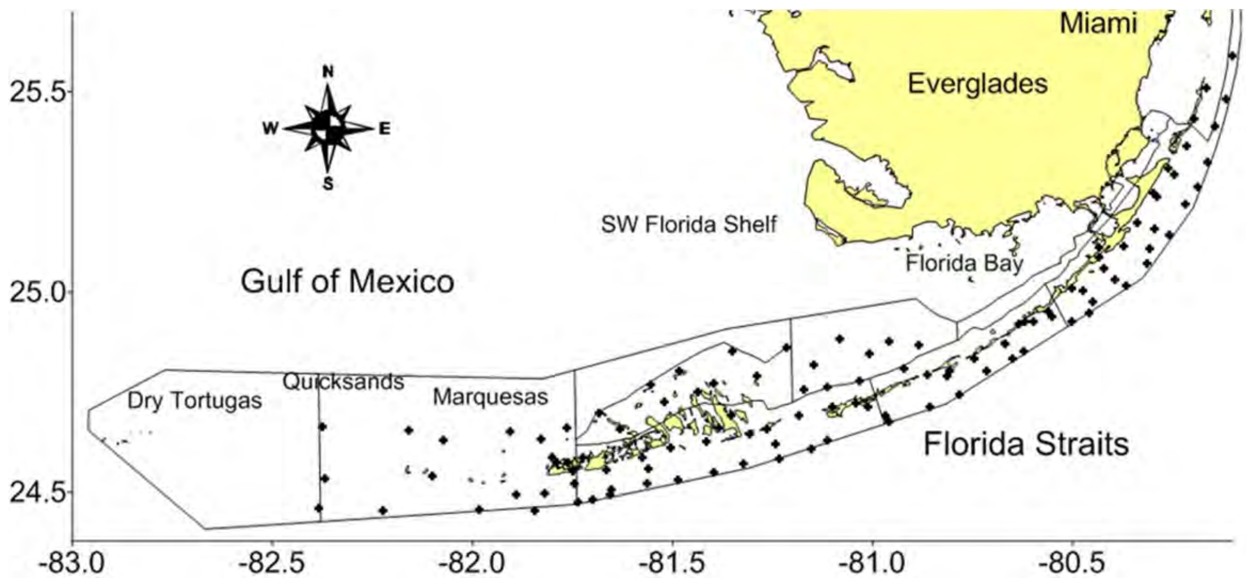
2013 ANNUAL REPORT
OF THE WATER QUALITY MONITORING PROJECT
FOR THE WATER QUALITY PROTECTION PROGRAM
OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY



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Principal Investigators

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Henry O. Briceño & Joseph N. Boyer

Funded by the Environmental Protection Agency (X7 00D02412)

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. 2013 and includes data from 73 quarterly sampling events within the FKNMS. This annual report reflects funding cutbacks in 2012 resulting in reduction of spatial sampling from 155 to 112 sites.

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 µg l^{-1} and the vertical attenuation coefficient for downward irradiance (K_d, i.e., light attenuation) should be less than or equal to 0.13 m^{-1}. For all monitoring sites in FKNMS, dissolved inorganic nitrogen should be less than or equal to 0.75 µM (0.010 ppm) and total phosphorus should be less than or equal to 0.2 µM (0.0077 ppm). Table 1 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2013.

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) introduces a bias to the dataset which results in a reporting problem, perhaps requiring a revision of SP-47 to correct this deviation. To avoid such complications, we have not included the recently added locations (#500 to #509) in the calculation of compliances.

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

For reef stations, chlorophyll less than or equal to 0.2 micrograms liter^{-1} (ugl^{-1}) and vertical attenuation coefficient for downward irradiance (K_d, i.e., light attenuation) less than or equal to 0.13 per meter; for all stations in the FKNMS, dissolved inorganic nitrogen less than or equal to 0.75 micromolar and total phosphorus less than or equal to 0.2 micromolar; water quality within these limits is considered essential to promote coral growth and overall health. The "number of samples" exceeding these targets is tracked and reported annually. 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

Year	REEF Stations		All Stations (excluding SHORE sites)	
	CHLA ≤ 0.20 µg l^{-1}	K_d ≤ 0.13 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 1000 (84.3%)	738 of 1,003 (73.6%)
2011	146 of 215 (67.9%)	156 of 213 (73.2%)	813 of 1012 (80.3 %)	911 of 1013 (89.9 %)
2012	142 of 168 (84.5%)	135 of 168 (80.4%)	489 of 683 (71.6 %)	634 of 684 (92.7 %)
2013	148 of 172 (86.0%)	150 of 172 (87.2%)	496 of 688 (72.1 %)	603 of 688 (87.6 %)

Important Results Realized from this Monitoring Project

1. Land-based Influence on Water Quality

We documented elevated nutrient concentrations (DIN, TN, TP, and SiO_2) in waters close to shore along the Keys, and their corresponding responses from the system, such as higher phytoplankton biomass (CHLA), turbidity, as well as lower salinity and DO in the water column. These changes, associated to human impact, have become even more obvious by the addition of 10 stations (# 500 to #509) located very close to shore, (within the so-called 500 m Halo; FDEP 2011) sampled since Nov 2011 (SHORE).

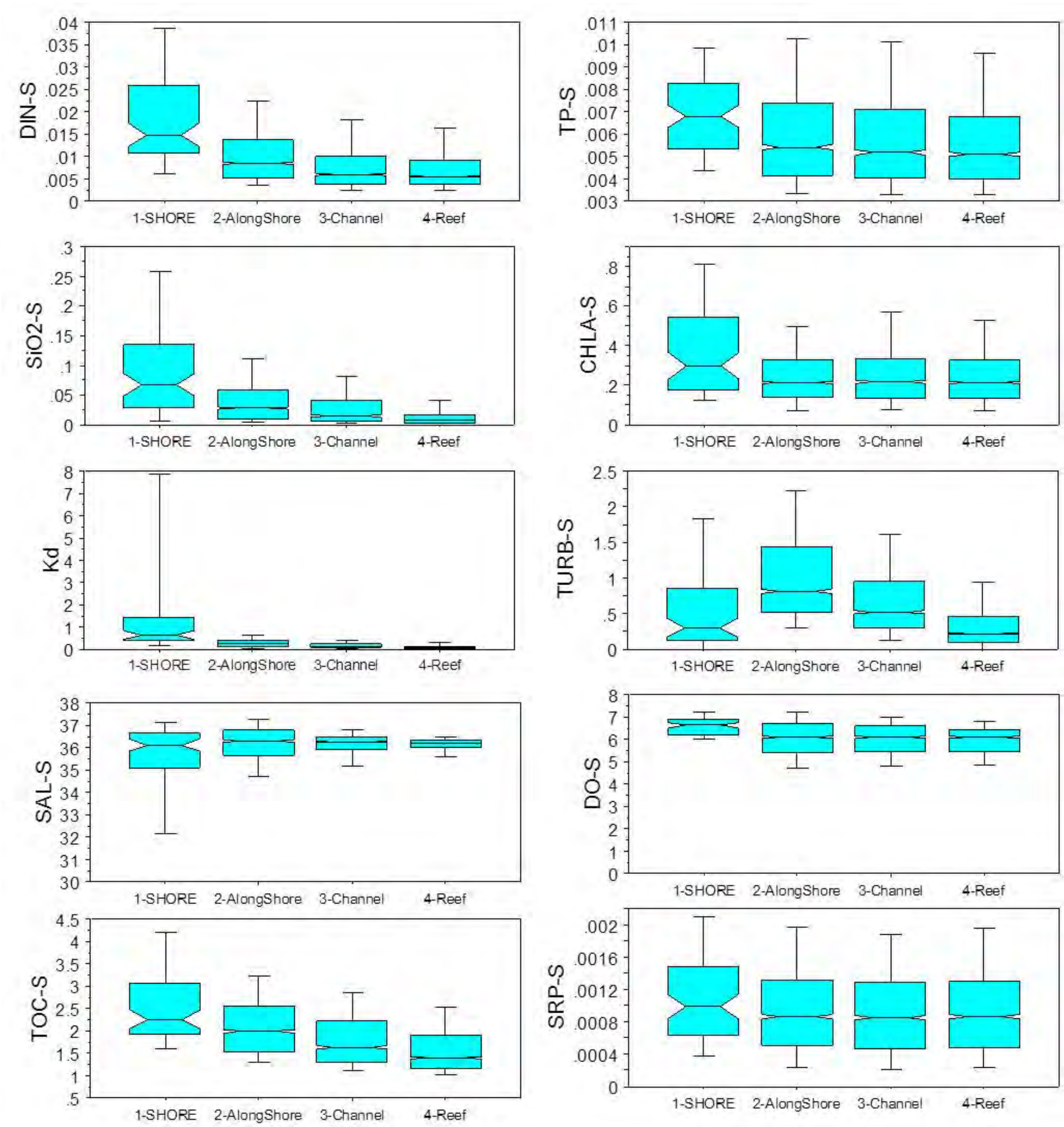

Figure i. *Nutrient and response changes along transect from shore sites to reef-track*

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. 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. Inclusion of new stations close to shore highlights where human impact is more evident.

2. Numeric Nutrient Criteria Development

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 (Briceño et al. 2013, Fig. ii).

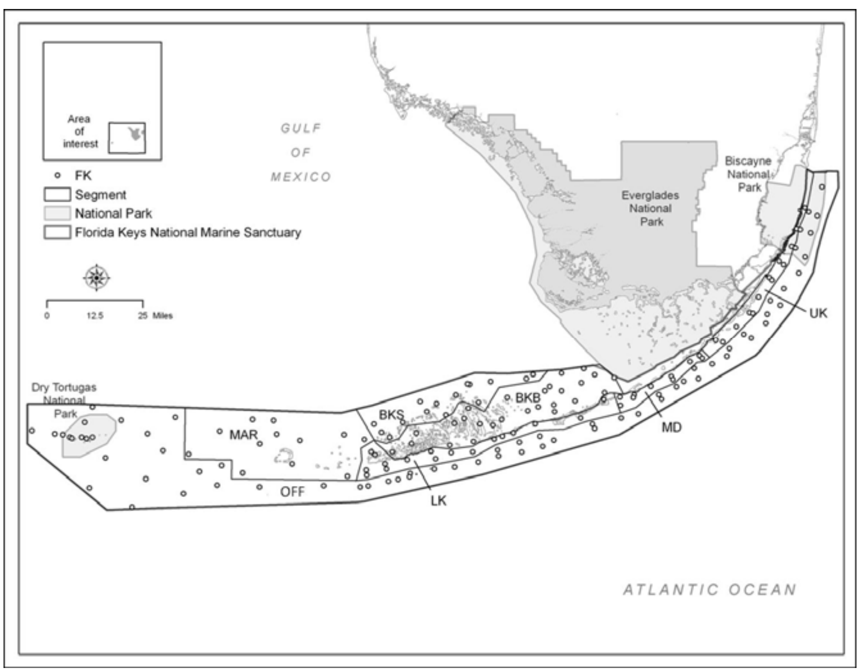

Figure ii. *Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys*

This segmentation was proposed to EPA and FDEP for use in developing numeric nutrient criteria for FL estuaries and coastal waters. The statistical approach was adopted by FDEP and referenced as Eight Maps of FL Marine Nutrient Regions, https://www.flrules.org/Gateway/reference.asp?No=Ref-01215, dated Oct. 19, 2011. The nutrient criteria for this region was subsequently developed using data from this Florida Keys Water Quality Monitoring Project and submitted to EPA in March 2013 as FDEP Implementation of FL Numeric Nutrient Standards, NNC_Implementation_3-11-13.pdf. On June 27, 2013, EPA approved 062713_epa_approval_nnc_implementation_document.pdf, FDEP Rule 62.300 (19) F.A.C. which includes 62.302.532 Estuary-Specific Numeric Interpretations of the Narrative Nutrient Criterion (the Coastal Estuary Rule), 62_302_final.pdf.

We believe that this accomplishment is an important achievement for a Federally-funded, University-operated water quality monitoring program and should be a model for future projects.

3. Trend analysis

Most Atlantic side reef sites experienced increased surface DO over the 18 year period of record (Fig. iii). Declines in surface DO were generally observed on the Gulf side of the Middle and Lower Keys and in some inshore areas on the Atlantic side. Bottom DO trends showed a similar pattern as surface with more increased DO than surface sites (Fig. iv). Increased DO is beneficial for animal life.

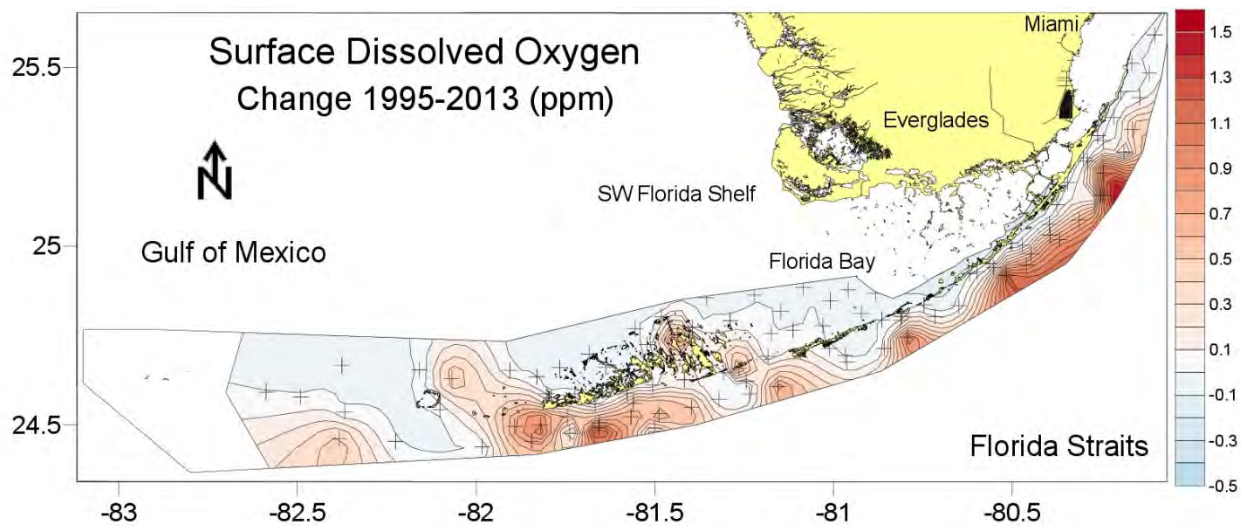

Figure iii. *Total change in DO of surface waters for 18 year period calculated from significant trends (p<0.10).*

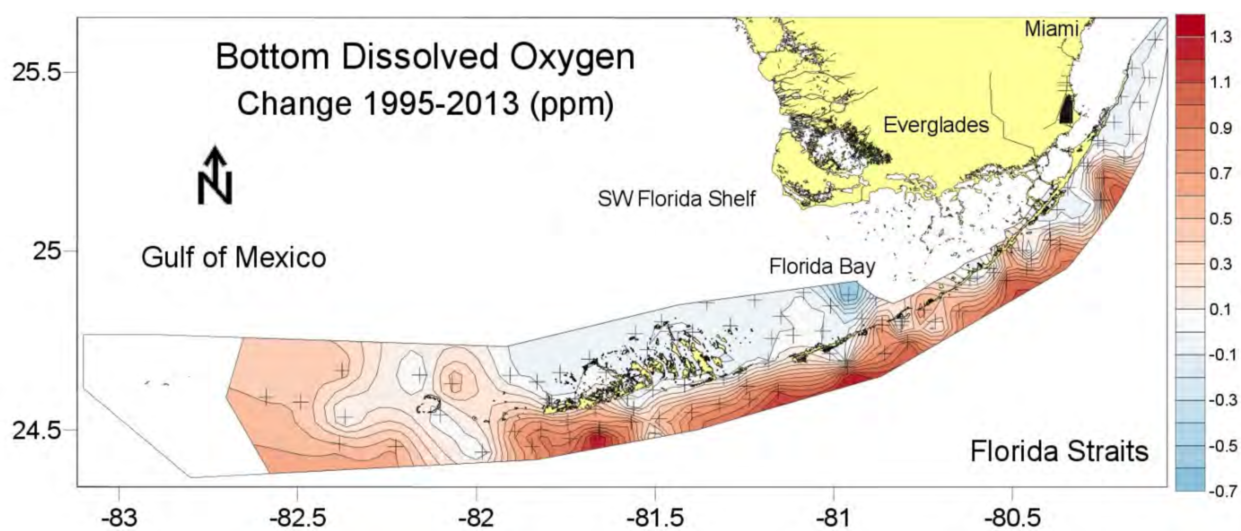

Figure iv. *Total change in DO of bottom waters for 18 year period calculated from significant trends (p<0.10).*

Water column turbidity, or cloudiness, declined throughout the FKNMS during the 18 year period (Fig v). There was no significant change in turbidity in bottom waters. The largest declines in turbidity occurred in western Florida Bay and Marquesas.

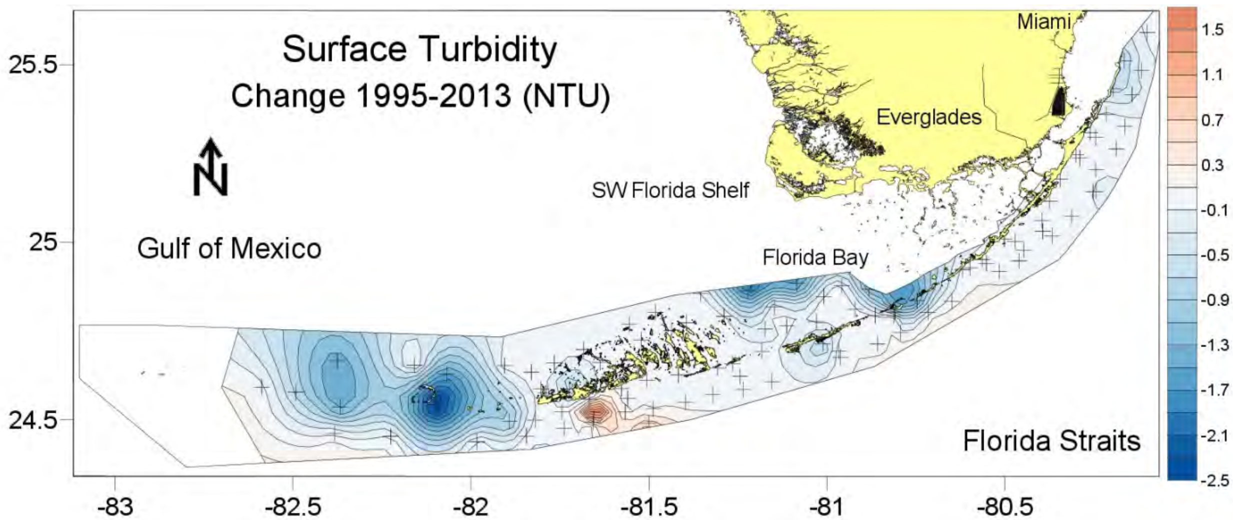

Figure v. *Total change in Turbidity in surface waters for 18 year period calculated from significant trends ($p<0.10$).*

Light extinction in the water column (K_d) also declined throughout most of the FKNMS, mostly as a result of decreased turbidity (Fig. vi). The smaller the K_d, the clearer the water column. This trend was the result of a general decrease in turbidity throughout the Keys (Fig. v).

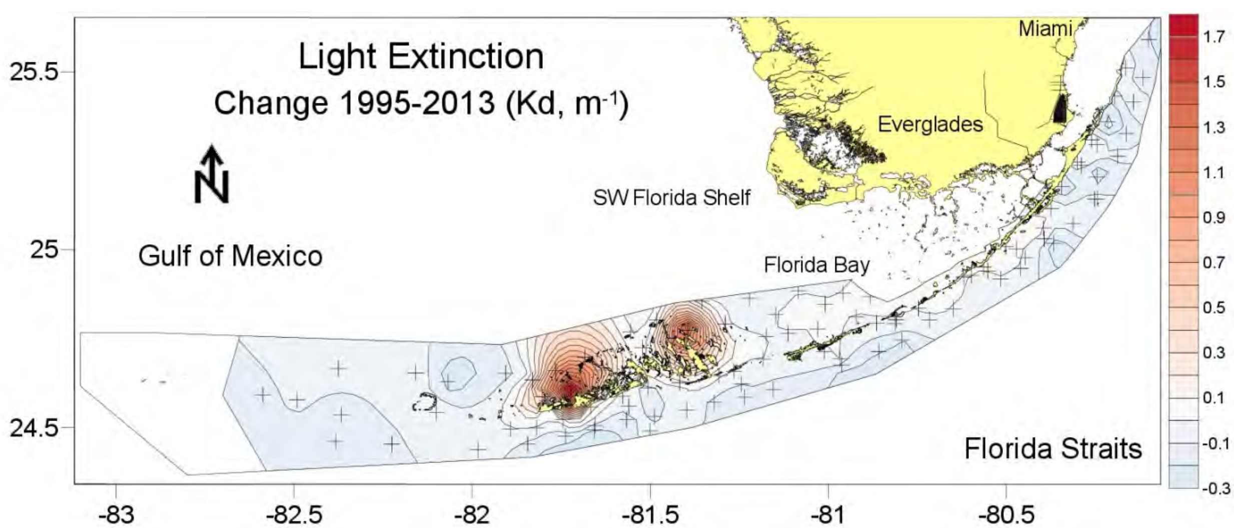

Figure vi. *Total change in K_d of water column for 18 year period calculated from significant trends ($p<0.10$).*

As a further consequence, the percent of ambient light reaching the bottom (I_o) increased at most reef sites throughout the Keys (Fig. vii). More light on the bottom is beneficial to corals, seagrass, and algae. Interestingly, the Backcountry area of the lower Keys experienced increases in K_d which lead to corresponding decreases in I_o (Fig vii).

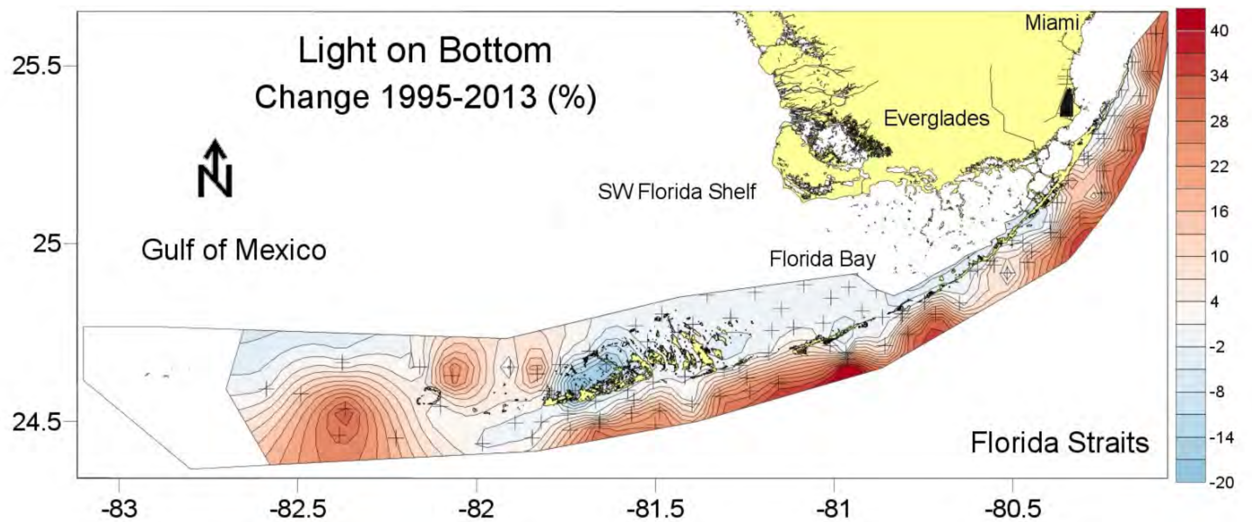

Figure vii. *Total change in bottom I_o for 18 year period calculated from significant trends (p<0.10).*

Nitrate in the surface waters declined significantly, especially along Middle and Lower Keys (Fig. viii). NO_3^- was the only N variable which showed any significant trend (NO_2^- concentrations are too small to be of any significance). Declines were greatest in surface waters of the Backcountry and inshore of Middle Keys.

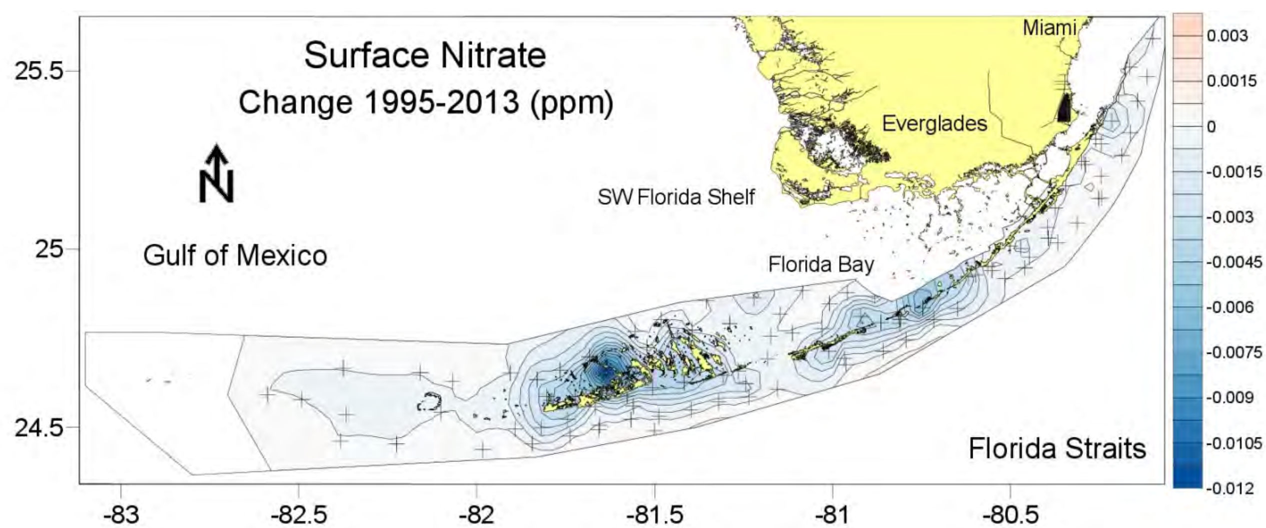

Figure viii. *Total change in NO_3^- in surface waters for 18 year period calculated from significant trends (p<0.10).*

Silicate in surface waters increased mostly in western Florida Bay/Sluiceway but declined slightly across the region (Fig ix). The source of SiO_2 in this region is Everglades runoff (diatomaceous periphyton). Overall results in bottom waters have slightly declined with a local exception offshore the Middle Keys (Fig. x).

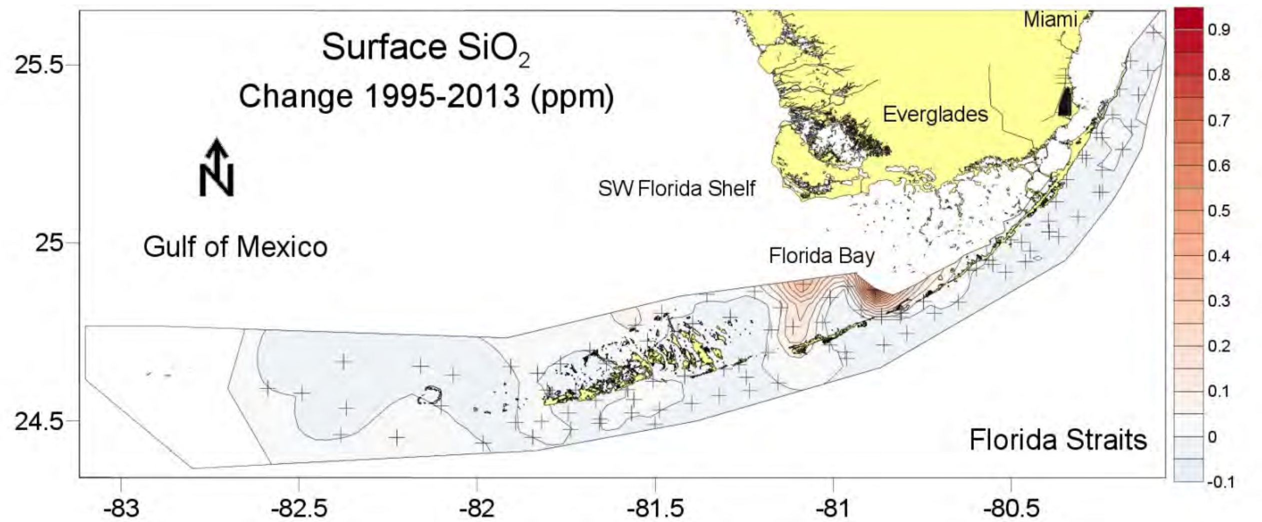

Figure ix. *Total change in SiO_2 in surface waters for 18 year period calculated from significant trends ($p<0.10$).*

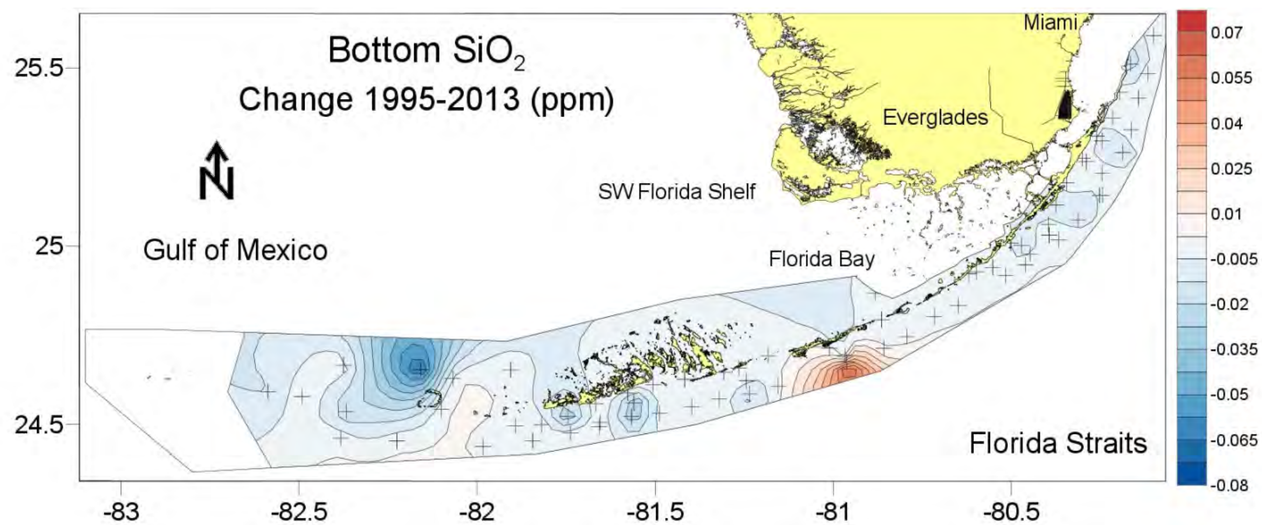

Figure x. *Total change in SiO_2 in bottom waters for 18 year period calculated from significant trends ($p<0.10$).*

No significant trends in TP were observed, however concentrations of SRP did increase in most surface and bottom waters (Fig. xi & xii). It must be noted that concentrations of SRP are generally an order of magnitude lower than TP and are usually below kinetic uptake threshold of phytoplankton, meaning it is not all that accessible.

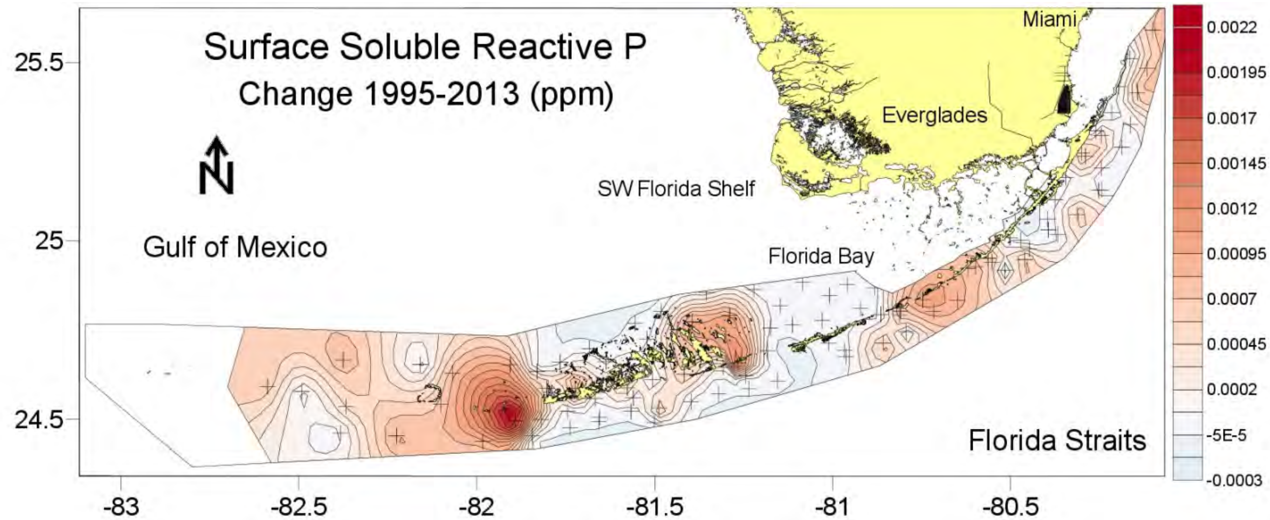

Figure xi. *Total change in SRP in surface waters for 18 year period calculated from significant trends (p<0.10).*

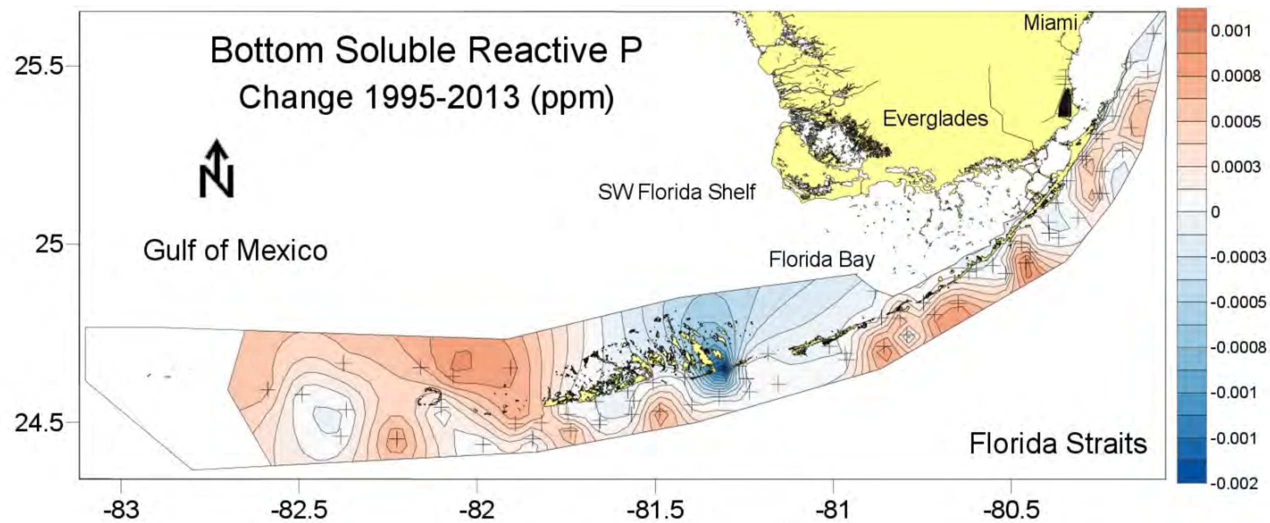

Figure xii. *Total change in SRP in bottom waters for 18 year period calculated from significant trends (p<0.10).*

Clearly, there have been some changes in the FKNMS water quality over time, but the <u>largest sustained monotonic trend has been the decline in surface TOC concentration</u>. There were strong declines in surface TOC throughout the FKNMS, especially in the Backcountry and the Marquesas (Fig. xiii). This is part of a regional trend in TOC observed on the SW Shelf, Florida Bay, and the mangrove estuaries draining the Everglades. This decline could be considered favorable given that TOC corresponds with CDOM (an important driver of water color and light penetration), but could also be an indication of decreased upstream primary production.

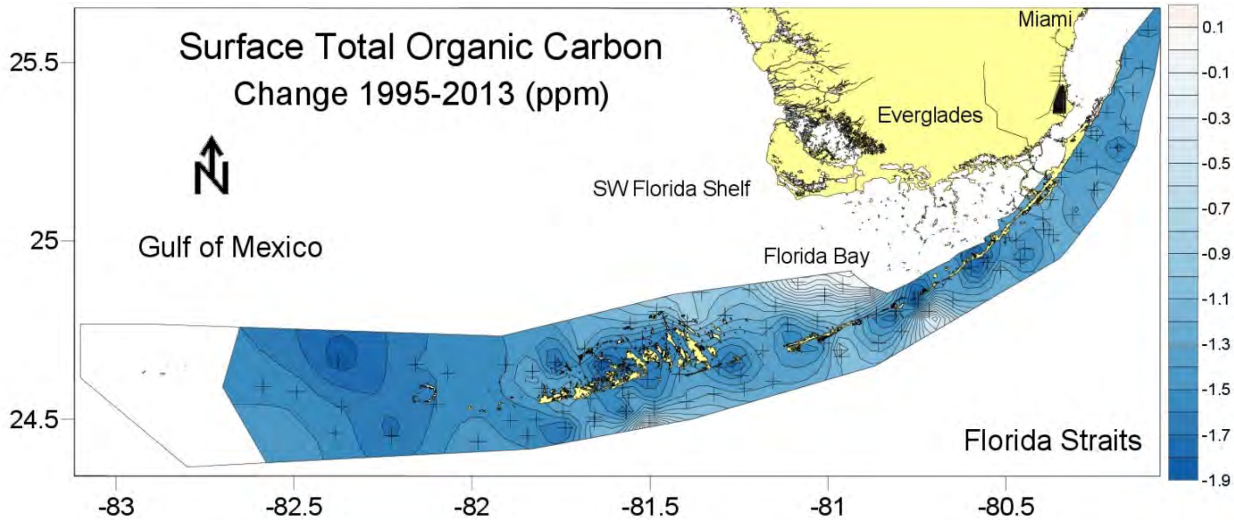

Figure xiii. *Total change in TOC in surface waters for 18 year period calculated from significant trends (p<0.10).*

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. 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.

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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.

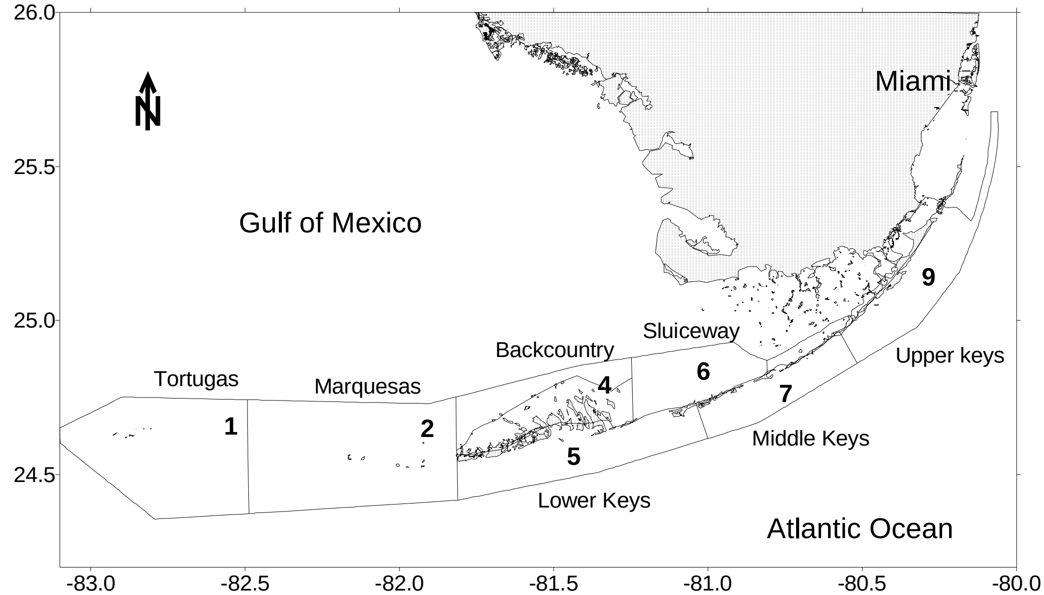

***Figure 1**: Map of original FKNMS boundary including collapsed segment numbers and common names. Modified after Klein and Orlando (1994)*

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. Sampling in the Dry Tortugas was finally halted since 2011 due to budget constraints. 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 (Briceño et al. 2013, Fig. 2).

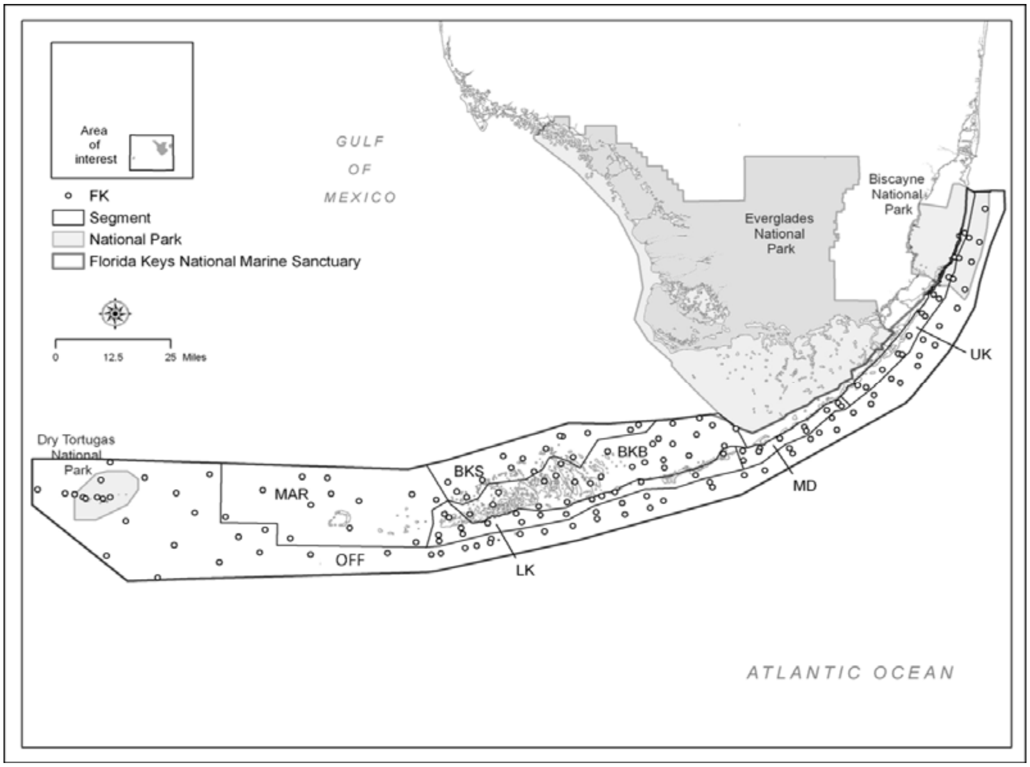

Figure 2: *Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys*

Although the original quarterly sampling of 155 stations was cut back to 112 (Fig. 3), 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 3*. 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 December 2013 which included 73 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 (N+N), nitrite (NO_2^-), total nitrogen (TN), soluble reactive phosphorus (SRP), total phosphorus (TP), total organic carbon (TOC), silicate (SiO_2), chlorophyll *a* (CHLA, µg 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 N+N 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 N+N - NO_2^-; total dissolved inorganic nitrogen (DIN) as N+N + 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. 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 $p<0.05$.

2.4. 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 (ArcView, ESRI) 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.

2.5. Trend Analysis

Temporal trends were quantified by simple regression with significance of the Ordinary Linear Regression slope set at $p<0.10$. Trend graphs were drawn only for those variables for which 20% of individual station trends were significant.

3. Results

3.1. Overall Water Quality of the FKNMS

Summary statistics for all water quality variables from calendar year 2013 sampling events are shown as number of samples (*n*), minimum, maximum, and median (Table 1). Overall, the region remains warm and euhaline with a median temperature of 25.88 °C and salinity of 36.07; dissolved 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 0.0014, 0.0057, 0.0051, and 0.009 mg l^{-1}, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (~70%). However, DIN comprised a small fraction (7%) of the TN pool (0.1007 mg l^{-1}) with TON being the bulk (median 0.0984 mg l^{-1}). SRP concentrations were very low (median 0.0007 mg l^{-1}) and comprised 14% of the TP pool (0.0051 mg l^{-1}). CHLA concentrations were also low overall, 0.237 µg l^{-1}, but ranged from 0.04 to 5.13 µg l^{-1}. TOC was 1. 429 mg l^{-1}; a value higher than open ocean levels but consistent with coastal areas.

Median turbidity was very low (0.06 NTU) as reflected in a low K_d (0.204 m^{-1}). Overall, 38.1% 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 = 42.6) but this must be tempered by the fact that much of the TN may not be bioavailable.

Table 1. *Summary statistics for each water quality variable in the FKNMS for the calendar year 2013. Data are summarized as number of samples (n), minimum value (Min.), maximum value (Max.), and Median.*

Variable	Depth	Count	Min.	Max.	Median
NO_3^-	Surface	440	0.0000	0.0342	0.0014
(mg l^{-1})	Bottom	271	0.0001	0.0192	0.0015
NO_2^-	Surface	446	0.0000	0.0019	0.0004
(mg l^{-1})	Bottom	282	0.0000	0.0013	0.0003
NH_4^+	Surface	448	0.0003	0.1097	0.0057
(mg l^{-1})	Bottom	282	0.0003	0.0395	0.0051
TN	Surface	448	0.0357	0.5073	0.1077
(mg l^{-1})	Bottom	282	0.0340	0.4616	0.0808
TON	Surface	448	0.0014	0.4947	0.0984
(mg l^{-1})	Bottom	282	0.0231	0.4596	0.0696
TP	Surface	448	0.0030	0.0181	0.0051
(mg l^{-1})	Bottom	282	0.0027	0.0097	0.0043
SRP	Surface	448	0.0001	0.0040	0.0007
(mg l^{-1})	Bottom	282	0.0001	0.0034	0.0007
CHLA (µg l^{-1})	Surface	444	0.039	5.126	0.237
TOC	Surface	448	0.932	6.877	1.429
(mg l^{-1})	Bottom	282	0.962	4.146	1.236
SiO_2	Surface	448	0.000	0.842	0.009
(mg l^{-1})	Bottom	282	0.000	0.768	0.003
Turbidity	Surface	424	0.000	31.000	0.065
(NTU)	Bottom	270	0.000	7.880	0.000
Salinity	Surface	447	26.28	37.80	36.07
	Bottom	445	27.21	37.81	36.06
Temp.	Surface	448	20.08	31.94	25.88
(°C)	Bottom	446	19.97	31.88	25.69
DO	Surface	448	4.23	8.87	6.54
(mg l^{-1})	Bottom	446	4.27	8.99	6.55
K_d		415	0.001	2.314	0.144
TN:TP	Surface	448	12.7	228.8	42.6
Si:DIN	Surface	448	0.0	74.4	0.6
DO Sat	Surface	448	64.6	131.9	97.4
(%)	Bottom	448	0.0	134.4	97.4
I_o (%)	Bottom	448	0.2	100.0	38.1
$\Delta\sigma_t$		448	-2.702	1.030	0.010

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 UK 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.

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.

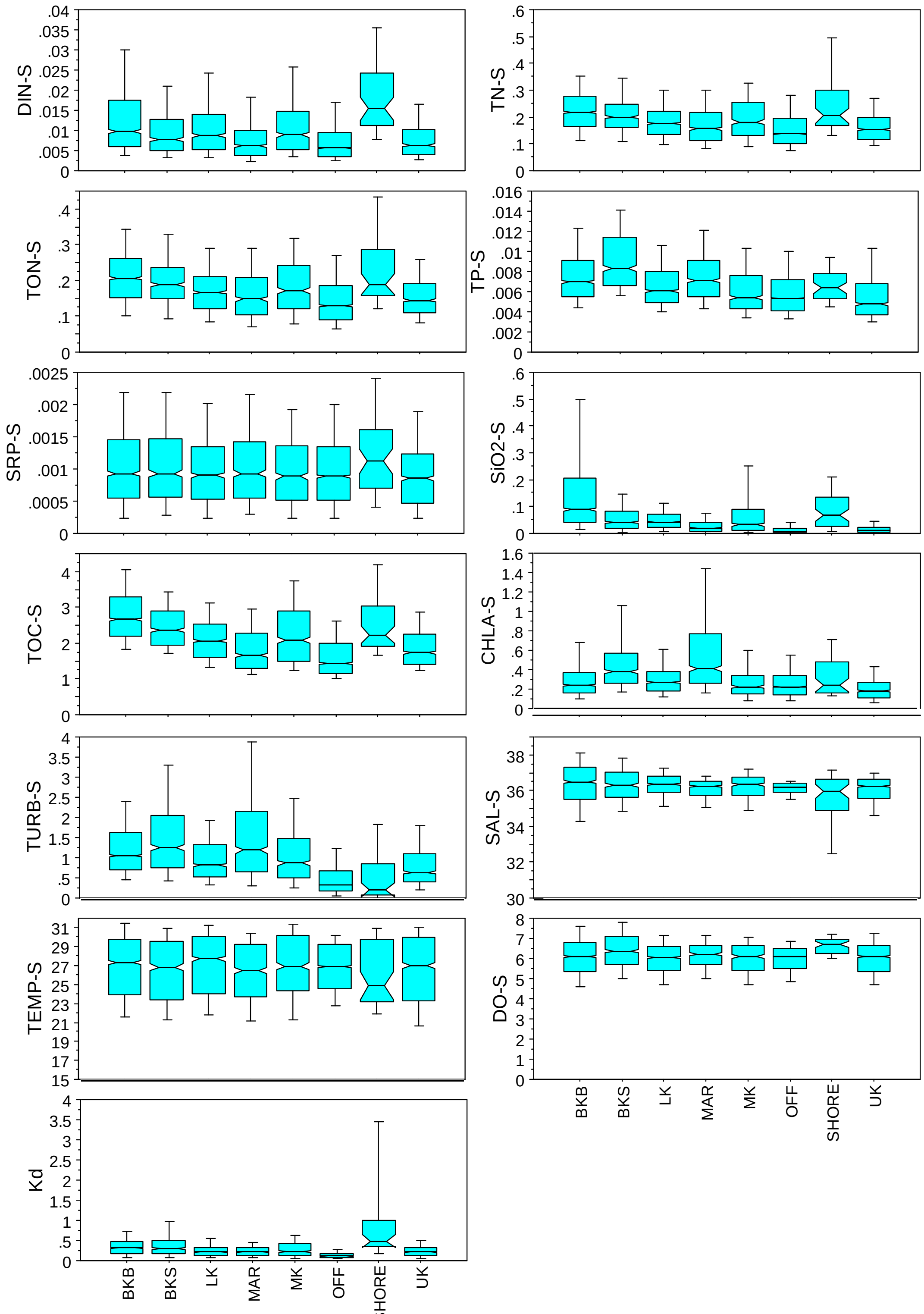

***Figure 4**. Box-and-whisker plots of surface samples showing median and distribution of DIN, TN, TP, CHLA, TOC, turbidity, salinity, temperature, DO and K_d as stratified by water quality cluster. Notches in the box that do not overlap with another are considered significantly different.*

3.2. Trend 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 5-7, where trends can be seen to be 1) monotonic, 2) episodically driven, and 3) reversing.

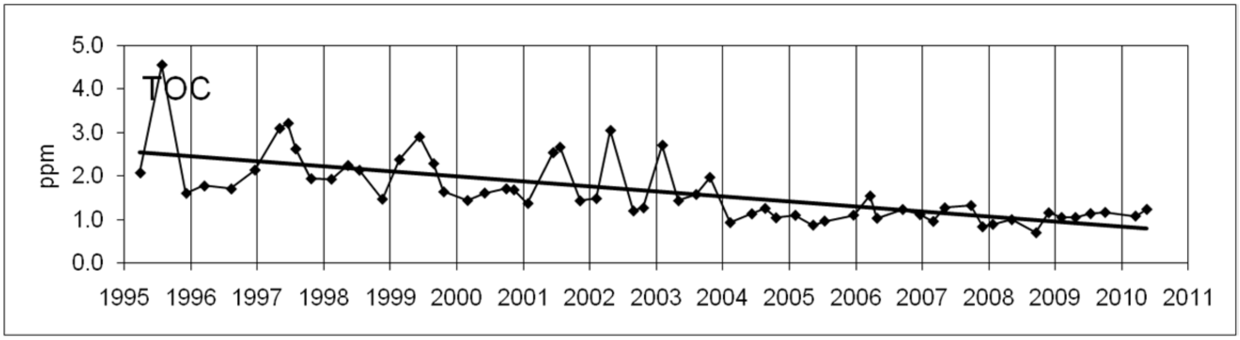

Figure 5. *Monotonic trend in TOC at Carysfort Reef.*

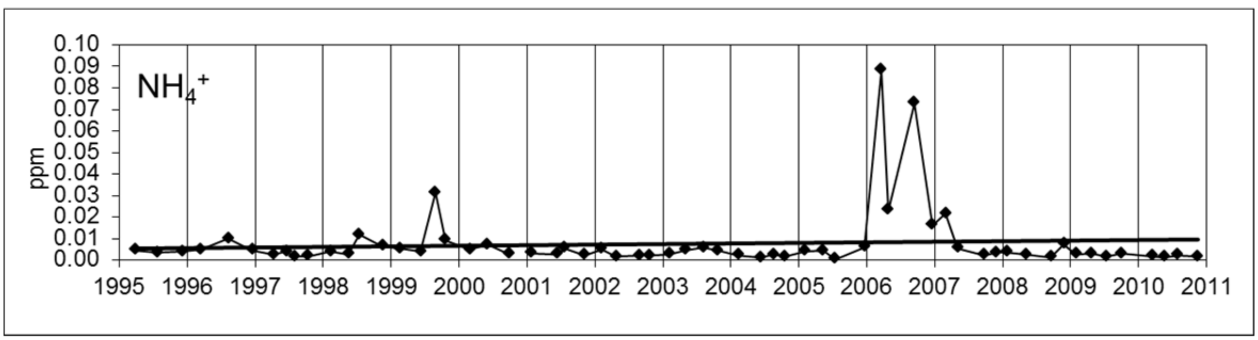

Figure 6. *Episodically (hurricane) driven pattern in NH_4^+ at The Elbow.*

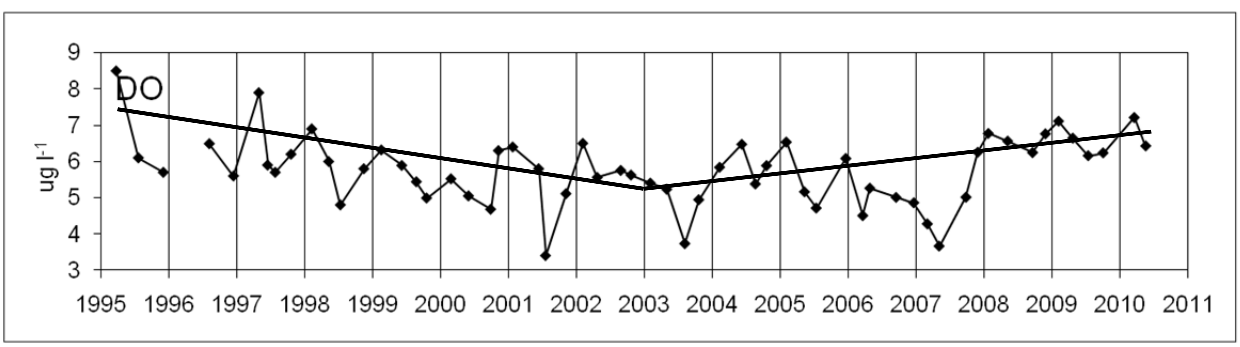

Figure 7. *Reversing trend in DO at Carysfort Reef.*

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. 8-18). Only those variables with >20% of sampling sites having significant slopes were displayed.

Surface DO has increased in some areas but declined in others (Fig. 8). Declines in surface DO were generally observed on the Gulf side of the Middle and Lower Keys and in some inshore areas on the Atlantic side. Most offshore/reef sites experience increased in DO over the period of record. Bottom DO trends showed a similar pattern as surface with more increased DO than surface sites (Fig. 9). Increased DO is beneficial for animal life.

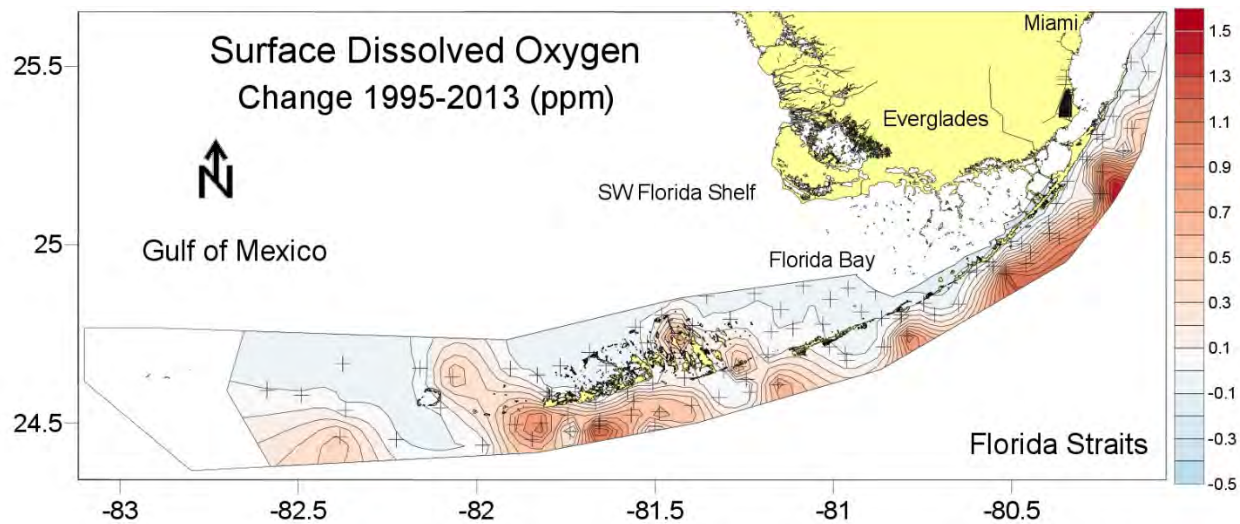

Figure 8. *Total change in DO of surface waters for 18 year period calculated from significant trends (p<0.10).*

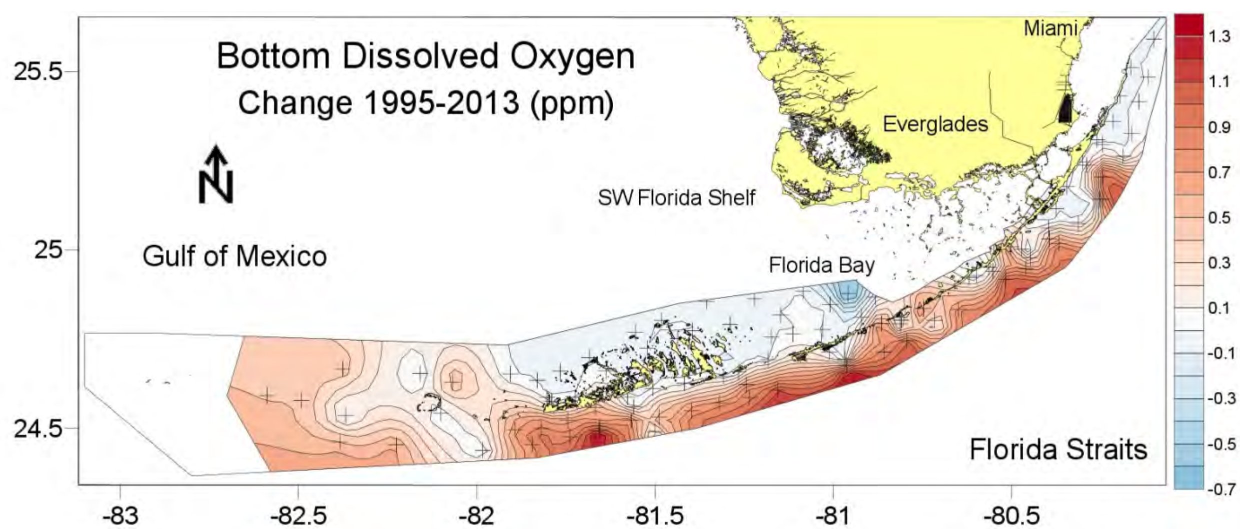

Figure 9. *Total change in DO of bottom waters for 18 year period calculated from significant trends (p<0.10).*

Water column turbidity, or cloudiness, declined throughout the FKNMS during the 18 year period (Fig 10). There was no significant change in turbidity in bottom waters. The largest declines in turbidity occurred in western Florida Bay and Marquesas.

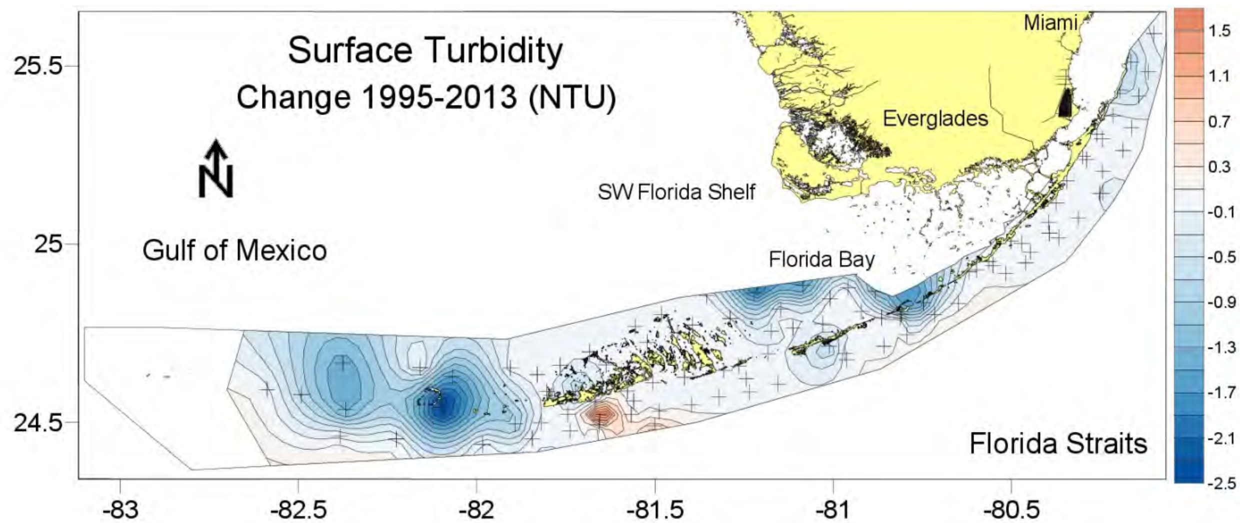

Figure 10. *Total change in Turbidity in surface waters for 18 year period calculated from significant trends (p<0.10).*

Light extinction in the water column (K_d) also declined throughout most of the FKNMS, mostly as a result of decreased turbidity (Fig. 11). This trend was the result of a general decrease in light extinction (K_d) throughout the Keys (Fig. 11). The smaller the K_d, the clearer the water column.

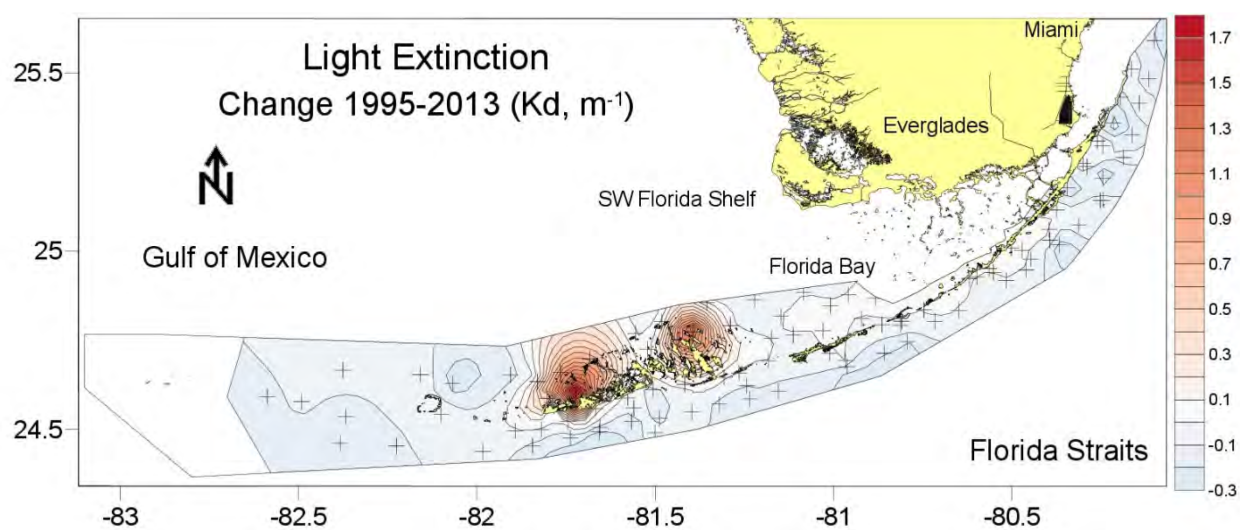

Figure 11. *Total change in K_d of water column for 18 year period calculated from significant trends (p<0.10).*

As a further consequence, the percent of ambient light reaching the bottom (%I_o) increased at most reef sites throughout the Keys (Fig. 11). More light on the bottom is beneficial to corals, seagrass, and algae. Interestingly, the Backcountry area of the lower Keys experienced increases in K_d which lead to corresponding decreases in I_o (Fig 10).

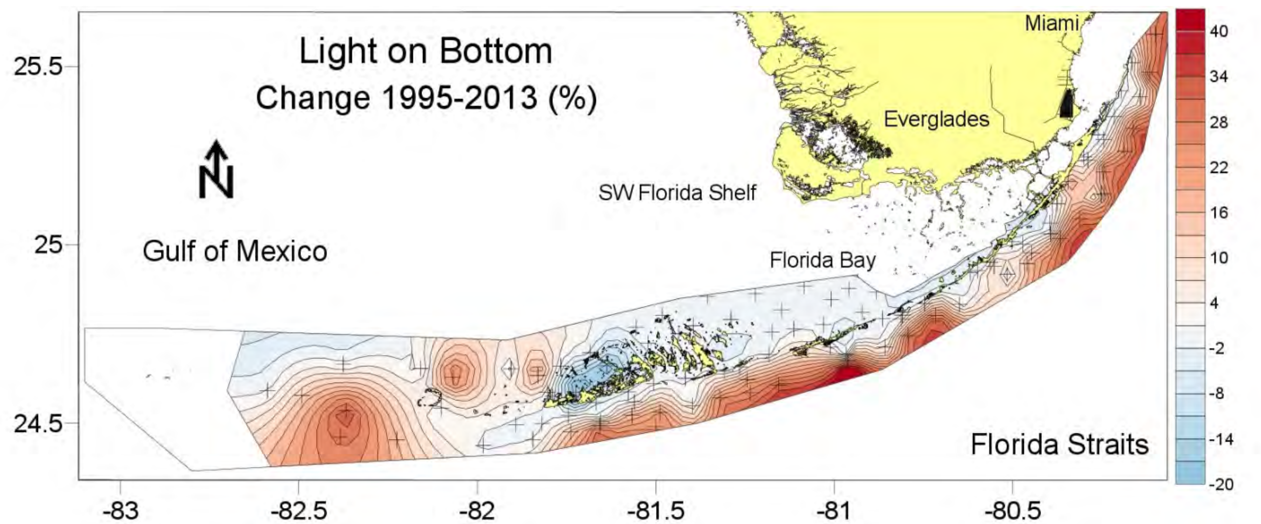

Figure 12. *Total change in bottom I_o for 18 year period calculated from significant trends (p<0.10).*

Nitrate in the surface waters declined significantly (Fig. 13). NO_3^- was the only N variable which showed any significant trend (NO_2^- concentrations are too small to be of any significance). Declines were greatest in surface waters of the Backcountry and inshore of Middle Keys.

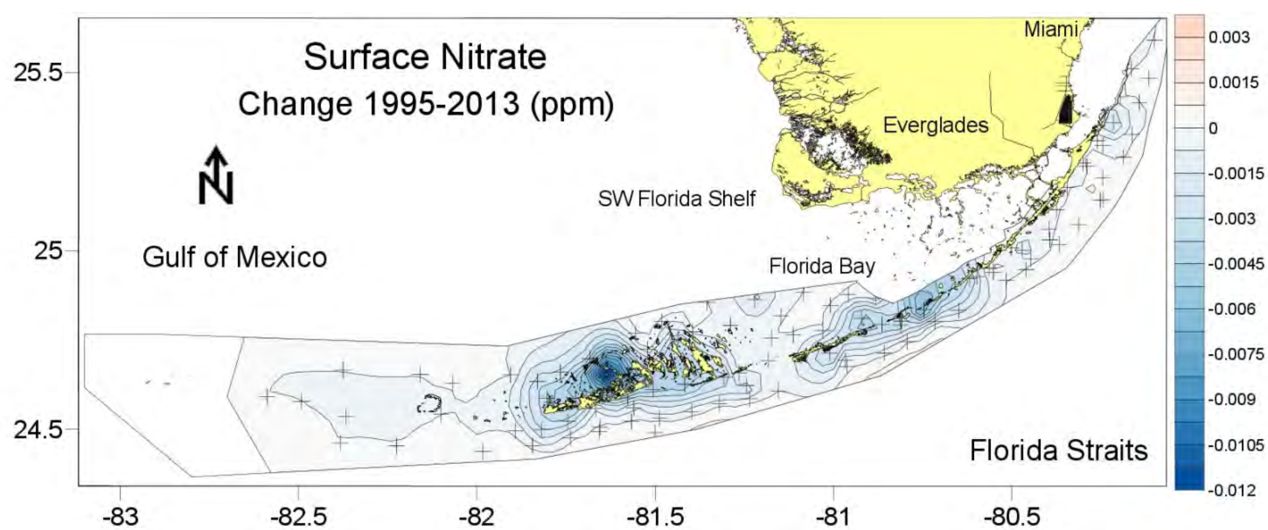

Figure 13. *Total change in NO_3^- in surface waters for 18 year period calculated from significant trends (p<0.10).*

Silicate in surface waters increased in western Florida Bay but declined slightly across the region (Fig 14). The source of SiO_2 in this region is Everglades runoff (diatomaceous periphyton). Overall results in bottom waters have slightly declined with a local exception offshore the Middle Keys (Fig. 15).

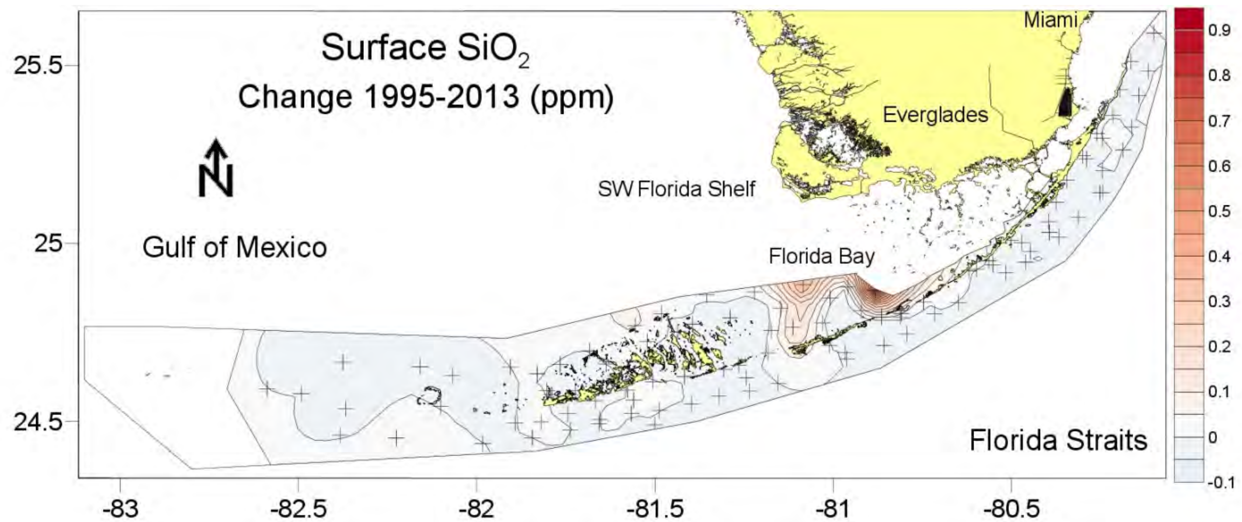

Figure 14. *Total change in SiO_2 in surface waters for 18 year period calculated from significant trends ($p<0.10$).*

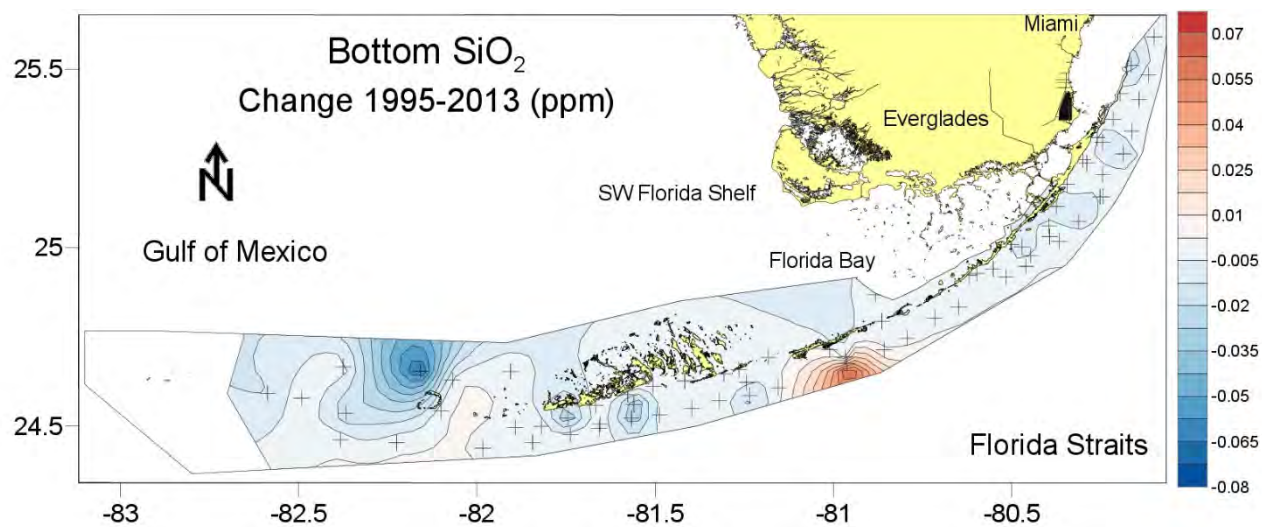

Figure 15. *Total change in SiO_2 in bottom waters for 18 year period calculated from significant trends ($p<0.10$).*

No significant trends in TP were observed, however concentrations of SRP did increase in most surface and bottom waters (Fig. 16 & 17). It must be noted that concentrations of SRP are generally an order of magnitude lower than TP and are usually below kinetic uptake threshold of phytoplankton, meaning it is not all that accessible.

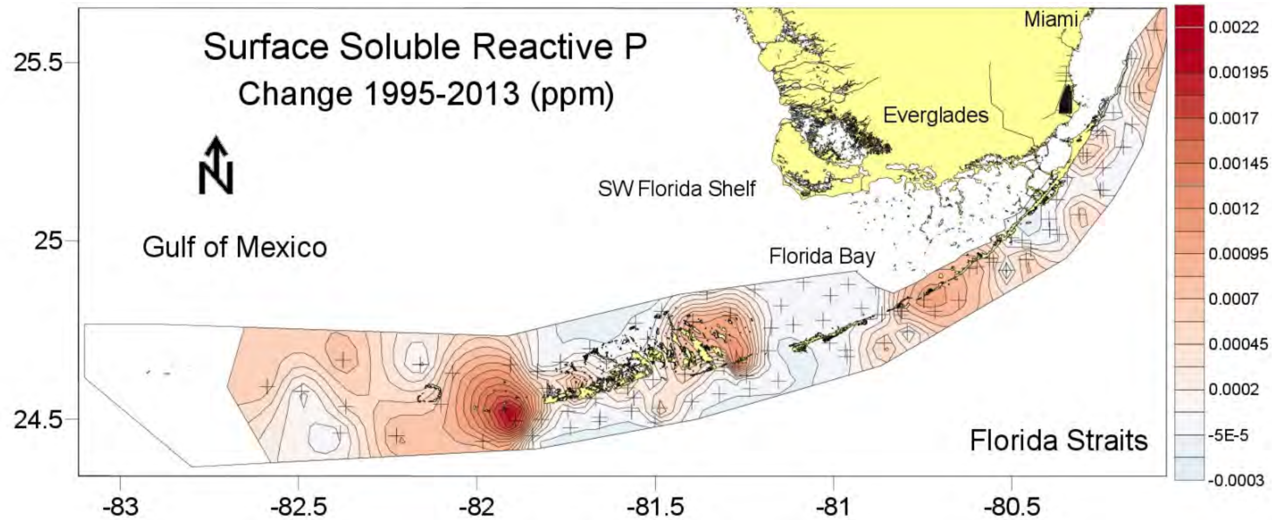

Figure 16. *Total change in SRP in surface waters for 18 year period calculated from significant trends (p<0.10).*

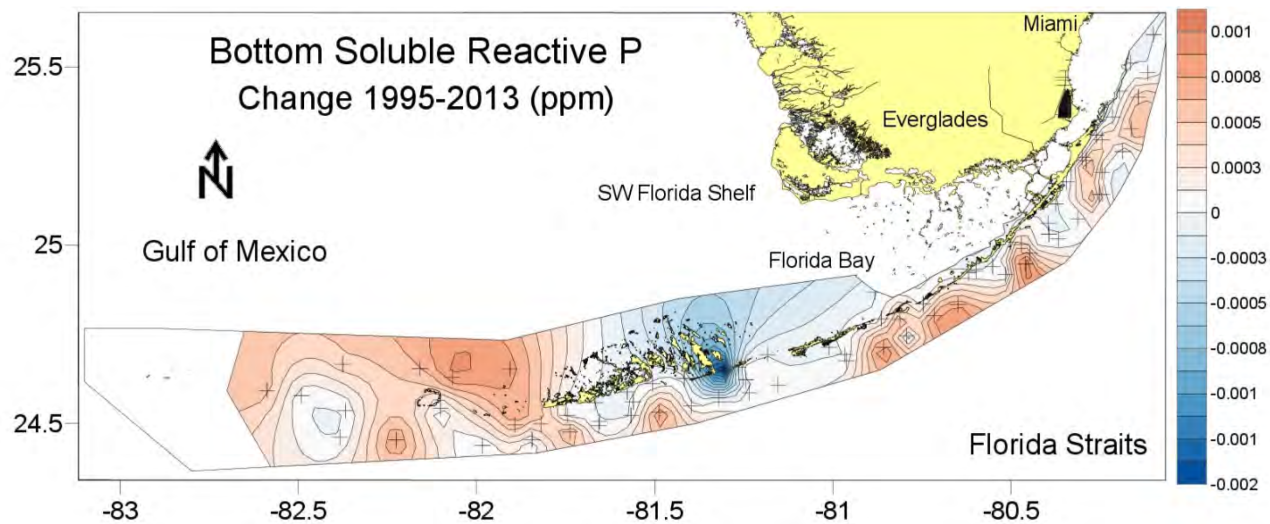

Figure 17. *Total change in SRP in bottom waters for 18 year period calculated from significant trends (p<0.10).*

Clearly, there have been some changes in the FKNMS water quality over time, but the largest sustained monotonic trend has been the decline in surface TOC concentration. There were strong declines in surface TOC throughout the FKNMS, especially in the Backcountry and the Marquesas (Fig. 18). This is part of a regional trend in TOC observed on the SW Shelf, Florida Bay, and the mangrove estuaries draining the Everglades. This decline could be considered favorable given that TOC corresponds with CDOM (an important driver of water color and light penetration), but could also be an indication of decreased upstream primary production.

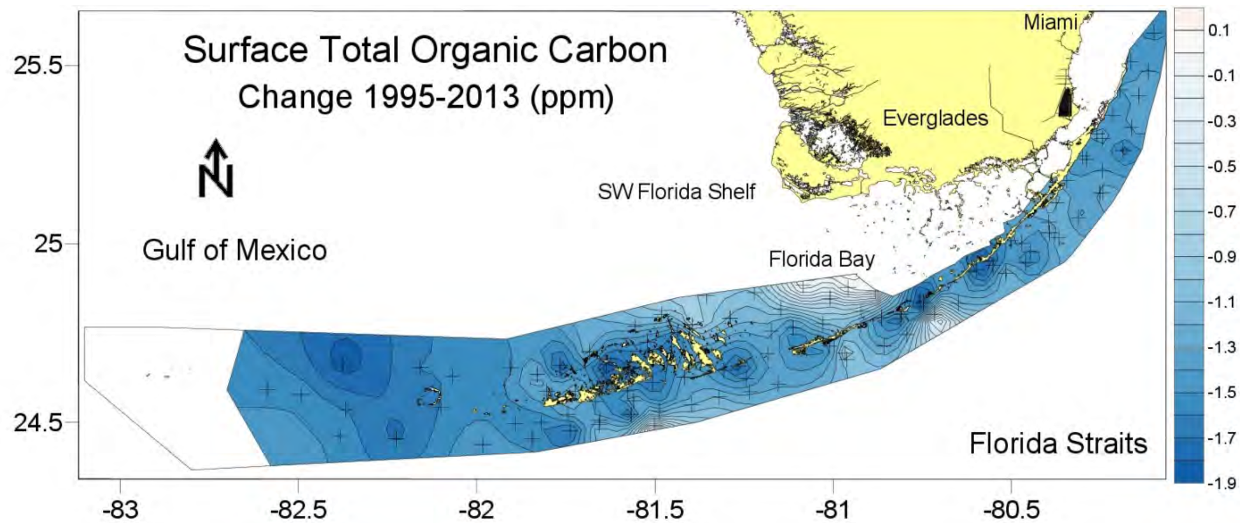

Figure 18. *Total change in TOC in surface waters for 18 year period calculated from significant trends (p<0.10).*

4. Overall Trends

Several important results have been realized from this monitoring project. First we documented elevated nutrient concentrations (DIN, TN, TP, and SiO_2) in waters close to shore along the Keys, and their corresponding responses from the system, such as higher phytoplankton biomass (CHLA), turbidity, as well as lower salinity and DO in the water column (Figure 19). These changes, associated to human impact, have become even more obvious by the addition of 10 stations (# 500 to #509) located very close to shore, sampled since Nov 2011 (SHORE).

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 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 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.

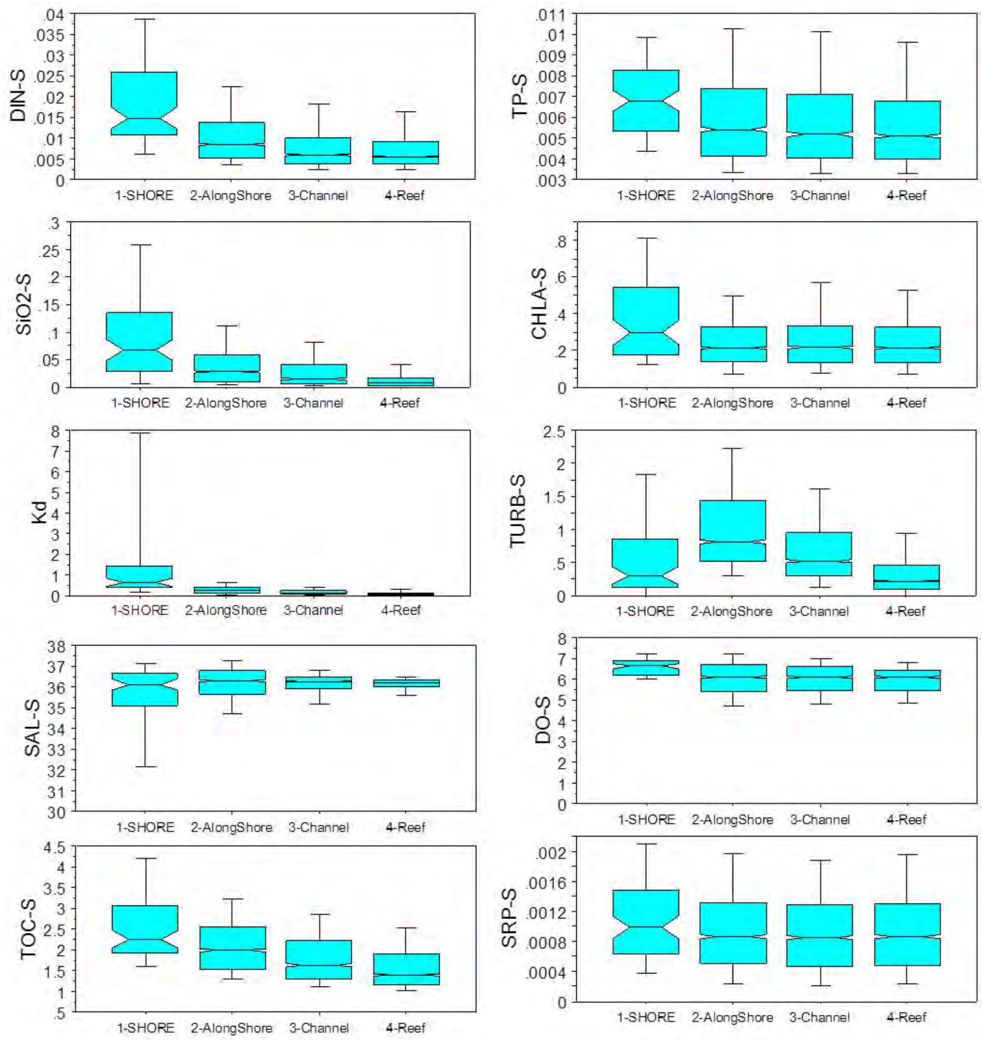

Figure 19: *Nutrient and response changes along transect from close-to-shore sites to the reef-track*

4.1.Strategic Targets

The EPA developed Strategic Targets for the Water Quality Monitoring Project which state that beginning in 2008 through 2013, 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 2 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2012.

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

For reef stations, chlorophyll less than or equal to 0.2 micrograms liter^{-1} (ug l^{-1}) and vertical attenuation coefficient for downward irradiance (K_d, i.e., light attenuation) less than or equal to 0.13 per meter; for all stations in the FKNMS, dissolved inorganic nitrogen less than or equal to 0.75 micromolar and total phosphorus less than or equal to 0.2 micromolar; water quality within these limits is considered essential to promote coral growth and overall health. The "number of samples" exceeding these targets is tracked and reported annually. 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

Year	REEF Stations		All Stations (excluding SHORE sites)	
	CHLA ≤ 0.20 µg l^{-1}	K_d ≤ 0.13 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 1000 (84.3%)	738 of 1,003 (73.6%)
2011	146 of 215 (67.9%)	156 of 213 (73.2%)	813 of 1012 (80.3 %)	911 of 1013 (89.9 %)
2012	142 of 168 (84.5%)	135 of 168 (80.4%)	489 of 683 (71.6 %)	634 of 684 (92.7 %)
2013	148 of 172 (86.0%)	150 of 172 (87.2%)	496 of 688 (72.1 %)	603 of 688 (87.6 %)

5. 2013 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. 20). 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. 21). 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.

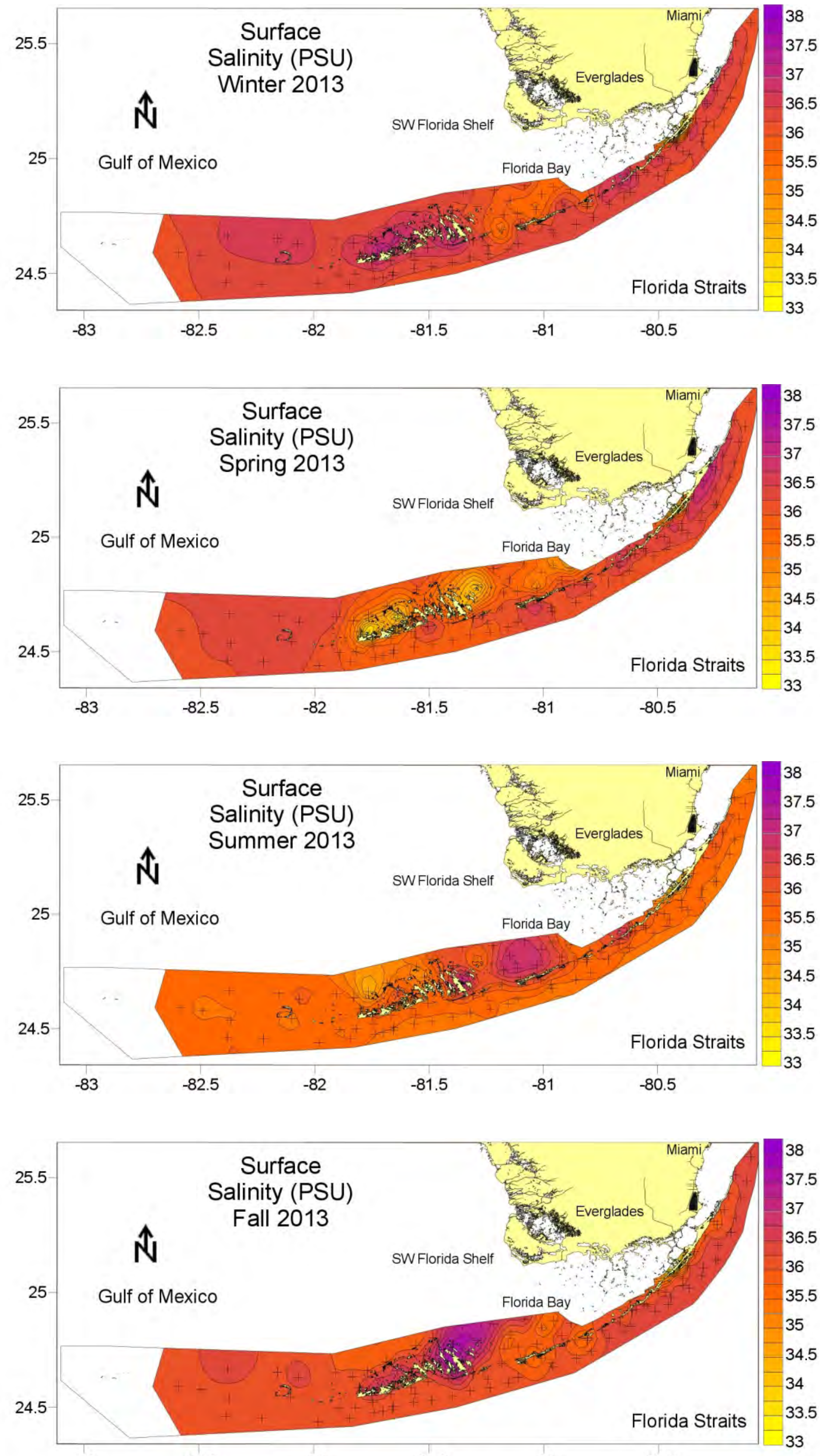

***Figure 20**. Surface salinity distributions across the region during 2013.*

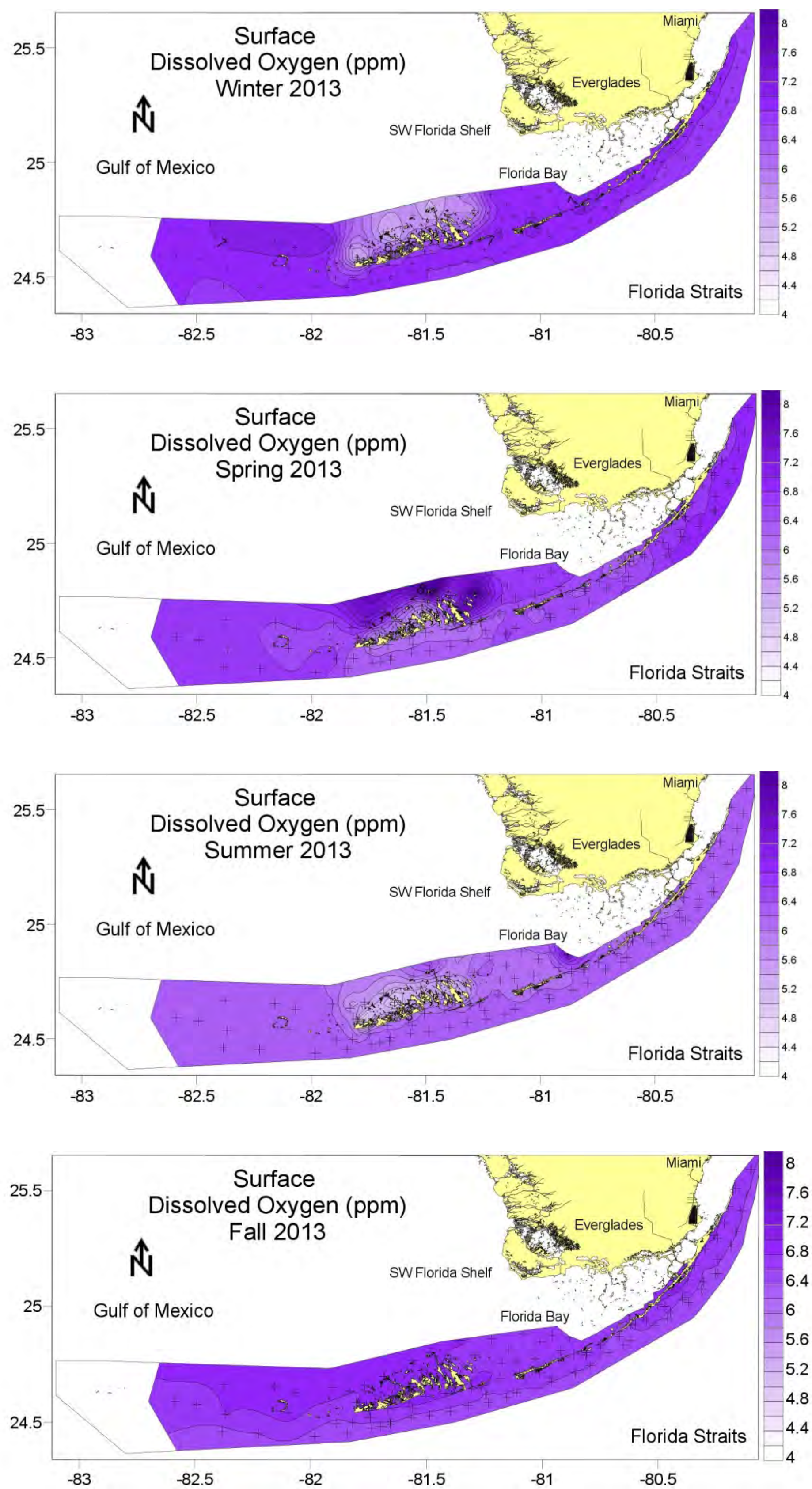

Figure 21 *Surface dissolved oxygen distributions across the region during 2013.*

Visualization of spatial patterns of NO_3^- concentrations over South Florida waters provides an extended view of source gradients over the region (Fig. 22). 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.

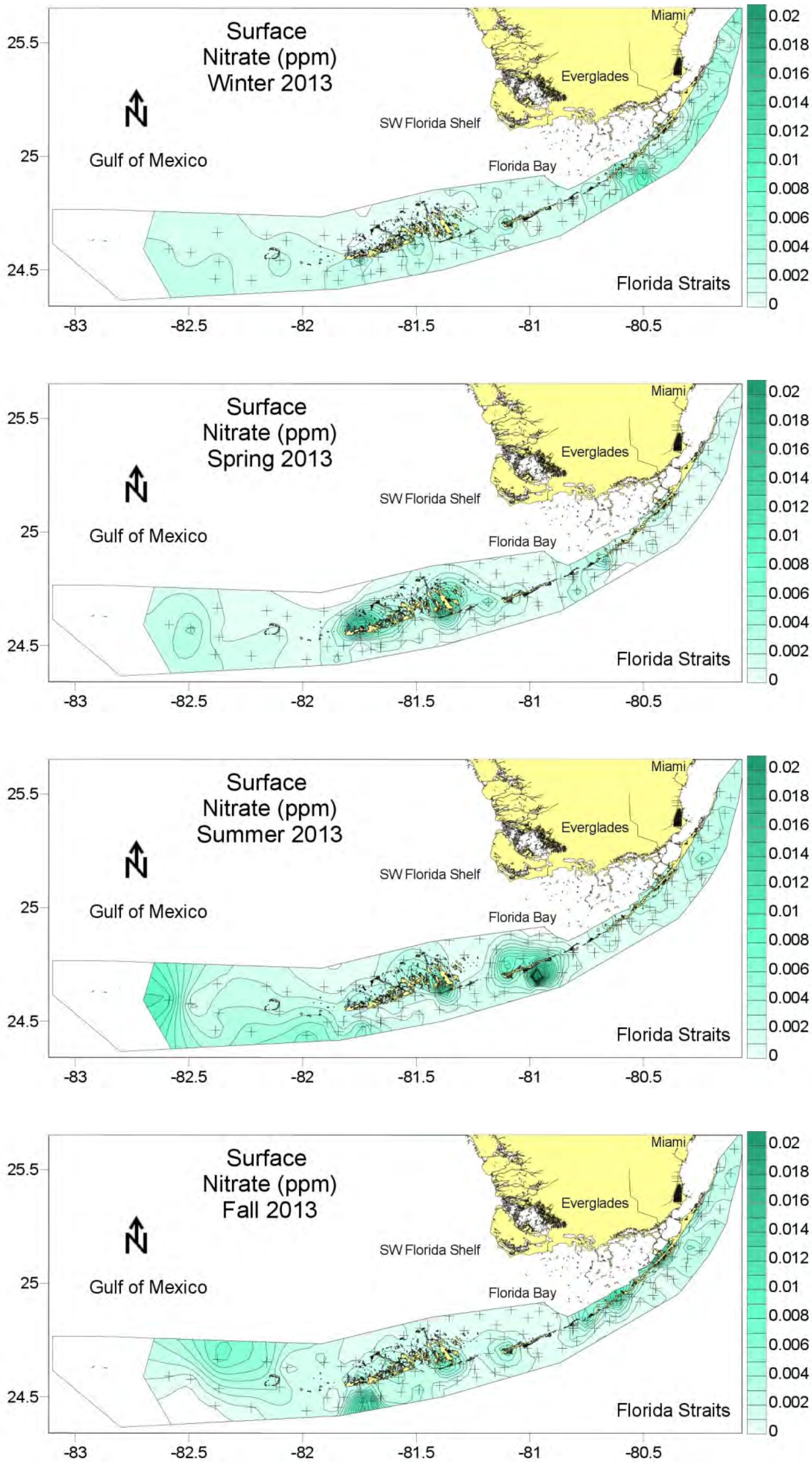

***Figure 22**. Surface nitrate distributions across the region during 2013.*

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. 23). 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.

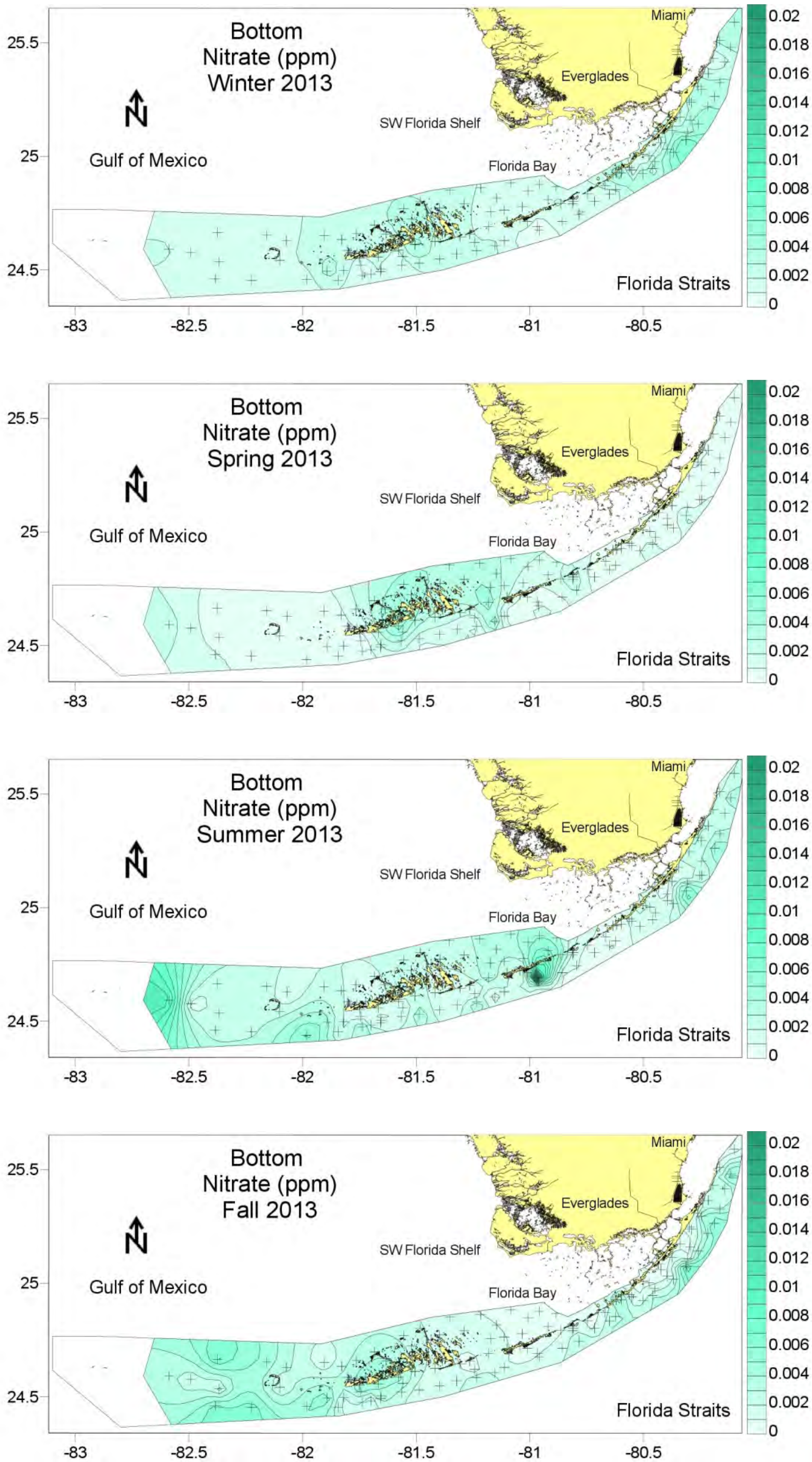

***Figure 23**. Bottom nitrate distributions across the region during 2013.*

NH_4^+ concentrations were distributed in a similar manner as NO_3^- with highest levels occurring in the Backcountry (Fig. 24). 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. 25). 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. 26) 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^{-1} TP) preferentially occurred on the Bay side of the Keys, and were probably supplied by Shelf waters (Fig. 27). Also, in some instances (i.e. Nov and Jan 2012) deeper offshore waters may have contributed TP to shallower localities in the Upper Keys.

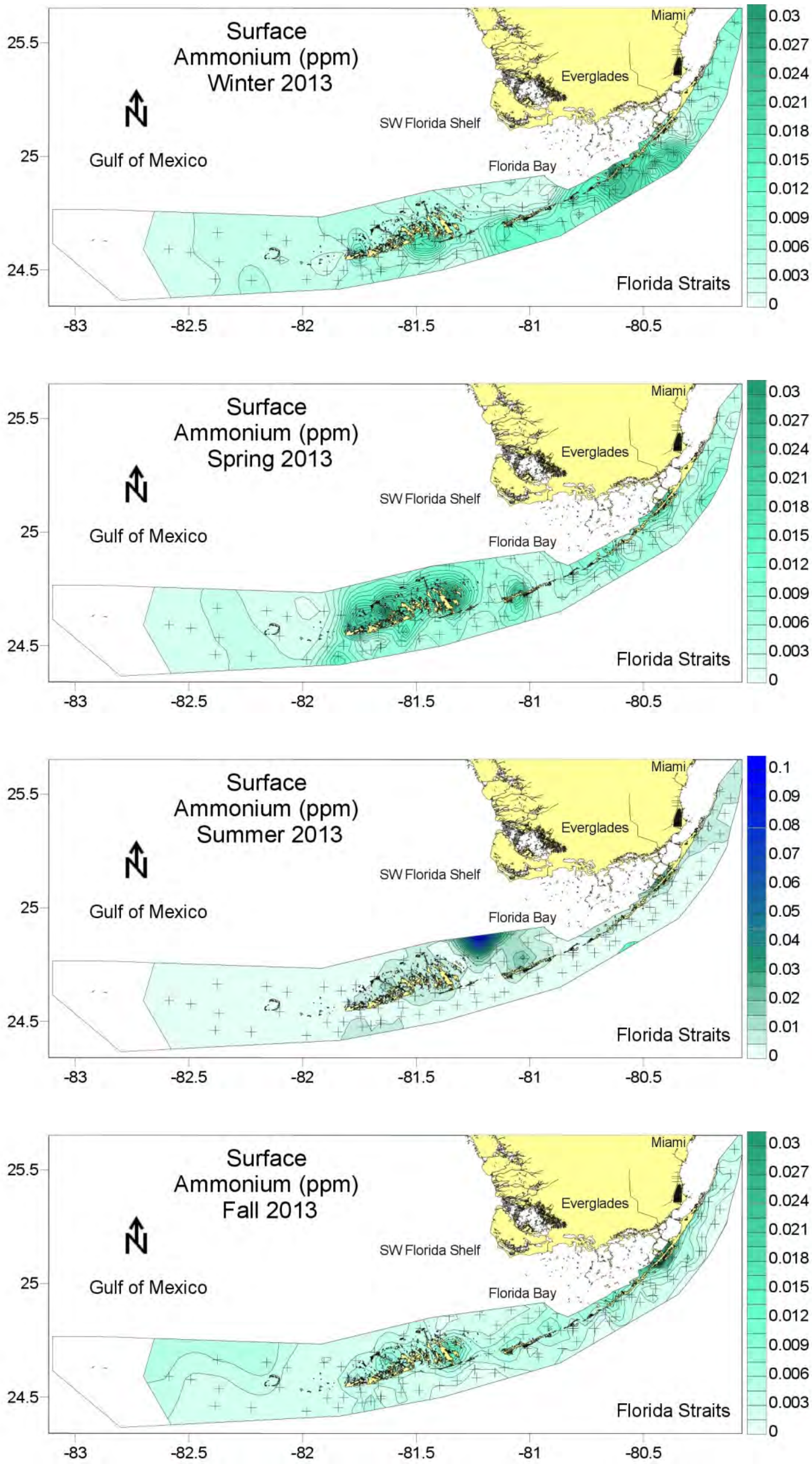

***Figure 24**. Surface ammonium distributions across the region during 2013.*

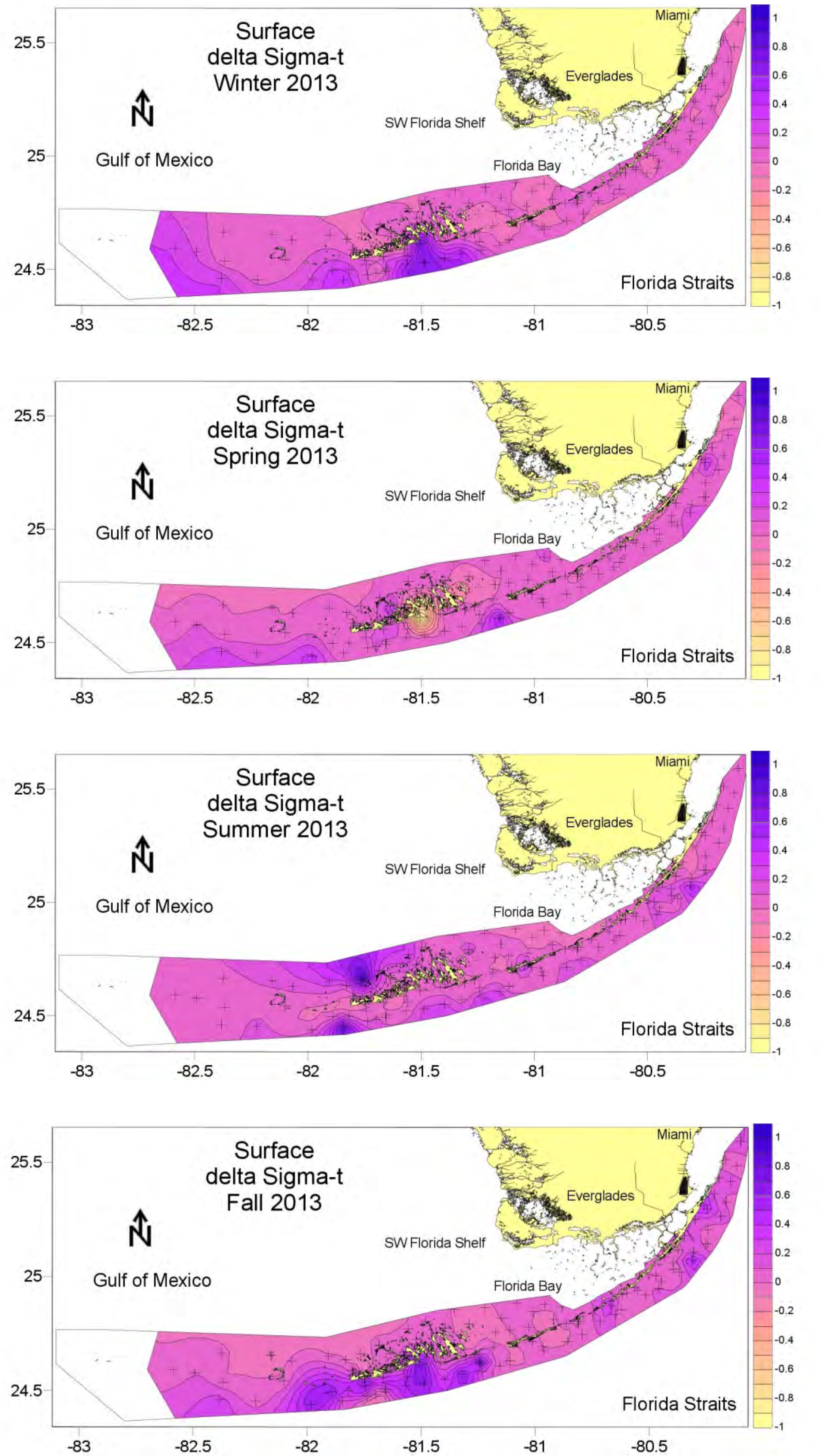

Figure 25*. Surface and bottom density differences ($\Delta\sigma_t$) across the region during 2013.*

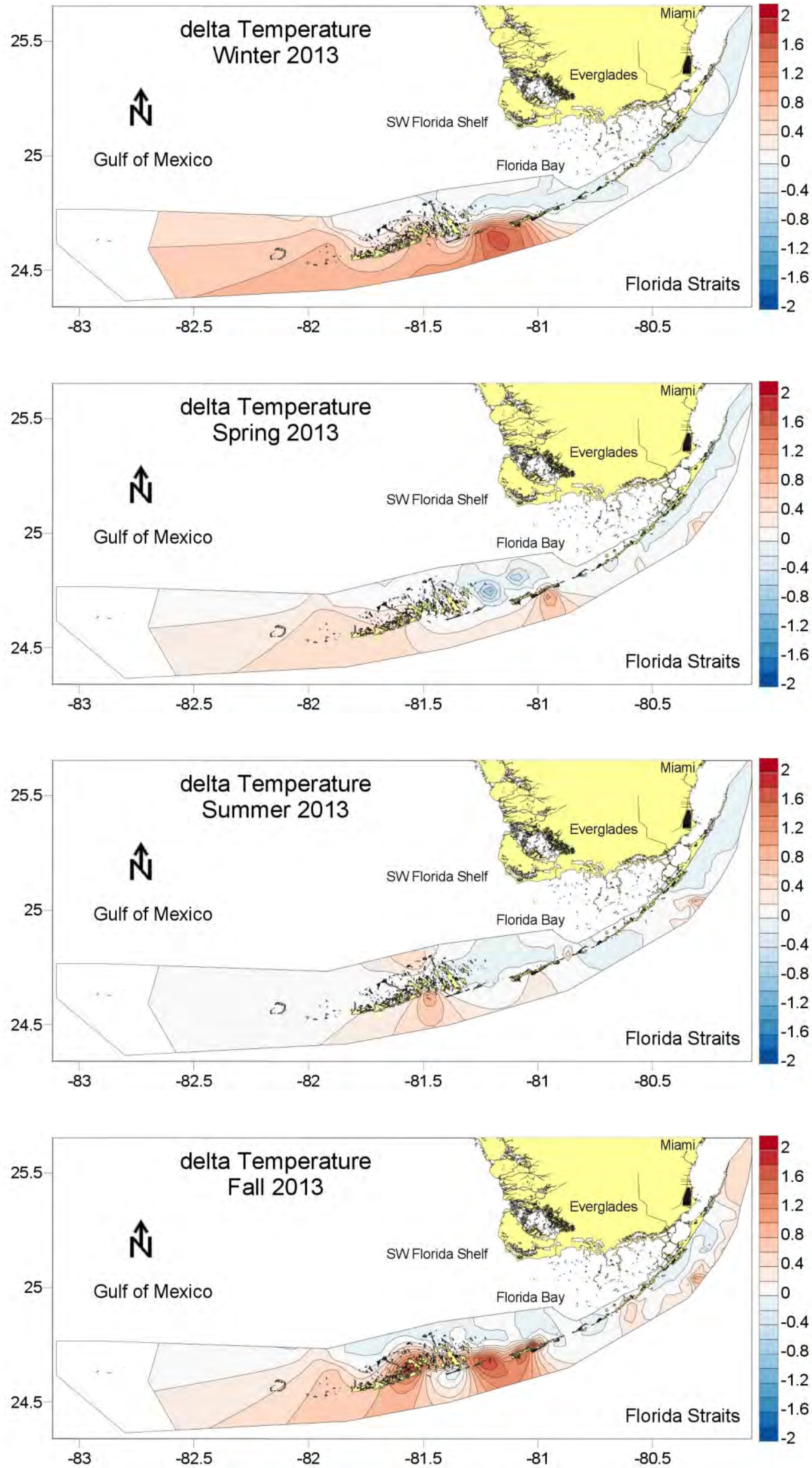

***Figure 26**. Surface and bottom temperature differences across the region during 2013.*

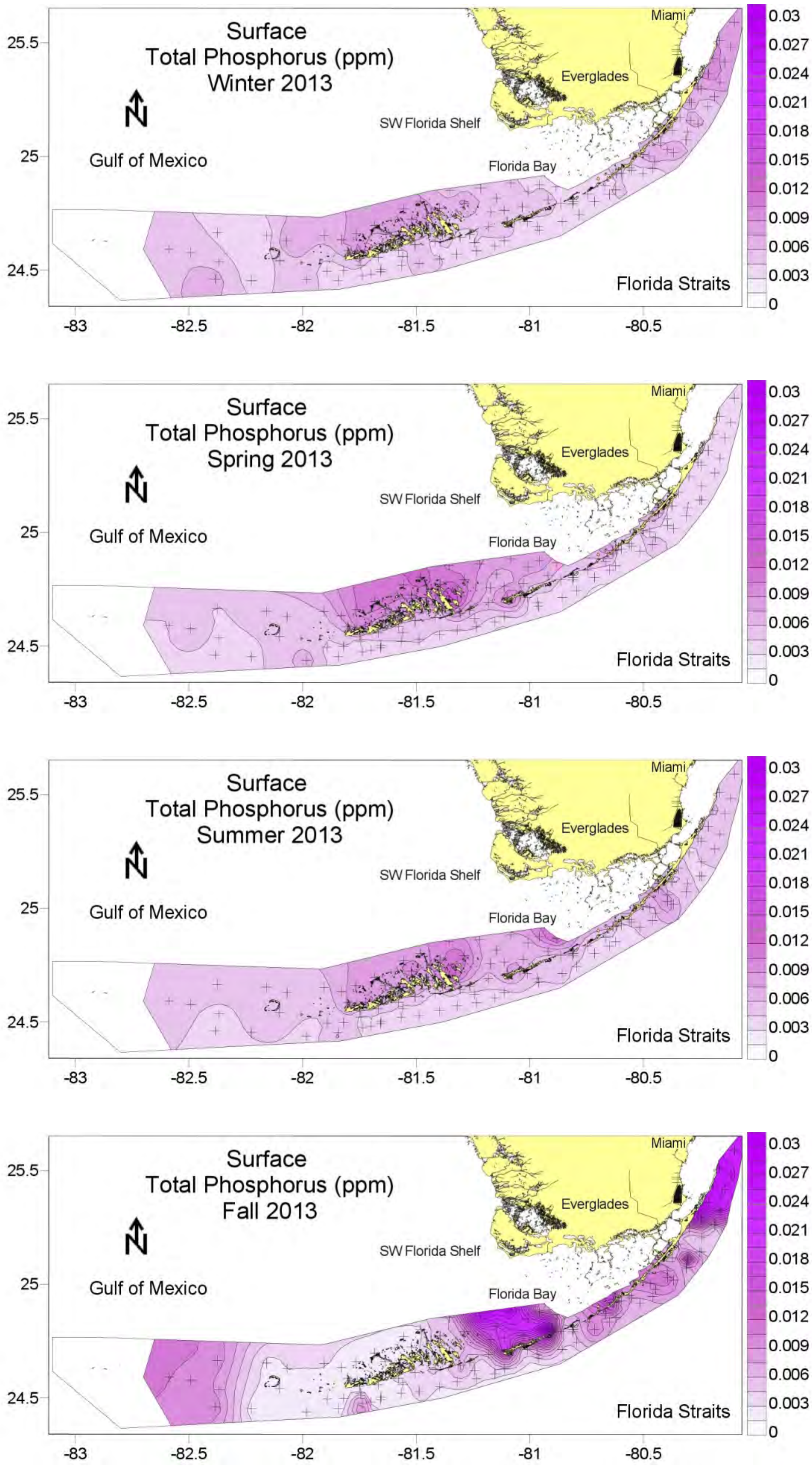

***Figure 27**. Distributions of surface total phosphorus across the region during 2013.*

Concentrations of TOC (Fig. 28) and TN (Fig. 29) are similar in pattern of distribution across the South Florida coastal hydroscape but do not always correspond. We believe this is due to differences in sources of dissolved organic matter. 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 28 and 29 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.

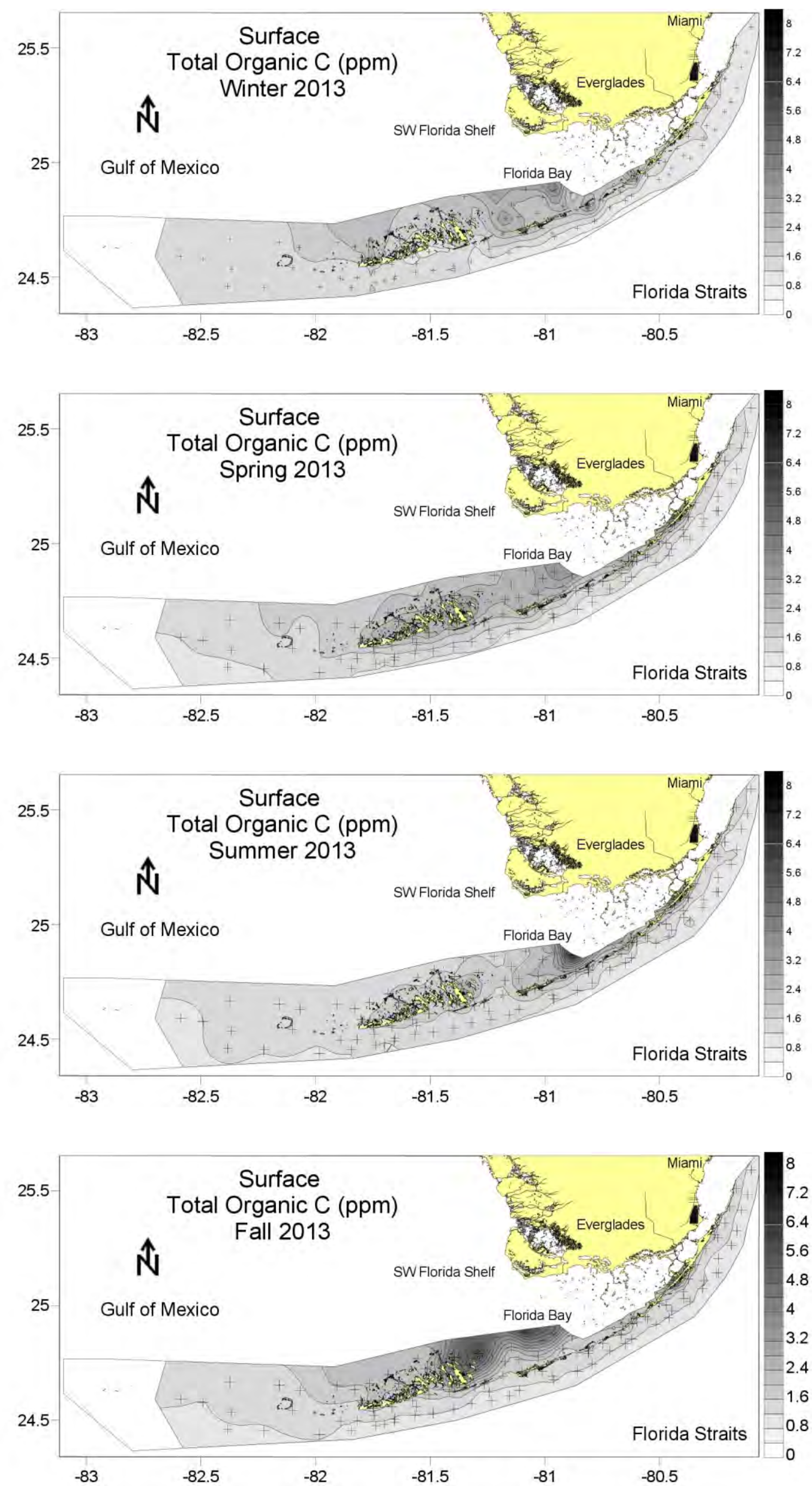

***Figure 28**. Distributions of surface total organic carbon across the region during 2013.*

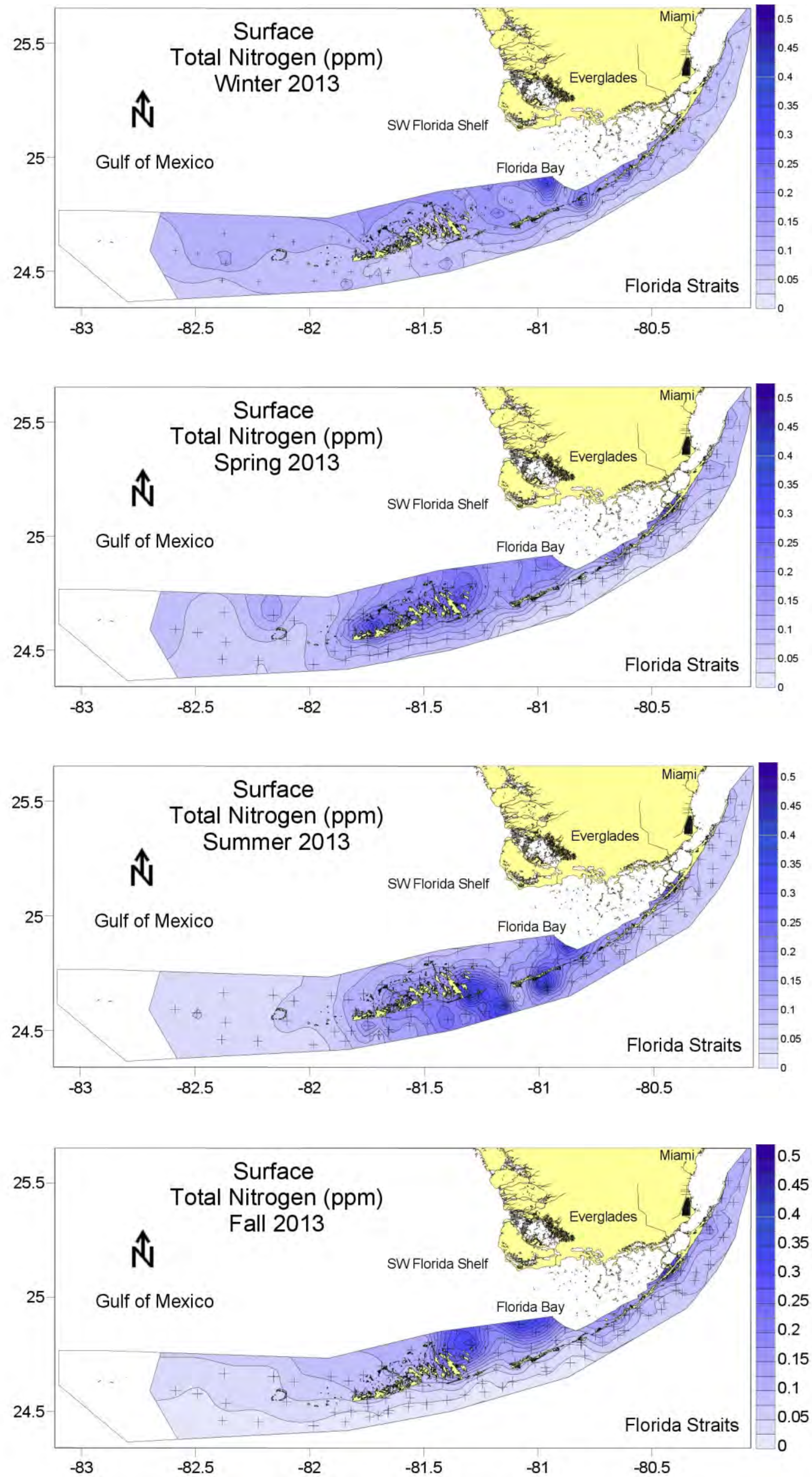

***Figure 29**. Distributions of surface total nitrogen across the region during 2013.*

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, 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. It is interesting that CHLA concentrations are typically higher in the Marquesas than in other areas of the FKNMS (Fig. 30). When examined in context with the whole South Florida ecosystem, it is obvious that the Marquesas zone should be considered a continuum of the Shelf rather than a separate management entity. This shallow sandy area (often called the Quicksands) acts as a physical mixing zone between the Shelf and the Atlantic Ocean and is a highly productive area for other biota as well as it encompasses the historically rich Tortugas shrimping grounds.

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

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

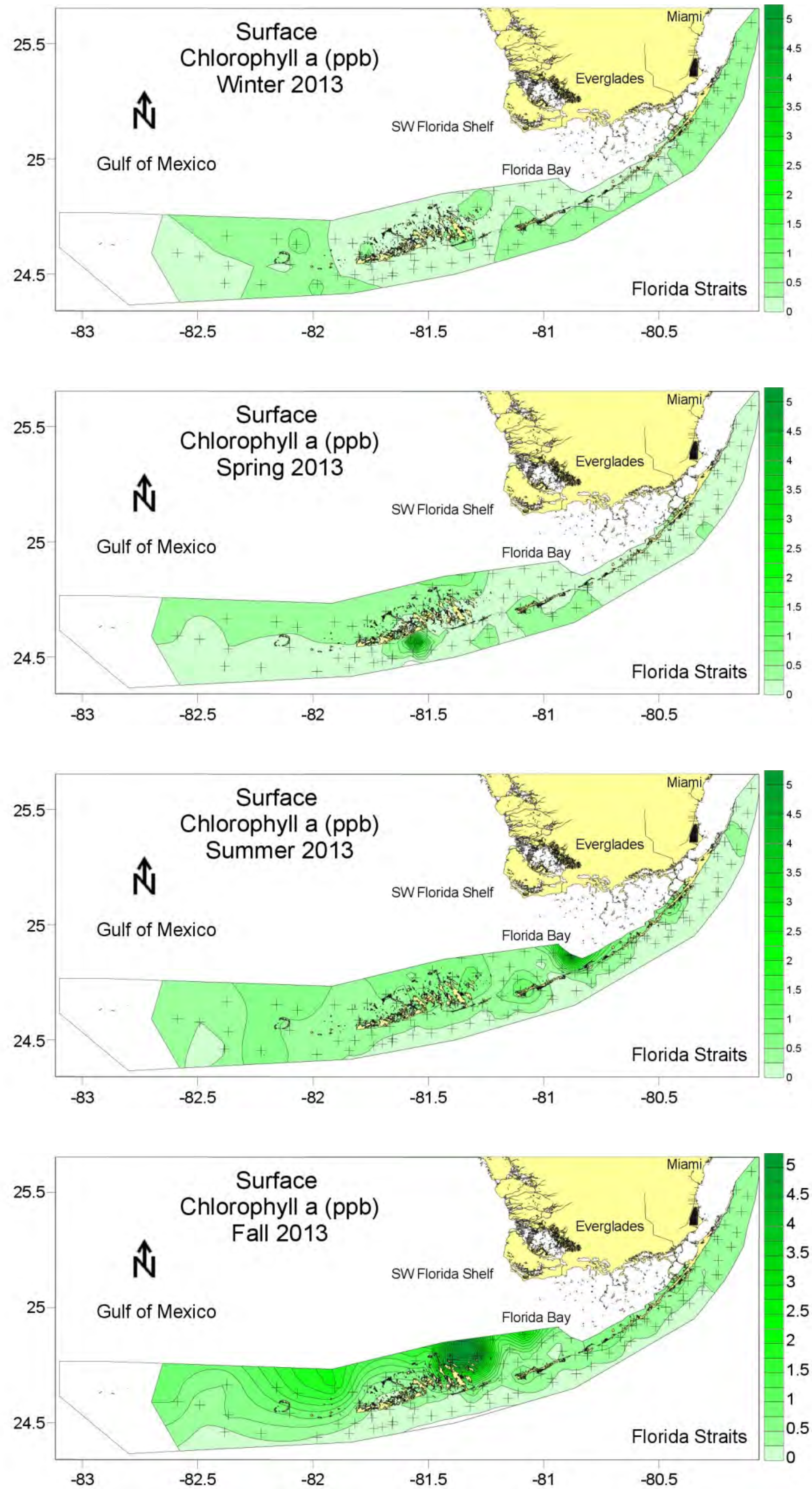

***Figure 30**. Distributions of surface chlorophyll a across the region during 2013.*

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 31). 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 in 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 32). However, in Keys waters, CDOM may be a more prominent driver of light penetration.

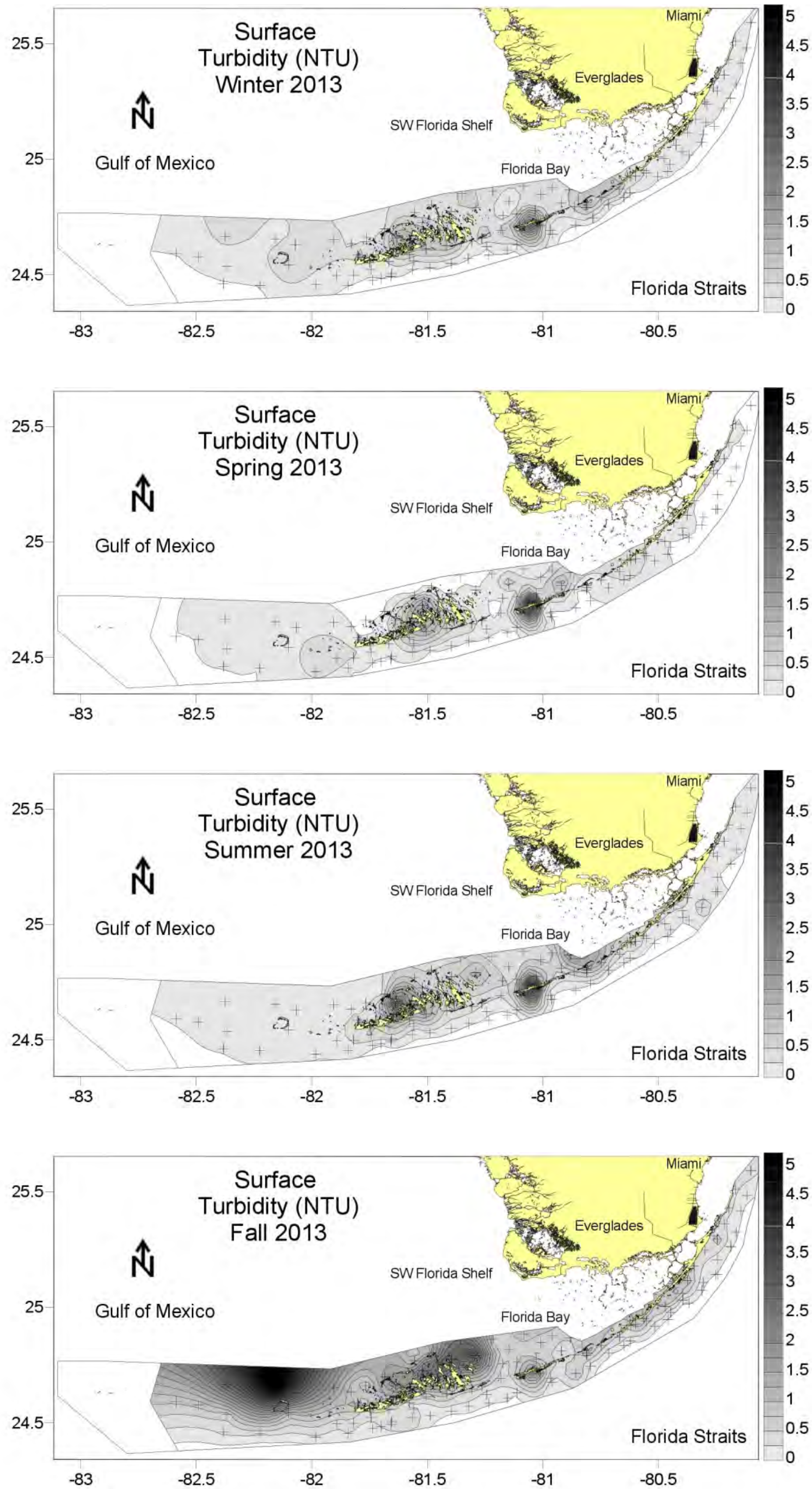

***Figure 31**. Distributions of surface turbidity across the region during 2013.*

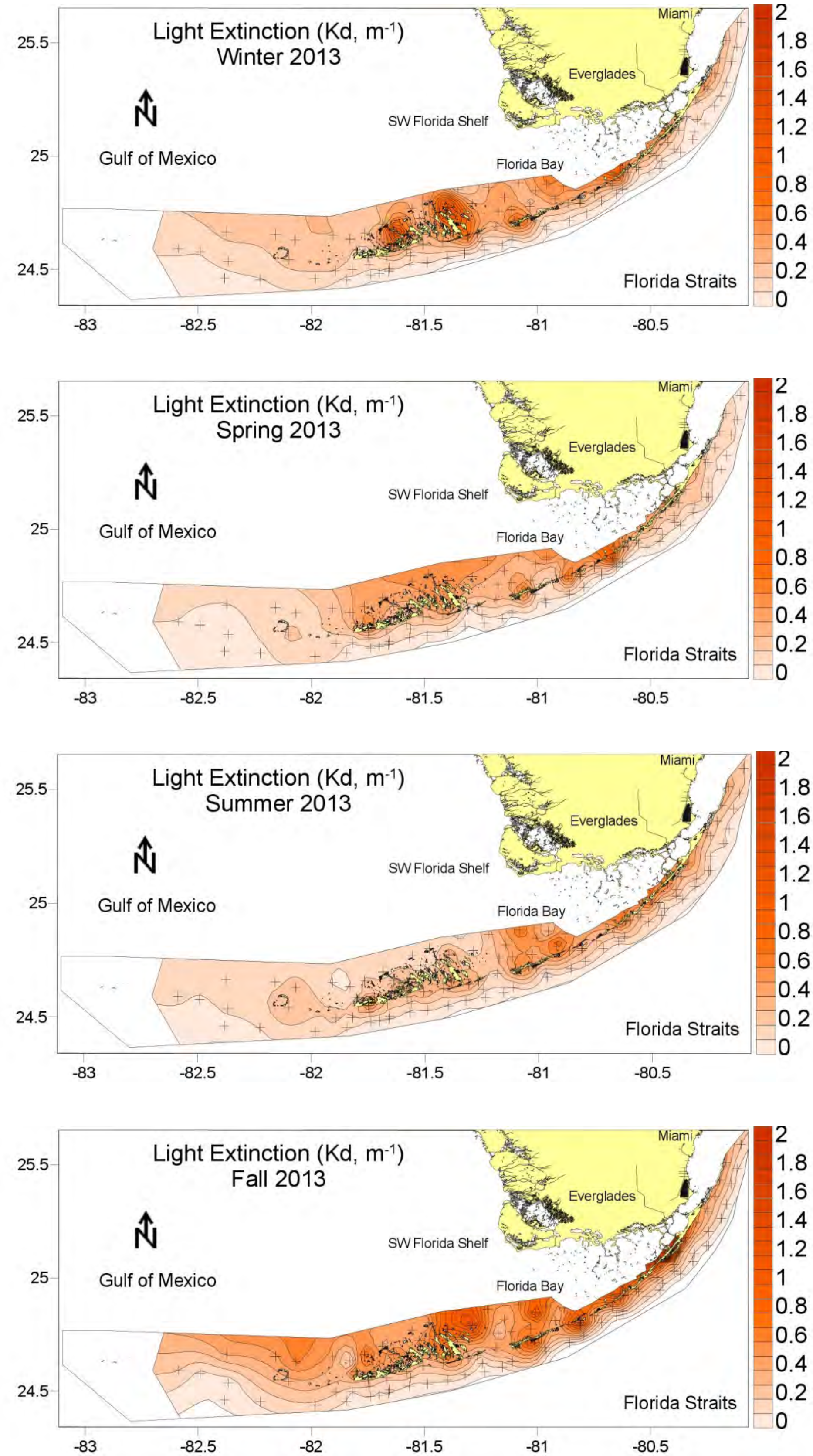

***Figure 32**. Distributions of Light extinction across the region during 2013.*

Surface SiO_2 concentrations exhibited a pattern similar to salinity (Fig. 33). 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. 33). 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. 34). 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).

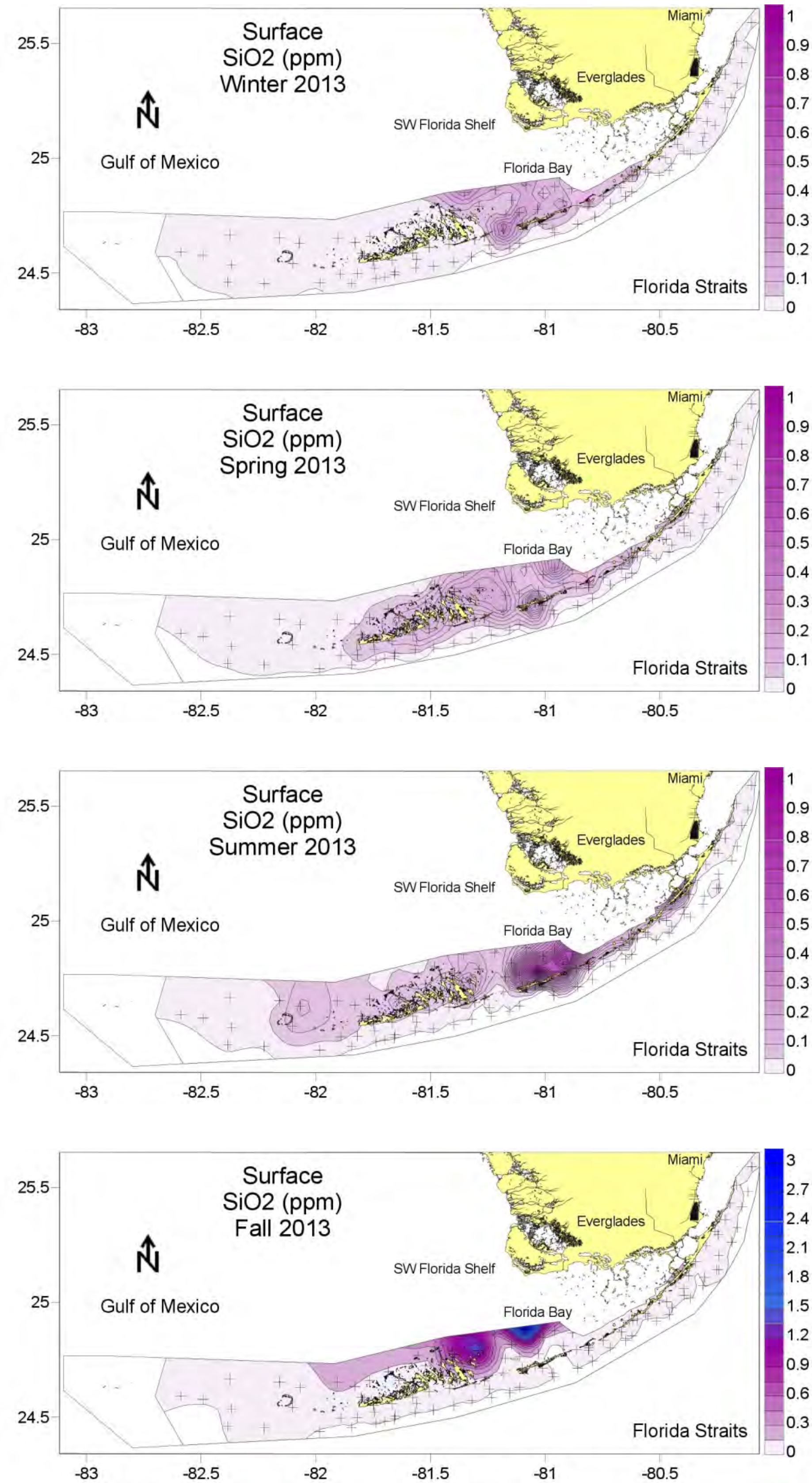

Figure 33. Distributions of surface silicate across the region during 2013.

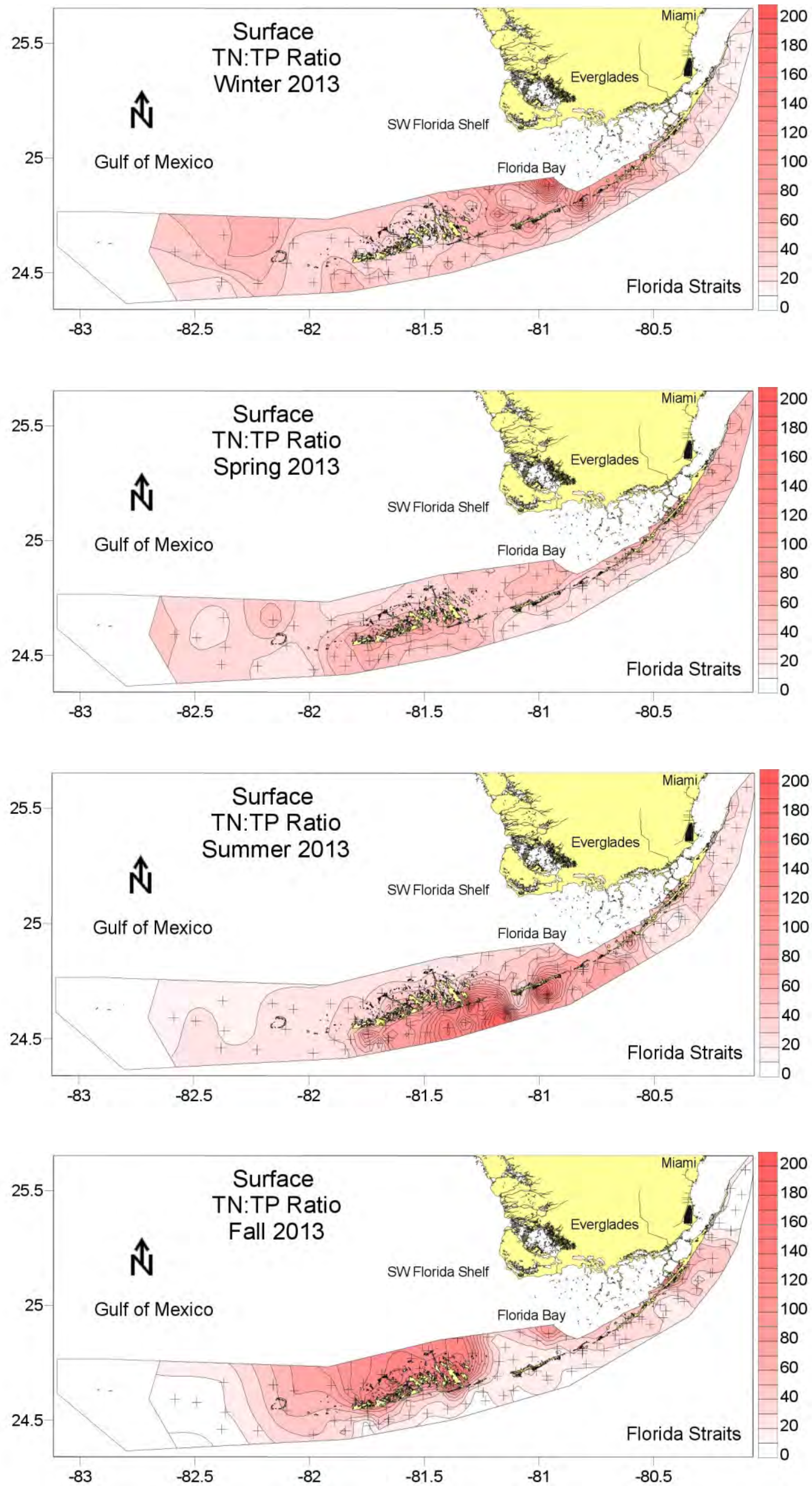

***Figure 34**. Distributions of surface TN:TP ratio across the region during FY2013.*

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.

6. Numeric Nutrient Criteria Development

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 (Briceño et al. 2013, Fig. 2).

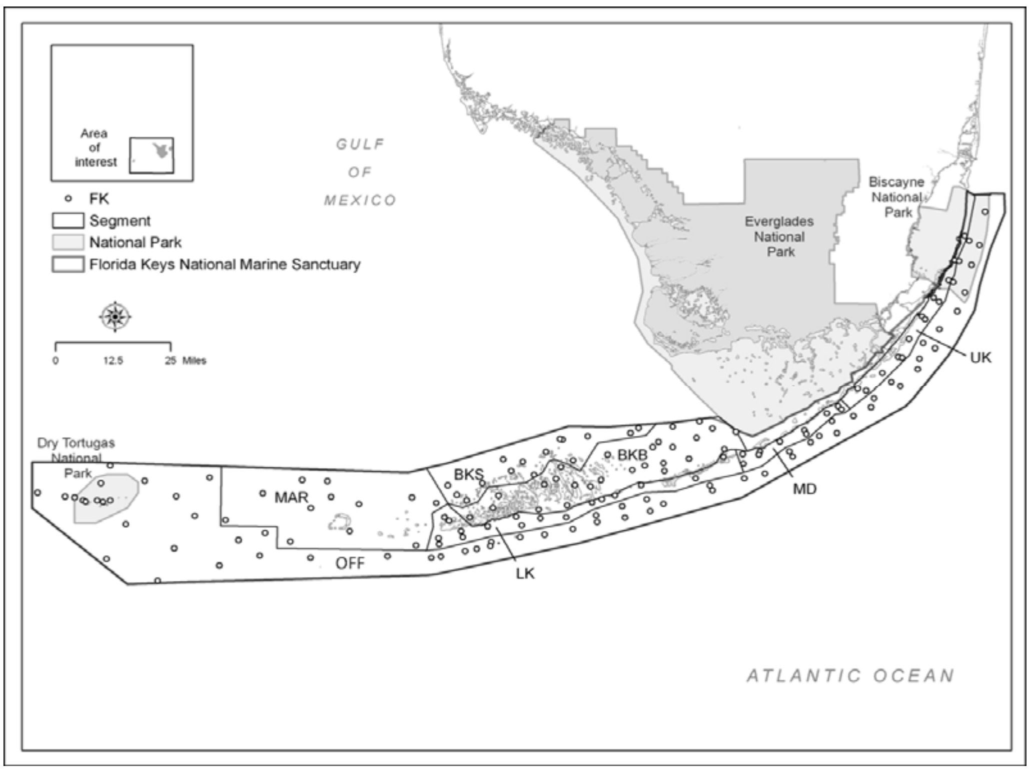

Figure 2. *Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys*

This segmentation was proposed to EPA and FDEP for use in developing numeric nutrient criteria for FL estuaries and coastal waters. The approach was adopted by FDEP as Eight Maps of FL Marine Nutrient Regions, https://www.flrules.org/Gateway/reference.asp?No=Ref-01215, dated Oct. 19, 2011. The nutrient criteria for this region was subsequently developed using data from this Florida Keys Water Quality Monitoring Project and submitted to EPA in March

2013 as Implementation of FL Numeric Nutrient Standards, NNC_Implementation_3-11-13.pdf. On June 27, 2013, EPA approved 062713_epa_approval_nnc_implementation_document.pdf, FDEP Rule 62.300 (19) F.A.C. which includes 62.302.532 Estuary-Specific Numeric Interpretations of the Narrative Nutrient Criterion (the Coastal Estuary Rule), 62_302_final.pdf.

We believe that this accomplishment is an important achievement for a Federally-funded, University-operated water quality monitoring program and should be a model for future projects.

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. 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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8. Appendix 1: Estimated tendency of parameters for the period 1995-2012

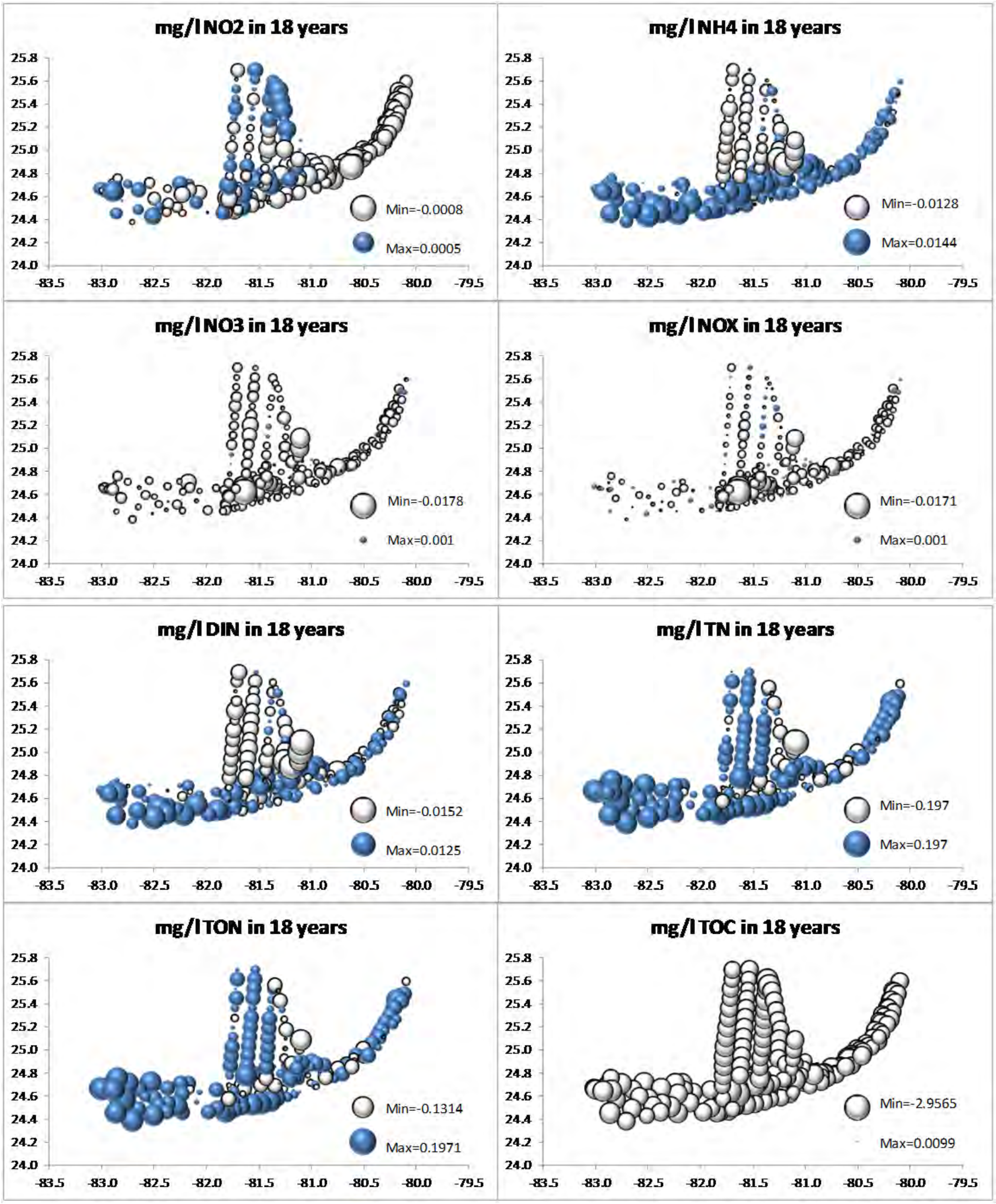

Figure A2.1: Estimated tendency of Nitrogen species for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance.

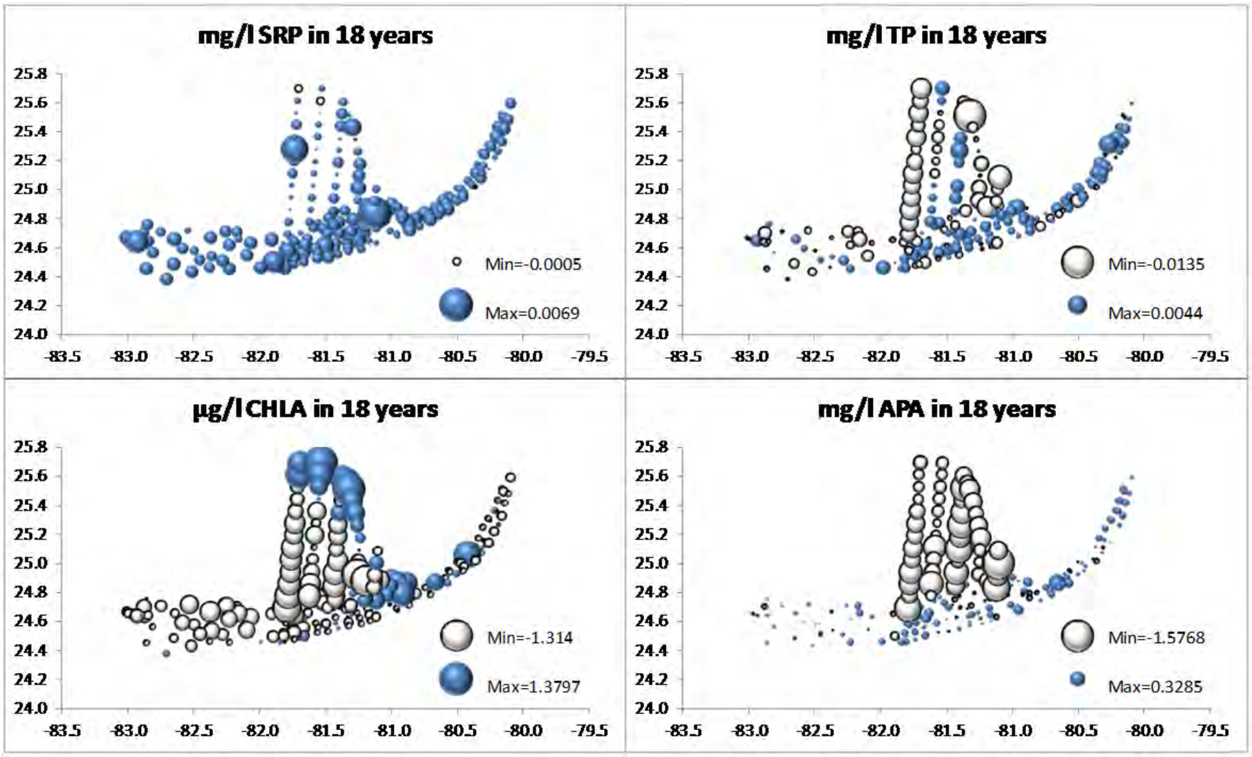

Figure A2.2: Estimated tendency of SRP, TP, CHLa and APA for the period 1995-2012, from slopes of Ordinary Linear Regression without considering statistical significance.

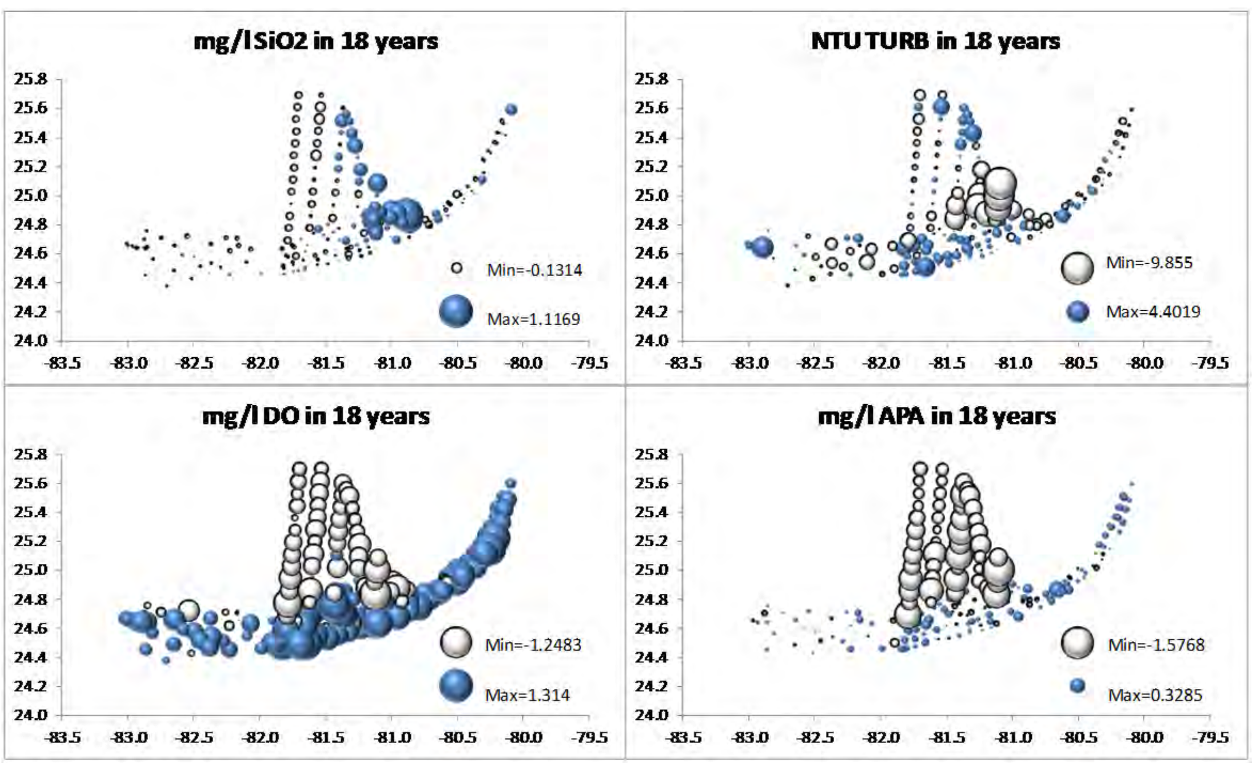

Figure A2.3: Estimated tendency of SiO2, Turbidity, DO and APA for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance.

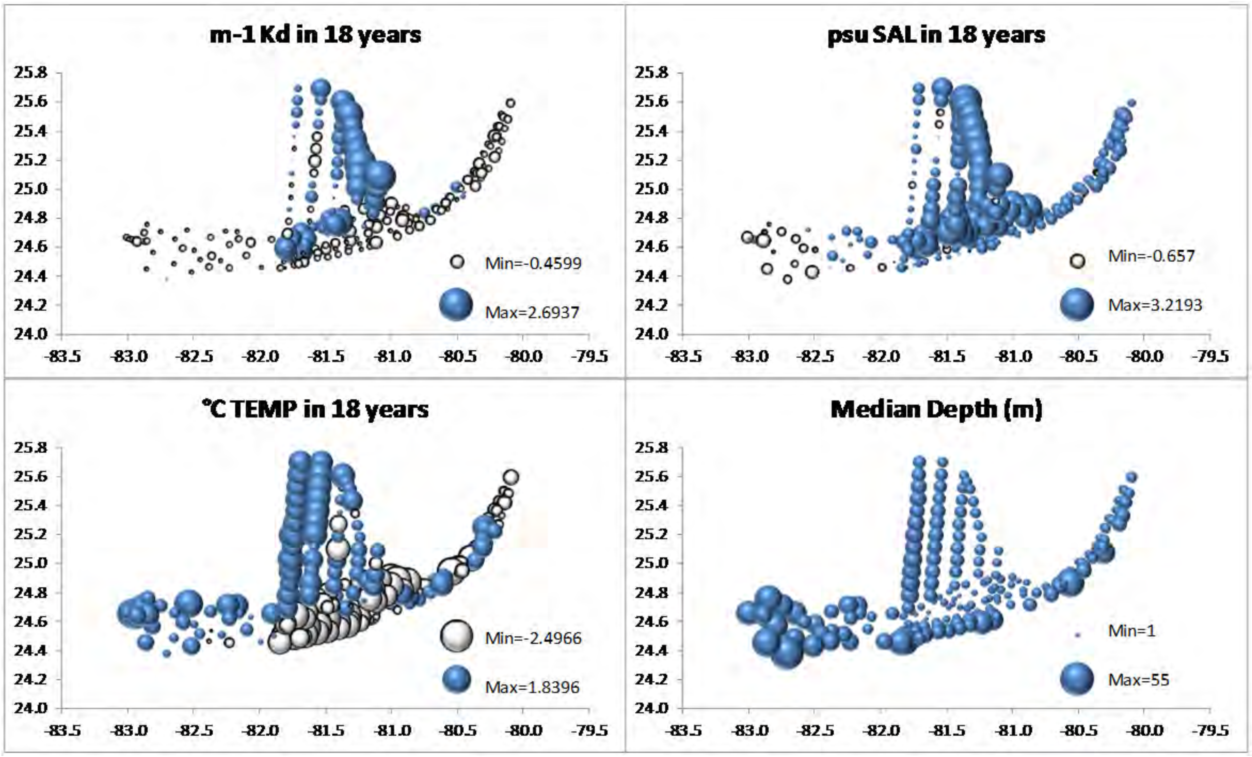

Figure A2.4: Estimated tendency of Kd, Salinity, Temperature for the period 1995-2012 derived from slopes of Ordinary Linear Regression without considering statistical significance. Also shown is Station median Depth,