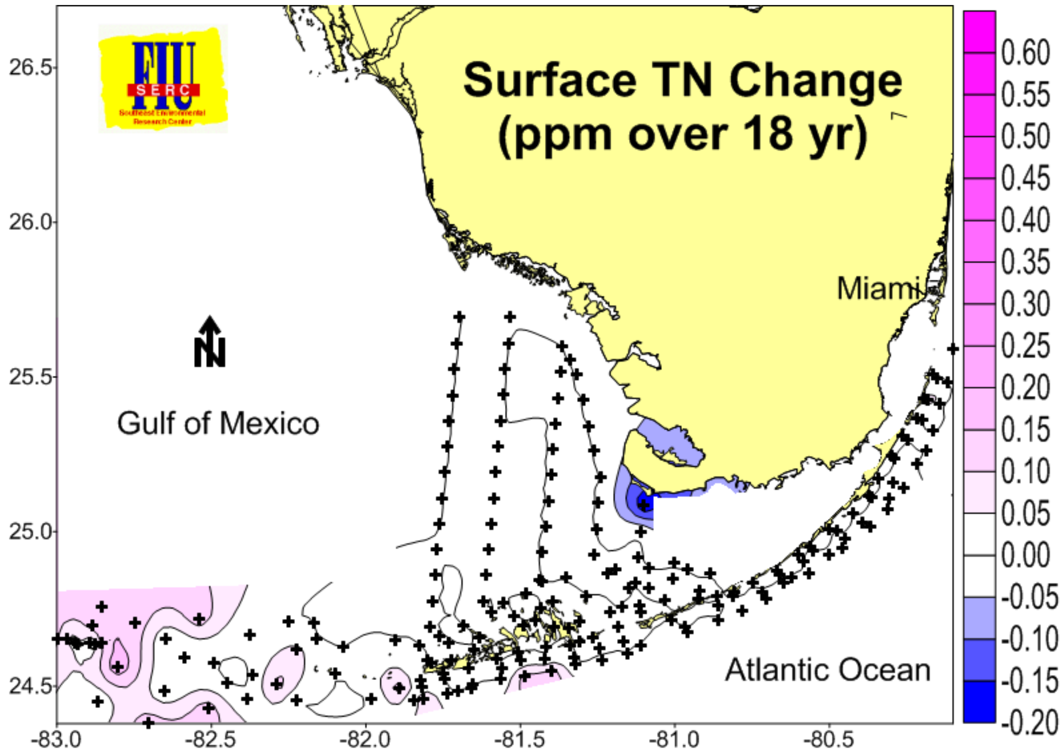

Figure 14. *Total change in TN in surface waters for 18 year period calculated from significant trends (p<0.10).*

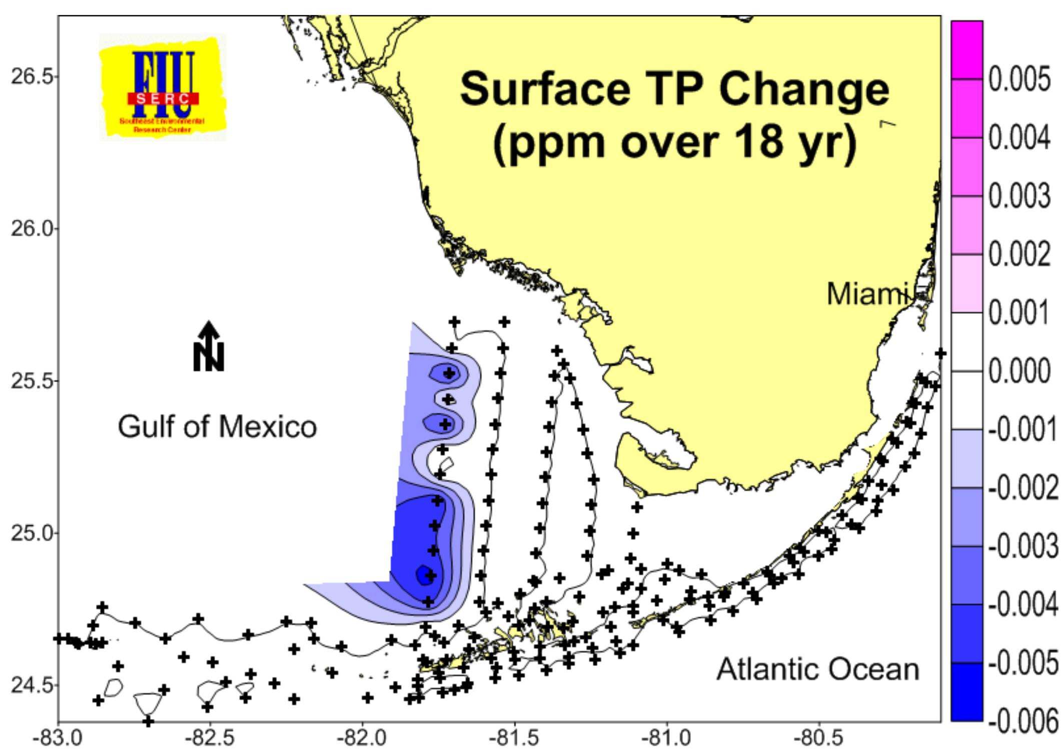

Figure 15. *Total change in TP in surface waters for 18 year period calculated from significant trends (p<0.10).*

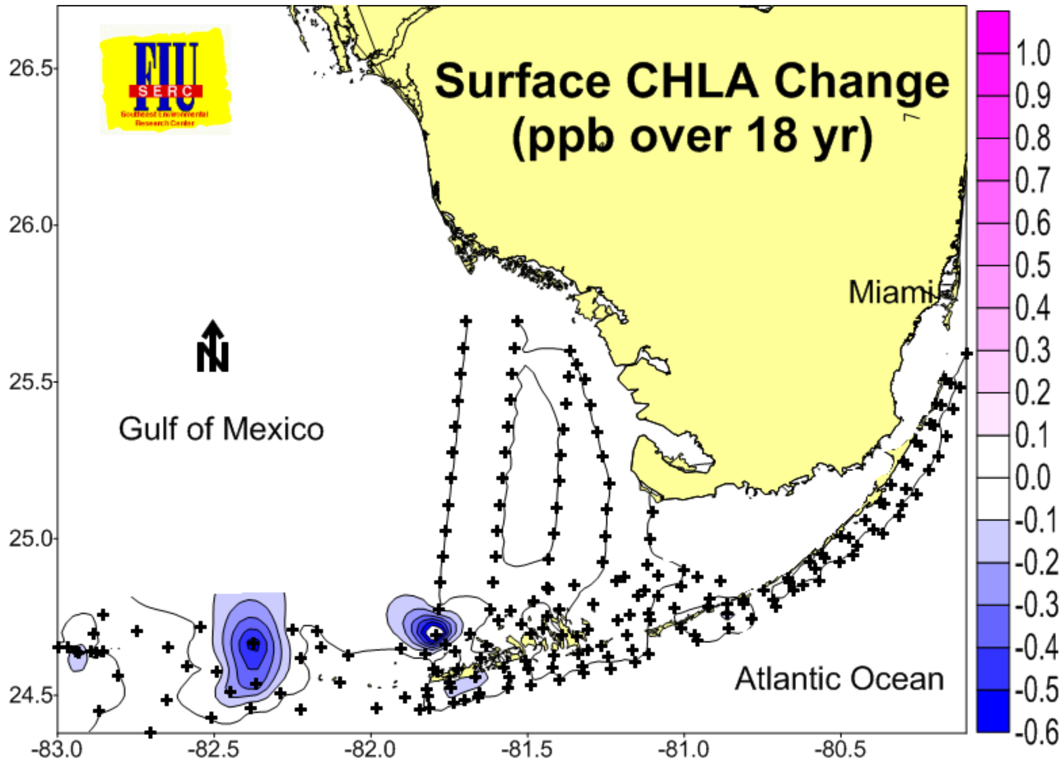

Figure 16. *Total change in CHLA in surface waters for 18 year period calculated from significant trends (p<0.10).*

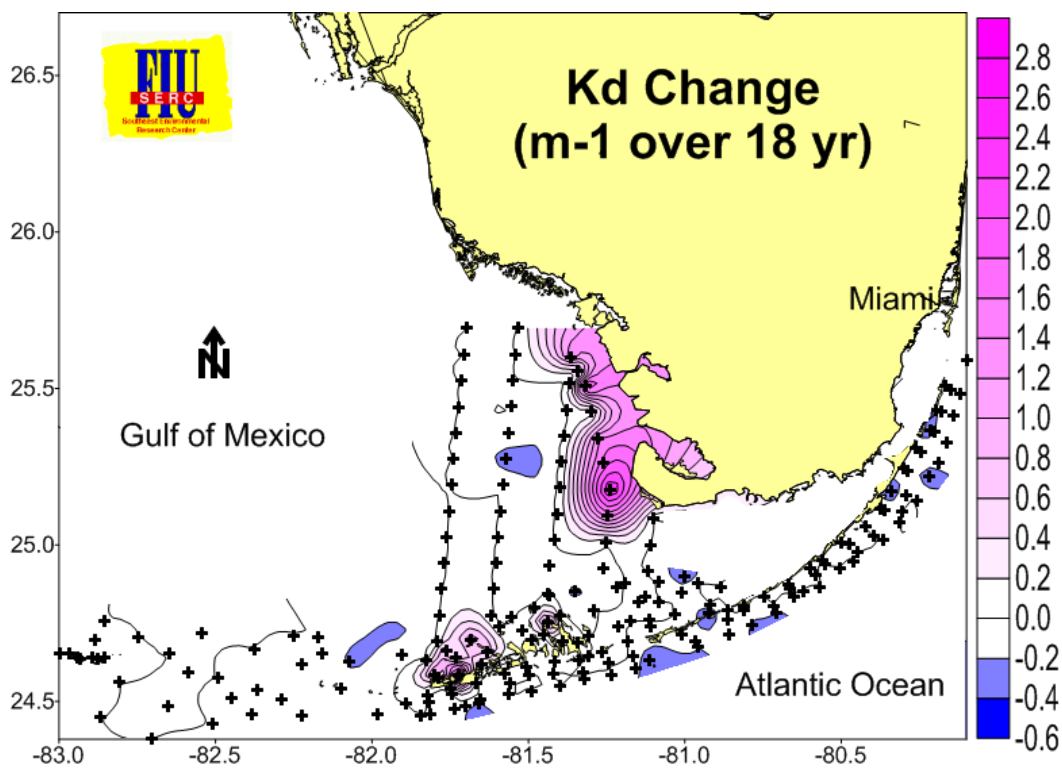

Figure 17. *Total change in K_d for 18 year period calculated from significant trends (p<0.10).*

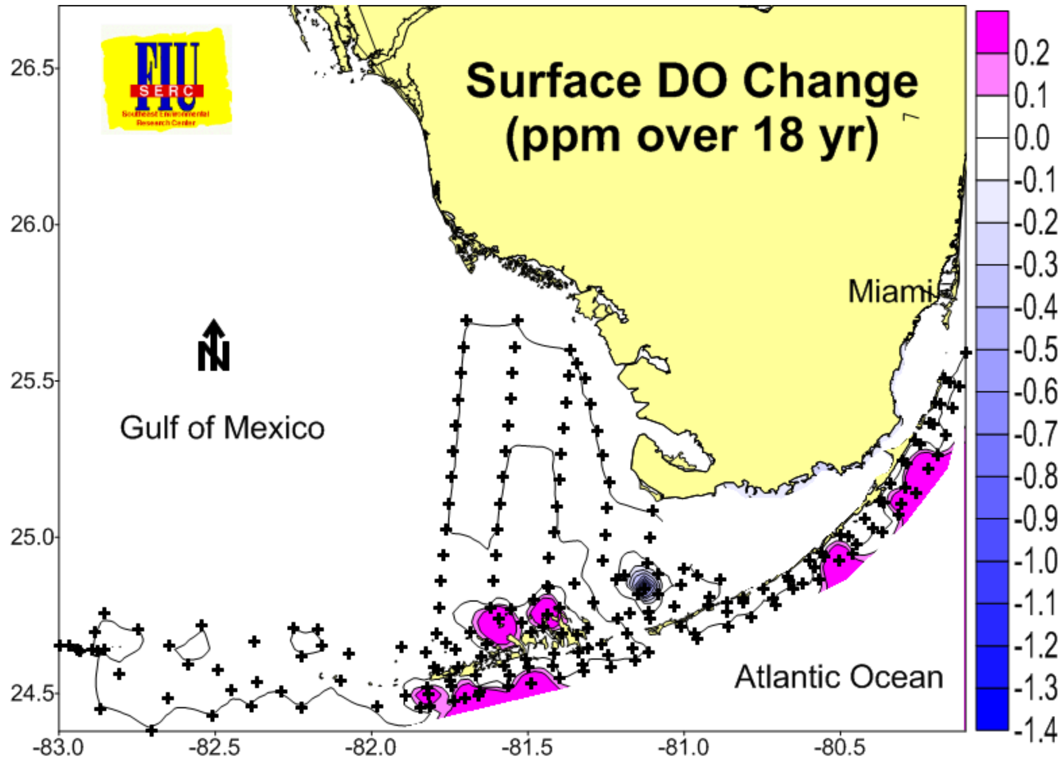

Figure 18. *Total change in DO in surface waters for 18 year period calculated from significant trends ($p<0.10$).*

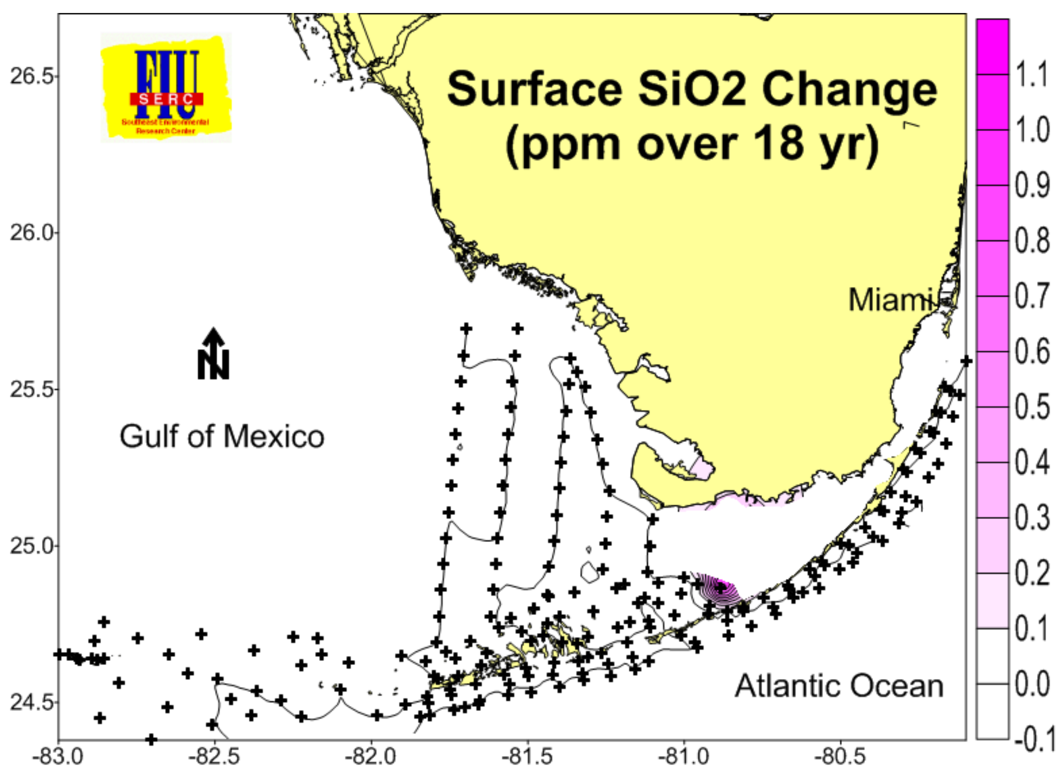

Figure 19. *Total change in SiO_2 in surface waters for 18 year period calculated from significant trends ($p<0.10$).*

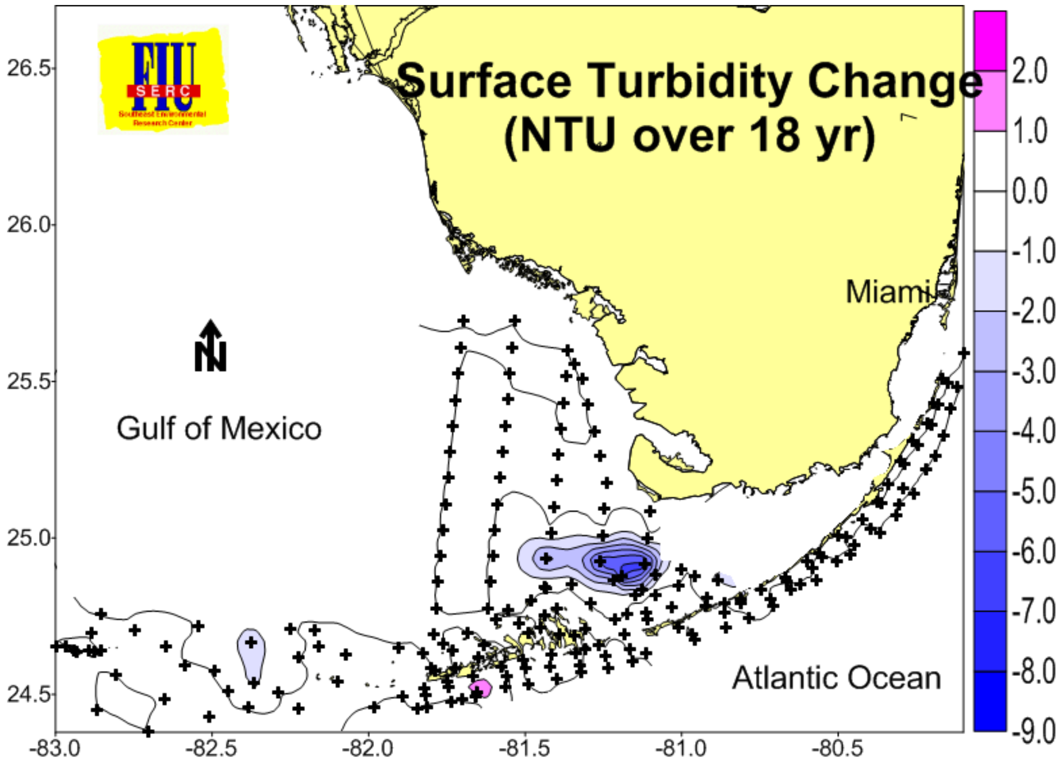

Figure 20. *Total change in Turbidity in surface waters for 18 year period calculated from significant trends (p<0.10).*

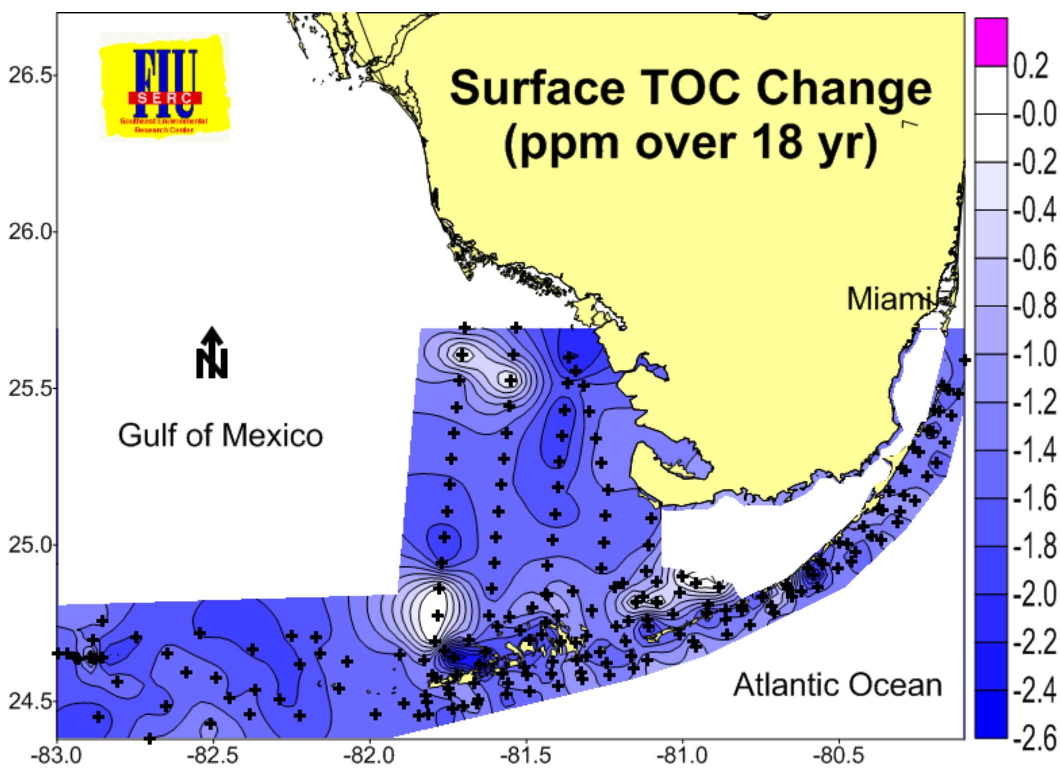

Figure 21. *Total change in TOC in surface waters for 18 year period calculated from significant trends (p<0.10).*

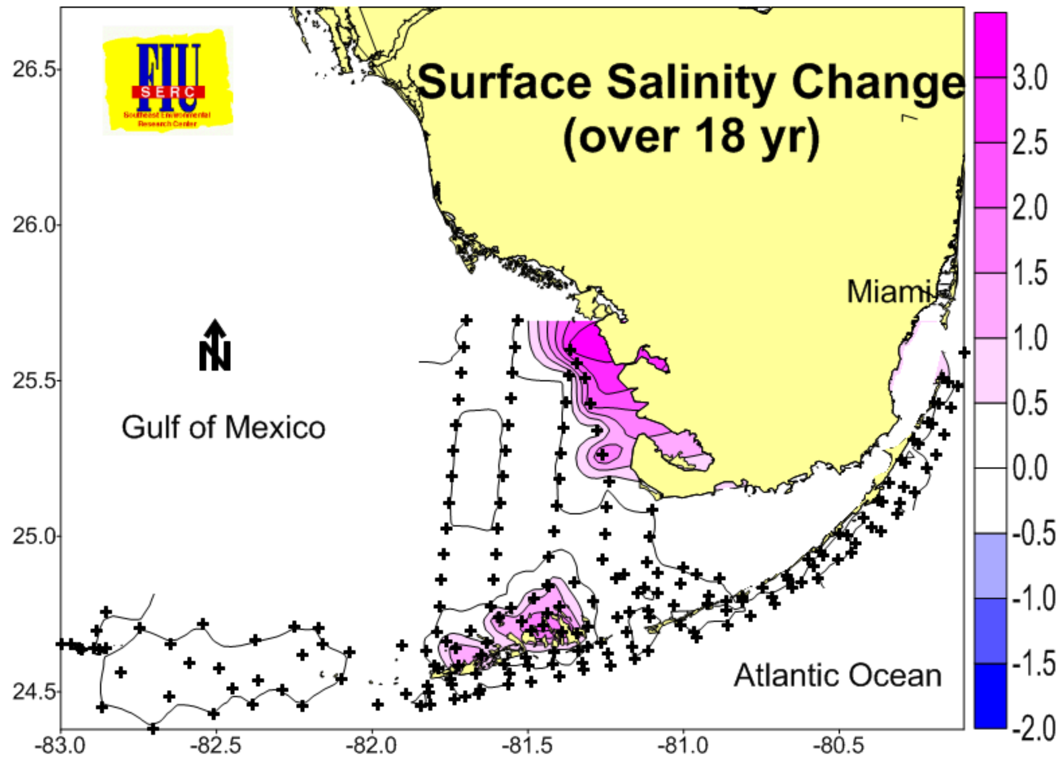

Figure 22. *Total change in Salinity in surface waters for 18 year period calculated from significant trends (p<0.10).*

4. Overall Trends

Several important results have been realized from this monitoring project. First is the documentation of elevated nutrient concentrations (DIN, TP and SiO2) in waters close to shore along the Keys, and corresponding responses from the system, such as higher phytoplankton biomass (CHLA), turbidity and light attenuation (K_d), as well as lower oxygenation (DO) and lower salinities of the water column (Figure 23). These changes, associated to human impact, have become more obvious in a new series of ten stations (# 500 to #509) located very close to shore and sampled since Nov 2011 (SHORE; Fig 23).

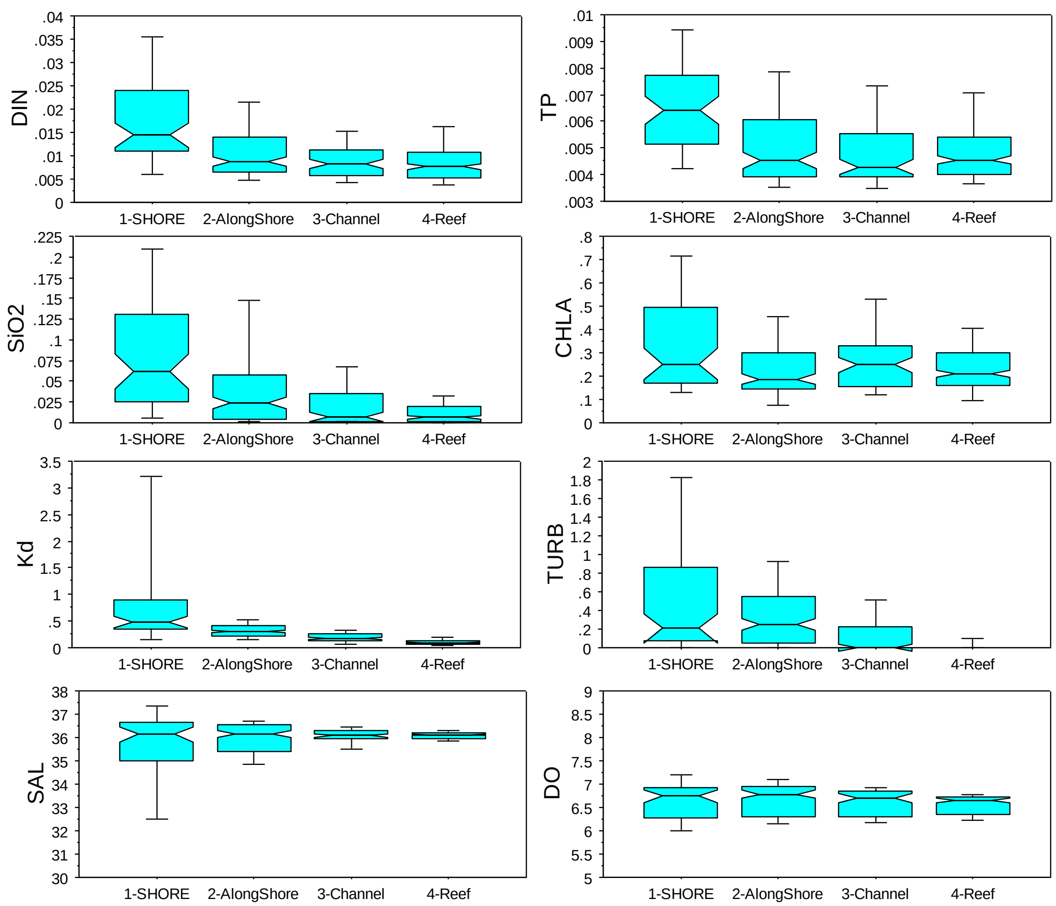

Figure 23: *Nutrient and response changes along transect from close-to-shore sites (~100 m) to the reef-track*

This trend, especially for DIN was evident from our first sampling event in 1995 and was not observed in a comparison transect from the Tortugas (no human impact). This pattern suggests a land-bound, freshwater end-member as the main nutrient source. The slight increase in TP in reef samples may indicate a contribution from ocean upwelling as well. In summary, this type of distribution would imply a relatively nutrient-rich land source which is diluted by low nutrient Atlantic Ocean waters.

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 a southwest gradient of TP concentrations on the Shelf from the Ten Thousand Islands-Whitewater Bay and from the SW Florida coast (Naples-Marco Island) towards the Marquesas as a result of southerly advection of TP-enriched water along the coast.

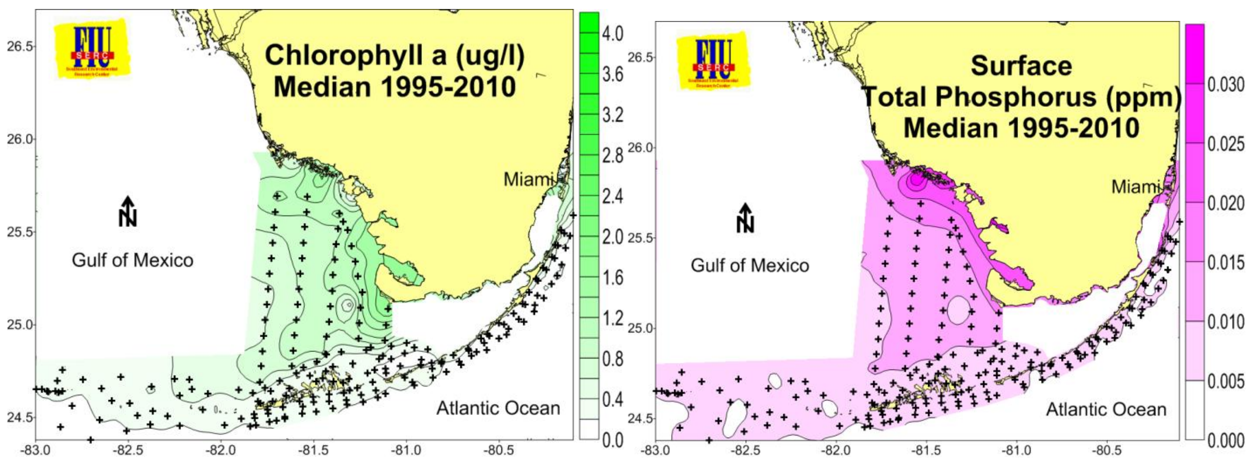

Figure 24

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

4.1.<u>Strategic Targets</u>

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 4 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2012.

Table 4: 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	
Year	CHLA ≤ 0.35 µg l^{-1}	K_d ≤ 0.20 m^{-1}	DIN ≤ 0.75 µM (0.010 ppm)	TP ≤ 0.25 µM (0.0077 ppm)
1995-05	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%)	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 of 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	146 of 215 (67.9%)	156 of 213 (73.2%)	432of 569 (75.9%)	507 of 569 (89.1%)
2012	142 of 168 (84.5%)	135 of 168 (80.4%)	268 of 447 (60.0%)	368 of 447 (82.3%)

5. FY2012 Condition 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).

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 may sometimes be 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 may sometimes affect the Backcountry because of its shallow nature but often 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 coolest 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.

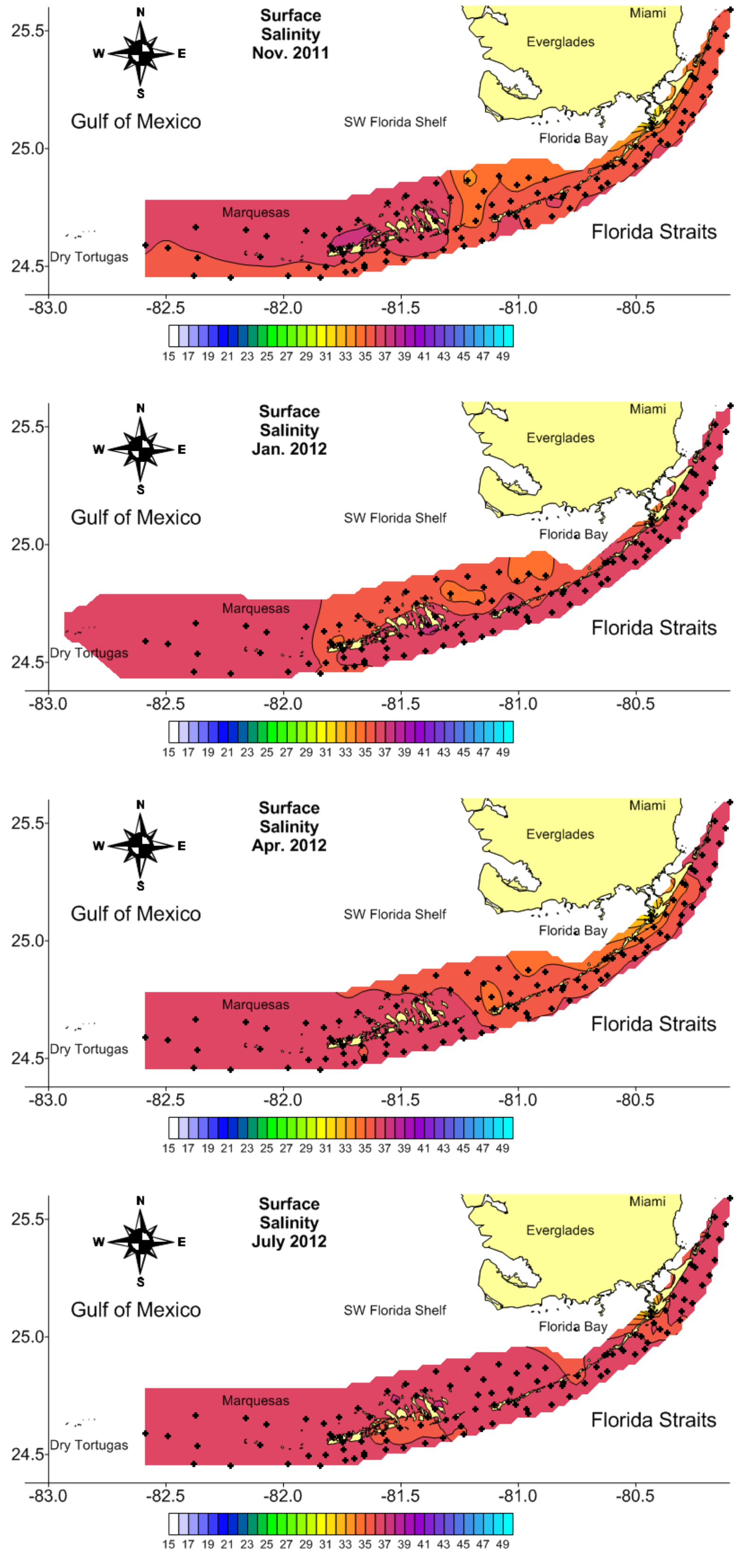

***Figure 25**. Surface salinity distributions across the region during FY2012.*

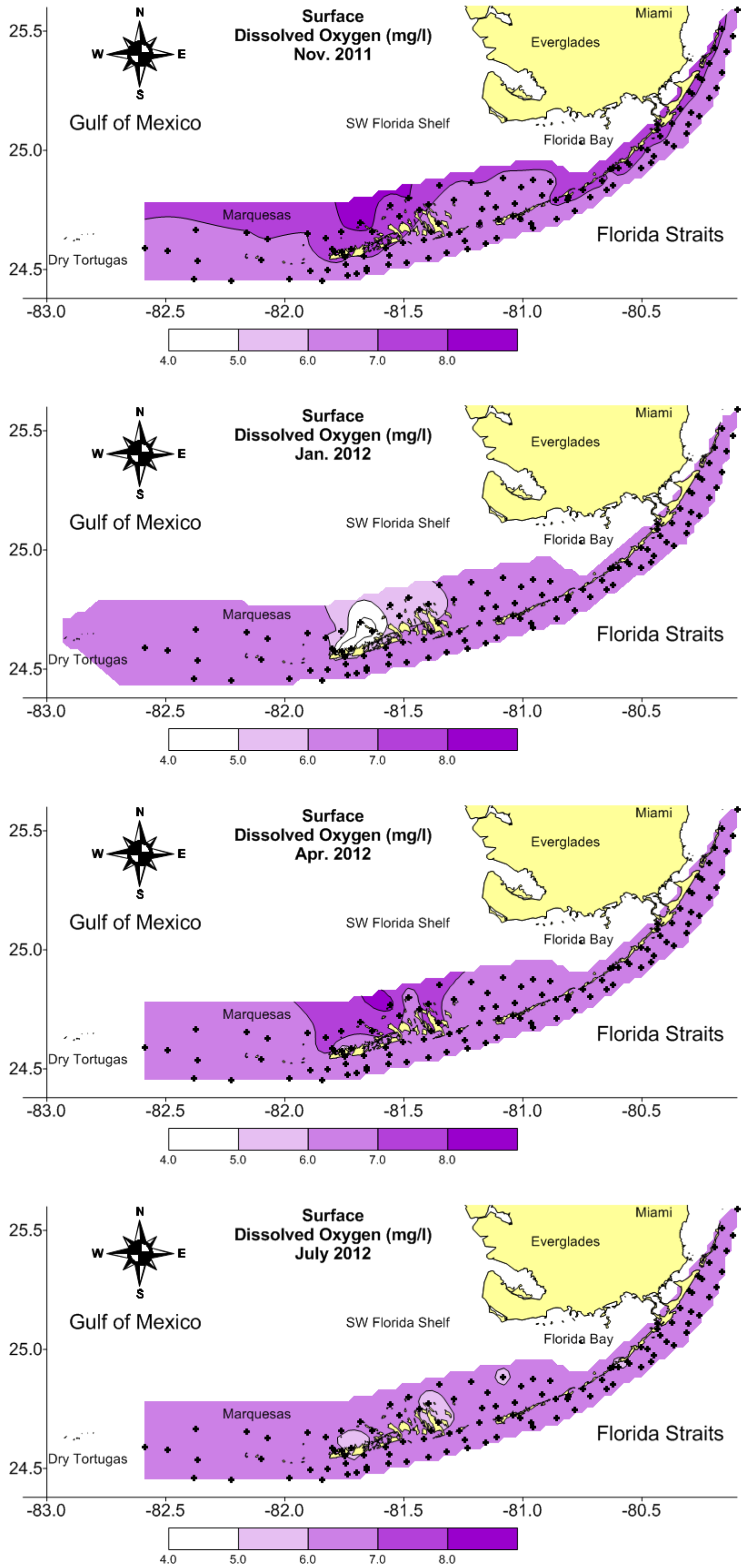

Figure 26*. Surface dissolved oxygen distributions across the region during FY2012.*

Visualization of spatial patterns of NO_3^- concentrations over South Florida waters provides an extended view of source gradients over the region (Fig. 27). Our previous work indicates that Biscayne Bay, Florida Bay and the Shark River area of the west coast usually exhibit higher NO_3^- concentrations relative to the FKNMS and Shelf (Caccia and Boyer 2005, Boyer and Briceño 2007). Elevated NO_3^- in Biscayne Bay is the result of loading from both the canal drainage system and from inshore groundwater (Alleman et al. 1995, Meeder et al. 1997, Caccia and Boyer 2007). A large source of NO_3^- to Florida Bay is the Taylor Slough and C-111 basin (Boyer and Jones, 1999; Rudnick et al., 1999) while the Shark River Slough impacts the west coast mangrove rivers and out onto the Shelf (Rudnick et al., 1999). We speculate that in both cases, elevated NO_3^- concentrations are the result of N_2 fixation/nitrification within the mangroves (Pelegri and Twilley 1998) 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_3^- compared to the Middle and Lower Keys. A similar pattern was observed in a previous transect survey from these areas (Szmant and Forrester 1996). They also showed an inshore elevation of NO_3^- relative to Hawk Channel and the reef tract which is also demonstrated for DIN in our previous analysis (Fig. 4). Interestingly, NO_3^- concentrations in all stations in the Tortugas transect were similar to those of reef tract sites in the mainland Keys; there was no inshore elevation of NO_3^- on the transect off uninhabited Loggerhead Key. We suggest this source of NO_3^- in the Keys is the due to human shoreline development.

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.

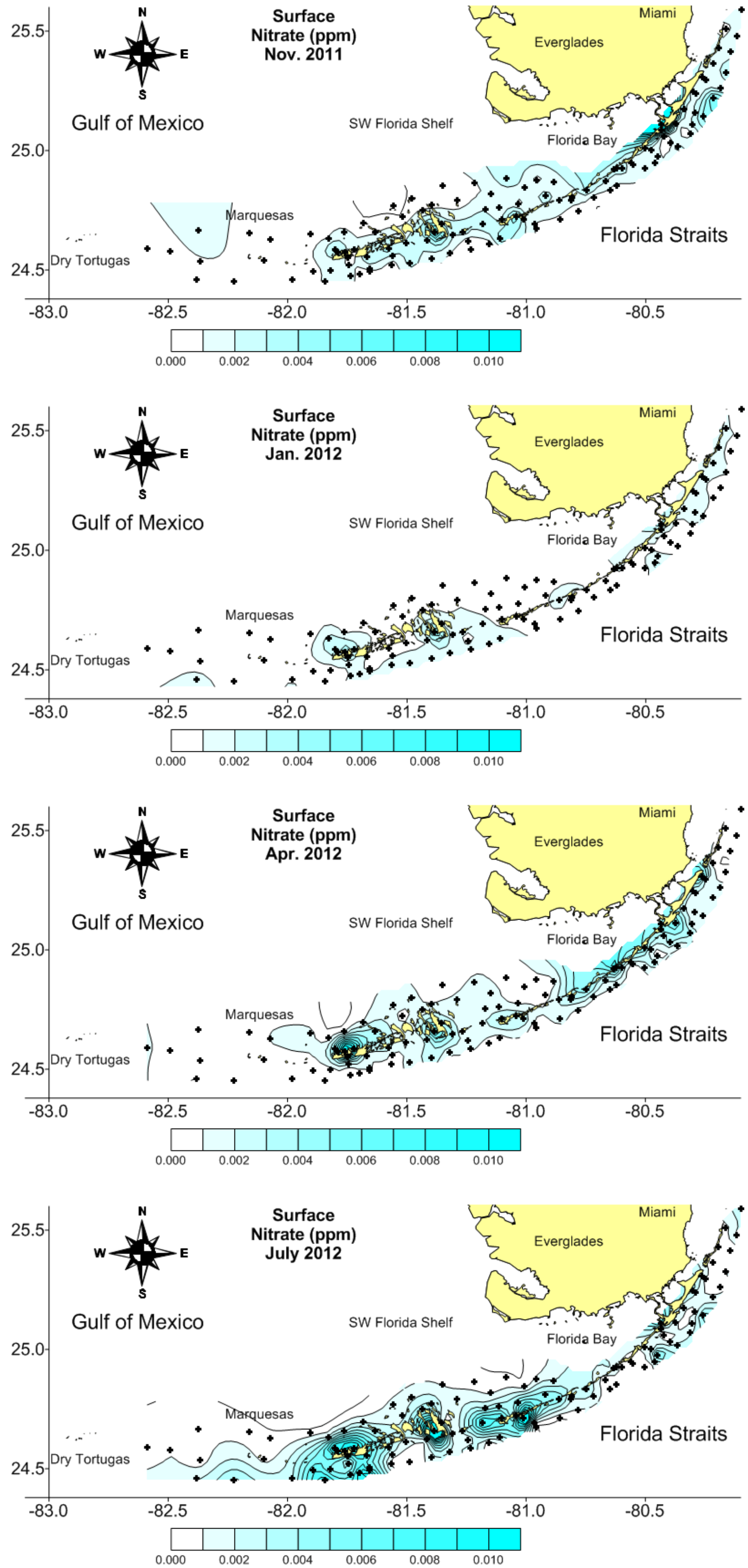

***Figure 27**. Surface nitrate distributions across the region during FY2012.*

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 (Fig. 28). 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.

Interestingly, in many cases for 2012 and other years, NO_3^- 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.

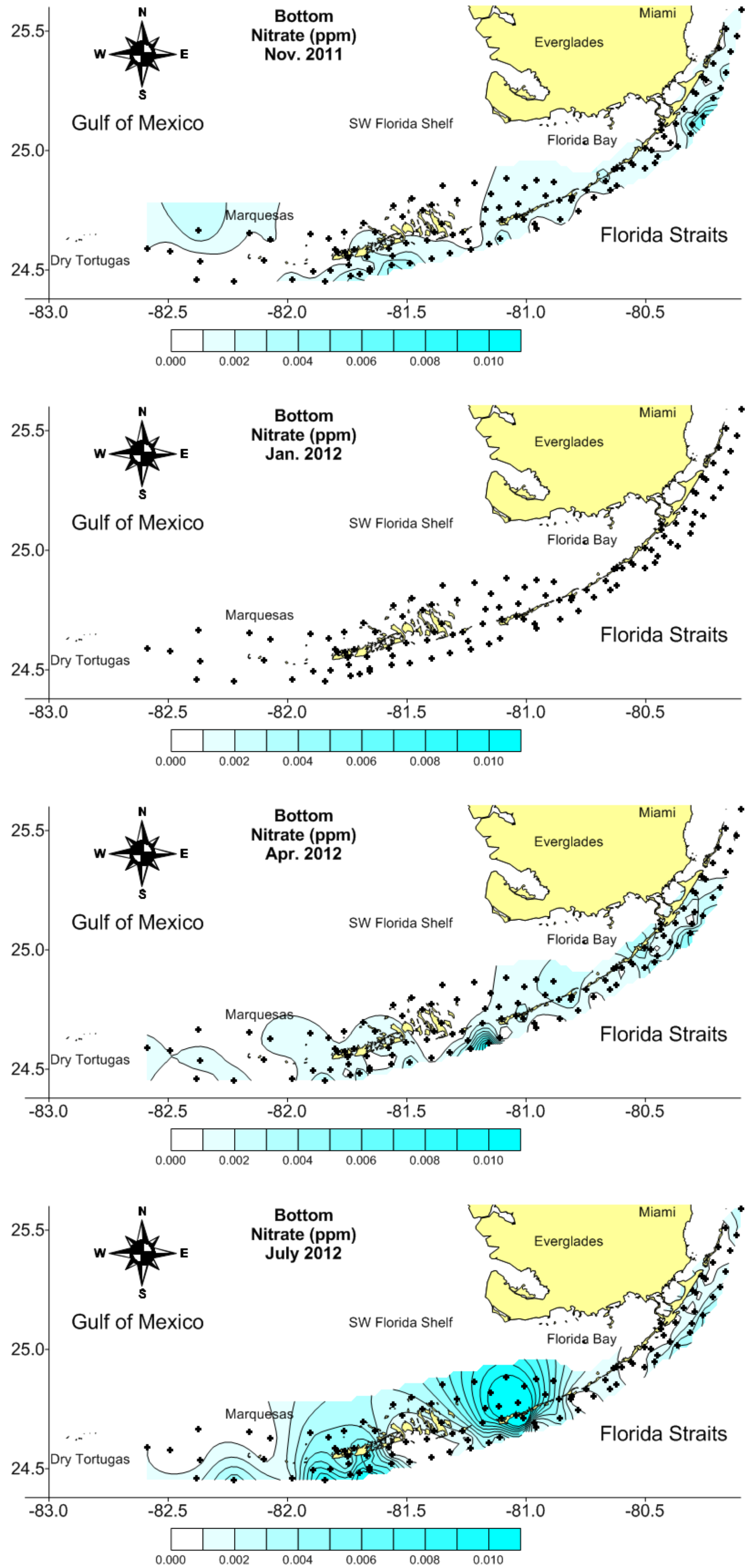

Figure 28*. Bottom nitrate distributions across the region during FY2012.*

NH_4^+ concentrations were distributed in a similar manner as NO_3^- with highest levels occurring in the Backcountry (Fig. 29). NH_4^+ also showed additional 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.

In many situations, independent water masses may be distinguished by difference in density (sigma-*t*, σ_t) between surface and bottom ($\Delta\sigma_t$, Fig. 30). 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 (ΔT, Fig. 31) from intrusion of deeper oceanic waters is clearly an indicator of increased NO_3^-. These upwelling events also affect other nutrient species such as NH_4^+, TP, and SRP in these bottom waters as well.

Spatial patterns in TP in South Florida coastal waters are strongly driven by the west coast sources (Boyer and Briceño 2007, 2011). 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). Little can be concluded regarding TP distribution in the Sanctuary during 2012, except that the highest concentrations (between 0.005 and 0.01 mg/l TP) preferentially occurred on the Bay side of the Keys, and were probably supplied by Shelf waters (Fig. 32). Also, in some instances (i.e. Nov and Jan 2012) deeper offshore waters may have contributed TP to shallower localities in the Upper Keys.

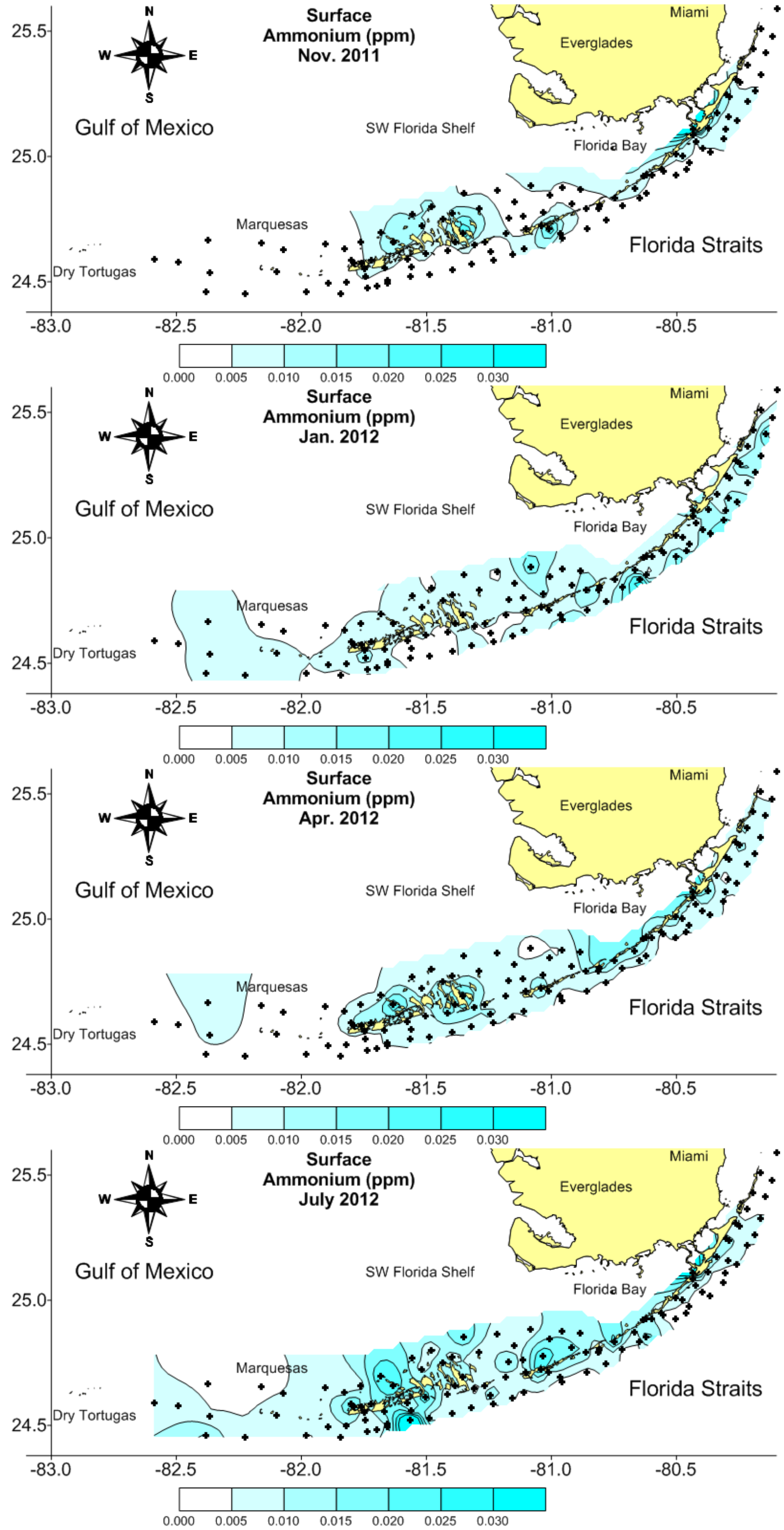

***Figure 29**. Surface ammonium distributions across the region during FY2012.*

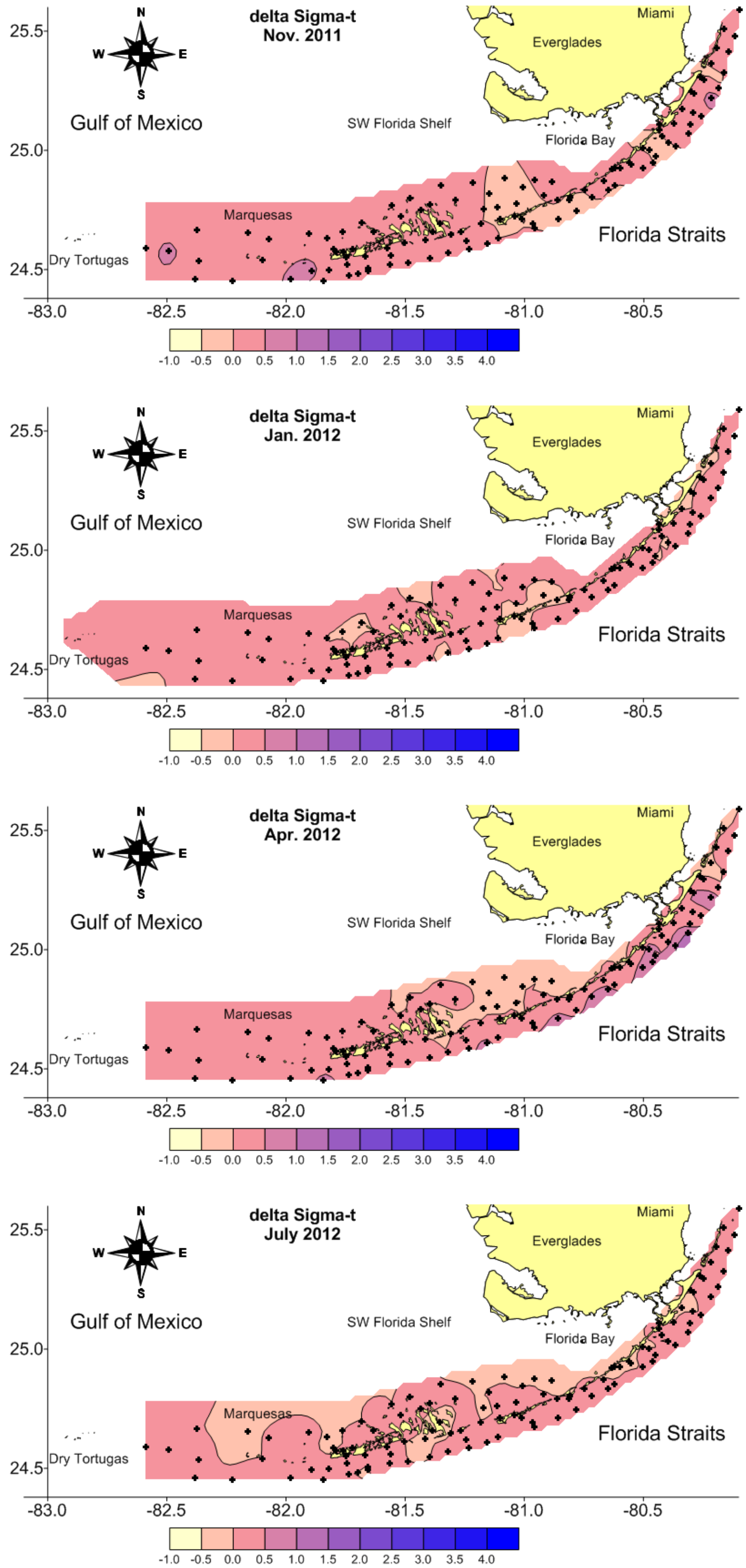

***Figure 30**. Surface and bottom density differences ($\Delta\sigma_t$) across the region during FY2012.*

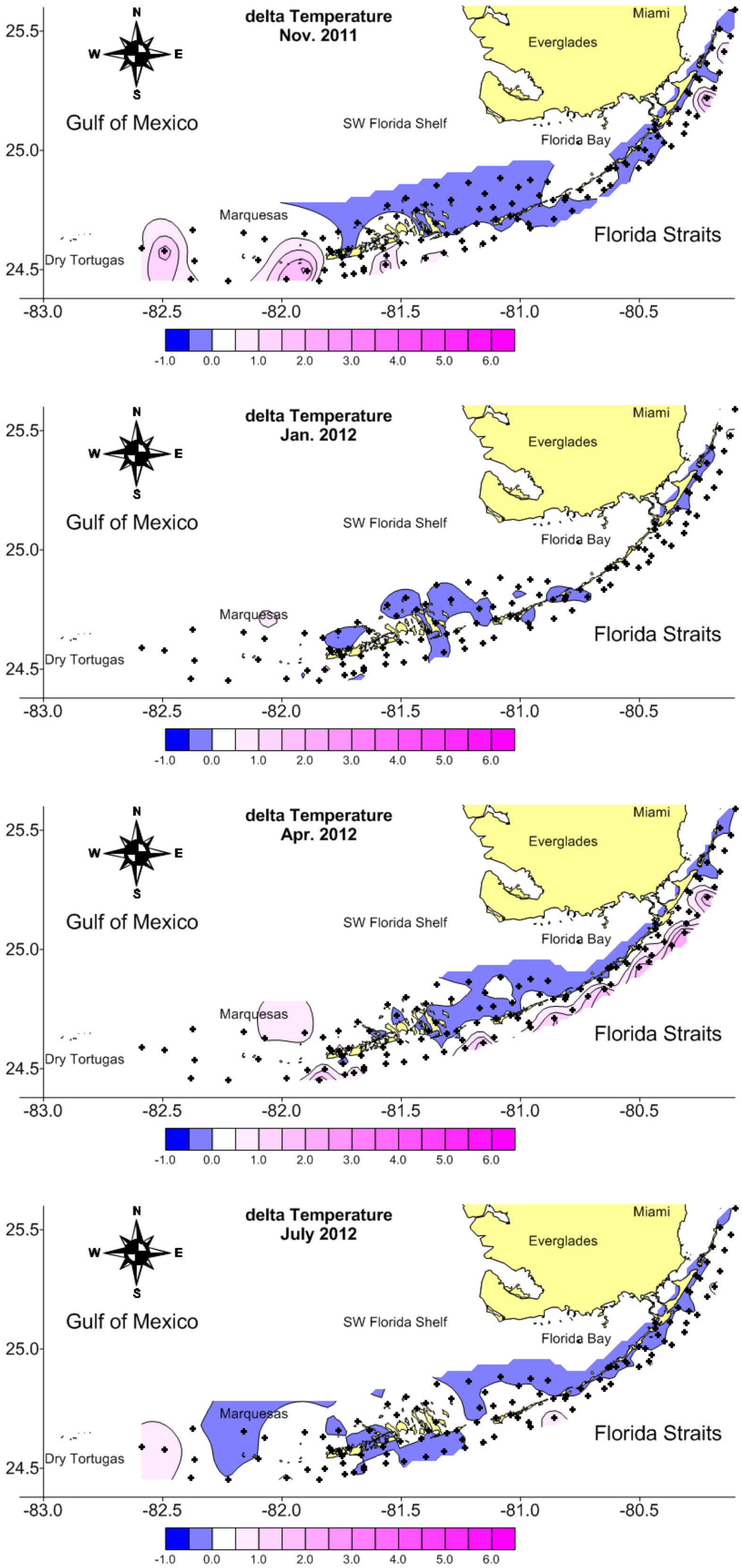

***Figure 31**. Surface and bottom temperature differences across the region during FY2012.*

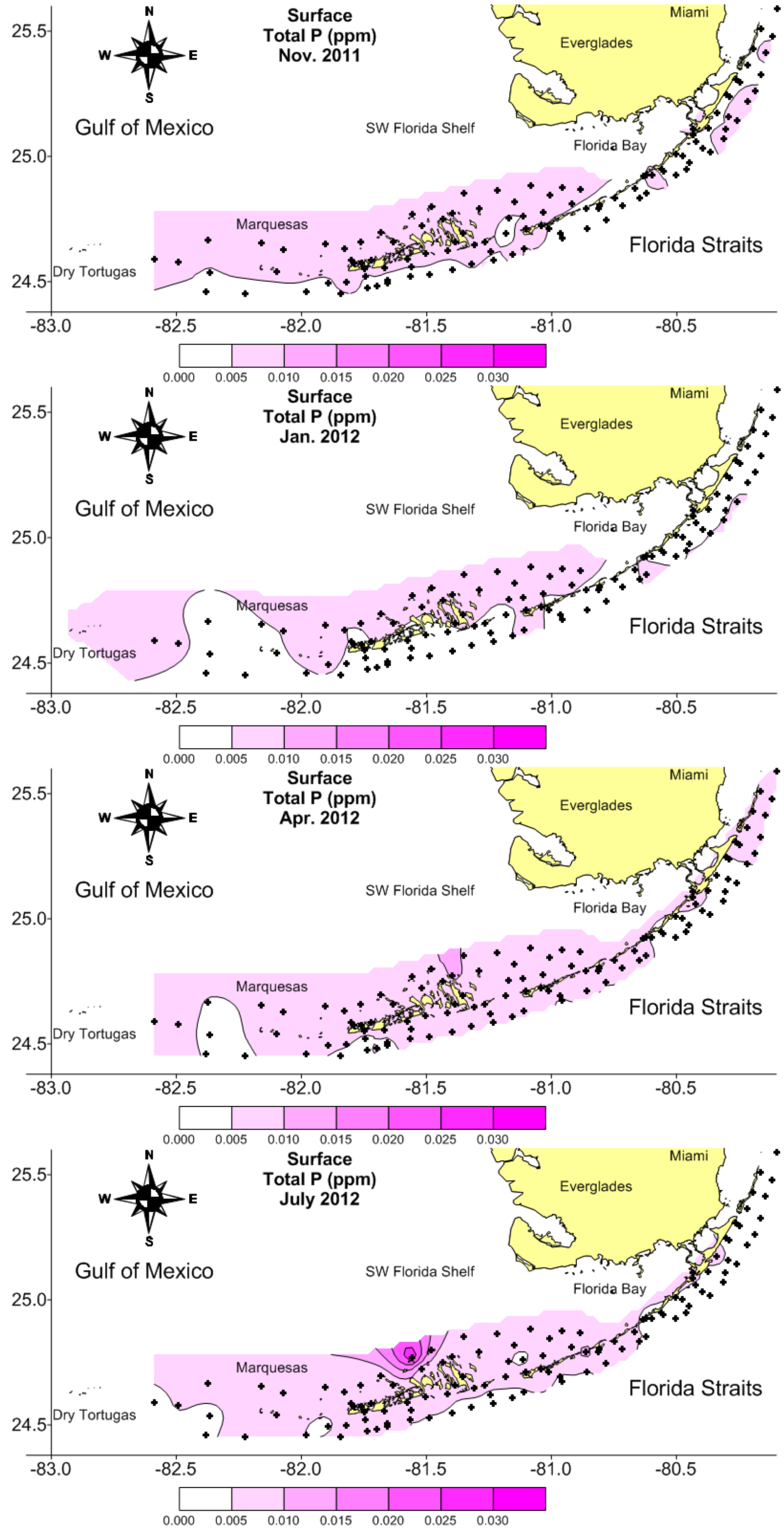

***Figure 32**. Distributions of surface total phosphorus across the region during FY2012.*

Concentrations of TOC (Fig. 33) and TN (Fig. 34) are remarkably similar in pattern of distribution across the South Florida coastal hydroscape. Regionally, 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 TN was from the mangrove forests. Our past data from this area showed that concentrations of TOC and TN increased from Everglades headwaters through the mangrove zone and then decrease with distance offshore. The high concentrations of TOC and TN 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 TN of the FKNMS. In fact, isolated high concentrations in Fig 33 and 34 correspond to the location of SHORE stations. Strong offshore gradients in TOC and TN existed for all mainland Keys segments (Fig 4) but not for the Tortugas transect (Boyer and Briceño 2007, 2010). 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 (anthropogenic) rather than simply benthic production and sediment re-suspension. Main Keys reef tract concentrations of TOC and TON were consistently the lowest in the FKNMS.

Much emphasis has been placed on assessing the impact of episodic phytoplankton blooms in Florida Bay on the offshore reef tract environment. In the past, patial 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. It is interesting that CHLA concentrations are typically higher in the Marquesas than in other areas of the FKNMS (Fig. 35). 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.

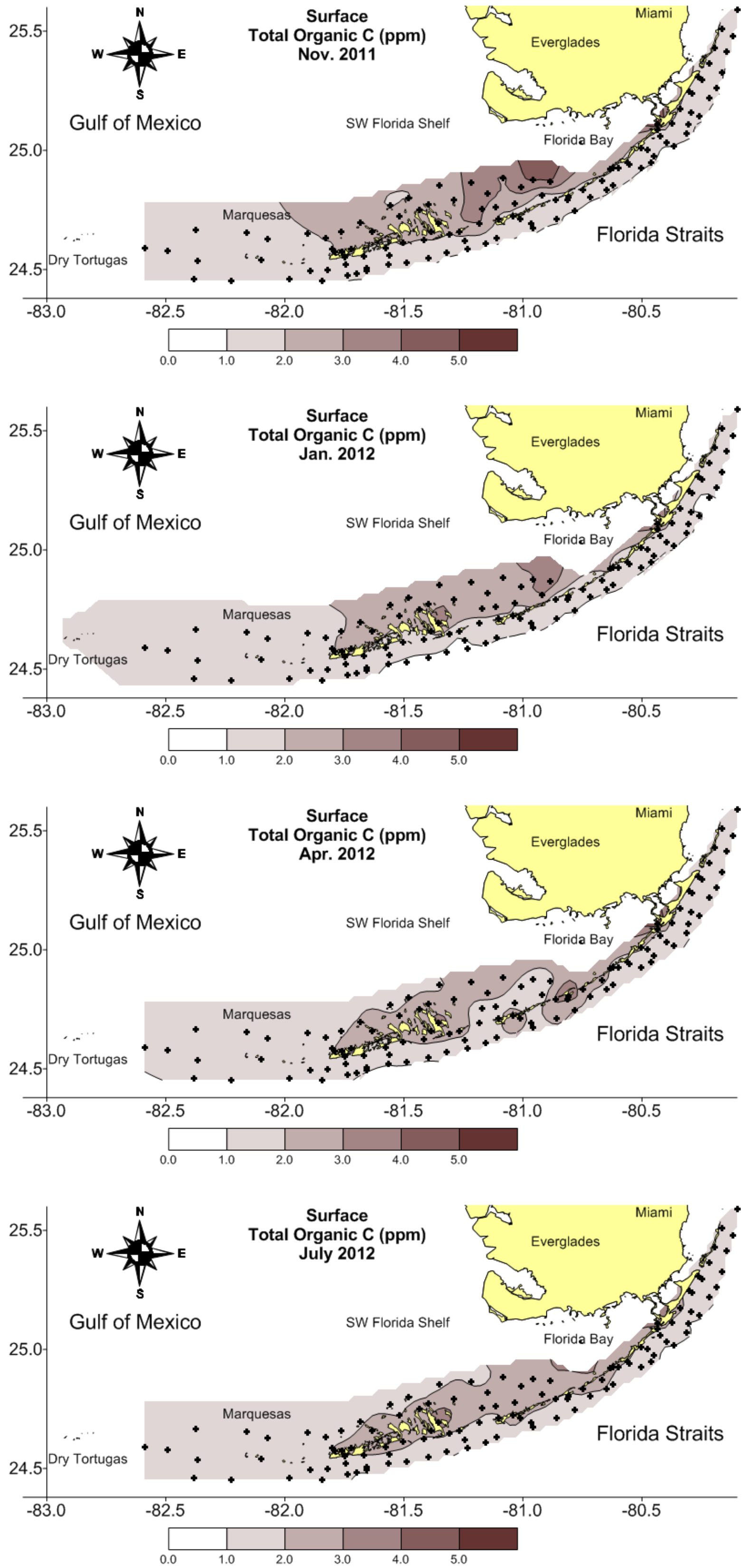

***Figure 33**. Distributions of surface total organic carbon across the region during FY2012.*

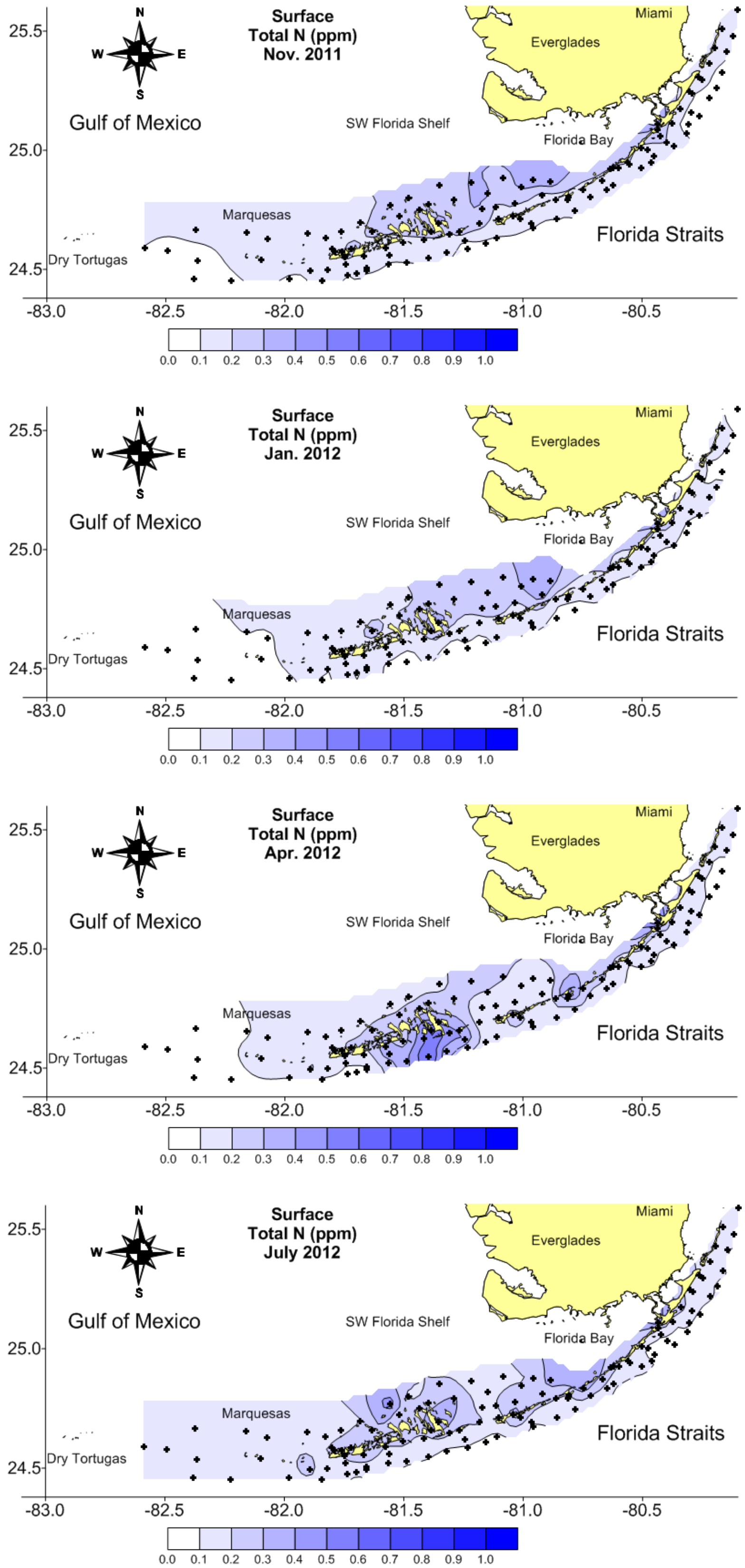

***Figure 34**. Distributions of surface total nitrogen across the region during FY2012.*

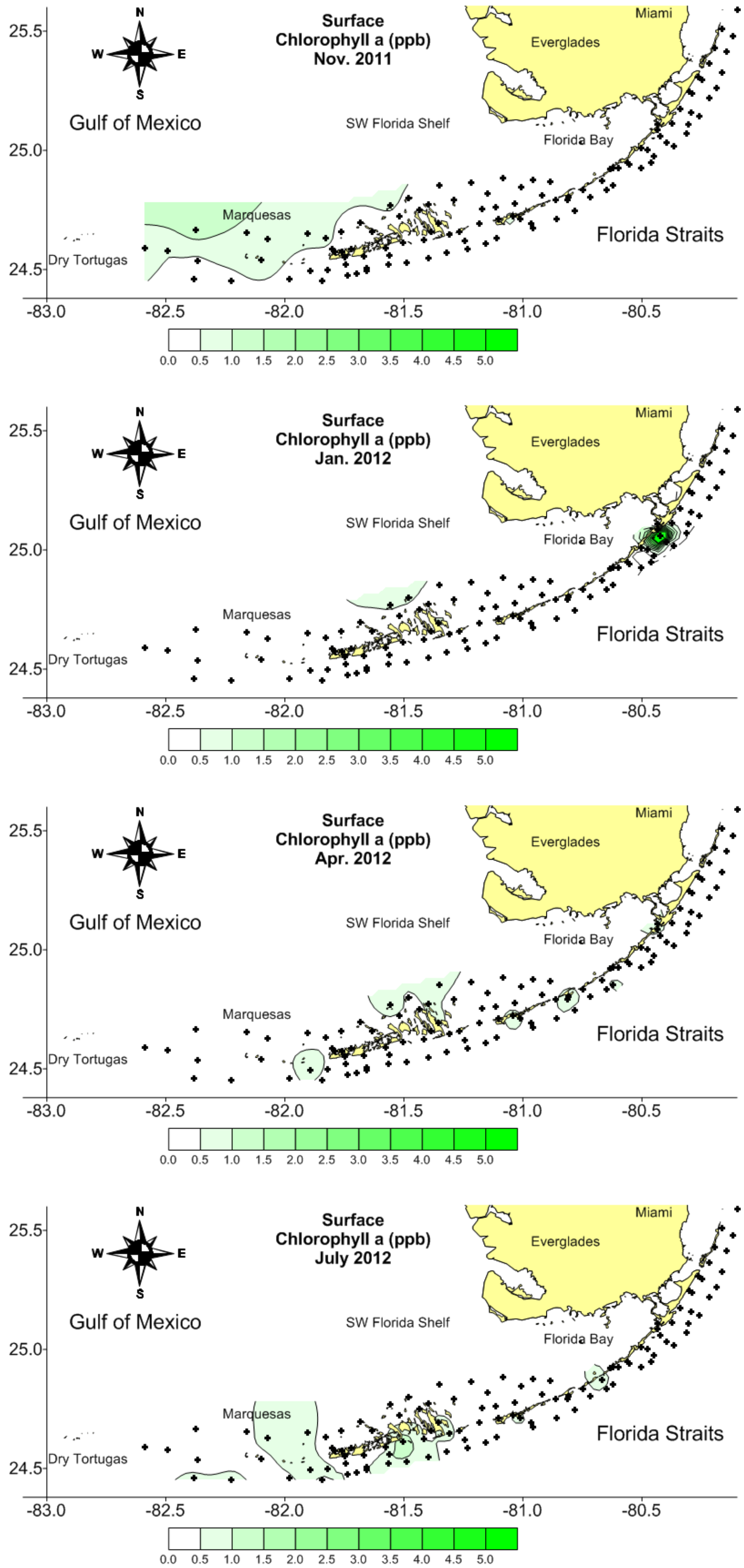

***Figure 35**. Distributions of surface chlorophyll a across the region during FY2012.*

A CHLA concentration of 2 µg l^{-1} in the water column of a reef tract might be considered an indication of eutrophication. Conversely, a similar CHLA level in the Quicksands indicates a productive ecosystem which feeds a valuable shrimp fishery.

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 (Boyer and Briceño 2007). 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. The recently installed SHORE stations show higher CHLA concentrations than those of LK, MD, UK and OFF stations underscoring the anthropogenic impact.

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 have been observed on the Shelf but reef tract levels remain remarkably low regardless of inshore levels. Elevated turbidity is the backcountry is most probably due to the shallow water column being easily re-suspended 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 37). However, in Keys waters, CDOM may be a more prominent driver of light penetration.

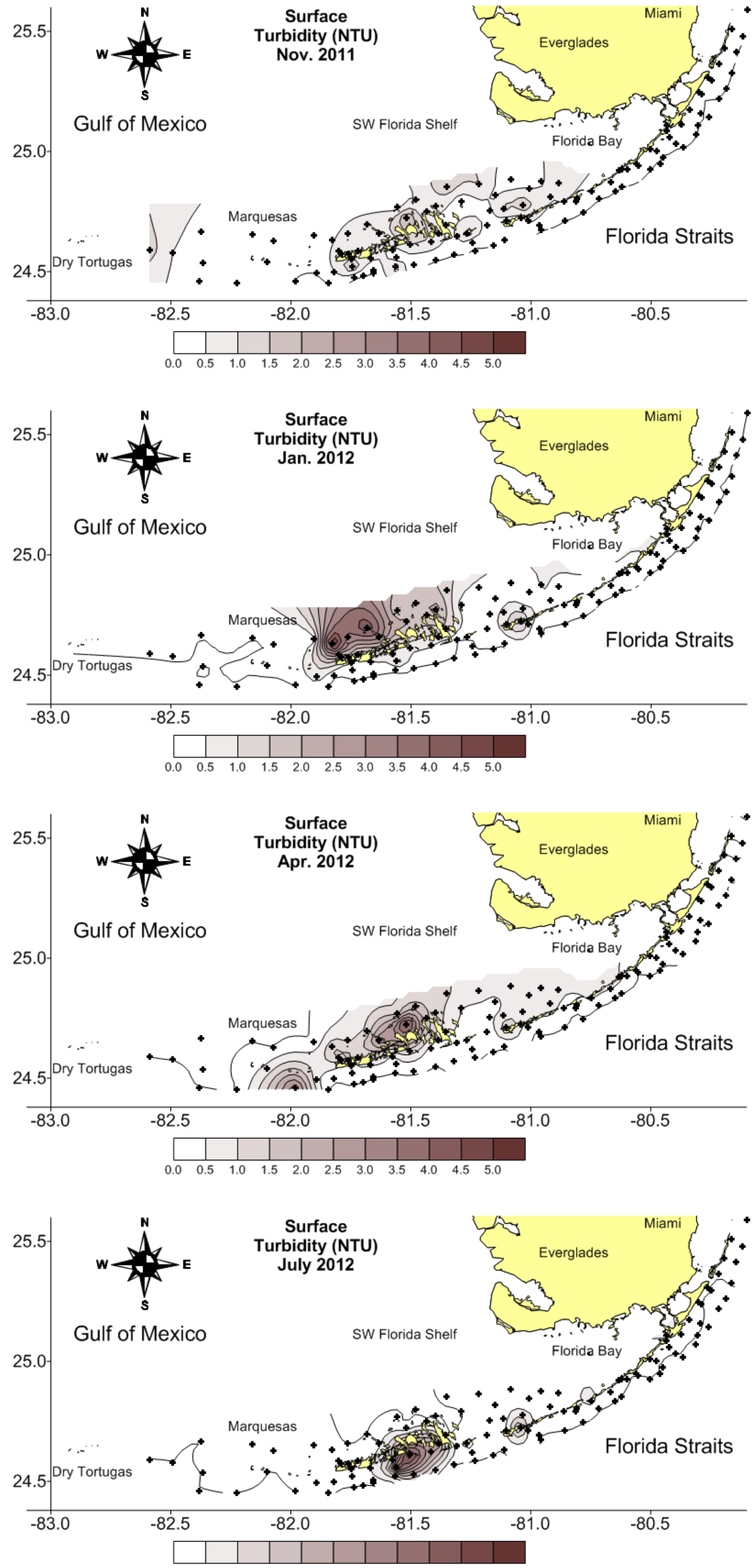

***Figure 36**. Distributions of surface turbidity across the region during FY2012.*

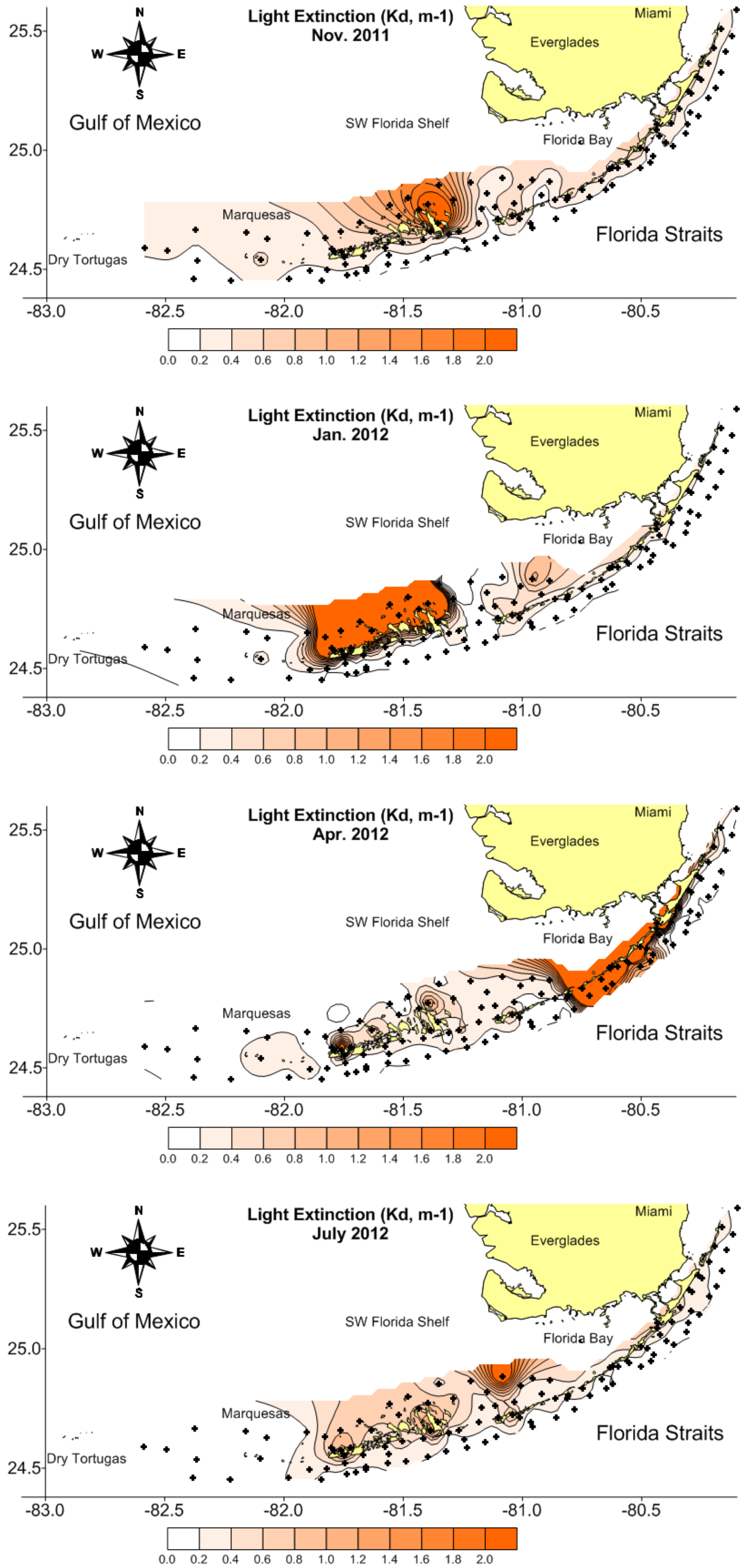

***Figure 37**. Distributions of Light extinction across the region during FY2012.*

Surface SiO_2 concentrations exhibited a pattern similar to salinity (Fig. 38). The source of SiO_2 in this geologic area of carbonate rock and sediments is from siliceous periphyton (diatoms) growing in the Shark River Slough, Taylor Slough, and C-111 basin watersheds. Unlike the Mississippi River plume with CHLA concentrations of 76 $\mu g\ l^{-1}$ (Nelson and Dortch 1996), phytoplankton biomass on the Shelf (1-2 $\mu g\ l^{-1}$ CHLA) was not sufficient to account for the depletion of SiO_2 in this area. Therefore, SiO_2 concentrations on the Shelf 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. 38). 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.

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.

Most of the FKNMS is routinely P limited using this metric. Interestingly, the Shelf and Tortugas areas were 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 land use and bedrock geochemistry of the watersheds (Boyer 2006; Briceño et al 2013). 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 land use changes from relatively undeveloped wetland (Big Cypress Basin) to a highly urban/agricultural mix (Naples, FL).

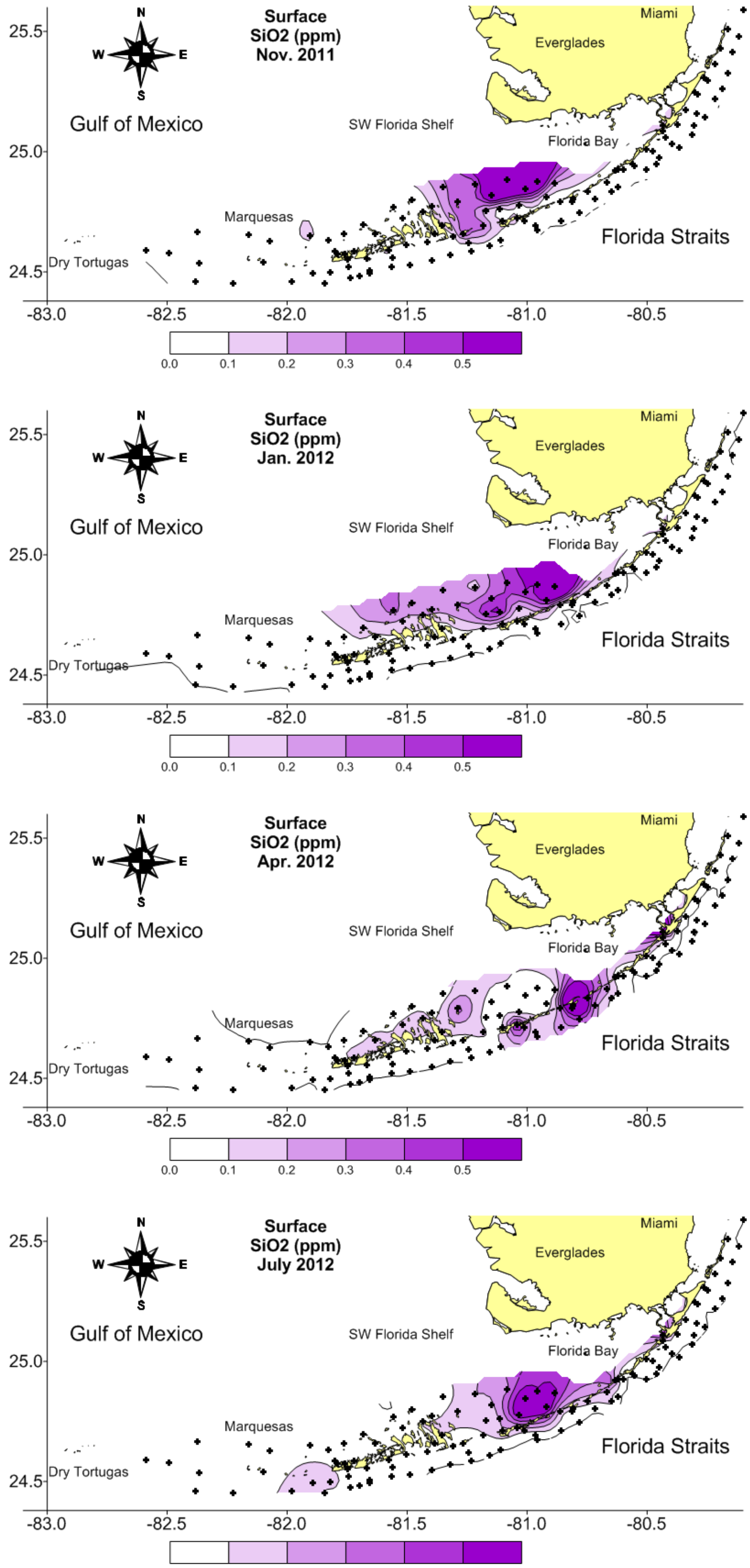

Figure 38. Distributions of surface silicate across the region during FY2012.

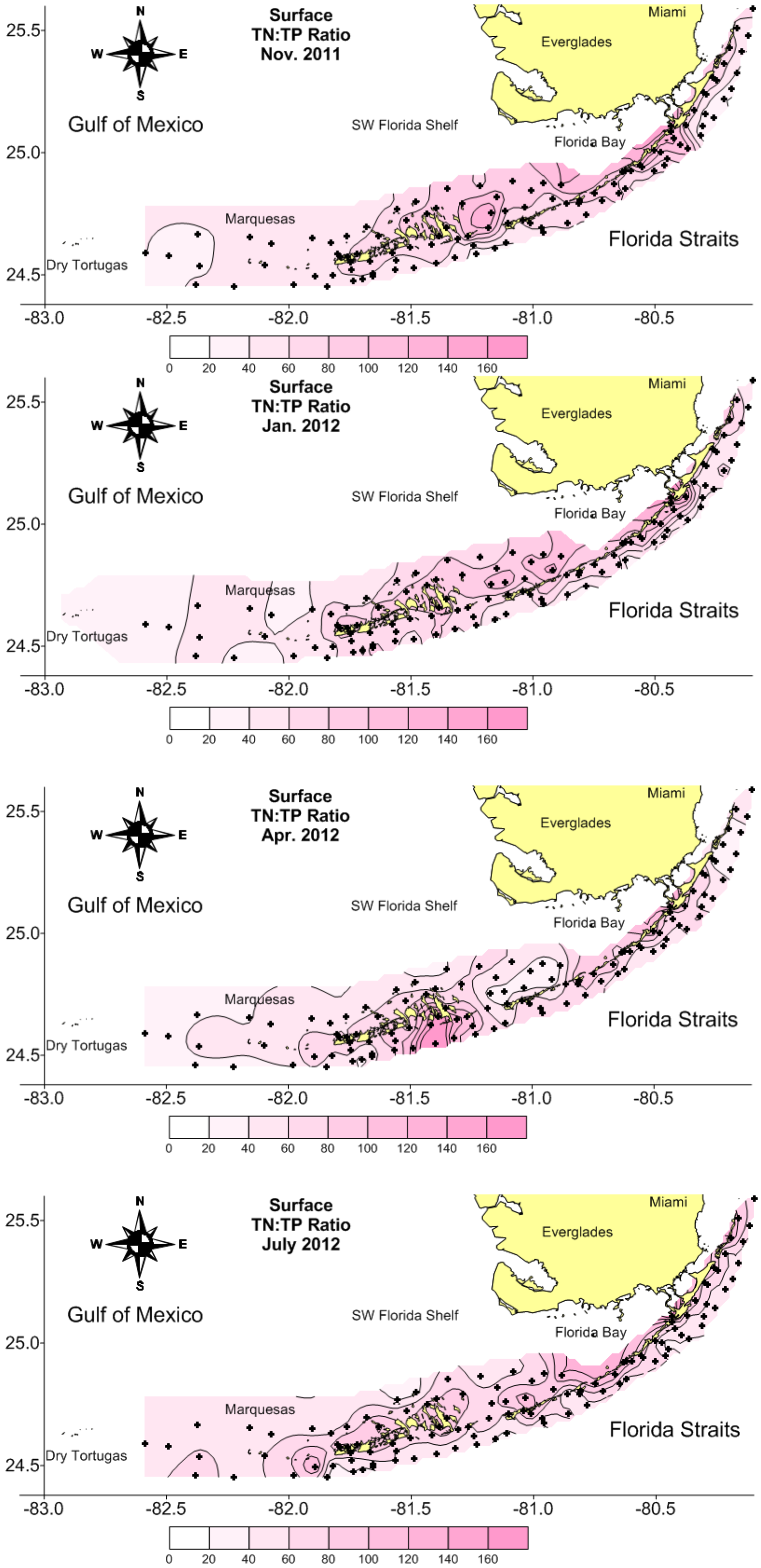

***Figure 39**. Distributions of surface TN:TP ratio across the region during FY2012.*

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.

The large scale of this monitoring program allowed us to assemble a much more holistic view of broad physical/chemical/biological interactions occurring over the South Florida hydroscape. We recently characterized and spatially subdivided South Florida's coastal and estuarine waters (Briceño et al. 2010, 2013), including the FKNMS which rendered seven biogeochemically distinct water bodies whose spatial distribution are closely linked to geomorphology, circulation, benthic community pattern, and to water management. This segmentation has been adopted with minor changes by federal (EPA) and state (FDEP) environmental agencies to derive numeric nutrient criteria. This confirms that 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.

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7. Appendix 1

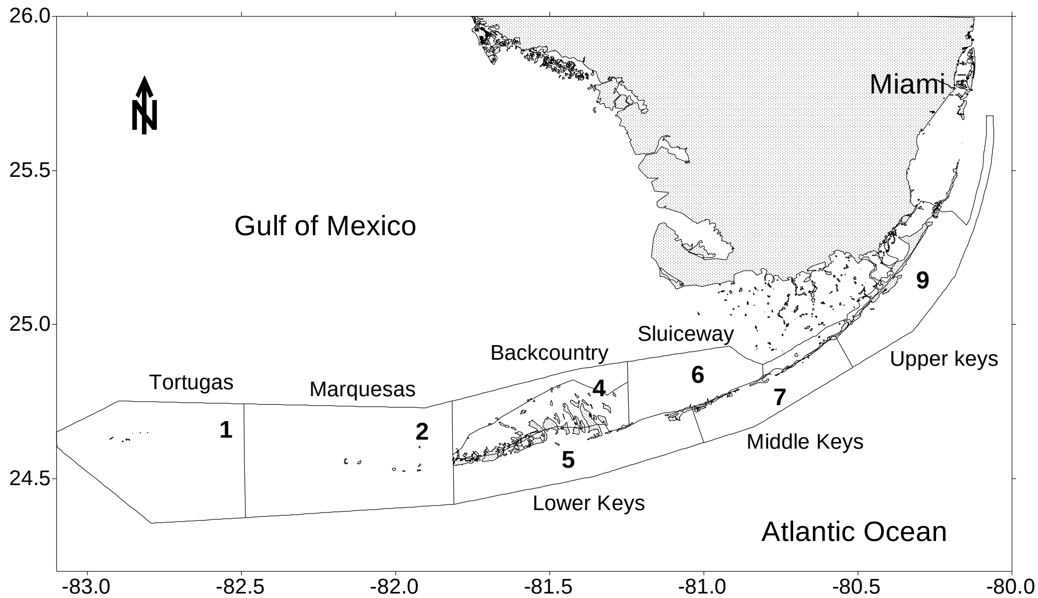

***Figure A1.1**: Map of original FKNMS boundary including collapsed segment numbers and common names. Modified after Klein and Orlando (1994)*

Table 5: Statistical summary of water quality in the FKNMS initial zones (Fig App 1.1) for the period of record. Data are summarized as median, minimum (Min.), maximum value (Max.), and number of samples (*n*).

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	0.10	0.00	3.04	586
NO_3^-	2	0.09	0.00	1.33	82
(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_3^-	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

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	0.06	0.00	0.45	586
NO_2^-	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_2^-	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
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

Variable	Cluster	Median	Min.	Max.	*n*
Bottom TN (ppm)	1	11.88	2.47	43.09	43
	2				
	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 TON (ppm)	1	14.61	0.98	71.65	585
	2	14.51	3.41	62.91	82
	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 TON (ppm)	1	11.32	2.21	42.78	43
	2				
	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 TP (ppm)	1	0.26	0.07	1.09	585
	2	0.24	0.10	0.83	82
	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 TP (ppm)	1	0.21	0.08	0.45	42
	2				
	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

Variable	Cluster	Median	Min.	Max.	*n*
Surface SRP (ppm)	1	0.02	0.00	0.30	586
	2	0.02	0.00	0.22	82
	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 SRP (ppm)	1	0.02	0.00	0.17	43
	2				
	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
Surface Chl *a* ($\mu g\ l^{-1}$)	1	0.32	0.00	15.24	587
	2	0.30	0.00	4.95	82
	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 TOC (ppm)	1	230.01	88.54	1435.42	586
	2	231.33	135.31	505.54	82
	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 TOC (ppm)	1	178.54	88.11	446.04	43
	2				
	3	142.75	0.00	883.10	2343
	4				
	5	206.17	78.56	392.63	136
	6	162.54	21.69	2135.83	1007
	7	225.90	147.40	281.73	3
	8	161.79	75.83	847.71	335

Variable	Cluster	Median	Min.	Max.	*n*
Surface	1	1.53	0.00	89.00	557
SiO_2	2	4.74	0.00	55.16	78
(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_2	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
Surface	1	1.31	0.00	37.00	581
Turbidity	2	1.13	0.20	5.55	82
(NTU)	3	0.33	0.00	10.14	2486
	4	0.79	0.00	7.70	208
	5	0.86	0.00	16.20	821
	6	0.55	0.00	8.80	1221
	7	0.95	0.00	17.35	458
	8	1.33	0.00	11.84	493
Bottom	1	1.67	0.00	9.10	52
Turbidity	2				
(NTU)	3	0.36	0.00	11.18	2329
	4				
	5	0.77	0.00	16.90	156
	6	0.56	0.00	7.95	1020
	7	0.72	0.00	4.89	12
	8	1.58	0.00	15.96	331
Surface	1	36.14	28.79	39.64	585
Salinity	2	36.22	29.59	40.30	82
	3	36.19	26.70	37.80	2488
	4	36.10	27.69	40.90	208
	5	36.30	29.51	40.00	798
	6	36.24	28.02	38.50	1200
	7	36.40	27.95	40.39	452
	8	36.15	30.33	39.06	493

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

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

8. Appendix 2: Estimated tendency of parameters for the period 1995-2012

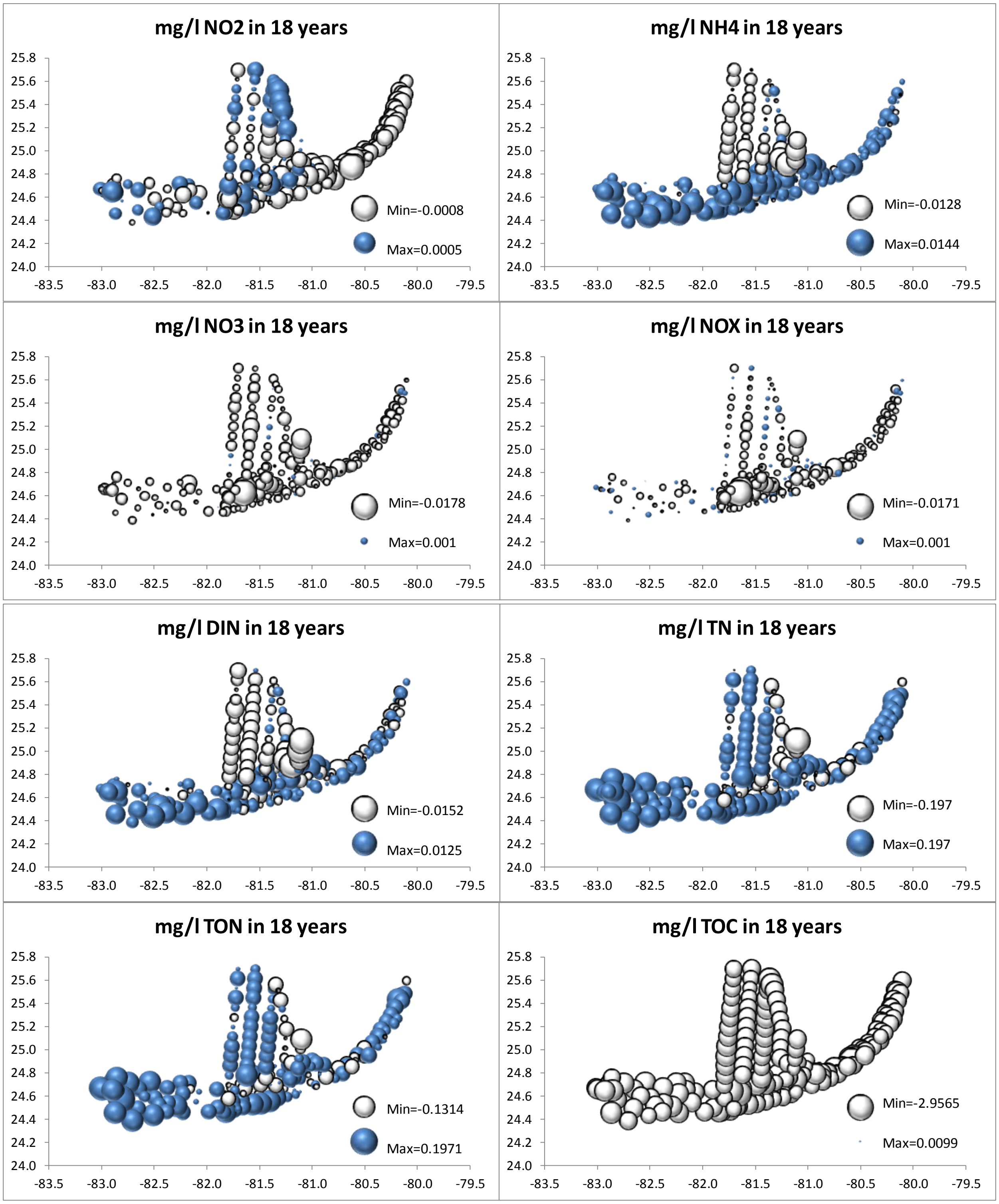

Figure A2.1: Estimated tendency of Nitrogen species for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance.

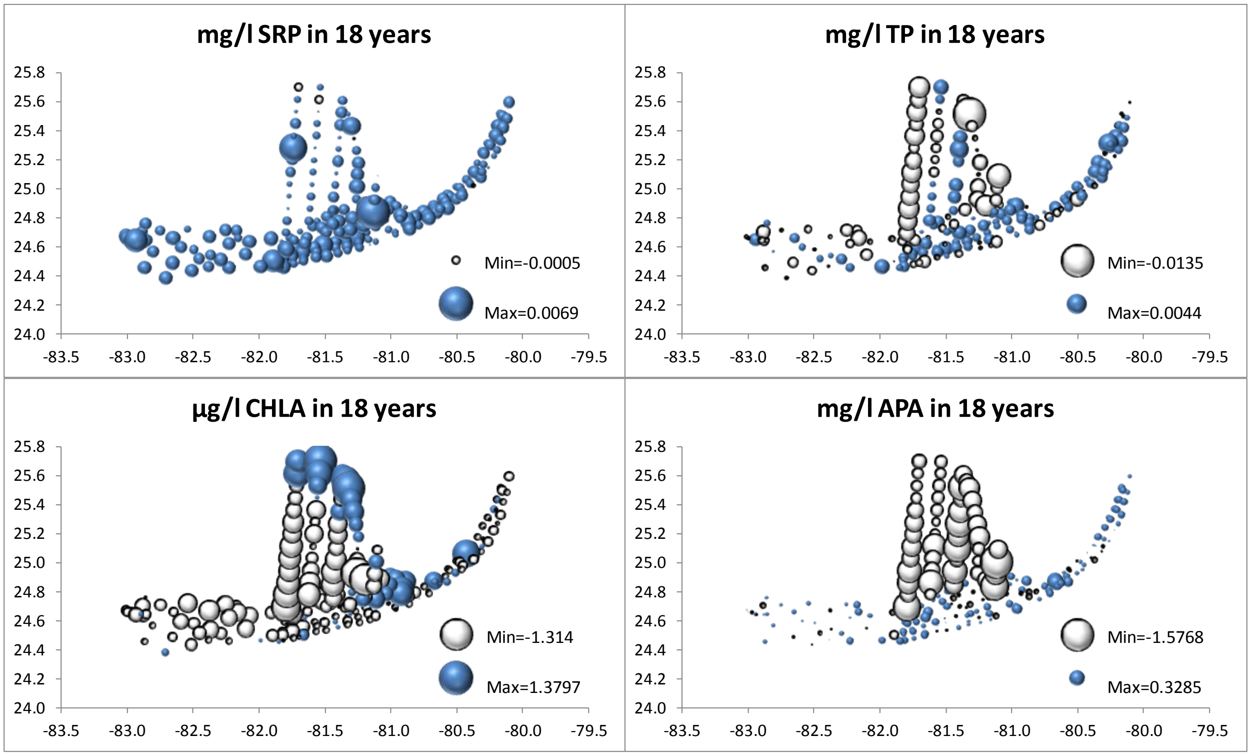

Figure A2.2: Estimated tendency of SRP, TP, CHLa and APA for the period 1995-2012, from slopes of Ordinary Linear Regression without considering statistical significance.

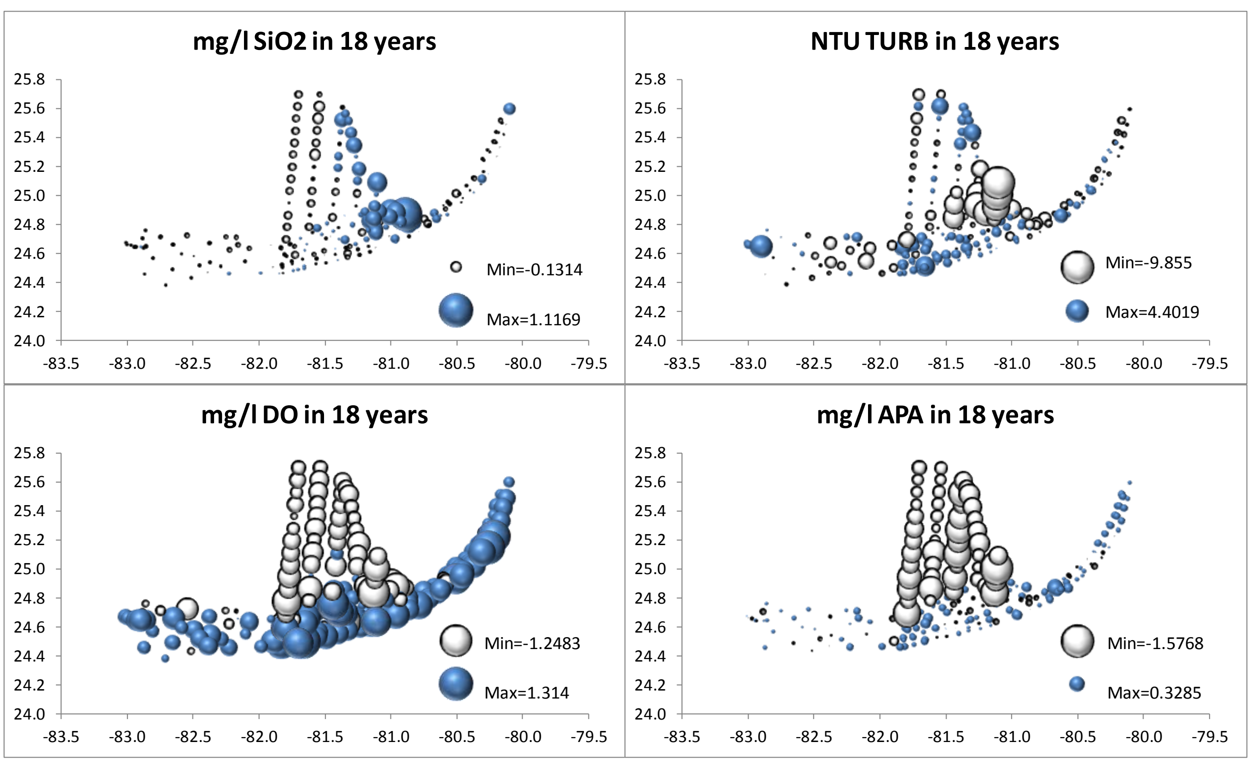

Figure A2.3: Estimated tendency of SiO_2, Turbidity, DO and APA for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance.

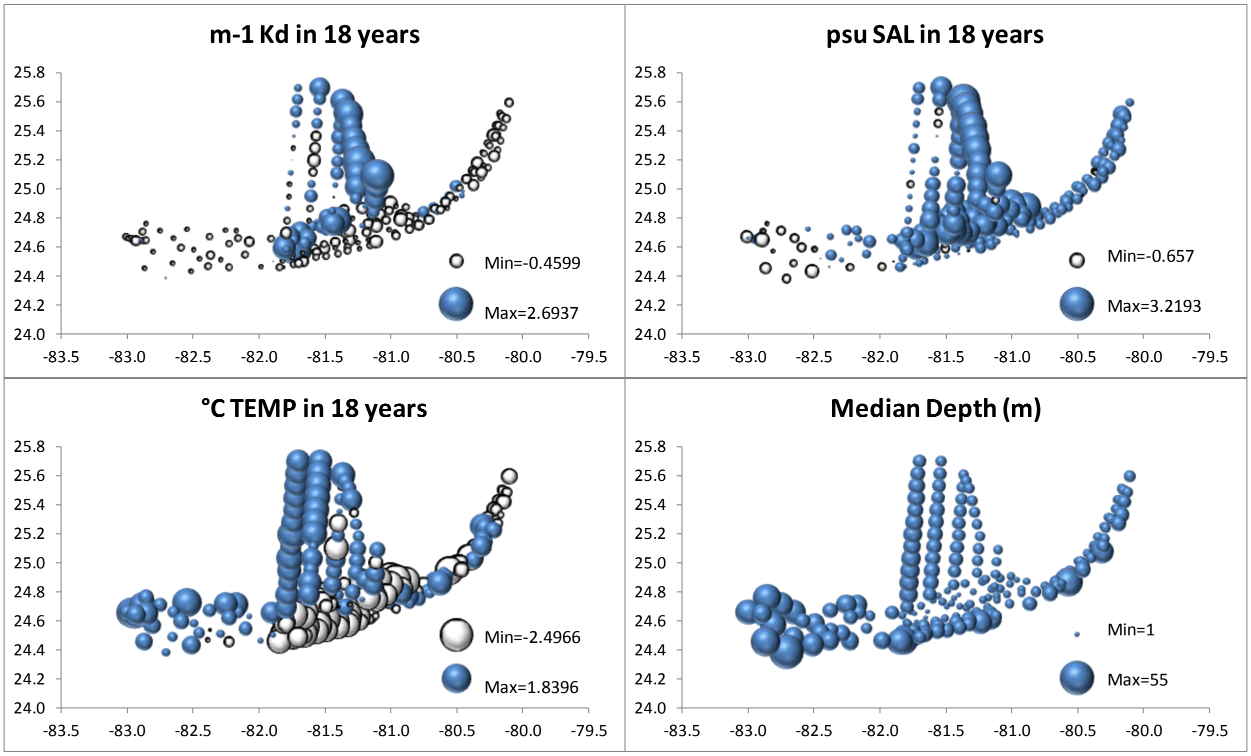

Figure A2.4: Estimated tendency of Kd, Salinity, Temperature for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance. Also shown is Station median Depth,