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2017 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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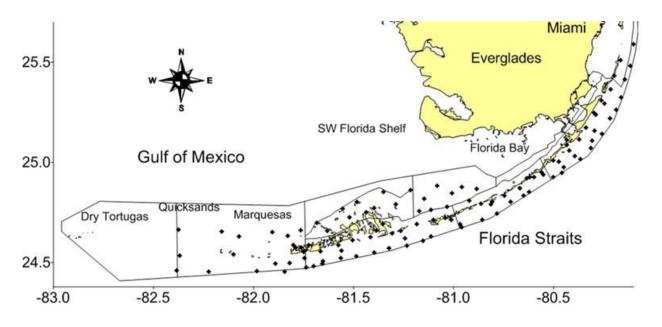
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2017 ANNUAL REPORT OF THE WATER QUALITY MONITORING PROJECT FOR THE WATER QUALITY PROTECTION PROGRAM OF THE FLORIDA KEYS NATIONAL MARINE SANCTUARY



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Henry O. Briceño & Joseph N. Boyer Funded by the Environmental Protection Agency (#X7-00049716-0)

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 Apr. 1995 – Dec. 2017 and includes data from 92 quarterly sampling events within the FKNMS (23 years).

Field parameters measured at each station (surface and bottom at most sites) include salinity (practical salinity scale), temperature (${}^{\circ}$ C), dissolved oxygen (DO, mg I $^{-1}$), turbidity (NTU), relative fluorescence, and light attenuation (K_d, m $^{-1}$). Water quality variables include the dissolved nutrients nitrate (NO₃ $^{-1}$), nitrite (NO₂ $^{-1}$), ammonium (NH₄ $^{+}$), and soluble reactive phosphorus (SRP). Total unfiltered concentrations include those of nitrogen (TN), organic carbon (TOC), phosphorus (TP), silicate (SiO₂) and chlorophyll α (CHLA, μ g I $^{-1}$).

The EPA developed Strategic Targets for the Water Quality Monitoring Project (SP-47) which state that beginning in 2008 through 2017, 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 α should be less than or equal to 0.35 μ g l⁻¹ and the vertical attenuation coefficient for downward irradiance (K_d, i.e., light attenuation) should be less than or equal to 0.20 m⁻¹. For all monitoring sites in FKNMS, dissolved inorganic nitrogen should be less than or equal to 0.75 μ M (0.010 ppm) and total phosphorus should be less than or equal to 0.25 μ M (0.0077 ppm). Table 1 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2017.

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 Water Quality Targets derived from 1995-2005 Baseline

For reef stations, chlorophyll less than or equal to 0.35 micrograms liter⁻¹ (ug l⁻¹) and vertical attenuation coefficient for downward irradiance (K_d , i.e., light attenuation) less than or equal to 0.20 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 0.25 micromolar. Water quality within these limits is considered essential to promote coral growth and overall health. The number of samples and percentage 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					
	REEF S	tations	All Stations (excluding SHORE sites)		
Year	a a a a a - 1-1	K _d ≤ 0.20 m ⁻¹	DIN ≤ 0.75 μM	TP ≤ 0.25 μM	
	CHLA ≤ 0.35 μg l ⁻¹		(0.010 mg l ⁻¹)	(0.008 mg l ⁻¹)	
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%)	813 of 1,012 (80.3 %)	911 of 1,013 (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 %)	
2014	141 of 172 (82.0%)	133 of 172 (77.3%)	426 of 690 (61.7%)	540 of 690 (78.3%)	
2015	122 of 172 (70.9%)	135 of 172 (78.5%)	487 of 688 (70.8%)	613 of 688 (89.1%)	
2016	131 of 172 (76.2%)	129 of 170 (75.9%)	427 of 687 (62.2%)	549 of 688 (79.8%)	
2017	106 of 172 (61.6%)	120 of 170 (70.6%)	440 of 575 (76.5 %)	581 of 683 (85.1 %)	

Trend Analysis – 23 years

No significant trends were observed for temperature or salinity however, surface and bottom dissolved oxygen did increase in most areas of the FKNMS. Greatest increases in DO occurred on the Atlantic side of the Keys, Marquesas, and in some inshore areas on the Bay side (Fig. ii). Bottom DO trends were similar (not shown). Increased DO is generally beneficial for animal life.

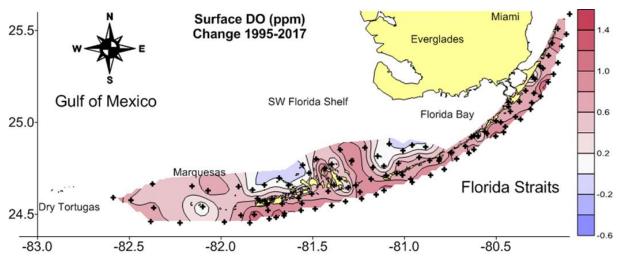


Figure ii. Total change in DO of surface waters for 23 year period calculated from significant trends.

Water column turbidity (cloudiness) declined throughout the FKNMS during the 23-year period (this is good). Some change in turbidity also occurred in bottom waters. The largest declines in turbidity occurred in western Florida Bay and west of the Marquesas (Fig iii).

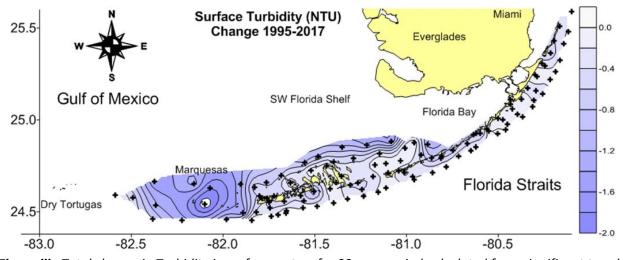


Figure iii. Total change in Turbidity in surface waters for 23 year period calculated from significant trends.

Decreased turbidity influenced light extinction (K_d) through the water column (Fig. iv) and inversely affected the percent of surface irradiance (I_o) reaching the bottom. Bottom light increased at most reef/offshore sites throughout the Keys and Marquesas (Fig. v). More light on the bottom is beneficial

to corals, seagrass, and algae. Interestingly, the Backcountry and Sluiceway areas experienced increases in K_d which lead to corresponding decreases in bottom light.

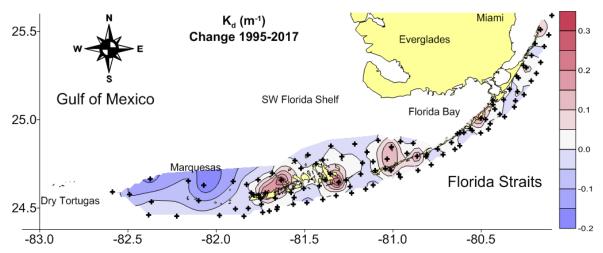


Figure iv. Total change in K_d in surface waters for 23 year period calculated from significant trends.

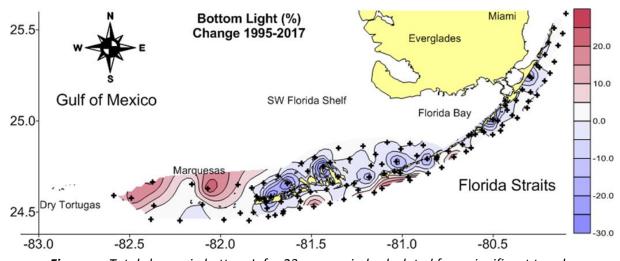


Figure v. Total change in bottom I_0 for 23 year period calculated from significant trends.

Significant Keys-wide trends in NH_4^+ , NO_3^- , TP, and SRP were detected but were very minor (not shown). However, chlorophyll α did exhibit variable trends, declining in the Marquesas while increasing in Backcountry, Sluiceway, and a few Keys areas (Fig. vi). The absolute changes were relatively small compared to normal concentrations (5-20% over 23 yr), but should be watched for continued increases.

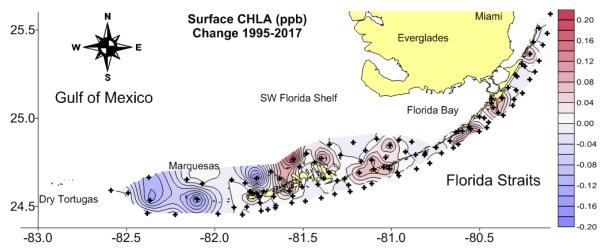


Figure vi. Total change in TOC in surface waters for 23 year period calculated from significant trends.

The largest sustained monotonic trends has been the decline in surface TOC and TON, especially in the Backcountry and the Marquesas (Fig. vii & viii). This is part of a regional trend in TOC observed on the SW Shelf, Florida Bay, and the Everglades mangrove estuaries. This decline could be considered favorable given that TOC is an important component of water color and affects light penetration, but could also be an indication of decreased upstream primary production.

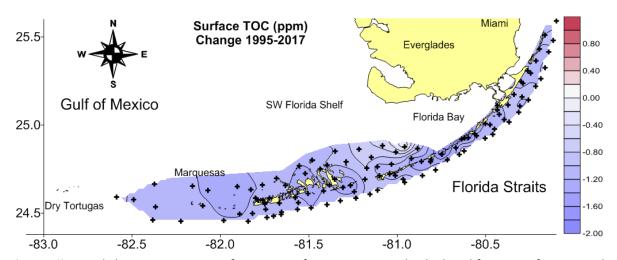


Figure vii. Total change in TOC in surface waters for 23 year period calculated from significant trends.

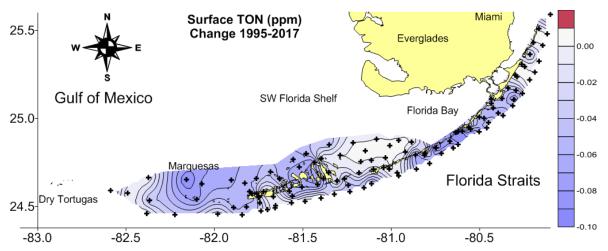


Figure viii. Total change in TON in surface waters for 23 year period calculated from significant trends.

As a result of this trend in TON, the TN:TP ratio has also declined overall (Fig. ix), especially in Upper and Lower Keys. The influence of the SW Shelf waters moving through the Middle Keys and Marquesas has attenuated any changes in those areas.

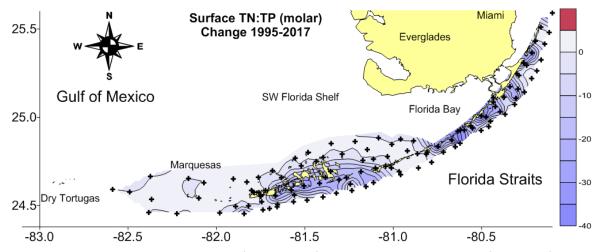


Figure ix. Total change in TN:TP ratio in surface waters for 23 year period calculated from significant trends.

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 programs.

Hurricane Irma

The 2017 Atlantic hurricane season was extreme, featuring multiple Category 5 hurricanes, including Hurricane Irma. Irma made landfall in Cudjoe Key (Lower Keys) at 13:00 UTC on September 10, at Category 4 intensity, with winds of 130 mph (215 km/h). Later that day, and after crossing the

Gulf Shelf while pounding Florida Bay and the Coastal Everglades, Irma made a second landfall on Marco Island. Measurement of high water marks indicate that the combination of surge and tide caused maximum inundation levels of 5 to 8 ft above ground level from Cudjoe Key to Big Pine Key and Bahia Honda Key. Middle and Upper Keys experienced inundation levels of 4 to 6 ft above ground level. West of Cudjoe Key, maximum elevation levels reached 4 ft.

Water sampling during our Survey #89 (third Quarter of 2017) was halted on 9/5/17 when Irma was approaching the Keys. By that time, only 20 samples belonging to Offshore, Lower Keys and Marquesas segments were pending. We resumed sampling operations two weeks later, on 9/27. Changes in water quality are summarized as follows: TN in the Lower Keys (LK) and Offshore (OFF=reef-track) remained unchanged after impact, but DIN increased, especially in the LK where it almost tripled. TP and SRP increased about 40% in both, OFF and LK segments. TOC increased dramatically in reef-track waters (6X), while silica increased mostly in LK waters (3X). Chlorophyll-a rose about 5X in the LK and doubled on the reef-track, while turbidity, although low, doubled after Irma in LK and OFF. Finally, salinity experienced a drop of 1.5 in LK and 0.5 in reef-track samples, underscoring the large input of freshwater brought by the hurricane.

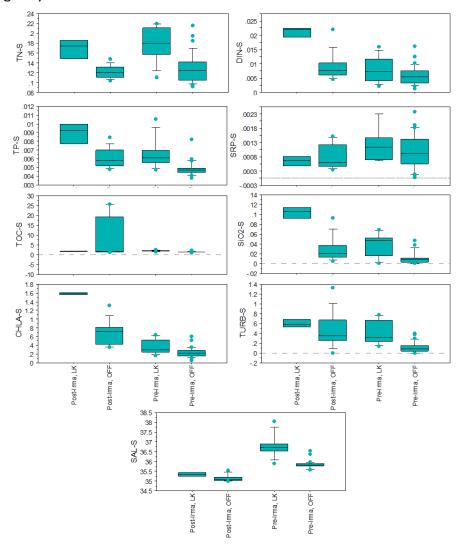


Figure x. Before-and-After Irma water quality in Lower Keys (LK segment) and coral reef (OFF segment)

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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.

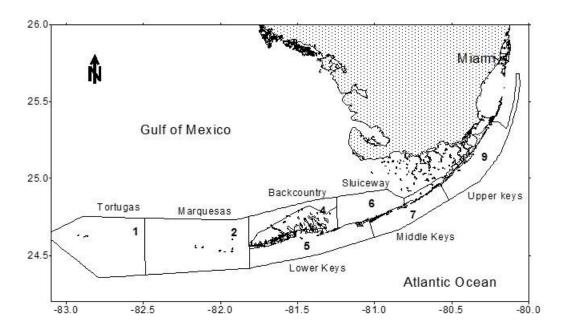


Figure 1: Map of original FKNMS boundary including collapsed segment numbers and common names.

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).

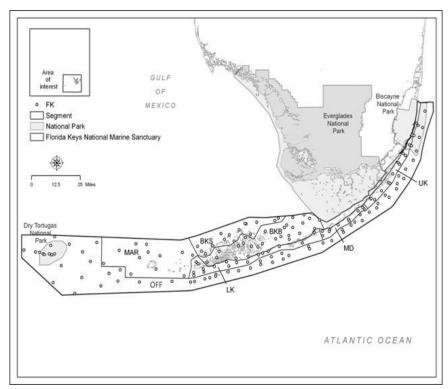


Figure 2: Map of FKNMS showing segments derived from biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys

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.

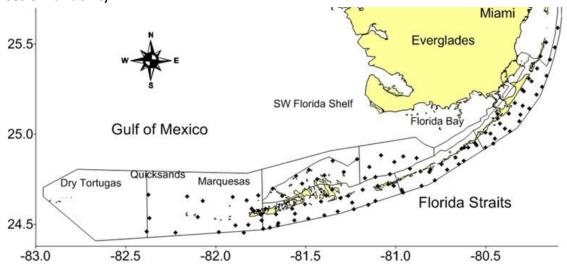


Figure 3. The SERC Water Quality Monitoring Network showing the distribution of fixed sampling stations within the FKNMS for 2017 sampling.

2. Methods

2.1. Field Sampling

The period of record of this study was from March 1995 to December 2017, which included 92 quarterly sampling events. For this year, field measurements and grab samples were collected from 112 fixed stations within the FKNMS boundary (Fig. 3). CTD casts (Seabird SBE 19) measured depth profiles of temperature (° C), salinity (practical salinity scale), dissolved oxygen (DO, mg l-1), photosynthetically active radiation (PAR, μE m-2 s-1), turbidity (NTU), and depth, as measured by pressure transducer (m). 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, Kd was reported for the upper layer. To determine the extent of stratification we calculated the difference between surface and bottom density as $\Delta \sigma_t$ (kg m⁻³), where positive values denoted greater density of bottom water relative to the surface. A $\Delta \sigma_t$ = 0-1 is considered weakly stratified, while instances >1 are strongly stratified. Negative $\Delta \sigma_t$ conditions occur rarely and denote an unstable water column where surface is denser than the bottom.

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 6600V2 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. Dissolved nutrients were defined using Whatman GF/F filters with a nominal pore size of 0.8 μ m. 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 α (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). An additional 120 ml sample was collected directly from the Niskin bottle for analysis of total nitrogen, total phosphorus, total organic carbon, and turbidity.

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 α (CHLA, $\mu g \ l^{-1}$), and turbidity (NTU) using standard laboratory methods. 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

NH₄⁺ was analyzed by the indophenol method (Koroleff 1983). NO₂⁻ 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 (NO₃⁻) was calculated as N+N - NO₂⁻; total dissolved inorganic nitrogen (DIN) as N+N + NH₄⁺, and total organic nitrogen (TON) as TN - DIN. All variables are reported in ppm (mg l⁻¹) unless otherwise noted.

2.3. <u>Summary Statistics - Box and Whisker Plots</u>

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. Spatial Analysis - 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 use contour maps (ArcView, ESRI) of specific water quality variables. 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 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. Time Series Analysis

Least squares, linear regression as a method for measuring change over time is useful for variables that change at relatively continuous rates. The simplicity of this method makes it appealing to those who are tracking water quality, but time series dominated by non-linear drivers may be skewed by endmember conditions. For this reason we used the nonparametric Sen slope estimation to determine temporal trends (unit yr^{-1}) for each water quality variable over the 23 year period of record. The Mann-Kendall Test was used to detect monotonic trends without the requirement that the measurements be normally distributed or that the trend be linear. Only those slopes having significant trends (p < 0.10) were reported; non-significant trends were coded as slope=0. Trend maps were drawn only for those variables for which 10% of individual station trends were significant (p<0.10). In an effort to show trend impact, significant trends are reported as the total change over the 23 year period of record.

While the Mann-Kendall Test tells us whether the overall trend is increasing or decreasing, it does not provide any information about short-term or reversing trends. To address this limitation, time series data stratified by segment (see above), were fitted using a locally-weighted approach (LOESS, SPSS Statistics). The LOESS algorithm is a non-parametric, locally weighted least squares method which combines multiple regression models in a k-nearest-neighbor approach (Cleveland 1979, SPSS Statistics). The Epanechnikov (1969) parabolic kernel with 10% data bandwidth was used as the time series smoother.

3. Results

3.1.Overall Water Quality of the FKNMS in 2017

Summary statistics for all water quality variables from calendar year 2016 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 27.6 °C and salinity of 36.2; dissolved oxygen saturation of the water column (DO_{sat}) was relatively high at 96.7%. On this coarse scale, the FKNMS exhibited very good water quality with median NO₃-, NH₄+, TP, and SiO₂ concentrations of 0.0019, 0.0053, 0.0058, and 0.0300 mg l⁻¹, respectively. NH₄+ was the dominant DIN species in almost all of the samples (64%). However, DIN comprised a small fraction (6.3%) of the TN pool (0.132 mg l⁻¹) with TON being the bulk (median 0.121 mg l⁻¹). SRP concentrations were low (median 0.0007 mg l⁻¹) and comprised only 12% of the TP pool (0.0058 mg l⁻¹). CHLA concentrations were also low overall, 0.28 μ g l⁻¹, but ranged from 0.07 to 3.34 μ g l⁻¹. Median TOC was 1.42 mg l⁻¹; a value higher than open ocean levels but consistent with coastal areas.

Median turbidity was higher than usual (0.26 NTU) compared to earlier years but is still low. Interestingly, K_d was still low (0.226 m⁻¹), comparable to last year. Overall, 34.1% of incident light (I_0) reached the bottom, which is up from last year's 33.7%. Molar ratios of N to P suggested a general P limitation of the water column (median TN:TP = 45.7) 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 2017. Data are summarized as number of samples (n), minimum value (Min.), maximum value (Max.), and Median.

Variable	Depth	n	Min.	Max.	Median
NO ₃ -	Surface	409	0.0000	0.0264	0.0020
(mg l ⁻¹)	Bottom	250	0.0001	0.0251	0.0019
NO ₂ -	Surface	433	0.0000	0.0045	0.0005
(mg l ⁻¹)	Bottom	269	0.0000	0.0031	0.0003
NH_4^+	Surface	426	0.0001	0.0361	0.0032
(mg l ⁻¹)	Bottom	265	0.0000	0.0285	0.0025
TN	Surface	448	0.0713	0.7176	0.1514
(mg l ⁻¹)	Bottom	280	0.0743	0.2492	0.1255
DIN	Surface	387	0.0001	0.0539	0.0062
(mg l ⁻¹)	Bottom	227	0.0002	0.0435	0.0051
TON	Surface	387	0.0677	0.6764	0.1485
(mg l ⁻¹)	Bottom	227	0.0630	0.2399	0.1190
TP	Surface	448	0.0002	0.0425	0.0060
(mg l ⁻¹)	Bottom	275	0.0036	0.0188	0.0052
SRP	Surface	329	0.0000	0.0390	0.0008
(mg l ⁻¹)	Bottom	194	0.0000	0.0073	0.0006
CHLA (μg l ⁻¹)	Surface	447	0.00	7.66	0.32
TOC	Surface	448	0.72	25.87	1.51
(mg l ⁻¹)	Bottom	280	0.73	26.06	1.18
SiO ₂	Surface	365	0.000	1.066	0.037
(mg l ⁻¹)	Bottom	212	0.000	0.570	0.022
Turbidity	Surface	448	0.000	5.620	0.320
(NTU)	Bottom	281	0.000	8.710	0.260
Salinity	Surface	448	25.31	40.61	36.25
	Bottom	448	25.35	40.60	36.28
Temp.	Surface	448	17.78	34.80	26.29
(°C)	Bottom	448	17.75	34.76	26.08
DO	Surface	448	5.65	7.75	6.55
(mg l ⁻¹)	Bottom	448	5.65	7.76	6.57
K _d		444	0.000	8.234	0.257
TN:TP	Surface	448	19.2	884.6	53.4
Si:DIN	Surface	327	0.0	57.3	2.4
DO Saturation	Surface	448	90.6	105.1	97.7
(%)	Bottom	448	90.7	101.7	97.7
I _o (%)	Bottom	444	0.1	99.5	33.9
Δσt		448	-0.387	1.466	0.017

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 were 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 Sluiceway (Fig. 4). This class was highest in nutrients, especially TN, TON, TOC, SiO₂, 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, SiO₂, 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 SiO₂, 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 resuspension.

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, SiO₂ 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. This zone had very low nutrients, TP, CHLA, and turbidity.

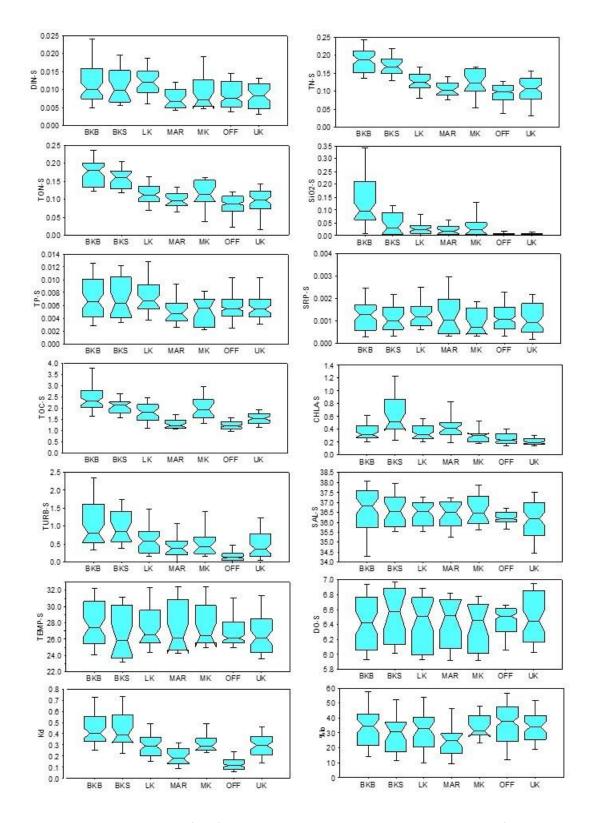


Figure 4. Box-and-whisker plots of surface samples showing median and distribution of water quality variables as stratified by water quality cluster. Notches in the box that do not overlap with another are considered significantly different.

3.2. Hurricane Irma

The 2017 Atlantic hurricane season was extreme, featuring multiple Category 5 hurricanes, including Hurricane Irma (Fig. 5). Irma made landfall in Cudjoe Key (Lower Keys) at 13:00 UTC on Sept. 10, at Category 4 intensity, with winds of 130 mph (215 km/h). Later that day, and after crossing the Gulf Shelf while pounding Florida Bay and the Coastal Everglades, Irma made a second landfall on Marco Island. Measurement of high water marks indicate that the combination of surge and tide caused maximum inundation levels of 5-8 ft above ground level on Cudjoe Key, Big Pine Key, and Bahia Honda Key. Middle and Upper Keys experienced inundation levels of 4-6 ft. West of Cudjoe Key, maximum elevation levels reached 4 ft.



Figure 5: Hurricanes Katia (left), Irma (center), and Jose (right) on September 8th 2017 (credit: <u>NOAA View Global Data Explorer</u>)

Major storms affect coastal and estuarine water quality by disturbing the delivery and processing of nutrients and organic matter, altering the physical—chemical properties, and disrupting ecosystem structure and function. Defoliation and destruction of mangrove forest are common in South Florida. Among the important drivers causing water chemistry changes is the huge and sudden input of organic debris, dissolved organic matter, nutrients, and the increase in suspended load due to hurricane impact. Receding waters after Irma's storm surge brought large amounts of debris from freshwater marshes, mangrove forest, and decaying seagrass from the large seagrass die-off affecting Florida Bay since 2015. Furthermore, there was already an algal bloom in Florida Bay onset since 2016 and canals were choked with debris.

Water sampling during our Survey #89 (3rd Quarter of 2017) was halted on 9/5/17 when Irma was approaching the Keys. By that time, only 20 samples belonging to Offshore, Lower

Keys and Marquesas segments were pending. We resumed sampling operations two weeks later, on 9/27. Changes in water quality are summarized as follows: TN in the Lower Keys (LK) and Offshore (OFF=reef-track) remained unchanged after impact (Fig. 6), but DIN increased, especially in the LK where it almost tripled. TP and SRP increased about 40% in both, OFF and LK segments. TOC increased dramatically in reef-track waters (6X), while silica increased mostly in LK waters (3X). CHLA rose about 5X in the LK and doubled on the reef-track, while turbidity, although low, doubled after Irma in LK and OFF. Finally, salinity experienced a drop of 1.5 in LK and 0.5 in reef-track samples, underscoring the large input of freshwater brought by the hurricane.

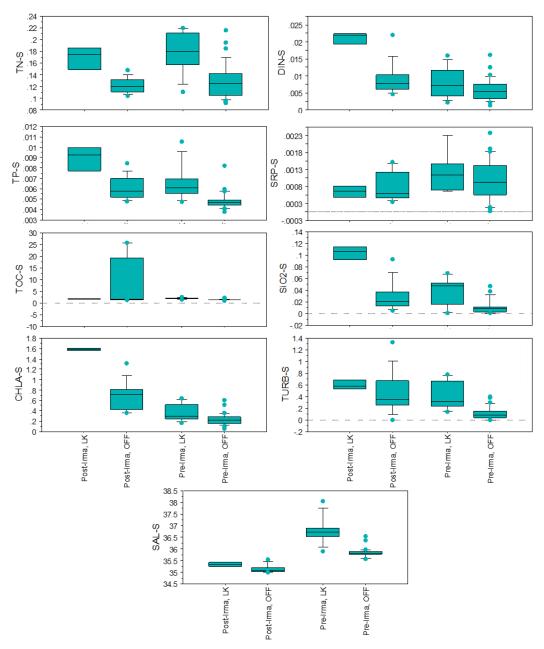


Figure 6: Before-and-After Irma water quality in Lower Keys (LK segment) and coral reef (OFF segment)

NOAA/AOML and NOAA/NESDIS perform monthly surveys of south Florida's coastal waters aboard the R/V Walton Smith. FIU participated in this effort as collaborator for a survey on October 9-13, 2017. The survey aim was to assess the response of south Florida coastal water quality to Hurricane Irma's impacts. Sampling was performed along the Florida Keys and southwest Florida shelf. We analyzed 73 water samples collected during the cruise for their nutrient content, namely TN, TP, and TOC, and for sucralose, a chemical species that is unique to human consumption, recently proposed as indicator to follow the intrusion of human derived wastewater into aquatic ecosystems (Briceño et al 2016). Simultaneous nutrient and Sucralose analyses of canal waters of the Florida Keys strongly suggest that Sucralose values exceeding a threshold of 57 ng l⁻¹ are indicative of human inputs.

We should keep in mind that the survey took place a little over one month after Irma's landfall in the Keys. Hence, results may reflect the effects of multiple modifiers occurring after hurricane impact. Larger TN and TP concentrations cluster on the Gulf Shelf area closer to the Everglades (Fig. 7), suggesting a source in the Everglades and/or a source from coastal waters farther north. There is a high and positive correlation between TN and TP statistically significant at p=0.05. This positive correlation differs from pre-Irma data for the region, but is the usual in waters impacted by human activities, like urban canal waters.

TOC values are also strongly bimodal (Fig 8), with higher TOC concentrations occurring mostly on the ocean side of the Florida Keys. Those high concentrations are ten times higher than pre-Irma data for ocean-side waters (Table 2), underscoring the magnitude and extension of the impact. Lower TOC concentrations (<20 mg/l) sites cluster in the Gulf Shelf.

The geographical bimodality of TOC, TN and TP distributions may indicate significantly different sources. The high concentration of TOC along the ocean side of the Keys may have three sources, the impacted Keys, upwelling, or finally, the Gulf current. There is a slight declining gradient of TOC and Sucralose from the shoreline of the Keys offshore to the reeftrack, suggesting the Keys as main source. Additionally, there is a slight declining trend from west to east, from the Lower Keys to Middle to Upper Keys. This gradient seems to highlight the geographically asymmetric impact where most disturbance and damage occurred in the Lower Keys and gradually declined eastwards, towards the Upper Keys. Again, the data suggest the Keys as immediate source of TP.

In summary, the immediate changes in water quality brought about by Hurricane Irma were significant, and from previous experience, its effects may last several years. EPA targets for 2017 were only breached by Chl a, and the rest of parameters (DIN, K_d and TP) do not reflect mayor deleterious changes due to the impact.

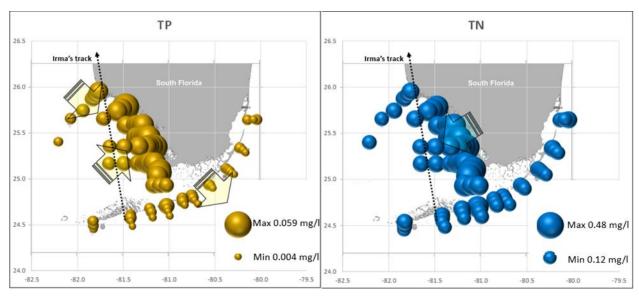


Figure 7. Post-Irma concentration of TN and TP in South Florida coastal waters.

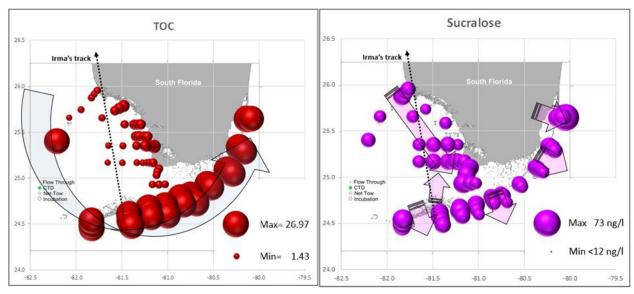


Figure 8. Post-Irma concentration of TOC and Sucralose in South Florida coastal waters.

Table 2. Comparison between pre-Irma (long-term) and just post-Irma nutrients and sucralose

		TN mg/L	TP mg/L	TOC mg/L	Sucralose ng/L
Post-IRMA	Bay Side	0.2830	0.0314	3.5647	22
	Atlantic Side	0.1532	0.0081	24.8476	27
Long-TERM	Bay Side	0.2245	0.0011	2.6502	-
	Atlantic Side	0.1623	0.0063	1.7765	-

3.3. Geographical Differences

Several important results have been realized from this monitoring project. First we documented elevated nutrient concentrations (DIN, TN, TP, and SiO₂) 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 9). These changes, associated with land/human development, have become even more obvious by the addition of 10 stations located very close to shore, sampled since Nov 2011 (SHORE).

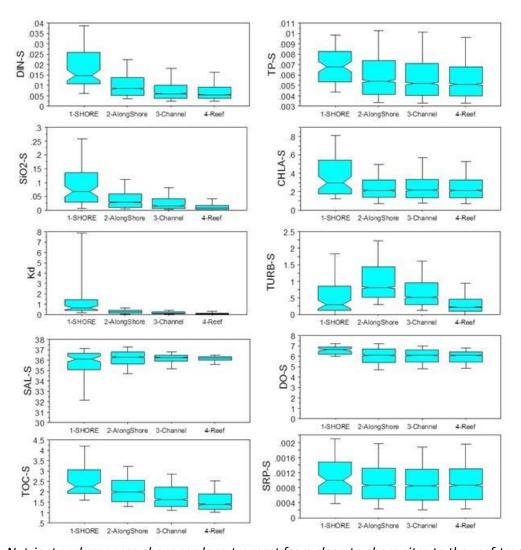


Figure 9. Nutrient and response changes along transect from close-to-shore sites to the reef-track

3.4.2017 Spatial Analysis

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; Shinn 1999a, 1999b; Paul et al. 1995, 1997; Reich et al. 2001; Briceño et al. 2015).

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. 10). 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, clearly impacts 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, such as DO (Fig. 11). Lowest DO concentrations tend to develop inside the Backcountry during warmest months.

In addition to surface currents there is evidence that internal tidal bores regularly impact the Key Largo reef tract (Leichter et al. 1996; Leichter and Miller 1999). Internal bores are episodes of higher density, deep water intrusion onto the shallower shelf or reef tract. Depending on their energy, internal tidal bores can promote stratification of the water column or cause complete vertical mixing as a breaking internal wave of sub-thermocline water.

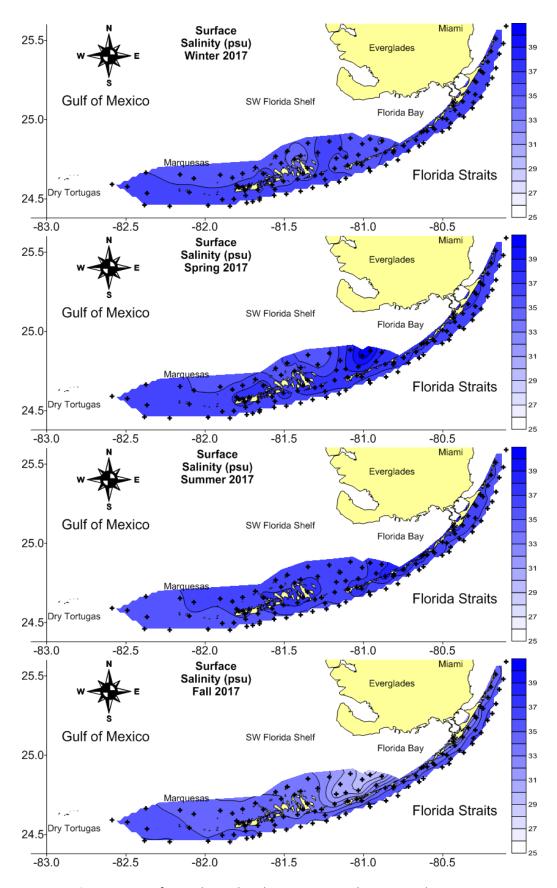


Figure 10. Surface salinity distributions across the FKNMS during 2017.

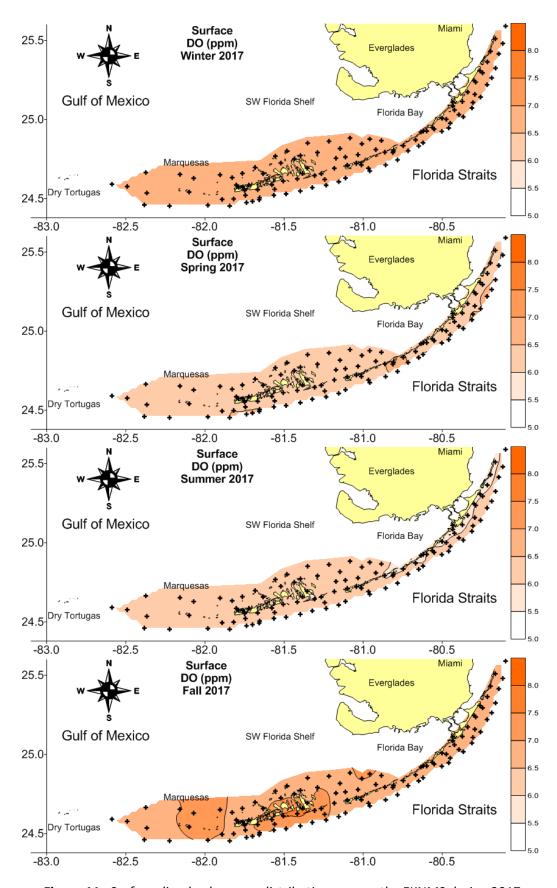


Figure 11. Surface dissolved oxygen distributions across the FKNMS during 2017.

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. 12). Since density is driven more by salinity than temperature, we do not always observe differences in σ_t between surface and bottom during upwelling events. However, decreased temperature of bottom waters from intrusion of deeper oceanic waters is clearly an indicator of increased NO₃. These upwelling events also affect other nutrient species such as NH₄+, TP, and SRP in these bottom waters as well.

Relatively high σ_t are widespread on the Atlantic side of the Keys during winter and spring, except south of Islamorada. Marquesas waters displayed high σ_t in winter, spring and summer, and values are high year around in the Lower Keys (Fig 12).

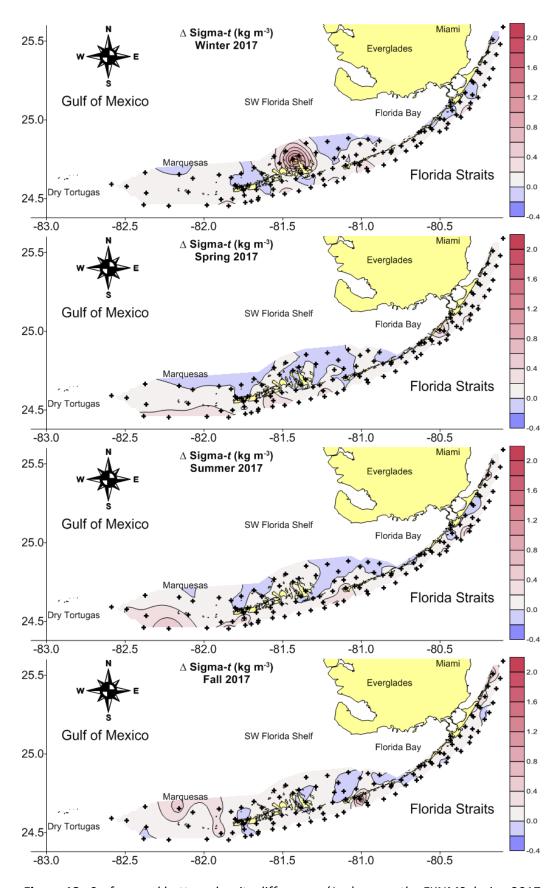


Figure 12. Surface and bottom density differences ($\Delta \sigma_t$) across the FKNMS during 2017.

Visualization of spatial patterns of NO_3^- concentrations over South Florida waters provides an extended view of source gradients over the region (Fig. 13). 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 as shown for DIN in our previous analysis (Fig. 9).

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. Another possibility is a contribution of benthic N_2 fixation/nitrification in this very shallow area.

The elevated DIN concentrations in the Backcountry are not easily explained. We think that the high concentrations found there are due to a combination of anthropogenic loading, physical entrapment, and benthic N_2 fixation. The relative contribution of these potential sources is unknown. Lapointe and Matzie (1996) showed 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 would result in a concentration effect of only 5-6%. Additionally, NO_3 - concentration declines for salinities above ~35.3 region-wide.

Benthic N₂ fixation may potentially be very important in the N budget of the Backcountry. Measured rates of N₂ fixation in a *Thalassia* bed in Biscayne Bay, having very similar physical and chemical conditions, were 7.56 ppm N m⁻² d⁻¹ (Capone and Taylor 1980). Without the plant community N demand, one day of N₂ fixation has the potential to generate a water column concentration much greater than typical ambient NH₄⁺ concentrations. Much of this NH₄⁺ is probably nitrified and may account for the elevated NO₃⁻ concentrations observed in this area (Fig. 13). Clearly, N₂ fixation may be a significant component of the N budget in the Backcountry and that it may be exported as DIN to the FKNMS in general.

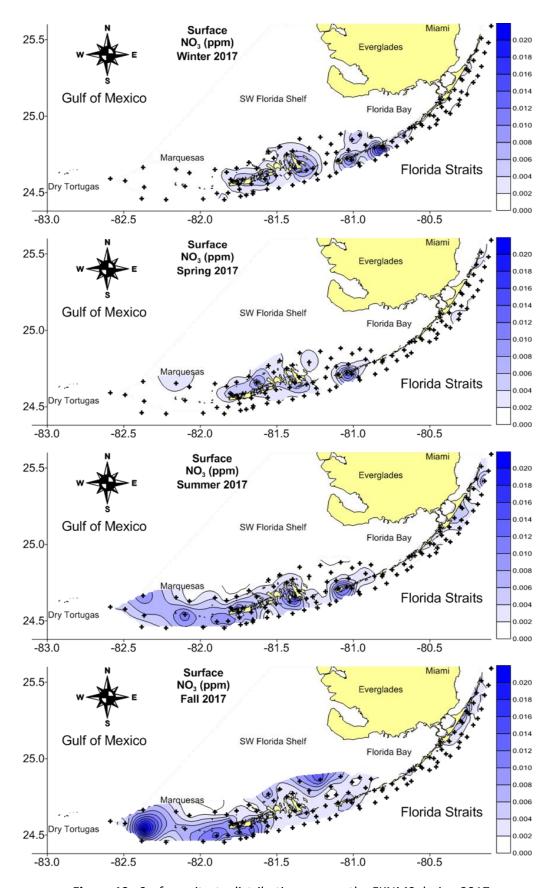


Figure 13. Surface nitrate distributions across the FKNMS during 2017.

Surface and bottom water concentrations are not always coincident. Interestingly, in many cases for 2017 and other years, we observe elevated NO₃⁻ in the bottom waters on the offshore reef tract (Fig. 14). We attribute this to regular "upwelling" (actually internal tidal bores) of deep water onto the reef tract (Leichter et al. 2003). This deep ocean water transport is a regular and persistent phenomenon which may deliver high nutrient waters to the offshore reef tract independent of any anthropogenic source. During the Summer & Fall 2017 sampling events, an extensive water mass offshore the Marquesas and Lower Keys exhibited relatively high NO₃⁻ concentrations in bottom waters. It is important to note that because of their shallowness, no bottom water samples are collected for nutrients in the Backcountry or Sluiceway regions. Therefore contour maps of bottom nutrient distributions do not reflect ambient conditions in those areas.

 NH_4^+ concentrations were distributed in a similar manner as NO_3^- with highest levels occurring in the Marquesas and Lower Keys (Fig. 15). NH_4^+ also showed additional similarities with NO_3^- in its spatial distribution, being lowest in the Upper Keys (except in the winter) and highest inshore relative to offshore. This pattern of decline offshore implies an onshore N source which is diluted with distance from land by low nutrient Atlantic Ocean waters. During the Summer & Fall 2017 sampling events, an extensive water mass offshore the Marquesas and Lower Keys exhibited relatively high NH_4^+ concentrations in bottom waters (Fig. 16).

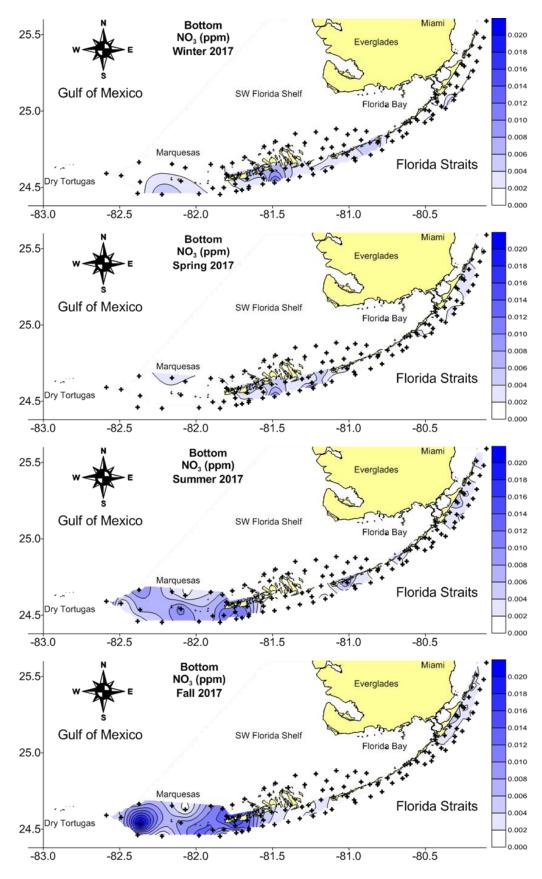


Figure 14. Bottom nitrate distributions across the FKNMS during 2017.

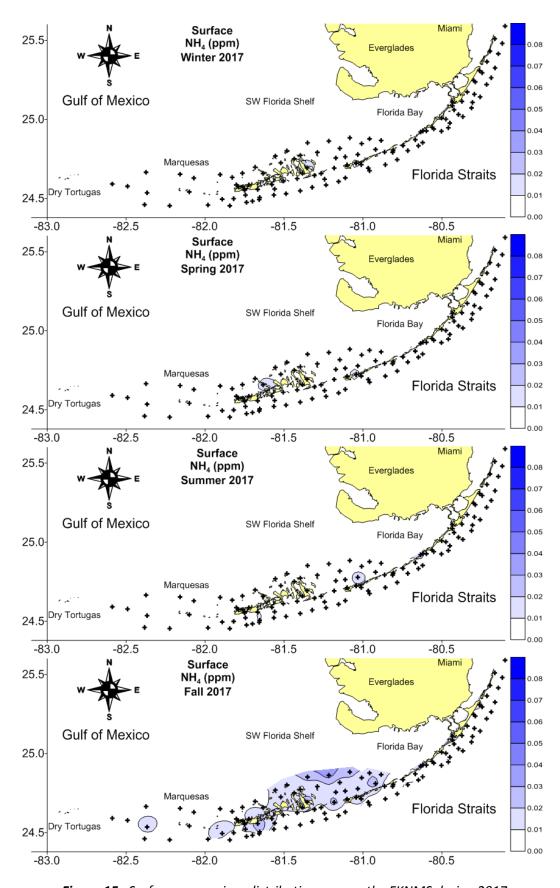


Figure 15. Surface ammonium distributions across the FKNMS during 2017.

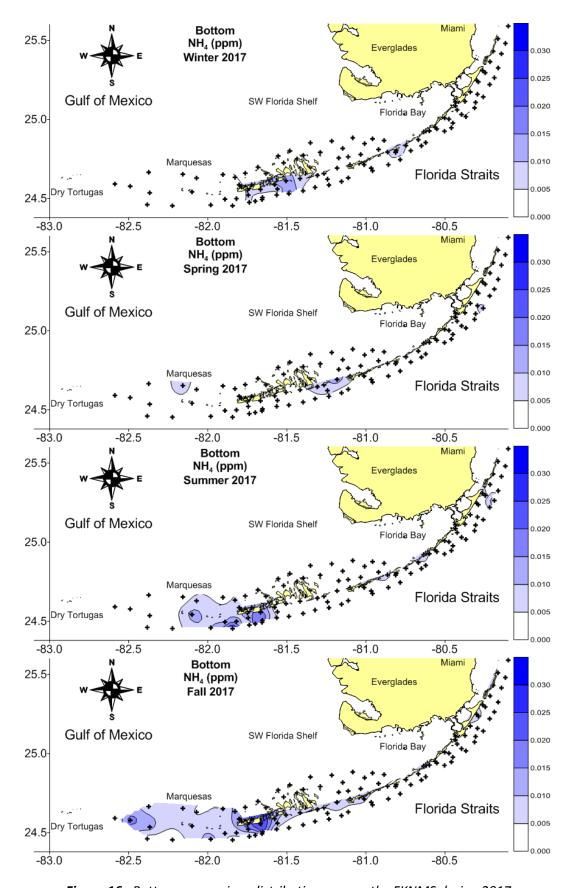


Figure 16. Bottom ammonium distributions across the FKNMS during 2017.

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 typically extends from the inshore waters of Whitewater Bay - Ten Thousand Islands mangrove complex out onto the Shelf and Tortugas. Gradients also extend 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). During 2017, highest TP concentrations occurred mostly along the northern boundary of the Sluiceway, and Marquesas (Fig 17).

Concentrations of TOC (Fig. 18) and TN (Fig. 19) are similar in pattern of distribution across the South Florida coastal hydroscape suggesting that most nitrogen is organic. We believe that deviations from this common pattern are due to differences in sources of dissolved organic matter. Our past data from this area showed that concentrations of TOC and TN increased from the 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). During Fall 2017, very high TOC concentrations were observed in the Marquesas coincident to high NO₃-, NH₄+, and TP. Interestingly, no elevated levels of TN were observed.

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. Strong offshore gradients in TOC and TN existed for all mainland Keys segments. The higher concentrations of TOC and TON in the inshore waters of the Keys may have a terrestrial source (anthropogenic) or may be derived from decomposition of weed-rack 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.

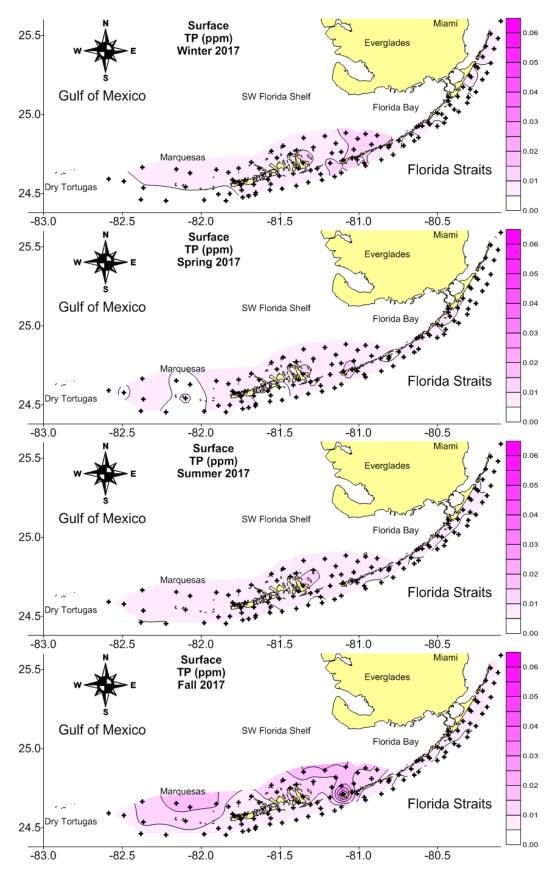


Figure 17. Distributions of surface total phosphorus across the FKNMS during 2017.

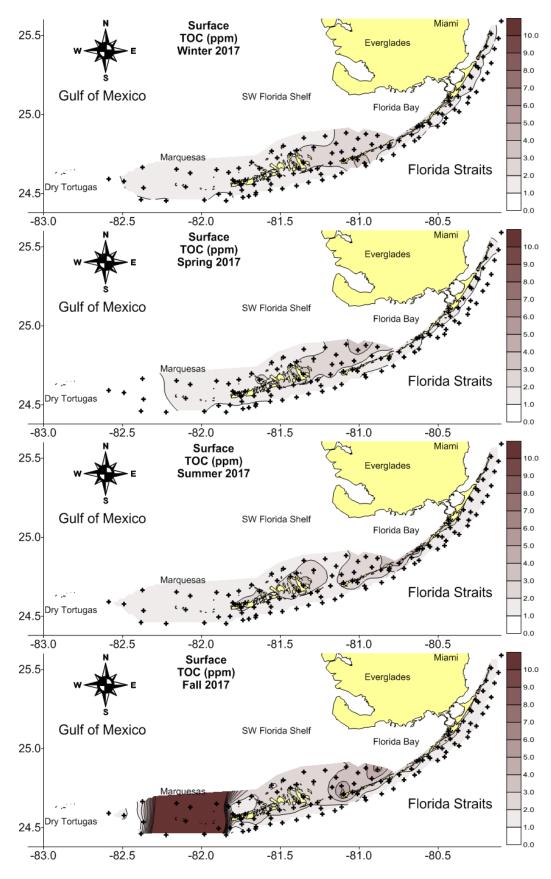


Figure 18. Distributions of surface total organic carbon across the FKNMS during 2017.

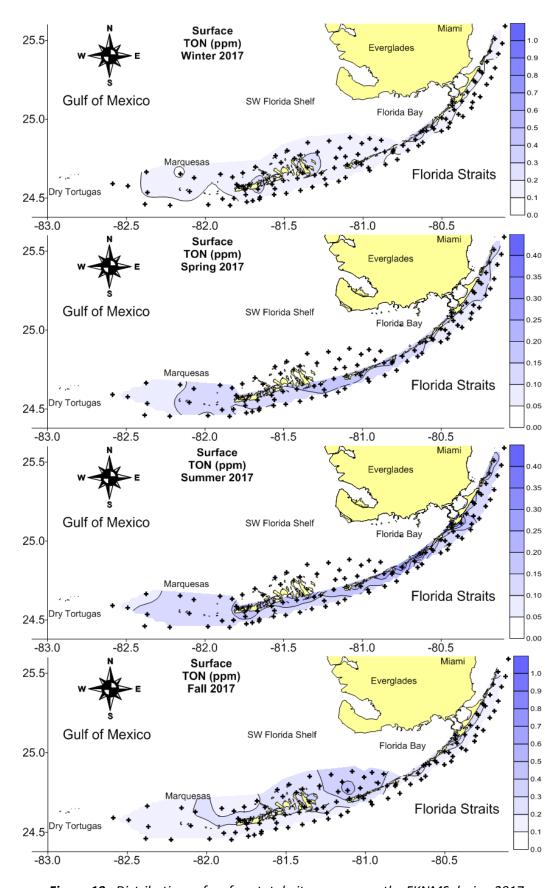


Figure 19. Distributions of surface total nitrogen across the FKNMS during 2017.

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, Northern Florida Bay, and the Ten Thousand Islands exhibited high levels of CHLA relative to the FKNMS. Also it showed that CHLA concentrations were typically higher in the Marquesas than in other areas of the FKNMS. When examined in context with the whole South Florida ecosystem, it is obvious that the Marquesas zone should be considered a continuum of the Shelf rather than a separate management entity. This shallow sandy area (often called the Quicksands) acts as a physical mixing zone between the Shelf and the Atlantic Ocean and is a highly productive area for other biota as well as it encompasses the historically rich Tortugas shrimping grounds. A CHLA concentration of 2 μ 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.

In 2017 highest CHLA values occurred mostly along the northern boundary of the Middle Keys, Lower Keys, and Marquesas suggesting an important contribution from the Shelf (Fig. 20). This contribution was especially large beginning in Summer and extending into the Fall.

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. Inshore and Hawk Channel CHLA concentrations among Middle Keys, Lower Keys and Tortugas sites were not significantly different. The recently installed SHORE stations show higher CHLA concentrations than those of LK, MD, UK and OFF stations underscoring the anthropogenic impact.

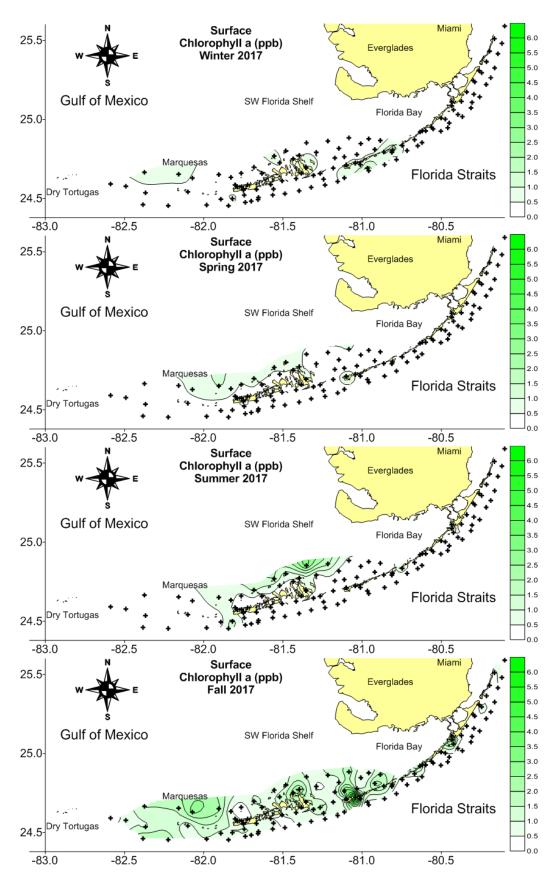


Figure 20. Distributions of surface chlorophyll a across the FKNMS during 2017.

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 21). The fine grained, low density carbonate sediments in this area are easily re-suspended, 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.

In 2017 highest turbidity values occurred mostly along the northern boundary of the Lower Keys, and Marquesas suggesting an important contribution from the Shelf (Fig. 21). This contribution was especially large in the Fall.

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 22). However, in Keys waters, CDOM (an important driver of water color and light penetration) may be a more prominent driver of light penetration. For 2017, highest K_d was observed mostly along the northern boundary of the Lower Keys, and Marquesas suggesting an important contribution from the Shelf (Fig. 22). This contribution was especially large in the Fall.

Both turbidity and K_d affect the amount of ambient light reaching the bottom (Fig. 23). For 2017, lowest bottom light was observed in the Marquesas during Fall sampling, suggesting an important contribution from the Shelf.

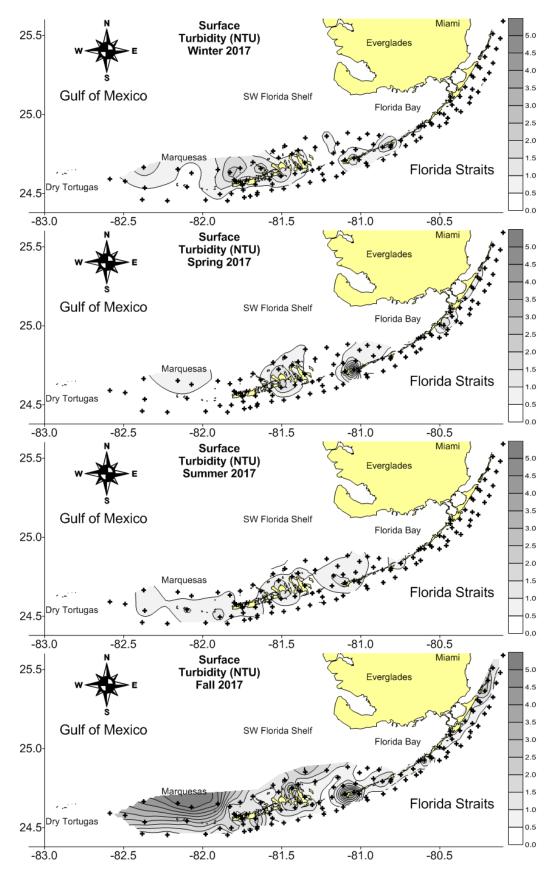


Figure 21. Distributions of surface turbidity across the FKNMS during 2017.

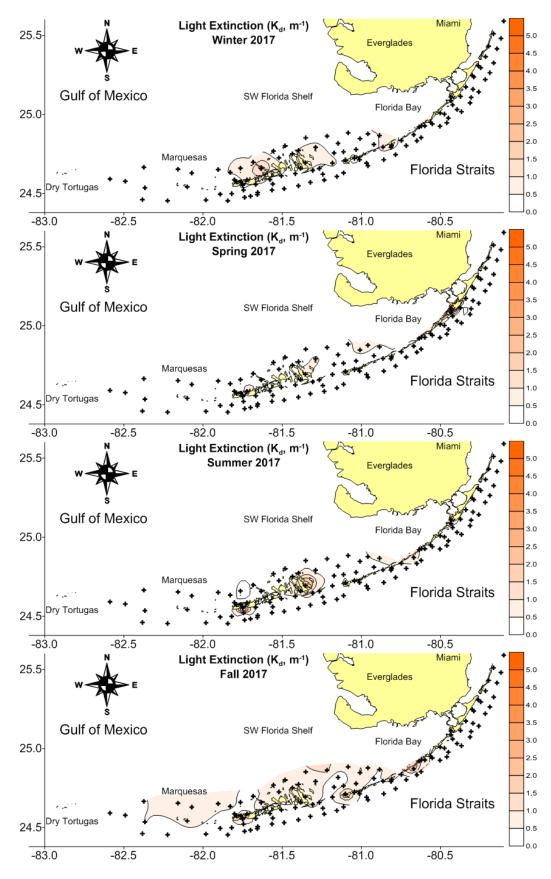


Figure 22. Distributions of light extinction across the FKNMS during 2017.

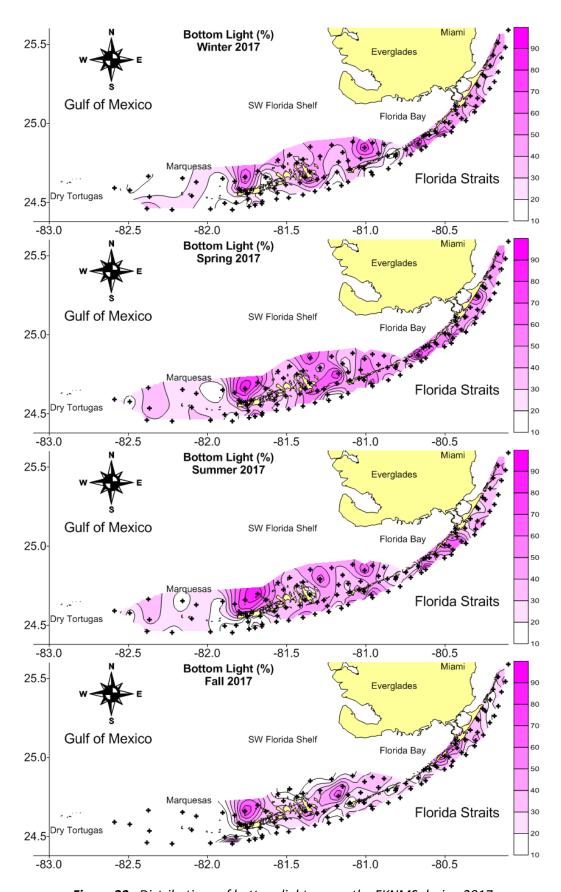


Figure 23. Distributions of bottom light across the FKNMS during 2017.

Surface SiO_2 concentrations exhibited a pattern similar to salinity (Fig. 24). 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 μ g l⁻¹ (Nelson and Dortch 1996), phytoplankton biomass on the Shelf (1-2 μ 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. 24). SiO_2 concentrations near the coast were elevated relative to the reef tract with higher concentrations occurring in the Lower and Middle Keys than the Upper Keys, where extensive wetlands as those of the John Pennekamp State Park separate urban developed areas from the Atlantic.

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. 25). 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.

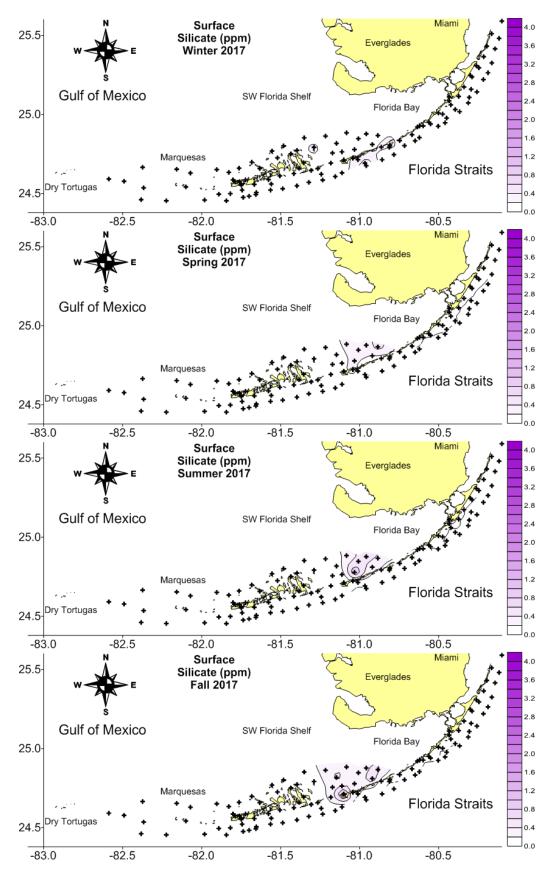


Figure 24. Distributions of surface silicate across the FKNMS during 2017.

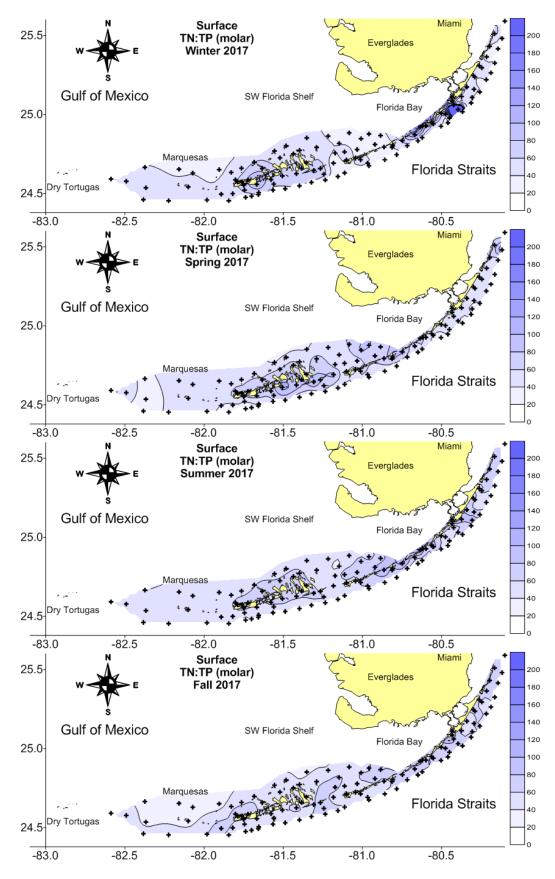


Figure 25. Distributions of surface TN:TP ratio across the FKNMS during FY2017.

3.5.Time Series Analysis

Clearly, there have been some 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 and method of analysis. Also, 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.

Time series analysis is limited to the window of observation and 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. Examples of trends can be seen to be monotonic (Fig. 26), episodically driven with no net trend (Fig. 27), and reversing or discontinuous with change point (Fig. 28).

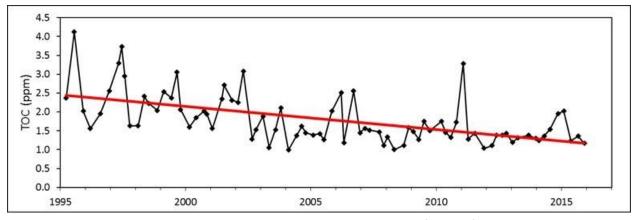


Figure 26. Monotonic trend in TOC at Carysfort Reef.

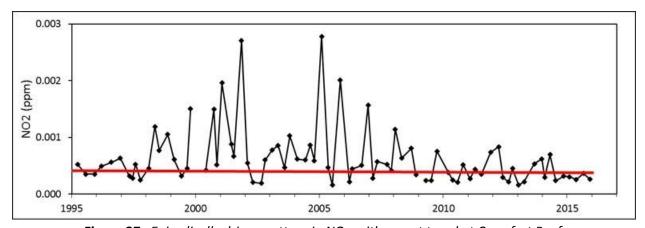


Figure 27. Episodically driven pattern in NO_2^- with no net trend at Carysfort Reef.

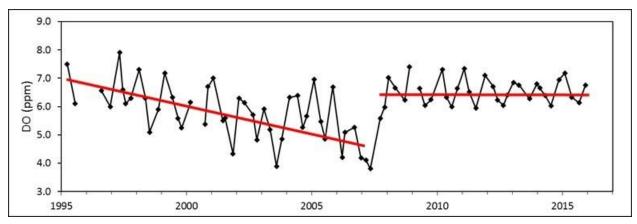


Figure 28. Discontinuous trend in DO at Carysfort Reef.

Therefore, linear regression approaches may not be optimal for long term time series influenced by fluctuating conditions or disturbance events. Instead, locally weighted regressions, such as LOESS, are especially useful for showing trend reversals and cycles in the time series (Fig 29).

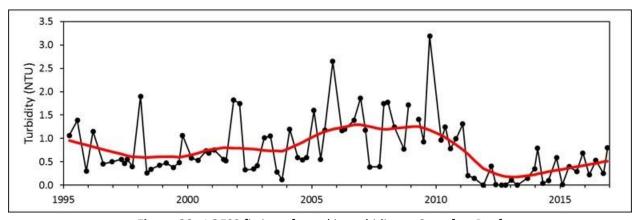


Figure 29. LOESS fitting of trend in turbidity at Carysfort Reef.

Sen slope regressions for each water quality variable were calculated for the 23 year period of record. Only those slopes having significant Mann-Kendall trends (p < 0.10) in ppm yr⁻¹, or as noted were reported. Some of the slopes were very small, so to get a better idea of change over the period of record, the annual slopes were multiplied by number of years sampled and plotted as contour maps of total change for 23 year period.

For the 23 year POR, all variables exhibited significant trends except for salinity and temperature. Surface DO increased at most sites the FKNMS (Fig. 30). Greatest increases in surface DO were generally observed on the Atlantic side of the Keys. Decreasing trends were observed in the Sluiceway areas closest to Florida Bay and north Backcountry sites.

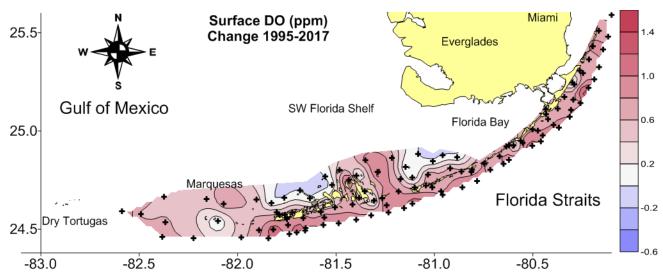


Figure 30. Total change in DO of surface waters for 23 year period calculated from significant trends.

By looking at the map, one might assume that DO has experienced a slow, incremental increase of between 0.5 and 1.5 ppm over the 23 year period. However, the LOESS regression of surface DO showed a small decline in most zones (Fig. 31) and then a rapid decline from 2004 to early 2007 with strong rebound in late 2007 to levels slightly higher than pre-2004. The DO drop seems to be linked to eight major hurricane impacts during 2004 (Charley, Frances, Ivan and Jeanne) and 2005 (Dennis, Katrina, Rita, and Wilma) whose effects lasted until 2007. Interestingly, DO in the Backcountry was relatively stable for the period of record and was not affected like other areas. Net DO changes over the 23-year period were small but significant; the range of internal variability during those impacted years was larger and significant reaching up to 2.75 ppm in Inshore, 2.5 ppm in Bay, 2 ppm in REEF and Marquesas, and 1.25 ppm in the Backcountry (Fig 31).

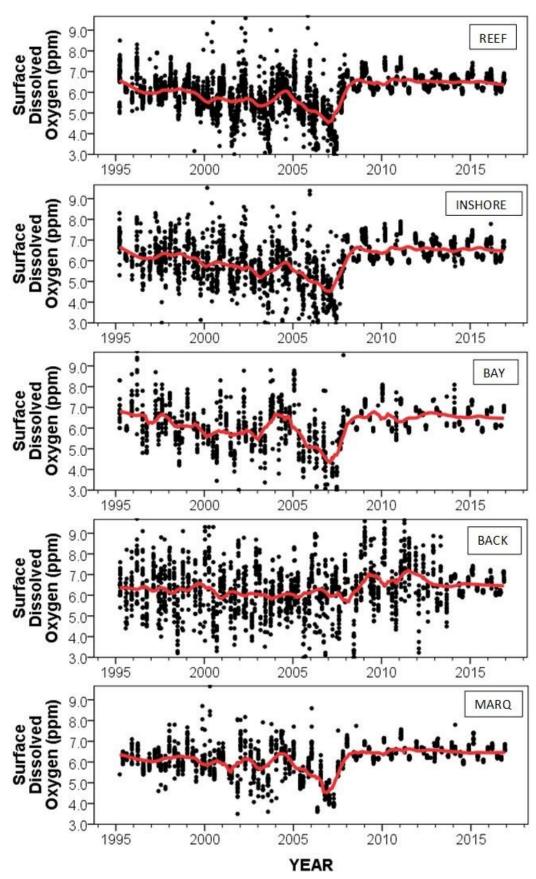


Figure 31. Time series of surface DO by segment showing depression 2005-07. The red line is LOESS fit.

Bottom DO trends showed a similar pattern as surface with more increased DO than surface sites (Fig. 32). Increased DO is beneficial for animal life. (Fig. 33).

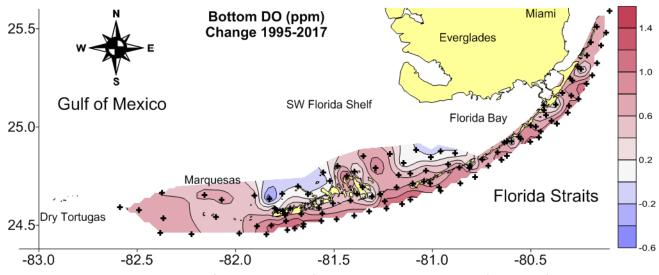


Figure 32. Total change in DO of bottom waters for 23 year period calculated from significant trends.

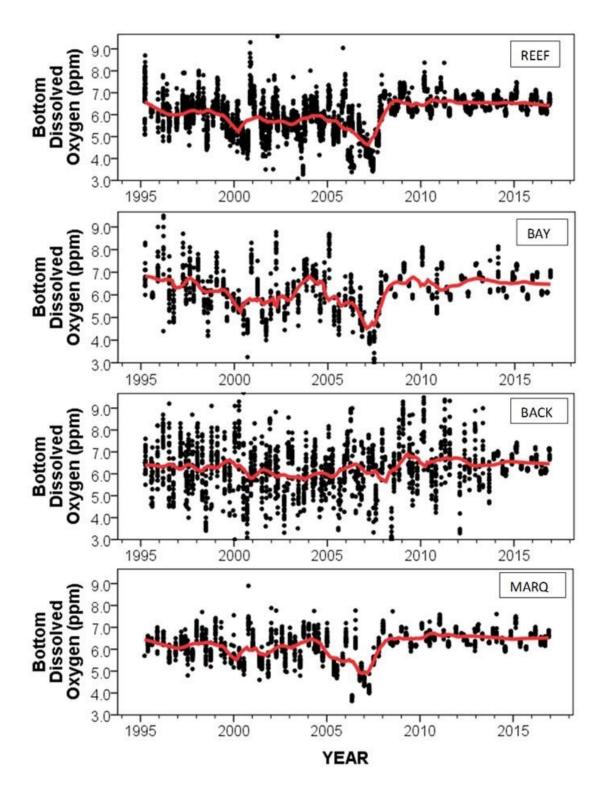


Figure 33. Time series of bottom DO by segment showing depression 2005-07. The red line is LOESS fit.

Water column turbidity (cloudiness) declined throughout the FKNMS (a beneficial result) during the 23 year period (Fig 34). There was no significant change in turbidity in bottom waters. The largest declines in turbidity occurred in western Florida Bay and Marquesas.

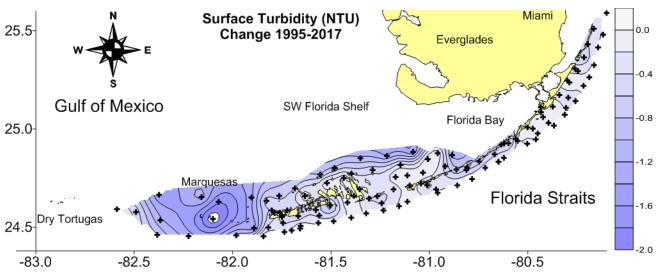


Figure 34. Total change in surface turbidity for 23 year period calculated from significant trends.

The time series plots of turbidity (Fig. 35) gives more information on the nature of the trend. It's clear that turbidity was relatively consistent for the period 1995-2005 and then increased during the 2005 hurricanes. Interestingly, the turbidity levels then returned to previous levels. Around 2010, turbidity across the region has dropped to lower levels than before the disturbance and have remained so.

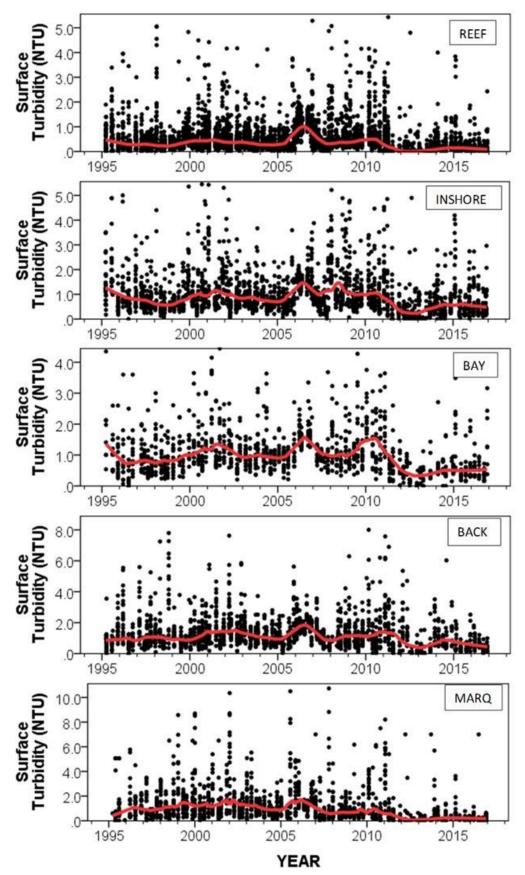


Figure 35. Time series of surface turbidity (NTU) by segment. The red line is LOESS fit.

Light extinction (K_d) also showed significant declining trend (Fig. 36) as a result of decreased turbidity. This tends to increase the amount of light reaching the bottom (I_0 in %). I_0 increased mostly at reef sites throughout the Keys (Fig. 37). More bottom light is beneficial to corals, seagrass, and algae. At the same time, the Backcountry area of the lower Keys experienced increases in K_d , decreases in I_0 and therefore less light on the bottom.

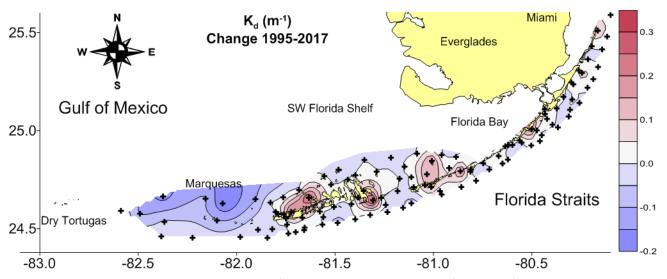


Figure 36. Total change in bottom I_o for 23 year period calculated from significant trends.

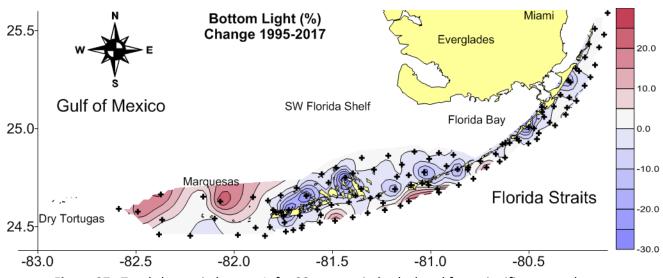


Figure 37. Total change in bottom I_0 for 23 year period calculated from significant trends.

The time series plots of K_d (Fig. 38) and I_o (Fig. 39) tell a similar story. There is a region-wide and sustained increase in I_o since 2004, except for Marquesas where values have remained about constant since 2007. Light reaching bottom I_o has oscillated widely, experiencing a strong decline in 1999-2000 and a sharp increase in 2001-2002, especially in REEF, Inshore and BAY sites. BACK sites experienced a significant drop from 2006 to 2008. Finally, MARQ sites increased markedly their I_o in 2011.

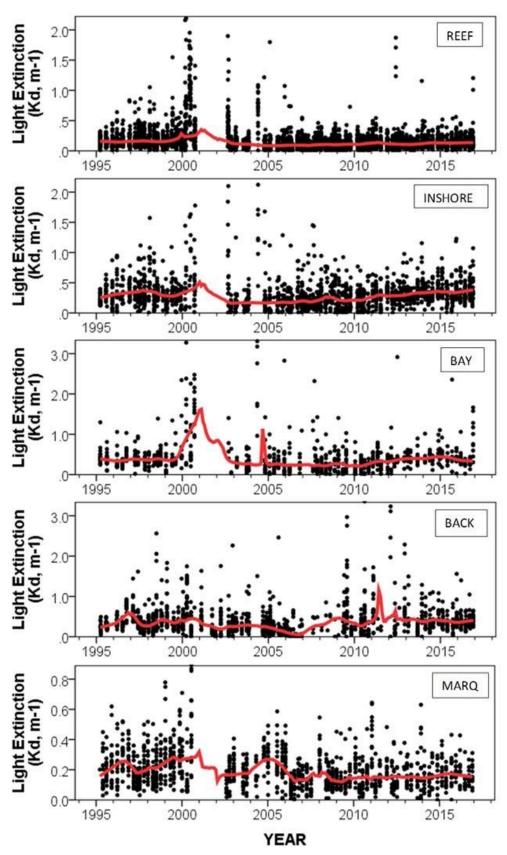


Figure 38. Time series of Light Extinction (K_d) by segment. The red line is LOESS fit.

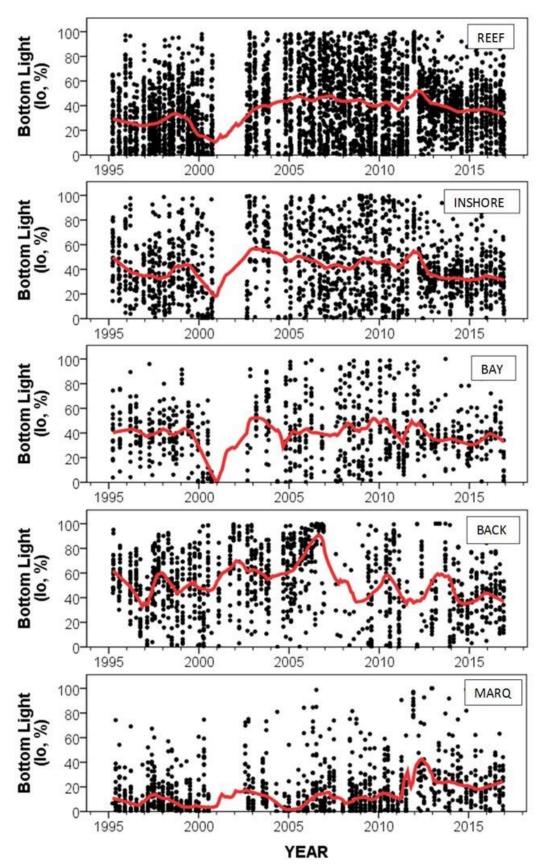


Figure 39. Time series of % of surface light reaching the bottom (I_0) by segment. The red line is LOESS fit.

Small but significant declining trends in TP were observed in most surface waters (Fig. 40). Small declining trend was observed offshore with small increases in the Sluiceway and inshore northern Keys.

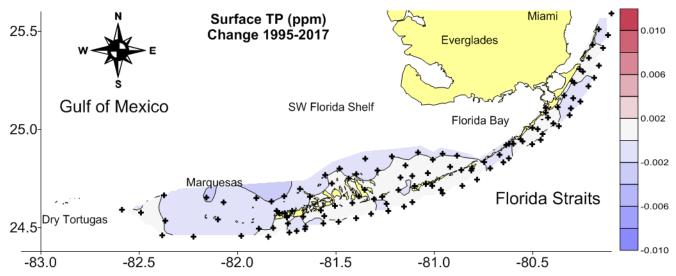


Figure 40. Total change in TP in surface waters for 23 year period calculated from significant trends.

The TP time series (Fig. 41) shows some slightly elevated time periods in the record, especially during 2000 and 2006-7 time period. As described for DO changes, TP positive deviations seems to be linked to major hurricane impacts during 1998-1999 and 2004-2005 whose effects lasted until 2000 and 2007 respectively. We believe the bay and land-based disturbance from hurricanes Mitch and Georges (1998) and Irene (1999) lasted until 2001, and those of Katrina-Rita-Wilma persistent until 2007. Otherwise, TP is consistently low (<0.01 ppm).

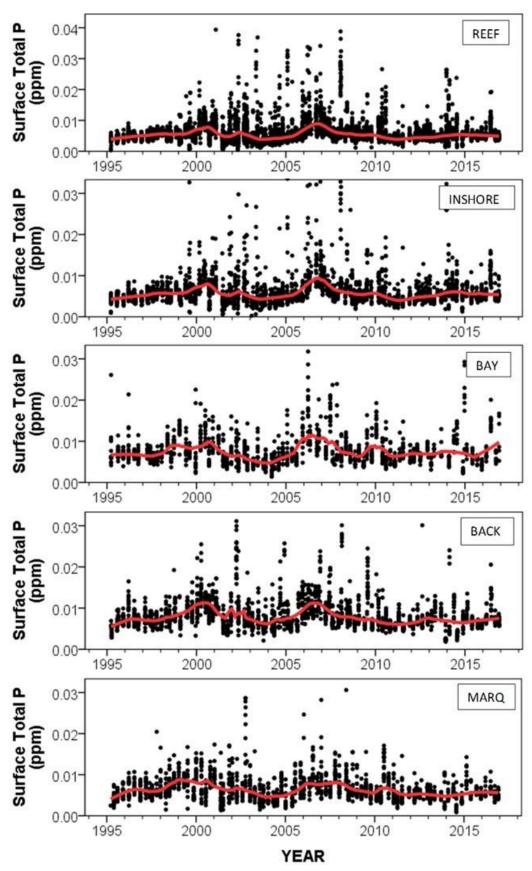


Figure 41. Time series of surface TP (ppm) by segment. The red line is LOESS fit.

Very small increases in SRP, up to 0.002 ppm over 23 years, were observed (Fig. 42). Concentrations of SRP are generally an order of magnitude lower than TP and usually below kinetic uptake threshold of phytoplankton, meaning that not all SRP is accessible to phytoplankton.

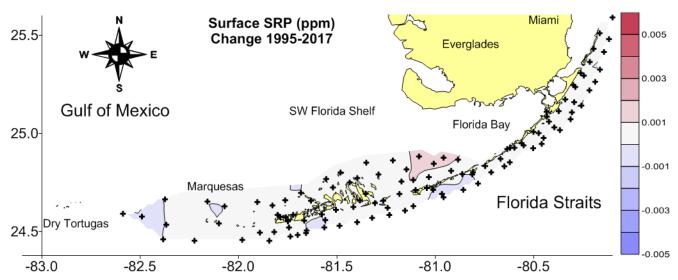


Figure 42. Total change in SRP in surface waters for 23 year period calculated from significant trends.

The SRP time series (Fig. 43) shows 2-3 year cyclical fluctuations in concentrations. However, the concentrations are very low and may not be significant biologically.

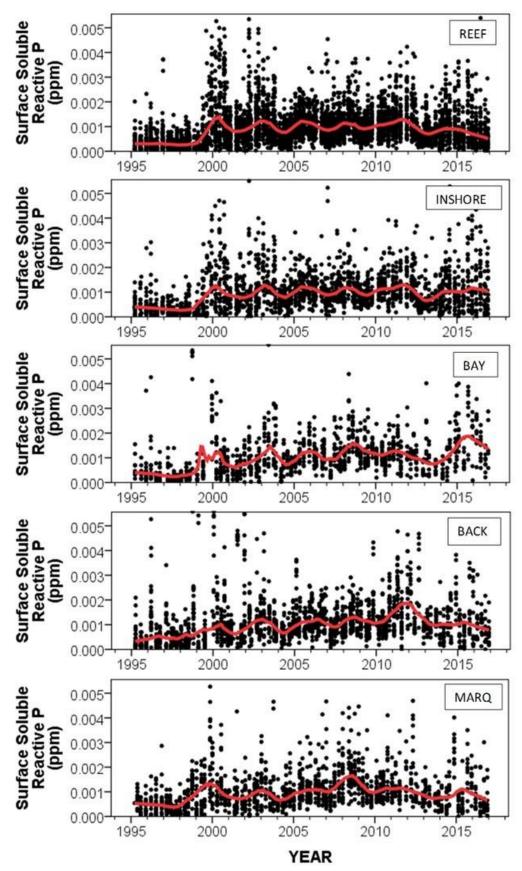


Figure 43. Time series of surface SRP (ppm) by segment. The red line is LOESS fit.

Nitrate showed very small declines over most of the FKNMS for the record (Fig. 44) as did NH_4^+ . (Fig. 45).

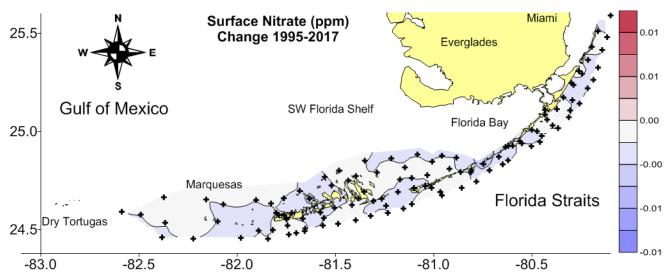


Figure 44. Total change in NO_3^- in surface waters for 23 year period calculated from significant trends.

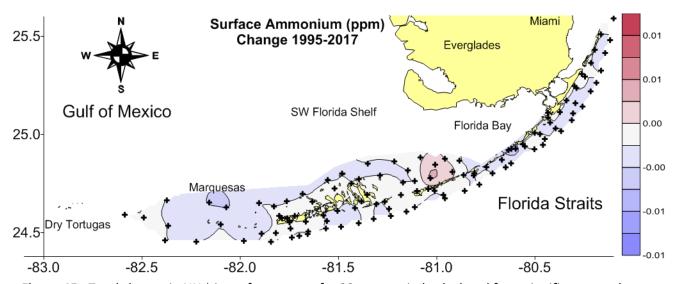


Figure 45. Total change in NH_4^+ in surface waters for 23 year period calculated from significant trends.

The NO_3^- time series (Fig. 46) was relatively consistent with a distinct elevation across the FKNMS during 2000 and smaller ones during 2003-4 and 2006-7. The 1999-2000 NO_x high coincides with elevated concentrations in Florida Bay, which have been linked to hurricane Irene impacts, exacerbated by extreme freshwater discharges (Briceño and Boyer 2013).

The NH₄⁺ time series was interesting as it showed large elevation in concentrations during 2006-7, the year following the Fall 2005 hurricane season (Fig. 47). We believe the land-based disturbance from Katrina-Rita-Wilma had a persistent effect on the FKNMS for the following two years. Interestingly, the effect in the Marquesas did not show up possibly as dampening due to Gulf of Mexico circulation.

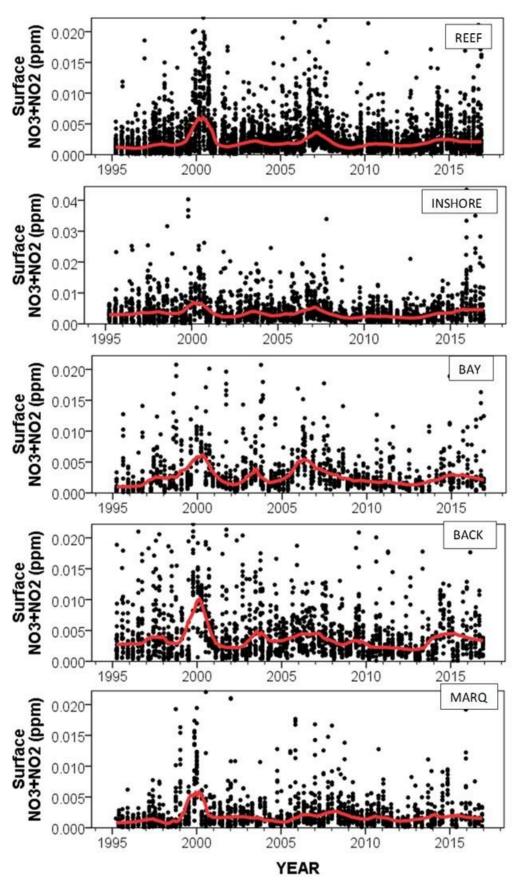


Figure 46. Time series of surface $NOx = NO_3^- + NO_2^-$ (ppm) by segment. The red line is LOESS fit.

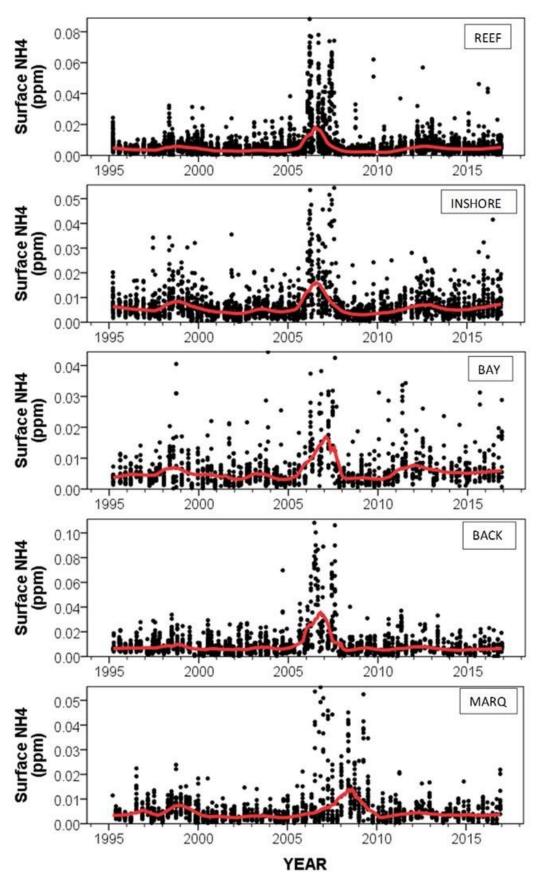


Figure 47. Time series of surface NH_4^+ (ppm) by segment. The red line is LOESS fit.

Total nitrogen continued to decline especially along the Keys and northern Marquesas (Fig. 48). Most of this is due to decline in the organic N fraction as it makes up ~96% of the TN pool.

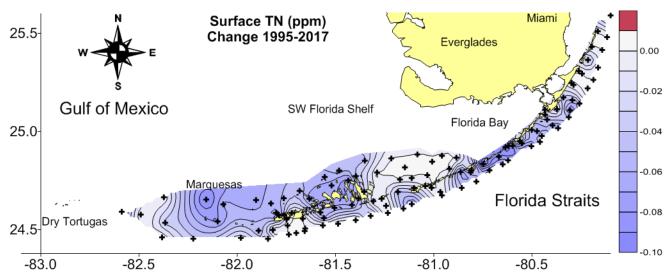


Figure 48. Total change in TN in surface waters for 23 year period calculated from significant trends.

The TN time series shows elevated concentrations across the region during 2003-4 and 2010 (Fig. 49). The long-term decline in TN is especially evident in inshore waters of the Keys.

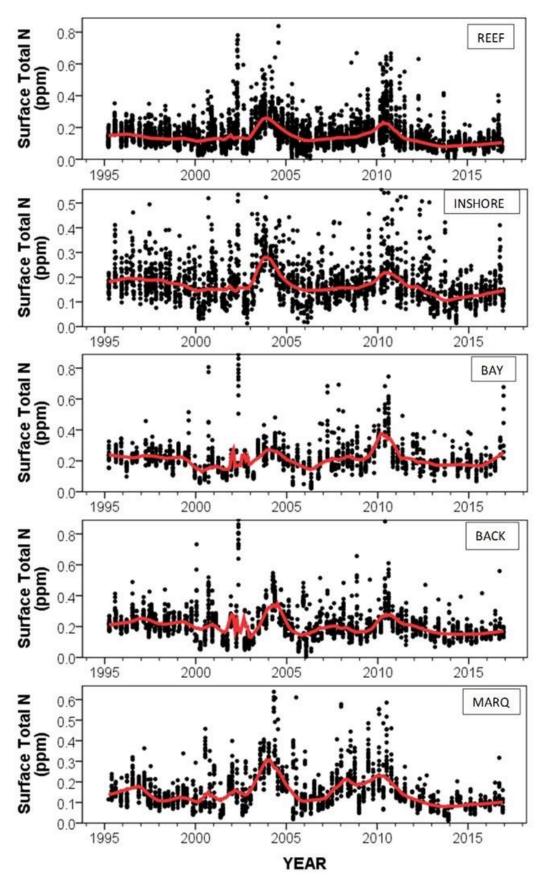


Figure 49. Time series of surface TN (ppm) by segment. The red line is LOESS fit.

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, Marquesas, and inshore (Fig. 50). 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.

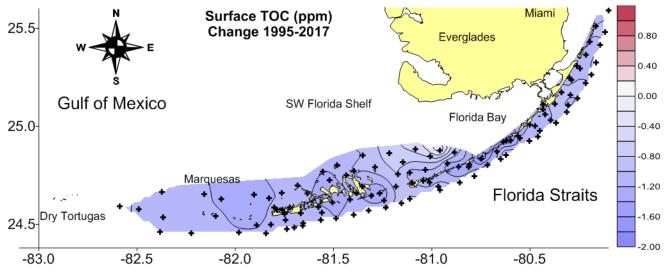


Figure 50. Total change in TOC in surface waters for 23 year period calculated from significant trends.

The TOC time series show relatively steep declines in the beginning of the time series with a leveling out around 2005 (Fig. 51). This declining trend has been observed also on Shelf, west coast mangrove estuaries and Florida Bay (Briceño and Boyer 2007), highlighting the importance of a regional contribution of organic carbon from the Everglades to Florida Bay and this, in turn, to the Florida Keys. Regier et al. (2016) found that dissolved organic carbon (DOC) fluxes from the Everglades were primarily controlled by hydrology but also by seasonality and long-term climate patterns (AMO) as well as episodic weather events. Lowest DOC concentrations in water coincide with extended droughts in 2007 and 2010-2011.

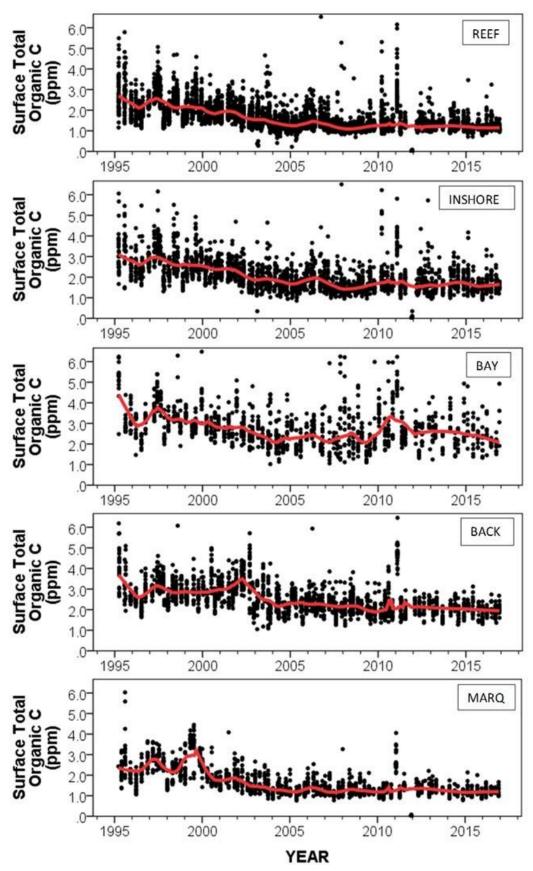


Figure 51. Time series of surface TOC (ppm) by segment. The red line is LOESS fit.

Silicate experience declines throughout the FKNMS except at sites in the Sluiceway adjacent to Florida Bay which showed increases (Fig. 52). We expect these increases are from a more Bay-wide trend but do not have data to show this. The SiO₂ time series shows small declines in the beginning with bump around 2010 for most regions (Fig. 53).

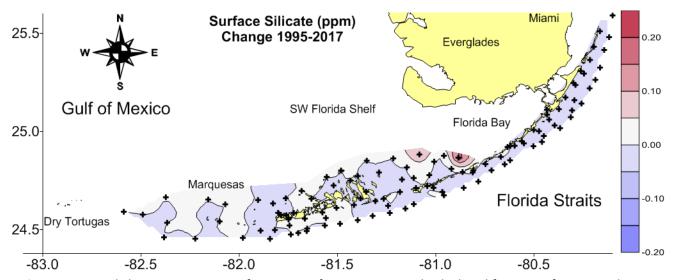


Figure 52. Total change in SiO2 in surface waters for 23 year period calculated from significant trends.

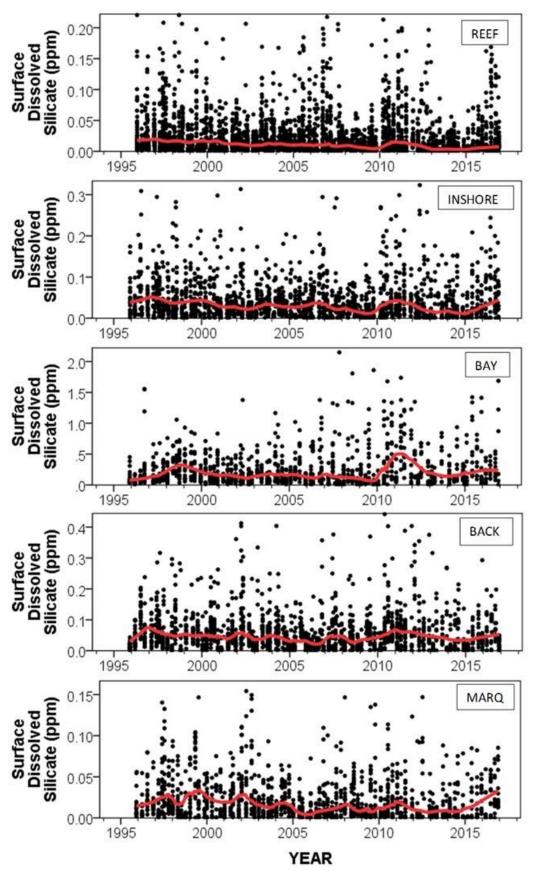


Figure 53. Time series of surface SiO_2 (ppm) by segment. The red line is LOESS fit.

Chla exhibited statistically significant long-term trends, both increasing and decreasing across the FKNMS (Fig. 54). Chla increased offshore Upper and Middle Keys as well as areas in the Sluiceway and north Backcountry. Large decline in Chla were observed in the Marquesas.

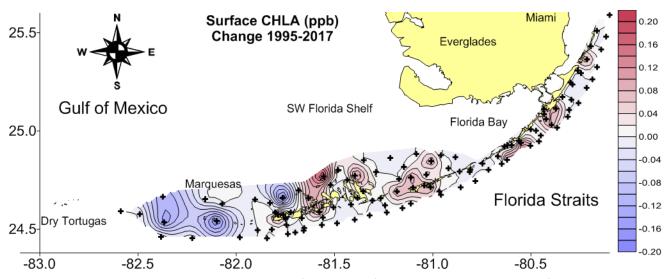


Figure 54. Total change in chlorophyll a in surface waters for 23 year period calculated from trends.

Additionally Chla did show a common perturbation marked by elevated Chla concentrations occurring during 1999-2000, coincident with peaks in NOx, especially NO₃-, and SRP (Fig. 55). Additionally, similar events occur in Marquesas during 2001-2002 and 2005-2006

Surface Salinity did not exhibit any long-term trends. Nonetheless, salinity time series shows relative difference in variability across regions (Fig. 56). Salinity on the Reef and Inshore areas was most consistent. Largest variations occurred in the Bay and Backcountry, areas that are most influenced by land sources and because of their shallow waters subjected to high evaporation rates causing high salinity or heavy rain causing salinity drops. The Backcountry displays salinity cycles lasting 4-5 years. Notice the large depression in salinity in the Marquesas during 2005-7. We believe this is due to legacy of 2005 hurricane season which affected salinity in the Gulf of Mexico for an extended period.

Temperature did not exhibit a significant long-term trend but the time series shows relative difference in variability across regions (Fig. 57). The time series also shows that the most variability occurs in the shallowest areas such as the Backcountry and Bay.

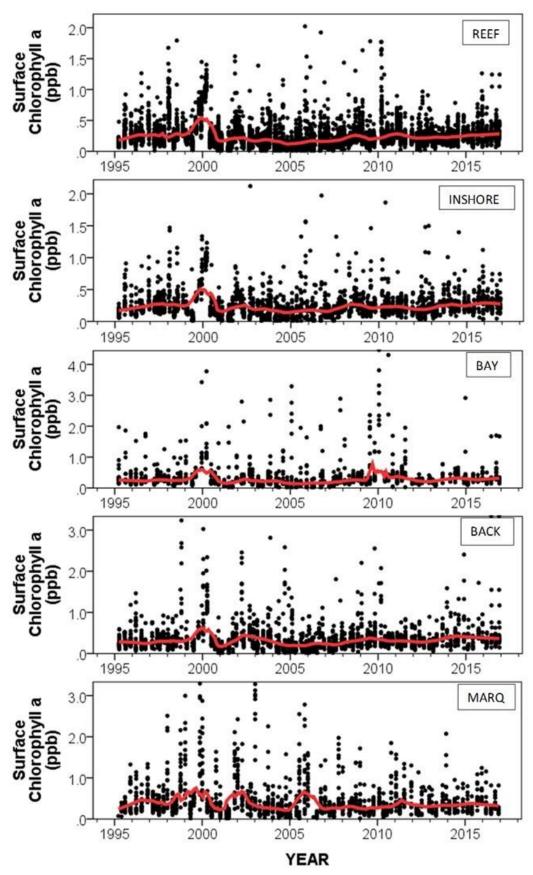


Figure 55. Time series of surface Chlorophyll a (ppb) by segment. The red line is LOESS fit.

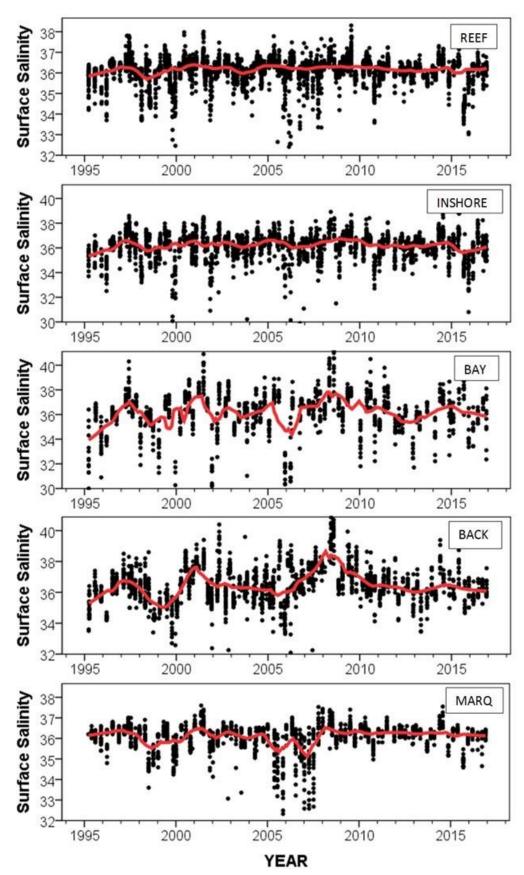


Figure 56. Time series of surface Salinity by segment. The red line is LOESS fit.

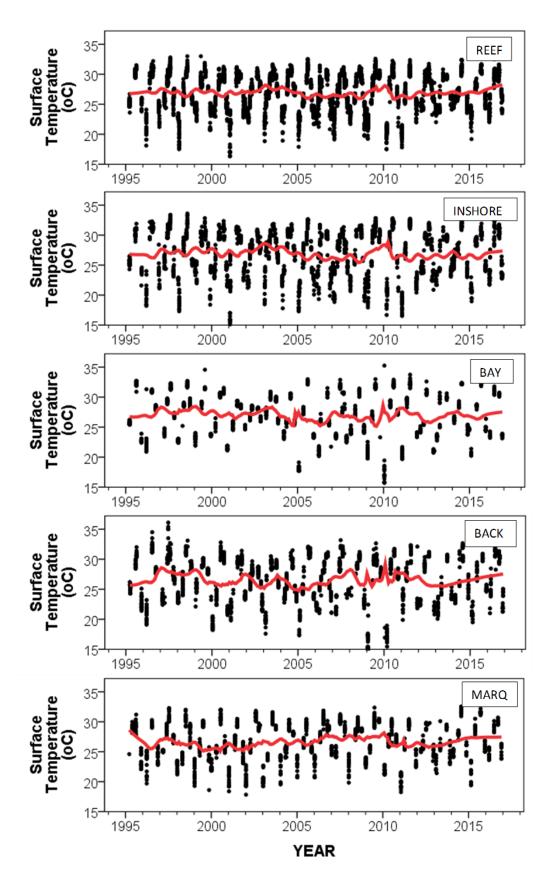


Figure 57. Time series of surface Temperature (°C) by segment. The red line is LOESS fit.

4. Strategic Targets

The EPA developed Strategic Targets for the Water Quality Monitoring Project which state that beginning in 2008, to annually maintain the overall water quality of the near shore and coastal waters of the FKNMS according to 2005 baseline. For reef sites, chlorophyll α should be less than or equal to 0.2 micrograms/I 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 μ M (0.010 mg I⁻¹) and total phosphorus should be less than or equal to 0.2 μ M (0.0077 mg I⁻¹). Table 3 shows the number of sites and percentage of total sites exceeding these Strategic Targets for the period of record to 2017.

Table 3: EPA WQPP Water Quality Targets derived from 1995-2005 Baseline

For reef stations, chlorophyll less than or equal to 0.35 micrograms liter⁻¹ (ug l⁻¹) and vertical attenuation coefficient for downward irradiance (K_d , i.e., light attenuation) less than or equal to 0.20 per meter; for all stations in the FKNMS, dissolved inorganic nitrogen less than or equal to 0.75 μ M and total phosphorus less than or equal to 0.25 μ M; water quality within these limits is considered essential to promote coral growth and overall health. The number of samples and percentage 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				
	REEF Stations		All Stations (excluding SHORE sites)	
Year	CHLA ≤ 0.35 μg l ⁻¹	K _d ≤ 0.20 m ⁻¹	DIN ≤ 0.75 μM	TP ≤ 0.25 μM
			(0.010 mg l ⁻¹)	(0.008 mg l ⁻¹)
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%)	813 of 1,012 (80.3 %)	911 of 1,013 (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 %)
2014	141 of 172 (82.0%)	133 of 172 (77.3%)	426 of 690 (61.7%)	540 of 690 (78.3%)
2015	122 of 172 (70.9%)	135 of 172 (78.5%)	487 of 688 (70.8%)	613 of 688 (89.1%)
2016	131 of 172 (76.2%)	129 of 170 (75.9%)	427 of 687 (62.2%)	549 of 688 (79.8%)
2017	106 of 172 (61.6%)	120 of 170 (70.6%)	440 of 575 (76.5 %)	581 of 683 (85.1 %)

5. 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 that 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. 58).

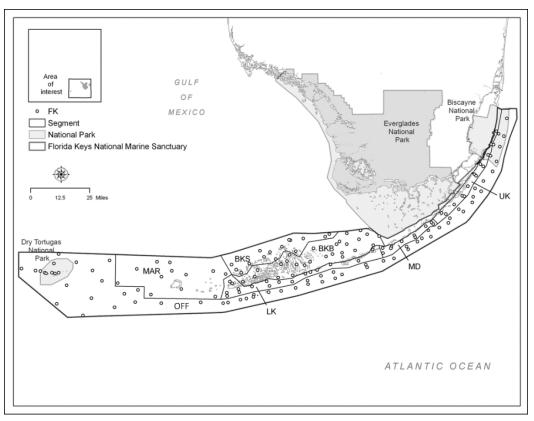


Figure 58. Map of FKNMS showing segments derived from Factor and Cluster Analysis of biogeochemical data: OFF=Offshore; MAR=Marquesas; BKS=Back Shelf; BKB= Back Bay; LK= Lower Keys; MK= Middle Keys; UK= Upper Keys

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 <u>Eight Maps of FL Marine Nutrient Regions</u>, 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 of EPA in March 2013 as Implementation of EPA in March 2013 as <a href="https://www.flrules.org/Gateway/reference.asp?No=R

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.

6. Acknowledgements

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