2018 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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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. 2018 and includes data from 94 quarterly sampling events within the FKNMS (24 years).

Field parameters measured at each station (surface and bottom at most sites) include salinity (practical salinity scale), temperature (°C), 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 (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺), and soluble reactive phosphorus (SRP). Total unfiltered concentrations include those of nitrogen (TN), organic carbon (TOC), phosphorus (TP), silicate (SiO₂) and chlorophyll *a* (CHLA, μ g l⁻¹). All variables are reported in ppm (mg l⁻¹) unless otherwise noted.

The EPA developed Strategic Targets for the Water Quality Monitoring Project (SP-47) which state that beginning in 2008 through 2018, they shall annually maintain the overall water quality of the near shore and coastal waters of the FKNMS according to 2005 baseline. For reef sites, chlorophyll *a* should be less than or equal to 0.35 µg l⁻¹ and the vertical attenuation coefficient for downward irradiance (K_d, i.e., light attenuation) should be less than or equal to 0.20 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 0.25 µM (0.0077 ppm). Table 1 shows the number of sites and percentage of total sites exceeding these Strategic Targets for 2018.

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		K _d ≤ 0.20 m ⁻¹	DIN ≤ 0.75 μM	TP ≤ 0.25 μM		
	CHLA ≤ 0.35 μg I		(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 %)		
2018	92 of 170 (54.1%)	108 of 152 (71.7%)	558 of 689 (81.0 %)	573 of 689 (82.3 %)		

Trend Analysis – 24 years

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



Water column turbidity (cloudiness) declined throughout the FKNMS during the 24 year period (beneficial trend). Some change in turbidity also occurred in bottom waters (not shown). The largest declines in turbidity occurred in northern bayside waters and the Marquesas (Fig iii).



Decreased turbidity influenced light extinction (K_d) through the water column (Fig. iv) and inversely affected the percent of surface light (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 with corresponding decreases in bottom light, but were not the result of increased turbidity (Fig. iii).



Significant Keys-wide trends in NH_4^+ , NO_3^- , TP, and SRP were detected but were very minor (not shown). However, chlorophyll *a* exhibited variable trends, declining in the Marquesas while increasing in Backcountry, Sluiceway, and some Keys areas (Fig. vi). The absolute changes were relatively small compared to normal concentrations (5-20% increase over 24 yr), but should be watched for continued trends.



Figure vi. Total change in CHLA in surface waters for 24 year period.

The largest sustained monotonic trends have been the decline in surface total organic carbon and nitrogen, especially in the Backcountry and the Marquesas (Fig. vii & viii). This is part of a regional trend in TOC observed in earlier monitoring 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 negatively affects light penetration, but could also be an indication of decreased terrestrial primary production and export. It might also be characteristic of a Gulf-wide trends



Figure vii. Total change in TOC in surface waters for 24 year period.



Figure viii. Total change in TON in surface waters for 24 year period.

The DIN:TP ratio, a way to assess phytoplankton nutrient limitation, has also declined overall (Fig. ix), especially in Upper and Lower Keys. This implies that primary production in those areas may be becoming more N limited. 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 DIN: TP ratio in surface waters for 24 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 (<u>http://serc.fiu.edu/wqmnetwork/</u>) where data and reports from the FKNMS are integrated with other 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 may significantly effect 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 by both external nutrient transport and internal nutrient loading sources (Gibson et al. 2008). Therefore, the geographical extent of the FKNMS as a political/regulatory boundary should not be thought of in any way 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 discontinued in 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 challenging 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 in 2011 (Fig. 3), it still provides a unique opportunity to explore the spatial component of water quality variability in the FKNMS, but decreases the ability 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 2018 sampling.

2. Methods

2.1. Field Sampling

The period of record of this study was from March 1995 to December 2018, which included 94 quarterly sampling events. For this year, field measurements and grab samples were collected from 112 fixed stations within the FKNMS boundary (Fig. 3). 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 (m), 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 $\Delta \sigma_t$ (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 µm. 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). 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 (NH₄⁺), nitrate+nitrite (NO_x), nitrite (NO₂⁻), total nitrogen (TN), soluble reactive phosphorus (SRP), total phosphorus (TP), total organic carbon (TOC), total silicate (SiO₂), chlorophyll *a* (CHLA, μ 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

 NH_4^+ was analyzed by the indophenol method (Koroleff 1983). NO_2^- was analyzed using the diazo method and NO_x was measured as nitrite after cadmium reduction (Grassoff 1983a,b). The ascorbic acid/molybdate method was used to determine SRP (Murphy and Riley 1962). High temperature combustion and high temperature digestion were used to measure TN (Frankovich and Jones 1998; Walsh 1989) and TP (Solórzano and Sharp 1980), respectively. TOC was determined using the high temperature combustion method of Sugimura and Suzuki (1988). Silicate was measured using the heteropoly blue method (APHA 1995). Samples were analyzed for CHLA content by spectrofluorometry of acetone extracts (Yentsch and Menzel 1963). Protocols are presented in EPA (1993) and elsewhere as noted. All elemental ratios discussed were calculated on a molar basis. DO saturation in the water column (DO_{sat} as %) was calculated using the equations of Garcia and Gordon (1992). Some parameters were not measured directly but calculated by difference. Nitrate (NO_3^-) was calculated as $NO_x - NO_2^-$; total dissolved inorganic nitrogen (DIN) as $NO_x + NH_4^+$, and total organic nitrogen (TON) as TN - DIN. All variables are reported in ppm (mg l⁻¹) unless otherwise noted.

2.3. 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 (SURFER, Golden Software) of specific water quality variables. Kriging was used 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.

Because quarterly field surveys occurred over more than one month period, we define the quarterly surveys as: Winter (Jan.-Mar.), Spring (Apr.-Jun.), Summer (Jul.-Sep.), and Fall (Oct.-Dec.).

2.4. 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 24 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. Trend maps were drawn using all stations regardless whether trends were significant (p < 0.10). In an effort to show trend impact, trends are reported as the <u>total change</u> over the 24 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 were stratified by segment (see above) and 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, except for SHORE sites where 20% was used because of shorter period of record.

3. Results

3.1. Overall Water Quality of the FKNMS in 2018

Summary statistics for all water quality variables from calendar year 2018 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 25.9 °C and salinity of 36.1; 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 0.0090 mg l⁻¹, respectively. NH_4^+ was the dominant DIN species in almost all of the samples (72%). However, DIN comprised a small fraction (7.3%) of the TN pool (0.108 mg l⁻¹) with TON being the bulk (median 0.098 mg l⁻¹). SRP concentrations were low (median 0.0007 mg l⁻¹) and comprised only 13.7% of the TP pool (0.0051 mg l⁻¹). CHLA concentrations were also low overall (median 0.24 µg l⁻¹), but ranged from 0.04 to 5.13 µg l⁻¹. Median TOC was 1.43 mg l⁻¹; a value higher than open ocean levels but consistent with coastal areas.

For 2018, median turbidity returned to previously low levels (0.065 NTU) resulting in low K_d (0.20 m⁻¹). Overall, 38.1% of incident light (I_o) reached the bottom, which was up from last year's 34.1%. 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.

The recently implemented stations very close to shore (within 500 m from 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 end as compared to the rest of the sites. Hence, we have grouped these ten stations as an additional class (SHORE), not for analytical purposes at this time, but for later comparison and exploration of human impacts on water quality.

3.2.2018 Spatial Analysis

Water quality is a subjective measure of ecosystem well-being. Aside from the physicalchemical composition of the water there is also a human perceptual element which varies according to our intents for use (Kruczyinski and McManus 2002). Distinguishing internal from external sources of nutrients in the FKNMS is a difficult task. The finer discrimination of internal sources into natural and anthropogenic inputs is even more difficult. Most of the important anthropogenic inputs are regulated and most likely controlled by management activities, however, recent studies have shown that nutrients from shallow sewage injection wells may be leaking into nearshore surface waters (Corbett et al. 1999; 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

Table 1. Summary statistics for water quality variables measured in the FKNMS for calendar year 2018 summarized by sampling depth as number of samples (n), minimum value (Min.), maximum value (Max.), and median value.

Variable	Depth	n	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
DIN	Surface	448	0.0014	0.1103	0.0079
(mg l⁻¹)	Bottom	282	0.0018	0.0434	0.0072
TON	Surface	448	0.0014	0.4947	0.0984
(mg l⁻¹)	Bottom	282	0.0231	0.4596	0.0696
ТР	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
тос	Surface	448	0.932	6.877	1.429
(mg l ⁻¹)	Bottom	282	0.962	4.146	1.236
SiO2	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 (m⁻¹)		415	0.001	4.314	0.204
TN:TP	Surface	448	12.7	228.8	42.6
DIN:TP	Surface	448	0.47	6.10	1.55
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
$\Delta \sigma_{ m t}$ (kg m ⁻³)		448	-24.702	1.030	0.010

to have more than just local impacts (Fig. 4). 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.

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.

All these forces have large influence on other water quality variables, such as DO (Fig. 5). Lowest DO concentrations tend to develop inside the Backcountry during warmest months.



Figure 4. Surface salinity distributions across the FKNMS during 2018; Winter being Jan.-Mar., etc.



Figure 5. Surface dissolved oxygen distributions across the FKNMS during 2018.

In many situations, independent water masses may be distinguished by difference in density (sigma-t or σ_t) between surface and bottom (Fig. 6). 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 $\Delta \sigma_t$ are widespread on the Atlantic side of the Keys during winter and spring, except south of Islamorada. Marquesas waters displayed high $\Delta \sigma_t$ in winter, spring and summer, and values are high year around in the Lower Keys (Fig 6).



Figure 6. Surface and bottom density differences ($\Delta \sigma_t$) across the FKNMS during 2018.

Visualization of spatial patterns of DIN concentrations over South Florida waters provides an extended view of source gradients over the region (Fig. 7-10). The oceanside transects off the uninhabited Upper Keys (off Biscayne Bay) exhibited the lowest alongshore NO_3^- compared to the Middle and Lower Keys (Fig. 7). 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 earlier analysis.

A distinct intensification of NO_3^- occurs in the Backcountry region. 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, water residence time, benthic N_2 fixation, and most importantly, sponge-mediated benthic flux (Hoer et al. 2018).

Part of this increase may due to local sources of NO₃⁻, i.e. septic systems and stormwater runoff around Big Pine Key (Lapointe and Clark 1992). However, there are areas that also exhibit high NO₃⁻ which are uninhabited by man, which rules out the premise of septic systems being the only source of NO₃⁻ in this area. The Backcountry area is very shallow (~0.5 m) and hydraulically isolated from the SW Shelf and Atlantic Ocean which results in its having a relatively long water residence time. However, 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, assuming this is due to evaporation would result in a concentration effect of only 5-6%. Additionally, NO₃⁻ concentration usually declines for salinities above ~35.3 region-wide. Benthic N₂ fixation may also contribute some NH₄⁺to the Backcountry but much of this is used by seagrass to balance their N demand (Capone & Taylor 1980).

Sponge-mediated benthic flux may be the most significant influence on water quality in the Backcountry. Hoer et al. (2018, in review) found sponge population densities in Florida Bay ranged from 0.08 to 21 individuals m⁻² with biomass as high as 4.4 L sponge m⁻². They estimated an average DIN contribution from sponge biomass of 8.3 mg L⁻¹ N m⁻² d⁻¹, with peak N fluxes of 49.0 mg L⁻¹ N m⁻² d⁻¹. The Backcountry exhibits a similar sponge density (Boyer et al. 2005) therefore, we expect that benthic fluxes might be of similar magnitude in this region.

Surface and bottom water concentrations are not always coincident. Interestingly, in many years (but not 2018), we observed elevated NO₃⁻ in the bottom waters on the offshore reef tract (Fig. 8). This has been attributed to "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 can deliver high nutrient waters to the offshore reef tract independent of any anthropogenic source. During the winter and spring 2018 sampling events, an extensive water mass offshore the Marquesas and Lower Keys exhibited relatively high NO₃⁻ concentrations in bottom waters. This followed similar conditions observed in summer and fall of 2017 (Briceño & Boyer 2018). It is important to note that because of their shallowness, <u>no</u> 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.

NH₄⁺ concentrations were distributed in a similar manner as NO₃⁻ with highest levels occurring in the Marquesas and Lower Keys (Fig. 9). NH₄⁺ also showed additional similarities with NO₃⁻ in its spatial distribution, being lowest in the Upper Keys and highest inshore relative to offshore and in the Backcountry. This pattern of decline offshore implies an onshore N source which is diluted with distance from land by low nutrient Atlantic Ocean waters. Similar to NO₃⁻, during the spring 2018 sampling event, an extensive bottom water mass offshore the Marquesas and Lower Keys exhibited relatively high NH₄⁺ concentrations (Fig. 10).



Figure 7. Surface nitrate distributions across the FKNMS during 2018.



Figure 8. Bottom nitrate distributions across the FKNMS during 2018.



Figure 9. Surface ammonium distributions across the FKNMS during 2018.



Figure 10. Bottom ammonium distributions across the FKNMS during 2018.

Spatial patterns in TP in South Florida coastal waters are strongly driven by 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 usually 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 2018, highest TP concentrations occurred mostly along the northern boundary of the Sluiceway, and Marquesas (Fig 11). Bottom TP was generally less than 0.01 ppm (Fig 12).



Figure 11. Distributions of surface total phosphorus across the FKNMS during 2018.



Figure 12. Distributions of bottom total phosphorus across the FKNMS during 2018.

Concentrations of TOC (Fig. 13 & 14) and TN (Fig. 15 & 16) 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).

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 13. Distributions of surface total organic carbon across the FKNMS during 2018.



Figure 14. Distributions of surface total organic carbon across the FKNMS during 2018.



Figure 15. Distributions of surface total nitrogen across the FKNMS during 2018.



Figure 16. Distributions of bottom total nitrogen across the FKNMS during 2018.
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 SW Shelf, Northern Florida Bay, and the Ten Thousand Islands exhibited higher CHLA levels relative to the FKNMS. Historical data also 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 2018, highest CHLA values occurred mostly along the northern boundary of the Sluiceway and Middle Keys, suggesting an important contribution from the SW Shelf and Florida Bay (Fig. 14). This contribution was especially large in 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, and Lower Keys sites were not significantly different.



Figure 14. Distributions of surface chlorophyll a across the FKNMS during 2018.

Along with TP, turbidity is probably the second most important determinant of local ecosystem health (Fig. 15). 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 and thereby limiting seagrass and coral growth. 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 resuspended by wind and wave action. In 2018, highest turbidity values occurred in the Backcountry during the Winter and the following Fall mostly along the northern boundary with the SW Shelf (Fig. 15).

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 16). However, in Keys waters, CDOM (an important driver of water color and light penetration) may be a more prominent driver of light penetration. For 2018, highest K_d was observed mostly in the Sluiceway and Backcountry areas (Fig. 16), with Fall being highest.

Turbidity and TOC affect K_d , while site depth also affects the amount of ambient light reaching the bottom (Fig. 17). Even when the water column is clear, the deeper the water depth, the less light relative to surface. For 2018, lowest bottom light was observed in the oceanside Marquesas and Backcountry.



Figure 15. Distributions of surface turbidity across the FKNMS during 2018.



Figure 16. Distributions of light extinction across the FKNMS during 2018.



Figure 17. Distributions of bottom light across the FKNMS during 2018.

Surface SiO₂ concentrations usually exhibit a pattern similar to salinity. The source of SiO₂ 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 SiO₂ in this area. Therefore, SiO₂ concentrations on the Shelf are depleted mostly by mixing (although we no longer have data from the Shelf), allowing SiO₂ to be used as a semiconservative tracer of freshwater in this system (Ryther et al. 1967; Moore et al. 1986). In 2018, SiO₂ concentrations were very low, relative to other years. (Fig. 18).

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. 19). 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. A potentially better estimate of nutrient limitation may be the DIN:TP ratio (Fig. 20) which assumes that most of the TON is refractory and that all of the TP is bioavailable. Given those assumptions, the FKNMS would be considered an N-limited system (<16).



Figure 18. Distributions of surface silicate across the FKNMS during 2018.



Figure 19. Distributions of surface TN:TP ratio across the FKNMS during 2018.



Figure 20. Distributions of surface DIN:TP ratio across the FKNMS during 2018.

3.3. 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. 21), episodically driven with no net trend (Fig. 22), and reversing or discontinuous with change point (Fig. 23).



Figure 21. Monotonic trend in TOC at Carysfort Reef.



Figure 22. Episodically driven pattern in NO_2^- with no net trend at Carysfort Reef.



Figure 23. 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 24).



Figure 24. LOESS fitting of trend in turbidity at Carysfort Reef.

Sen slope regressions for each water quality variable were calculated for the 24 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 the number of years sampled and plotted as contour maps of <u>total change</u> for the record. For the 24 year period of record, most variables exhibited some significant trends except salinity and temperature.

Salinity did not exhibit any significant long-term trends, nonetheless, the change maps (Fig. 25) show differences across regions. Both surface and bottom salinity in the bayside area of the Middle Keys and oceanside Upper Keys showed increases in salinity while the Oceanside Lower Keys declined. Salinity on the Reef and Inshore areas was most consistent (Fig 26). 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 displayed salinity cycles lasting 4-5 years. Note 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.

What is obvious from Fig 25 and 26 is that long term trends are small, practically neglectable, but internal variability and amplitude of the signal is orders of magnitude larger than the long-term net change. As we will see, this is also true for most water quality variables measured in this study.





Figure 26. Time series of surface salinity by zone. The line is LOESS fit.

Temperature also did not exhibit a statistically significant long-term trend but the time series shows relative differences in direction of tendency across regions (Fig. 27). The Bay and Backcountry zones tended to decline while the oceanside Upper Keys and Marquesas increased. Time series (Fig. 28) also show that the most temperature variability occurred in the shallowest areas such as the Backcountry and Bay.



Figure 27. Total change in surface and bottom temperature for 24 year period.



Figure 28. Time series of surface temperature by zone. The line is LOESS fit.

Surface DO saturation increased at most sites the FKNMS (Fig. 29). Increased DO_{sat} is beneficial for animal life. Greatest increases in DO_{sat} were generally observed on the Atlantic side of the Keys. A few sites in the Sluiceway areas closest to Florida Bay and north Backcountry sites showed decreasing trends. Trends in bottom DO_{sat} were similar to surface sites (Fig. 30).



By looking at the map, one might assume that DO_{sat} has experienced a slow, incremental increase of over the 24 year period. However, the LOESS regression of surface DO_{sat} 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_{sat} 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_{sat} in the Backcountry was relatively stable for the period of record and was not affected like other areas.

The range of internal variability in all areas became smaller in 2007, where we use Seabird sondes which incorporated optical DO sensors in 2007. In the Backcountry, where variance reduction began in 2014 we had used YSI membrane type sensors until 2014. In summary, the change in variance is due to improving sensor technology from membrane sensors to optical DO sensors.



Figure 30. Time series of surface DO saturation by zone. The line is LOESS fit.



Figure 31. Time series of bottom DO saturation by zone. There are no bottom measurements for SHORE samples. The line is LOESS fit.

Water column turbidity declined throughout the FKNMS (a beneficial result) during the 24year period (Fig 34). There was no statistically significant change in turbidity in bottom waters, but there is a tendency to increase in the Sluice and NE Backcountry. The largest reduction in turbidity occurred in western Florida Bay and Marquesas.



Figure 34. Total change in surface and bottom turbidity for 24 year period.

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 had dropped to lower levels than before the disturbance and have remained so.



Figure 35. Time series of surface turbidity by zone. The line is LOESS fit.

Light extinction (K_d) also showed significant declining trends (a positive result, Fig. 36) offshore and in the Marquesas but increased in the Backcountry and Sluiceway. K_d is partially driven by turbidity and dissolved organic matter. Lower K_d tends to increase the amount of light reaching the bottom (I_o in %). I_o 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, and the inshore zone of the Mid and Upper Keys experienced increases in K_d , decreases in I_o and therefore less light on the bottom.



Figure 36. Total change in bottom K_d for 24 year period.



The time series of K_d (Fig. 38) and I_o (Fig. 39) tells 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 $I_{\rm o}$ in 2011.



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



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

Small but significant declining trends in TP were observed in most surface waters (Fig. 40). Small but increasing trends in bottom TP were observed at numerous oceanside inshore sites off the Upper and Middle Keys. These trends need to be watched as we expect them to decline as recent central sewering takes effect.



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. Hurricane Irma (2017) did not cause major changes in TP. Otherwise, TP is consistently low (<0.01 ppm).



Figure 41. Time series of surface TP by zone. The line is LOESS fit.

Very small decreases in SRP, up to 0.002 ppm over 24 years, were observed (Fig. 42), but these trends were not statistically significant. 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. Interestingly, weak trends in bottom SRP at oceanside inshore sites off the Upper and Middle Keys were opposite to those of TP.



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



Figure 43. Time series of surface SRP by zone. The line is LOESS fit.

Nitrate showed very small declines over most of the FKNMS for the record (Fig. 44), while trends in NH_4^+ were also small and variable (Fig. 45). Interestingly, the decreasing trends in bottom NH_4^+ were observed at many of the same oceanside inshore sites off the Upper and Middle Keys where TP was increasing. We are not sure if such trends are stoichiometrically related or not. Did increases in TP drive down NH_4^+ through biological uptake? Or did declines in NH_4^+ allow TP to be released to the water column?



Figure 44. Total change in surface and bottom NO_3^- for 24 year period.



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 $NO_3^2 + NO_2^2$ by zone. The line is LOESS fit.



Figure 47. Time series of surface NH_4^+ by zone. The 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.



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 by zone. The 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.



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 by zone. The line is LOESS fit.

Silicate experienced declines throughout the FKNMS except at sites in the Sluiceway adjacent to Florida Bay which showed increases (Fig. 52). We believe 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 surface and bottom SiO2 for 24 year period.



Figure 53. Time series of surface SiO_2 by zone. The 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. Largest declines in Chla were observed in the Marquesas.



Figure 54. Total change in chlorophyll a in surface waters for 24 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). Similar events occur in Marquesas during 2001-2002 and 2005-2006. These events seem closely linked to hurricane impact in 1998-1999 and 2004-2005 as discussed above.



Figure 55. Time series of surface Chlorophyll a by zone. The 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 *a* 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 l⁻¹) and total phosphorus should be less than or equal to 0.2 μ M (0.0077 mg l⁻¹). Table 3 shows the number of sites and percentage of total sites exceeding these Strategic Targets for the period of record to 2018.

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 %)
2018	92 of 170 (54.1%)	108 of 152 (71.7%)	558 of 689 (81.0 %)	573 of 689 (82.3 %)

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6. References

APHA. 1995. Automated method for molybdate-reactive silica. In A. D. Eaton, L. S. Clesceri, and

- A. E. Greenberg (Eds.), Standard Methods for the Examination of Water and Wastewater
- BOYER, J. N. 2006. Shifting N and P limitation along a north-south gradient of mangrove estuaries in South Florida. <u>Hydrobiologia</u> 269: 167-177.
- BOYER, J. N. AND H. O. BRICEÑO. 2007. FY2006 Annual Report of the South Florida Coastal Water Quality Monitoring Network. SFWMD/SERC Cooperative Agreement #4600000352. SERC Tech. Rep. T-351. <u>2006 CWQMN.pdf</u>.
- BOYER, J. N. AND H. O. BRICEÑO. 2011. 2010 Annual Report of the Water Quality Monitoring Project for the Water Quality Protection Program of the Florida Keys National Marine Sanctuary. US EPA/FIU Agreement #X7-96410604-6. SERC Tech. Rep. T-536
- BOYER, J. N., J. W. FOURQUREAN, AND R. D. JONES. 1997. Spatial characterization of water quality in Florida Bay and Whitewater Bay by multivariate analysis: Zones of similar influence (ZSI). <u>Estuaries</u> 20: 743-758.
- BOYER, J. N., AND R. D. JONES. 1999. Effects of freshwater inputs and loading of phosphorus and nitrogen on the water quality of Eastern Florida Bay, p. 545-561. *In* K. R. Reddy, G. A.
 O'Connor, and C. L. Schelske (eds.) Phosphorus biogeochemistry in sub-tropical ecosystems. CRC/Lewis Publishers, Boca Raton, Florida.
- BOYER, J. N., AND R. D. JONES. 2002. A view from the bridge: External and internal forces affecting the ambient water quality of the Florida Keys National Marine Sanctuary, p. 609-628. *In* J. W. Porter and K. G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press.
- BOYER, J. N., B. J. PETERSON, AND D. MIR-GONZALEZ. 2005. Water Quality Monitoring and Analysis for the Florida Keys National Wildlife Refuge. Final Report to the US Fish and Wildlife Services. SERC Tech. Rep. #T-244.
- BOYER, J. N., P. STERLING, AND R. D. JONES. 2000. Maximizing information from a water quality monitoring network through visualization techniques. <u>Estuarine, Coastal and Shelf Science</u> 50: 39-48.
- BRICEÑO, H. O., AND J. N. BOYER. 2007. SERC-WQMN: Long-term Declines in TOC, TON and TP export from the Everglades Mangrove Forest. Annual Science Meeting SFC CESU, Miami, Fl.
- BRICEÑO, H. O., AND J. N. BOYER. 2010. Climatic controls on nutrients and phytoplankton biomass in a sub-tropical estuary, Florida Bay, USA. <u>Estuaries and Coasts</u> 33: 541–553.
- BRICEÑO, H. O. AND J. N. BOYER. 2018. FY2017 Annual Report of the Water Quality Monitoring Project for the Florida Keys National Marine Sanctuary. EPA Agreement #X7-00049716-0. SERC Tech. Report #T-887.
- BRICEÑO, H. O., J. N. BOYER AND P. HARLEM. 2010. Proposed Methodology for the Assessment of Protective Numeric Nutrient Criteria for South Florida Estuaries and Coastal Waters. White paper submitted to Environmental Protection Agency Science Advisory Board. Dec 6 2010. FIU/SERC Contribution # T-501

- BRICEÑO, H.O. J.N. BOYER, J. CASTRO, AND P. HARLEM. 2013. Biogeochemical classification of south Florida's estuarine and coastal waters. <u>Marine Pollution Bulletin</u> 75: 187–204.
- BRICEÑO, H., R. GARCIA, P. GARDINALI, K. BOSWELL, A. SERNA AND E. SHINN. 2015. Design and implementation of dye-tracer injection test, Cudjoe Key, Florida Keys. FINAL REPORT. Submitted to CH2M Hills on behalf of Florida Keys Aqueduct Authority. FIU/SERC TR# T-723. 68 p
- CAPONE, D. G., AND B. F. TAYLOR. 1980. Microbial nitrogen cycling in a seagrass community, p. 153-161. *In* V. S. Kennedy (ed.), Estuarine Perspectives. Academic.
- CLEVELAND, WILLIAM S. 1979. Robust locally weighted regression and smoothing scatterplots. J. Amer. Stat. Assoc. 74: 829–836.
- CORBETT, D. R., K. DILLON, W. BURNETT, AND J. CHANTON. 2000. Estimating the groundwater contribution into Florida Bay via natural tracers ²²²Rn and CH₄. <u>Limnology and</u> <u>Oceanography</u> 45:1546-1557.
- EPA. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA 600/4-79-019. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH.
- EPA. 1993. Water Quality Protection Program for the Florida Keys national Marine Sanctuary: Phase II Report. Battelle Ocean Sciences, Duxbury, MA and Continental Shelf Associates, Inc., Jupiter, FL.
- EPA. 1995. Water quality protection program for the Florida Keys National Marine Sanctuary:
 Phase III report. Final report submitted to the Environmental Protection Agency under Work
 Assignment 1, Contract No. 68-C2-0134. Battelle Ocean Sciences, Duxbury, MA and
 Continental Shelf Associates, Inc., Jupiter FL.
- EPA-REGION 2. 1997. Non-Detect Policy. CENAN-OP-SD 28 February 1997
- EPANECHNIKOV, V. A. 1969. Non-parametric estimation of a multivariate probability density. <u>Theory Probab. Appl.</u> 14:153–158. doi:10.1137/1114019
- FRANKOVICH, T. A., AND R. D. JONES. 1998. A rapid, precise, and sensitive method for the determination of total nitrogen in natural waters. <u>Mar. Chem.</u> 60:227-234.
- FOURQUREAN, J.W., M.D. DURAKO, M.O. HALL AND L.N. HEFTY. 2002. Seagrass distribution in south Florida: a multi-agency coordinated monitoring program, p. 497-522. *In* J. W. Porter and K. G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press.
- FOURQUREAN, J. W., R. D. JONES, AND J. C. ZIEMAN. 1993. Processes influencing water column nutrient characteristics and phosphorus limitation of phytoplankton biomass in Florida Bay, FL, USA: Inferences from spatial distributions. <u>Estuarine, Coastal and Shelf Science</u> 36:295-314.
- GIBSON, P. J., J. N. BOYER, AND N. P. SMITH. 2008. Nutrient Mass Flux between Florida Bay and the Florida Keys National Marine Sanctuary. <u>Estuaries and Coasts</u> 31: 21–32.

- HOER, D. R., J. P. TOMMERDAHL, N. L. LINDQUIST, AND C. S. MARTENS. 2018. Dissolved inorganic nitrogen fluxes from common Florida Bay (U.S.A.) sponges. <u>Limnology and Oceanography</u> 63: 2563–2578.
- HOER, D. R., W. SHARP, G. DELGADO, N. L. LINDQUIST, AND C. S. MARTENS. (in review). Sponges represent a major source of inorganic nitrogen in Florida Bay (U.S.A.). <u>Limnology and Oceanography</u>.
- ISAAKS, E. H., AND R. M. SRIVASTAVA. 1989. An Introduction to Applied Geostatistics. Oxford Press, 561 pp.
- KAISER, H.F. 1958. The varimax criterion for analytic rotation in factor analysis". <u>Psychometrika</u> 23 (3).
- KLEIN, C. J., AND S. P. ORLANDO JR. 1994. A spatial framework for water-quality management in the Florida Keys National Marine Sanctuary. <u>Bulletin of Marine Science</u> 54: 1036-1044.
- Koroleff, F. 1983. Determination of ammonia. In K. Grasshoff, M. Erhardt, and K. Kremeling (Eds.), Methods of Seawater Analysis. Verlag Chemie, Weinheim, Germany.
- MURPHY, J., AND J. P. RILEY. 1962. A modified single solution method for the determination of phosphate in natural water. Anal. Chim. Acta 27: 31-36.
- LAPOINTE, B. E., AND M. W. CLARK. 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida Keys. <u>Estuaries</u> 15: 465-476.
- LAPOINTE, B. E., AND W. R. MATZIE. 1996. Effects of stormwater nutrient discharges on eutrophication processes in nearshore waters of the Florida Keys. <u>Estuaries</u> 19: 422-435.
- LEE, T. N., M. E. CLARKE, E. WILLIAMS, A. F. SZMANT, AND T. BERGER. 1994. Evolution of the Tortugas gyre and its influence on recruitment in the Florida Keys. <u>Bulletin of Marine Science</u> 54: 621-646.
- LEE, T. N., E. WILLIAMS, E. JOHNS, D. WILSON, AND N. P. SMITH. 2002. Transport processes linking South Florida ecosystems, p. 309-342. *In* J. W. Porter and K. G. Porter (eds.), The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press.
- LEICHTER, J. J., S. R. WING, S. L. MILLER, AND M. W. DENNY. 1996. Pulsed delivery of subthermocline water to Conch Reef (Florida Keys) by internal tidal bores. <u>Limnology and Oceanography</u> 41: 1490-1501.
- LEICHTER, J. J., AND S. L. MILLER. 1999. Predicting high-frequency upwelling: Spatial and temporal patterns of temperature anomalies on a Florida coral reef. <u>Continental Shelf Research</u> 19: 911-928.
- LEICHTER, J. J., H. L. STEWART, AND S. L. MILLER. 2003. Episodic nutrient transport to Florida coral reefs. <u>Limnology and Oceanography</u> 48:1394-1407.
- MOORE, W. S., J. L. SARMIENTO, AND R. M. KEY. 1986. Tracing the Amazon component of surface Atlantic water using ²²⁸Ra, salinity, and silica. <u>Journal of Geophysical Research</u> 91: 2574-2580.

- NELSON, D. M., AND Q. DORTCH. 1996. Silicic acid depletion and silicon limitation in the plume of the Mississippi River: evidence from kinetic studies in spring and summer. <u>Marine Ecology</u> <u>Progress Series</u> 136: 163-178.
- NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION. 1995. Florida Keys National Marine Sanctuary Draft Management Plan/Environmental Impact Statement.
- OVERLAND, J. E. AND R. W. PREISENDORFER. 1982. A significance test for principal components applied to cyclone climatology. <u>Monthly Weather Review</u> 110:1-4.
- PAUL J. H., ROSE J. B., BROWN J., SHINN E. A., MILLER S. AND FARRAH S. R. 1995. Viral tracer studies indicate contamination of marine waters by sewage disposal practices in Key Largo, Florida. <u>Appl. Environ. Microbiol.</u>61,2230-2234.
- PAUL, J.H., J.B. ROSE, S.C. JIANG, X. ZHOU, P. COCHRAN, C. KELLOGG, J.B. KANG, D. GRIFFIN, S. FARRAH AND J. LUKASIK. 1997. Evidence for groundwater and surface marine water contamination by waste disposal wells in the Florida Keys. <u>Water Research</u> 31:.
- PITTS, P. A. 1997. An investigation of tidal and nontidal current patterns in Western Hawk Channel, Florida Keys. <u>Continental Shelf Research</u> 17: 1679-1687.
- REDFIELD, A. C. 1958. The biological control of chemical factors in the environment. <u>American</u> <u>Scientist</u> 46: 205-222.
- REGIER, P., H. BRICEÑO AND R. JAFFE. 2016. Long-term environmental drivers of DOC fluxes: Linkages between management, hydrology and climate in a subtropical coastal estuary. <u>Estuarine</u>, <u>Coastal and Shelf Science</u> 182, 112-122
- REICH, C., E.A. SHINN, C. HICKEY AND A.B. TIHANSKY. 2001. Tidal and Meteorological Influences on Shallow Marine Groundwater Flow in the Upper Florida Keys in J. Porter and K.C Porter (Editors) The Everglades, Florida Bay, and Coral reefs of the Florida Keys. An Ecosystem Handbook. CRC Press. 1022 p.
- RUDNICK, D., Z. CHEN, D. CHILDERS, T. FONTAINE, AND J. N. BOYER. 1999. Phosphorus and nitrogen inputs to Florida Bay: the importance of the Everglades watershed. <u>Estuaries</u> 22: 398-416.
- RYTHER, J. H., D. W. MENZE, AND N. CORWIN. 1967. Influence of the Amazon River outflow on the ecology of the western tropical Atlantic, I. Hydrography and nutrient chemistry. <u>Journal of Marine Research</u> 25: 69-83.
- SHINN, E.A., C. REICH, D. HICKEY AND A.B. TIHANSKY. 1999a. Determination of Groundwater-Flow Direction and Rate Beneath Florida Bay, the Florida Keys and Reef Tract. http://sofia.usgs.gov/projects/index.php?project_url=grndwtr_flow. Accessed Oct 2014
- SHINN, E.A., R.S. REESE AND C.D. REICH. 1999b. Fate and Pathways of Injection-Well Effluent in the Florida Keys. <u>http://sofia.usgs.gov/publications/ofr/94-276/index.html Downloaded Oct 2014</u>
- Sмітн, N. P. 1994. Long-term Gulf-to-Atlantic transport through tidal channels in the Florida Keys. <u>Bulletin of Marine Science</u> 54: 602-609.
- SOLÓRZANO, L., AND J. H. SHARP. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. <u>Limnology and Oceanography</u> 25:754-758.
- STUMPF, R. P., M. L. FRAYER, M. J. DURAKO, AND J. C. BROCK. 1999. Variations in water clarity and bottom albedo in Florida Bay from 1985-1997. <u>Estuaries</u> 22: 431-444.

- SZMANT, A. M., AND A. FORRESTER. 1996. Water column and sediment nitrogen and phosphorus distribution patterns in the Florida Keys, USA. <u>Coral Reefs</u> 15: 21-41.
- WALSH, T. W. 1989. Total dissolved nitrogen in seawater: a new high temperature combustion method and a comparison with photo-oxidation. <u>Mar. Chem.</u> 26: 295-311.
- YENTSCH, C. S., AND D. W. MENZEL. 1963. A method for determination of phytoplankton chlorophyll and phaeophytin by fluorescence. <u>Deep Sea Res.</u> 10: 221-231.