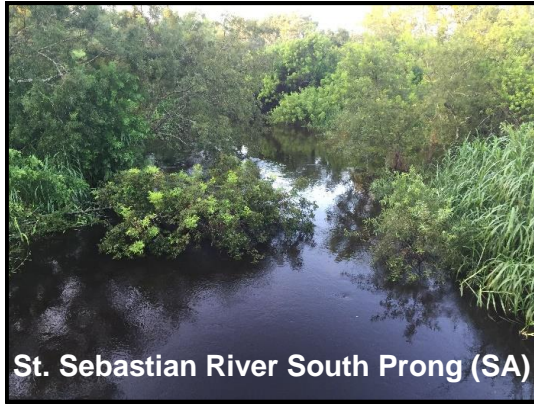


## Inputs of Nitrogen and Phosphorus from Major Tributaries to the Indian River Lagoon (Subtask 4b)



John H. Trefry, Austin L. Fox, Robert P. Trocine, Stacey L. Fox,  
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October 2017

**Impacts of Environmental Muck Dredging 2016-2017  
Inputs of Nitrogen and Phosphorus from Major Tributaries  
to the Indian River Lagoon (Subtask 4b)**

Final Project Report Submitted to  
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### **Executive Summary**

Muck removal and control of nutrient inputs are important components of the restoration of the Indian River Lagoon (IRL). Successful management plans for controlling muck and nutrients in the IRL require continuing assessment of external and internal inputs of substances that are precursors to algal blooms and future muck deposits. Runoff from large drainage basins in the IRL provide one major pathway for external inputs. Atmospheric inputs and direct runoff from hundreds of outfalls along the lagoon also are important external sources. The main source of internal inputs is fluxes of nutrients from IRL muck. More detailed composition data for tributaries to the IRL during regular and storm flow are among the much needed baseline information.

The goal for the first year of this study was to obtain and interpret composition data for selected dissolved and particulate chemicals, including nitrogen (N) and phosphorus (P), from major tributaries to the IRL. Surveys were carried out during (1) non-storm flow from December 2015 to February 2017 (15 months) and (2) nine storm events. Our sampling locations, all of which have active U.S. Geological Survey (USGS) flow gauges, are as follows: St. Sebastian River at the South Prong (SA), St. Sebastian River system in the Fellsmere Canal (SB), Turkey Creek (TC), Crane Creek (CC) and the Eau Gallie River (EG).

Continuous profiles for salinity, temperature, dissolved oxygen and pH, along with discrete water samples, were collected at each station monthly and on multiple occasions during rain events. Water samples were analyzed for (1) total dissolved solids (TDS in mg/L), turbidity (in NTU, nephelometric turbidity units) and total suspended solids (TSS in mg/L), (2) dissolved ammonium, nitrate + nitrite, organic carbon, organic nitrogen, organic phosphorus, phosphate, total dissolved nitrogen and phosphorus, plus iron, sulfate, calcium, chloride, silica and alkalinity, and (3) particulate nitrogen, phosphorus, organic carbon, iron, aluminum and silicon.

This first year of study yielded a wealth of data plus some preliminary interpretations and conclusions, including the following:

- Mean values for total (dissolved + particulate) N and P were  $890 \pm 120 \mu\text{g/L}$  and  $110 \pm 60 \mu\text{g/L}$ , respectively, for non-storm data for all tributaries, relative to Florida water quality criteria for rivers and streams of  $1540 \mu\text{g total N/L}$  and  $120 \mu\text{g total P/L}$  (USEPA, 2017).
- The forms of total N (dissolved + particulate) for all monthly samples ( $n = 73$ ) from all

tributaries averaged  $57 \pm 13\%$  dissolved organic N (DON),  $19 \pm 8\%$  particulate N,  $17 \pm 12\%$  nitrate + nitrite and  $7 \pm 4\%$  ammonium.

- The forms of total P (dissolved + particulate) for all tributaries averaged  $55 \pm 17\%$  dissolved phosphate,  $36 \pm 13\%$  particulate P, and  $9 \pm 17\%$  dissolved organic P (DOP).
- Lower fractions of nitrate + nitrite and higher fractions of DON were found in less urban tributaries such as Fellsmere Canal. The opposite trends (higher nitrate + nitrite and lower DON) were found in more urban areas including Crane Creek and the Eau Gallie River.
- Concentrations of TDS inversely tracked flow with decreased values during increased (storm) flow. Values for TSS showed an opposite, more positive trend with flow. Phosphate concentrations also tended to be higher during storm flow. Concentrations of nitrate + nitrite decreased below mean, non-storm values during peak storm flow and then slowly returned to mean, non-storm values as storm flow decreased. The other forms of dissolved N showed only minor changes in concentrations relative to flow. These differences may be linked to the relative importance of baseflow (e.g., nitrate + nitrite) versus surface runoff (e.g., phosphate) as sources of the various ions to tributary waters.
- Fluxes of all ions and solids were higher during storm flow. Particulate iron (Fe) values (as a percent of the mass of TSS) decreased significantly at the beginning of a storm event, most likely due to a decrease in the relative amount of groundwater input (i.e., baseflow) of dissolved Fe; the Fe content of the particles returned to mean values as flow decreased.
- Calculated annual fluxes of total N and P for the various creeks, based simply on total flow and average concentrations were as follows:

Tributary	Total N (tons/yr)	Total P (tons/yr)
Eau Gallie River	10	1
Crane Creek	20	2
Turkey Creek	80	5
St. Sebastian B	60	3
St. Sebastian A	60	9
Total	230	20

- Estimated annual inputs of total N and P from these major tributaries are close to estimated benthic fluxes of N (280 tons) and P (45 tons) from muck sediments in the North IRL (north of Melbourne Causeway, Highway 192; excludes Banana River Lagoon).
- Recommendations for future study include (1) continued study of major tributaries, (2) sampling and analysis of minor tributaries and outfalls plus (3) continued assessment of the relative importance of baseflow versus stormwater inputs for major ions and the various chemical forms of N and P.

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## **Inputs of Nitrogen and Phosphorus from Major Tributaries to the Indian River Lagoon (Subtask 4b)**

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### **Introduction**

The long-term goal of this study is to obtain a detailed data set that shows the composition and fluxes (inputs) of nitrogen (N), phosphorus (P) and other chemicals to the Indian River Lagoon (IRL) and from major tributaries and other outfalls to the lagoon. Such information is needed to (1) help determine the effectiveness of upland controls on nutrient and soil runoff and (2) assess the performance and success of removing IRL muck. Four major tributaries were the focus of this Year 1 (2016–2017) effort (St. Sebastian River, Turkey Creek, Crane Creek and Eau Gallie River). Selected other outfalls will be added to the tributary surveys during Year 2 (2017–2018). The stimulus for this study was to better quantify nutrient loading to the IRL because nutrients are a driving force that triggered an algae superbloom in 2011 and the related catastrophic collapse of IRL seagrass (SJRWMD, 2012). Sources of nutrients to the lagoon include direct discharges, runoff (baseflow and storm), fluxes from muck sediments and atmospheric inputs, each of which contributes ~20–40% of the total (dissolved + particulate) N and P added annually to the IRL system (Tetra Tech, 2016). Detailed data for the concentrations, fluxes and forms of N and P in major tributaries to the IRL are needed to better assess the relative importance of runoff, with its complement of natural, fertilizer and septic system sources, relative to internal (benthic fluxes) and atmospheric contributions.

Sampling and analysis were the major activities of the 15-month period that this report covers (December 2015 to February 2017). We have begun the process of tabulating, graphing and carrying out a variety of calculations with our large and varied data set. We are pleased with our progress and feel well prepared to capitalize during 2017–2018 on the insight that we have gained. The scope of our data set and possible avenues of interpretation are very broad. This report was written to give our sponsors and other readers an overview of the first-year's results, while sharing some of the concepts and pathways that we plan to follow as we move forward.

Results from our study are progressively being integrated with past (e.g., Trefry et al., 1989; Dierberg, 1991), and continuing tributary programs (e.g., USGS, 2017; SJRWMD, 2017). Previous efforts in Turkey Creek (e.g., Trefry et al., 1989; Dierberg, 1991) showed the importance of storm events to nutrient transport, especially for particulate N and P. For example, during a six-week period in January–February 1989, storms transported about one-third and one-half, respectively, of the total annual N and P loads of Turkey Creek (Dierberg, 1991). At present,

continuous data for dissolved nitrate + nitrite for Turkey Creek and Crane Creek (USGS, 2017) show that abrupt changes (2- to 5-fold) in concentrations can occur in response to storm events. So, let us tell you what we have learned to date.

## Approach

### Sample Locations

The tributaries study began in December 2015 as an early start to the Environmental Muck Dredging (EMD) projects for 2016–2017. This report presents and interprets results for water chemistry during 15 months (December 2015 to February 2017, referred to as 2016 for convenience) at the following tributaries: Eau Gallie River (EG), Crane Creek (CC), Turkey Creek (TC), St. Sebastian River at the Fellsmere Canal (SB) and at the South Prong (SA) (Figures 1–5, Table 1). All sampling stations were located near USGS gauging stations.

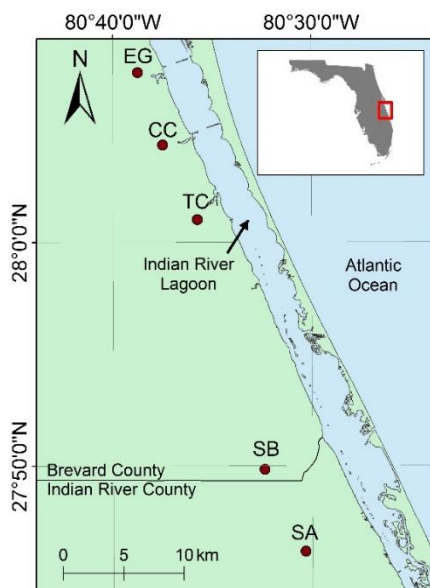


Figure 1. Locations of tributaries sampled for water chemistry [Eau Gallie River (EG), Crane Creek (CC), Turkey Creek (TC), St. Sebastian River, South Prong (SA) and St. Sebastian River, Fellsmere Canal (SB)]. Inset map shows study area along the central east coast of Florida

Table 1. Tributaries, identifications (ID), location names and coordinates for sampling sites.

Tributary	ID	Name of Sampling Site	Coordinates
Eau Gallie River	EG	North Apollo Blvd. Bridge	28° 7.608' N, 80° 38.762' W
Crane Creek	CC	Country Club Rd.	28° 4.364' N, 80° 37.501' W
Turkey Creek	TC	Port Malabar Blvd.	28° 1.021' N, 80° 35.764' W
St. Sebastian B	SB	Fellsmere Canal at SR 507	27° 49.839' N, 80° 32.384' W
St. Sebastian A	SA	South Prong at SR 512	27° 46.168' N, 80° 30.345' W

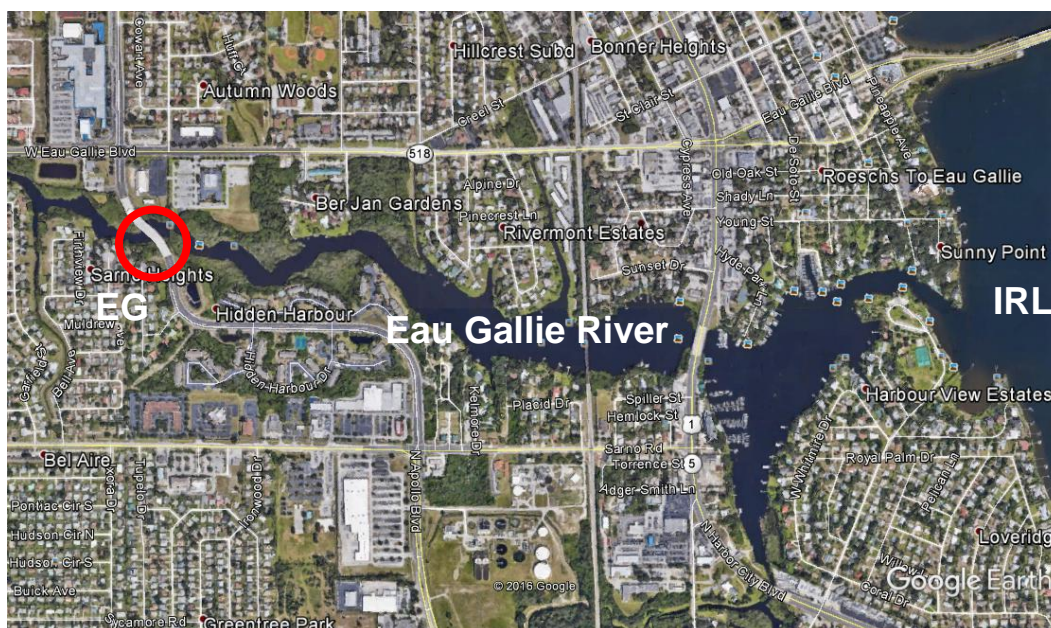


Figure 2. Location of sampling site on the Eau Gallie River (EG) at North Apollo Boulevard Bridge (within red circle). USGS website at [https://waterdata.usgs.gov/nwis/dv?referred\\_module=sw&site\\_no=02249007](https://waterdata.usgs.gov/nwis/dv?referred_module=sw&site_no=02249007).

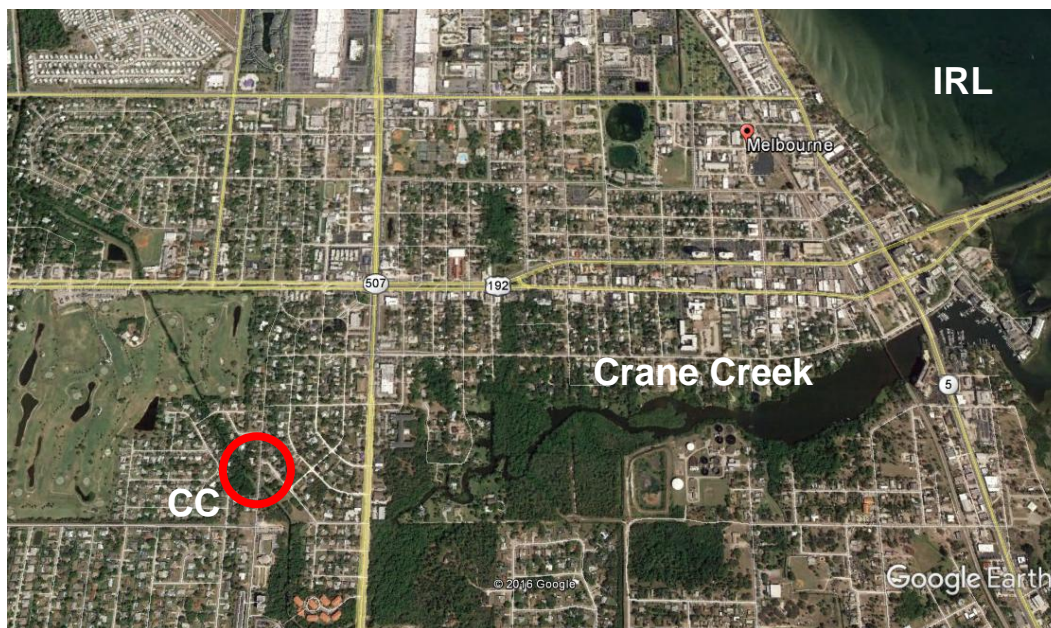


Figure 3. Location of sampling site on Crane Creek (CC) at Country Club Road (within red circle). USGS website at [https://waterdata.usgs.gov/nwis/uv/?site\\_no=02249500](https://waterdata.usgs.gov/nwis/uv/?site_no=02249500).





Figure 4. Location of sampling site at Turkey Creek (TC) on Port Malabar Boulevard (within red circle). USGS website at [https://waterdata.usgs.gov/usa/nwis/uv?site\\_no=02250030](https://waterdata.usgs.gov/usa/nwis/uv?site_no=02250030).

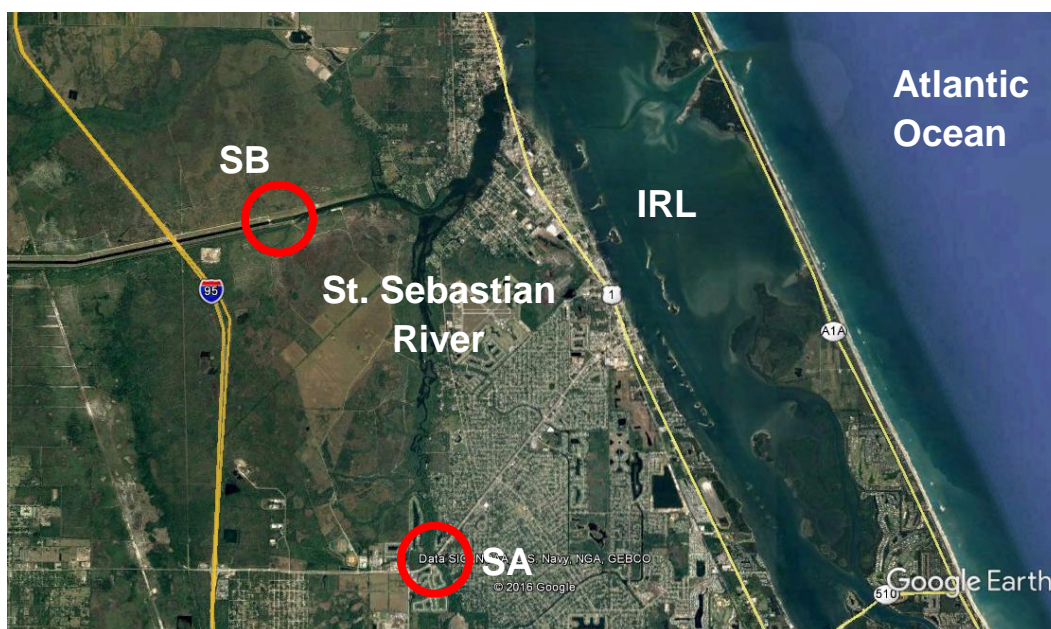


Figure 5. Locations of sampling sites on the St. Sebastian River system, Sebastian B (SB) at the Fellsmere Canal and State Road 507, upstream of control structure, and Sebastian A (SA) on the South Prong of the river at State Road 512 (within red circles). USGS websites at SA: [https://waterdata.usgs.gov/nwis/uv/?site\\_no=02251000](https://waterdata.usgs.gov/nwis/uv/?site_no=02251000) and SB: <https://waterdata.usgs.gov/nwis/uv?02251767>.

### *Sample Collection*

Surveys were carried out monthly at each tributary from December 2015 to February 2017. Vertical profiles for salinity, temperature, pH and dissolved oxygen were obtained first at each site using a YSI 6600 V2 or a YSI ProDSS (Yellow Springs Instruments, Figure 6a). The sondes were calibrated at the beginning of each day following manufacturer's specifications and intercalibrated regularly. During each survey, water samples were collected in acid-washed low-density polyethylene bottles at 0.5 m depth at each station. The open bottles were placed in a weighted sample holder (Figure 6b) and lowered from a bridge to the surface of the water and then quickly (1–2 seconds) lowered to 0.5 m, based on a marked line that held the sampler. A bottom water sample was collected at TC if a salt wedge was identified during the Sonde cast. Collection locations for the other tributaries were upstream of their respective salt wedges, as determined by the conductivity profiles; thus, no bottom samples were necessary. Samples were placed in coolers until returned to the Marine & Environmental Chemistry Laboratories at Florida Institute of Technology (FIT). Filtration was carried out within 2–3 hours through 47-mm diameter, 0.4- $\mu\text{m}$  pore size polycarbonate filters (for particulate Fe, Al, Si, P and dissolved forms of N, P and C) and 47-mm diameter, 0.7- $\mu\text{m}$  pore size glass fiber filters (for particulate C and N).

Filtered water samples and suspended particles were analyzed for a variety of dissolved and particulate chemicals (Table 2) following the techniques summarized below.

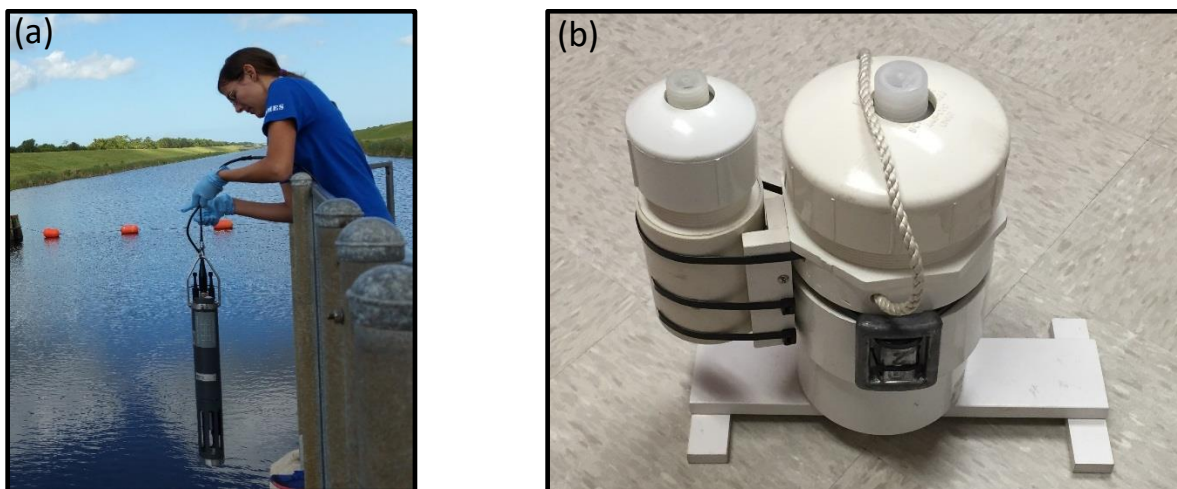


Figure 6. (a) Lowering YSI Sonde 6600 for continuous profile of salinity, temperature, dissolved oxygen and pH and (b) weighted sampler for collecting water samples.

Table 2. Chemical parameters analyzed during this study.

Parameter	Dissolved	Particulate
<i>In situ</i> water column	salinity, temperature, pH, dissolved oxygen	-
Nitrogen	ammonium, nitrate, nitrite, total dissolved nitrogen, dissolved organic nitrogen	total particulate N
Phosphorus	phosphate, total dissolved phosphorus, dissolved organic phosphorus	total particulate P
Dissolved & particulate solids	conductivity, total dissolved solids, salinity	total suspended solids (TSS) turbidity (in NTU)
Major elements	chloride, calcium, alkalinity sulfate, (sodium and magnesium on a subset)	silicon, aluminum, iron, carbon
Trace elements	iron, silica, organic carbon	-

*Laboratory Analyses: Dissolved Chemicals*

Samples for nutrient analysis were vacuum filtered through polycarbonate filters (Poretics, 47-mm diameter, and 0.4- $\mu$ m pore size) in a laminar-flow hood. Concentrations of nitrate + nitrite were determined using a SEAL AA3 HR Continuous Segmented Flow AutoAnalyzer following manufacturer’s method G-218-98. The National Institute of Standards and Technology (NIST) traceable Dionex 5-Anion Standard was analyzed as a reference standard with each batch of samples to ensure accuracy; all values were within 10% of the known concentration. Analytical precision for lab duplicates (relative standard deviation = RSD = [SD/mean] x100%) was  $6.1 \pm 4.8\%$ . Additional Quality Assurance and Quality Control (QA/QC) items are provided below.

Concentrations of total dissolved N were determined using a SEAL AA3 HR Continuous Segmented Flow AutoAnalyzer following manufacturer’s method G-218-98. Organic and inorganic N compounds were converted to nitrate using UV and persulfate digestion. Nitrate was reduced to nitrite using a cadmium column. All values were within 10% of the known concentration. Analytical precision for lab duplicates (RSD) was  $2.1 \pm 1.8\%$ .

Ammonium was quantified following standard methods (Rice et al., 2012) using UV-visible spectrometry. A Spex CertiPrep Cation Standard was analyzed as a reference standard with each batch of samples to ensure accuracy; all values were within 10% of the known concentration. Average analytical precision for lab duplicates (RSD) was 2.4%.

Concentrations of ortho-phosphate were determined using a SEAL AA3 HR Continuous



Segmented Flow AutoAnalyzer following manufacturer's method G-218-98. Ortho-phosphate was reacted with ascorbic acid, molybdate and antimony to yield a phospho-molybdenum blue complex; the absorbance at 880 nm was determined using UV-visible spectrometry. The NIST-traceable Dionex 5-Anion Standard was analyzed as a reference standard with each batch of samples to ensure accuracy; all values were within 10% of the known concentration. Analytical precision for lab duplicates (RSD) averaged 2%.

Concentrations of total dissolved P were determined using a SEAL AA3 HR Segmented Flow AutoAnalyzer following manufacturer's method G-219-98. UV and persulfate digestion were used to free organically-bound P. The NIST-traceable Dionex 5-Anion Standard was analyzed as a reference standard with each batch of samples to ensure accuracy; all values were within 10% of the known concentration. Analytical precision for lab duplicates (RSD) was  $2.6 \pm 2.4\%$ .

Alkalinity was determined following method 2320-B (Rice et al., 2012). Samples were titrated with 0.01N HCl and alkalinity was calculated using the Gran function. Alkalinity in mg CaCO<sub>3</sub>/L is directly proportional to the volume of acid added to reach the pK<sub>a</sub>. Standard seawater solution (OSIL, UK) was analyzed as a reference standard with each batch of samples; all values were within 95% confidence interval for the standard.

#### *Laboratory Analyses: Particulate Chemicals*

Samples of suspended matter were collected by vacuum filtering water through polycarbonate filters (Poretics, 47-mm diameter, 0.4- $\mu$ m pore size) in a laminar-flow hood in the FIT clean room. Prior to the field effort, filters were acid washed in 3N HCl, rinsed three times with deionized water, dried and then weighed to the nearest  $\mu$ g. Precision for replicate filtrations averaged <4% (i.e.,  $\pm 0.04$  mg/L). Samples for particulate organic carbon (POC) were filtered through pre-combusted Gelman Type A/E glass fiber filters mounted on acid-washed filtration glassware in a Class-100 laminar-flow hood. Particle-bearing filters were sealed in acid-washed petri dishes, labeled, double-bagged in plastic and stored until dried and re-weighed at FIT.

Suspended particles, as well as separate milligram quantities of standard reference material (SRM) #2704, a river sediment issued by the NIST, were digested in stoppered, 15-mL Teflon test tubes using Ultrex II HNO<sub>3</sub> and HF as described by Trefry and Trocine (1991). Concentrations of particulate Al, Fe and Si were determined by flame atomic absorption spectrometry and concentrations of particulate P were determined by inductively-coupled plasma mass spectrometry (ICP-MS) using a Varian 820 instrument. Analytical precision (RSD) for individual elements in sediments ranged from 1–5%. Additional QA/QC information and data are provided below.

Concentrations of POC and N (PON) were determined by first treating particles on the glass fiber filter with 10% (v/v) hydrochloric acid to remove any inorganic carbon, washed with carbon-free,

high purity water (HPLC grade) and dried. Then, the filters with approximately 200–800 mg of pre-treated suspended sediment were weighed into ceramic boats and combusted with pure oxygen at 950°C using a LECO TruMac C/N/S system with quantification of the resultant CO<sub>2</sub> gas using an infrared detection cell. Total N concentrations were determined using separate glass fiber filters that were untreated prior to analysis to avoid losses of nitrogen during acidification. Nitrogen analyses of suspended particles also were carried out using the LECO system at 950°C with quantification of the N<sub>2</sub> gas produced via a thermal conductivity detector. Concentrations of C and N in the sediment CRM MESS-3, SRM #2704 and LECO reference sample 502-309 were within the 95% confidence intervals for certified values. Analytical precision (RSD) averaged 1.5% for TOC and 2% for total N.

#### *Quality Assurance and Quality Control (QA/QC)*

The Quality Assurance Plan used in the Marine & Environmental Chemistry Laboratories at FIT was reviewed by Florida DEP. The plan meets the minimum requirements for description of research field and laboratory procedures according to rule 62-160.600, F.A.C. Our sediment and water collection and analyses followed the general guidelines listed below.

- (i) *Sample handling.* Sediment samples were transferred to a refrigerator. If sampled as cores, they were sub-sampled immediately and then refrigerated or frozen. Water samples were collected and preserved using appropriate containers and reagents. Solutes were measured within appropriate holding times. All water samples were kept chilled, either on ice or in refrigerators, until analyzed.
- (ii) *Quality control measurements for analyses.* Quality control measures included instrument calibration, matrix spike analysis, field replicates, duplicate sample analysis, standard reference material analysis, procedural blank analysis, and standard checks. With each batch of 20 field samples, a procedural blank, standard reference materials, a field and laboratory duplicate, and a matrix spike sample were analyzed. Data quality objectives are listed in Table 3.
- (iii) *Matrix spike analysis.* A matrix spike sample (method of additions analysis) was analyzed with every batch of 20 samples. Results from the method of additions analysis provide information on the extent of any signal suppression or enhancement due to the matrix. When necessary (spike results outside 85–115% limit), samples were analyzed by methods of additions.
- (iv) *Duplicate sample analysis.* To estimate analytical precision, a duplicate field sample was analyzed with each batch of 20 samples.
- (v) *Standard reference material analysis.* A common method to evaluate analytical accuracy is to analyze standard reference materials, samples for which consensus or "accepted" analyte concentrations exist. The marine sediment (MESS-3) from the NRC of Canada and a river bottom sediment from the NIST (#2704, Buffalo River Sediment) were analyzed with every batch of sediment samples.

- (vi) *Procedural blank analysis.* A procedural blank was processed and analyzed with each batch of samples to monitor potential contamination from laboratory reagents, glassware, and processing procedures.

Electronic balances used for weighing samples and reagents were calibrated prior to each use with their internal electronic calibration and then verified with certified standard weights (NIST-traceable). All pipets (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metal analysis was initially standardized with a three- to five-point calibration; a linear correlation coefficient of  $r \geq 0.999$  was required before sample analysis. Analysis of complete three- to five-point calibrations or single standard checks occurred after every eight samples until all analyses were complete. The RSD between complete calibration and standard checks was required to be <10% or recalibration and reanalysis of the previous samples were performed.

All weighing-related manipulation of the filters used for suspended solids quantification took place under cleanroom conditions, including controlled temperature and relative humidity. Each filter was weighed twice in random order, with a minimum of 5% of the filters being weighed in triplicate. Static effects on filter weight were controlled by the placement of two  $^{210}\text{Po}$  anti-static devices near the weighing-pan within the balance. The standard deviation in the weights for each filter had to be <2  $\mu\text{g}$  for the value to be accepted.

Table 3. Data quality objectives for the study.

Element or Sample Type Criteria	Minimum Frequency	Data Quality Objective/Acceptance
Initial Calibration	Prior to every batch of samples Standard Curve	3–5 point curve depending on the element and a blank Correlation coefficient $r \geq 0.999$ for all analytes
Continuing Calibration	Must end every analytical sequence or after every 8–10 samples	% RSD $\leq 10\%$ for all analytes
Certified and Standard Reference Materials	Two per batch of 20 samples	Results were within 10% of the accepted values for >85% of the certified analytes
Method Blank	Two per batch of 20 samples	No more than 2 analytes exceed 5x minimum detection limit
Matrix Spike and Spike Method Blank	Two per batch of 20 samples	85–115%
Lab Duplicate	Two per batch of 20 samples	RSD <15% for 75% of analytes

## **Results and Discussion**

### *Chemical Composition of Monthly Samples during Non-Storm Flow*

Trends in water flow and concentrations of the major components of the IRL tributaries are presented first to provide a framework for subsequent discussion of concentrations and fluxes of nutrients and suspended sediments to the IRL. Median water flows (from 30-year means of median daily values) vary by as much as 12-fold among the tributaries (Table 4). Water flow during 2016 was within 15% of the 30-year values for all tributaries except CC (Table 4). Even though the 2016 flow for CC was the highest recorded during the past 30 years, no consistent trend showing changes in the annual flow over time was observed for CC.

Average TDS values for these IRL tributaries ranged from 250 mg/L (SB) to 680 mg/L (SA, Table 4); all values were well above the global average TDS for river water of ~110 mg/L (Berner and Berner, 1996), yet below values for rivers that flow through ancient salt deposits such as the Pecos River (TDS = 2,600 mg/L) or seawater (TDS = 35,000 mg/L). An average of 71% of the TDS for the tributaries was  $\text{Cl}^-$  plus  $\text{Na}^+$  with average values of ~200 and ~130 mg/L, respectively (Table 4, Figure 7a). Average values for TDS of  $250 \pm 66$  mg/L for SB are ~2 times lower than the mean of  $530 \pm 100$  mg/L for the other four locations (Table 4). Water at SB is from a large drainage basin with mostly natural and agricultural land use; and, water is stored behind a weir for flood control and use of irrigation water. Lower TDS values at SB are likely influenced by the presence of more surface water than groundwater due, in part, to plugging of wells and retention of freshwater in the SB drainage basin (Wicklein and Gain, 1999; Morris and Gilbert, 2005).

The higher TDS values for all tributaries of the IRL studied are consistent with high salt content in the surface aquifer due to saltwater intrusion. Artesian wells and the Floridan Aquifer in Brevard County have concentrations of  $\text{Cl}^-$  and  $\text{Na}^+$  that range from ~700 to >1300 mg/L and 200 to >600 mg/L, respectively (Wander and Reitz, 1950; Planert and Aucott, 1985), all higher than found in the IRL tributaries (Table 4). Despite large differences in flow, plus some differences in values for TDS, the rivers show a commonality in river classification by major element composition as described below. Globally, rivers can be classified by TDS and the relative abundances of the major anions or cations (Gibbs, 1970; Stallard and Edmond, 1983) where (1) high TDS (>250 mg/L) and high  $\text{Cl}^- + \text{SO}_4^{2-}$  (>3,000  $\mu\text{equivalents/L}$  or ~200 mg/L for these tributaries) signify an evaporite-crystallization control of water composition and relatively low rainfall, (2) moderate TDS (40–250 mg/L) and higher  $\text{HCO}_3^-$  than  $\text{Cl}^- + \text{SO}_4^{2-}$  support a rock dominant control of water composition (igneous and sedimentary rock; limestone being most notable in this study) and (3) low TDS (<40 mg/L) and Si-rich water suggest that water composition is controlled by intensely-weathered igneous rocks and abundant rainfall. The composition of Florida rivers and streams, including the IRL tributaries, seems to fit an evaporite classification; however, the high  $\text{Na}^+$  and  $\text{Cl}^-$  fraction of the TDS show the influence of high-TDS groundwater, albeit less for SB (Table 4).

Table 4. Summary data (means  $\pm$  standard deviations) for flow and major chemicals in tributaries for monthly (non-storm) samples from December 2015 through February 2017 (15 months). (Note: iron (Fe) values are in  $\mu\text{g/L}$ )

Tributary	St. Sebastian (A)	St. Sebastian (B)	Turkey Creek	Crane Creek	Eau Gallie River
Median Flow <sup>1</sup> (30 yr) (CFS)	59 $\pm$ 27	64 $\pm$ 22	107 $\pm$ 52	12.6 $\pm$ 4.8	8.6 $\pm$ 3.6
Median Flow <sup>1</sup> (2016) (CFS)	65	68	115	24	7.4
Drainage Basin <sup>2</sup> Area (km <sup>2</sup> )	91	194	254	48	24
Conductivity ( $\mu\text{S/cm}$ )	1190 $\pm$ 290	430 $\pm$ 110	770 $\pm$ 90	980 $\pm$ 160	980 $\pm$ 240
TDS (mg/L)	680 $\pm$ 210	250 $\pm$ 66	430 $\pm$ 110	510 $\pm$ 100	510 $\pm$ 100
TSS (mg/L)	8.5 $\pm$ 4.8	2.3 $\pm$ 1.5	3.3 $\pm$ 1.3	2.8 $\pm$ 1.0	5.7 $\pm$ 1.8
pH	7.54 $\pm$ 0.18	7.70 $\pm$ 0.22	7.52 $\pm$ 0.17	7.03 $\pm$ 0.30	7.29 $\pm$ 0.21
Dissolved O <sub>2</sub> (mg/L) [%sat]	6.5 $\pm$ 0.9 [74 $\pm$ 6]	5.9 $\pm$ 1.8 [69 $\pm$ 18]	7.2 $\pm$ 1.4 [85 $\pm$ 10]	5.2 $\pm$ 1.3 [59 $\pm$ 12]	5.0 $\pm$ 1.2 [58 $\pm$ 13]
Chloride (mg/L)	294 $\pm$ 112	66 $\pm$ 26	214 $\pm$ 161	204 $\pm$ 40	222 $\pm$ 40
% of TDS as Na <sup>+</sup> + Cl <sup>-</sup>	71	55	82	74	72
Sulfate (mg/L)	76 $\pm$ 23	21 $\pm$ 10	55 $\pm$ 32	52 $\pm$ 12	48 $\pm$ 9
Alkalinity (mg CaCO <sub>3</sub> /L)	140 $\pm$ 30	87 $\pm$ 33	160 $\pm$ 40	170 $\pm$ 20	130 $\pm$ 30
HCO <sub>3</sub> <sup>-</sup> (mg/L)	168 $\pm$ 36	104 $\pm$ 40	192 $\pm$ 48	204 $\pm$ 24	156 $\pm$ 36
Ca (mg/L)	84 $\pm$ 16	44 $\pm$ 14	92 $\pm$ 19	104 $\pm$ 16	95 $\pm$ 19
Si (mg/L)	5.2 $\pm$ 1.1	2.8 $\pm$ 0.9	4.3 $\pm$ 1.5	4.6 $\pm$ 1.0	3.6 $\pm$ 0.9
DOC (mg/L)	14.7 $\pm$ 5.7	19.8 $\pm$ 3.6	11.5 $\pm$ 3.4	11.3 $\pm$ 3.4	14.0 $\pm$ 2.9
Fe ( $\mu\text{g/L}$ )	190 $\pm$ 130	303 $\pm$ 172	160 $\pm$ 150	87 $\pm$ 33	101 $\pm$ 48

<sup>1</sup>USGS (2017). <sup>2</sup>SJRWMD (2009).

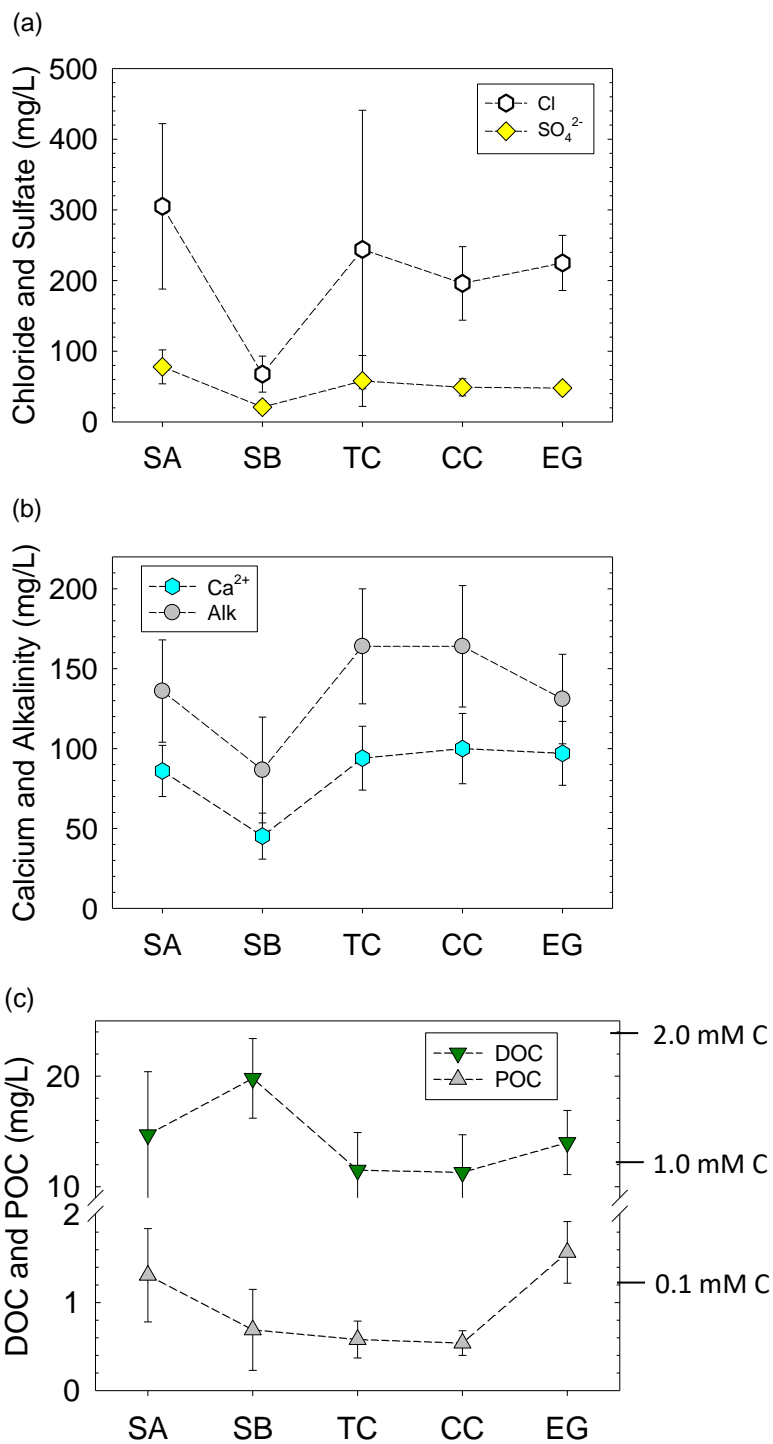


Figure 7. Mean values ( $\pm$  standard deviation) for (a) chloride and sulfate, (b) calcium and alkalinity and (c) dissolved organic carbon (DOC) and particulate organic carbon (POC) for tributaries during monthly surveys from December 2015 to February 2017. Dashed lines added to help show differences in values among tributaries.

Despite the importance of  $\text{Na}^+$  and  $\text{Cl}^-$  to TDS values in the IRL tributaries, concentrations of  $\text{Ca}^{2+}$  (44–105 mg/L) and  $\text{HCO}_3^-$  (104–204 mg/L) from our study also are much greater than average world river water ( $\text{Ca}^{2+} = 14$  mg/L;  $\text{HCO}_3^- = 53$  mg/L; Berner and Berner, 1996). Clearly, the baseflow of the IRL tributaries traverses subsurface limestone. This understanding helps show the importance of baseflow (groundwater) to the composition of the tributaries and set a framework for evaluating concentrations of nutrients and other chemicals in the system. Data for anions from the IRL tributaries and the St. Johns River plot closest to the  $\text{Cl}^- + \text{SO}_4^{2-}$  vertex (i.e., 100%  $\text{Cl}^- + \text{SO}_4^{2-}$ ) on the anion ternary diagram (Figure 8) in support of the previous discussion. The impact of limestone weathering also shows on the ternary diagram because the tributaries plot between ~20 and 40%  $\text{HCO}_3^-$  (Figure 8). The IRL tributaries are more similar in anion sources to the Ohio and Rio Grande rivers than the Yukon River or average world river water.

Concentrations of  $\text{Cl}^-$  correlated very strongly ( $r > 0.9$ ) with TDS due to the dominance of  $\text{Cl}^-$  and  $\text{Na}^+$  in the IRL tributaries (Figure 9a; Table 4). Sulfate and chloride also correlated strongly because ~55% of the sulfate, and essentially all of the  $\text{Cl}^-$  and  $\text{Na}^+$ , in tributary waters could be traced to an original seawater source (note that the  $[\text{SO}_4^{2-}/\text{Cl}^-]$  for the tributaries is greater than

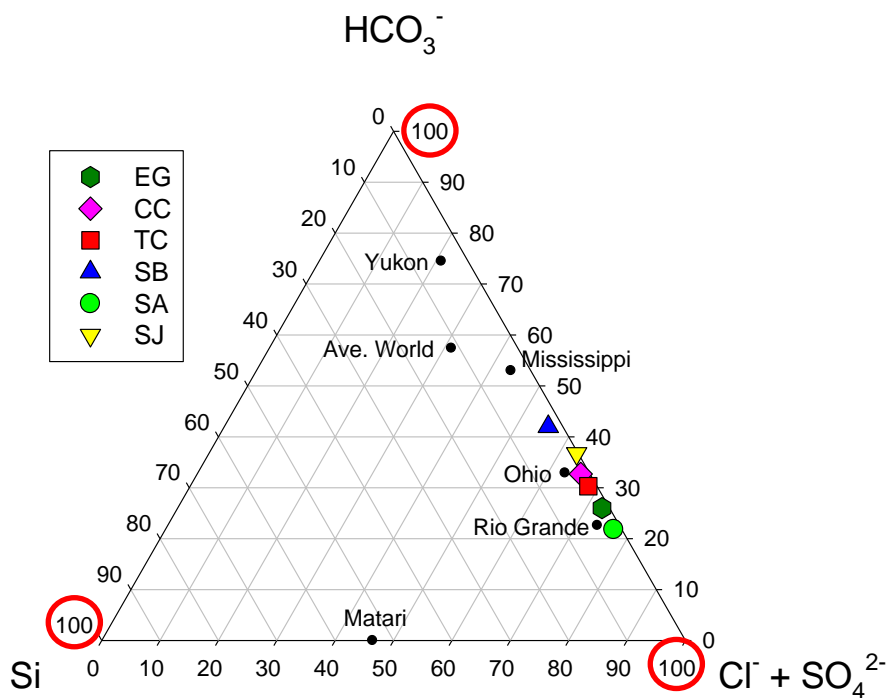


Figure 8. Ternary diagram showing relative chemical compositions of IRL tributaries, the St. Johns River near Cocoa, FL (SJ) and selected world rivers. The data point for the Eau Gallie River, for example, shows that the rivers had the following percentage distribution: 1.3% Si, 72.7%  $\text{Cl}^- + \text{SO}_4^{2-}$ , and 26.0%  $\text{HCO}_3^-$ . Units are as follows: Si ( $\mu\text{mol/L}$ ),  $\text{Cl}^- + \text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  ( $\mu\text{eq/L}$ ). Data for St. Johns River from Wendy Tweedale (SJRWMD, written communication).

the ratio for seawater, Figure 9b). The source of excess sulfate (the 45% of the sulfate not having seawater source) is discussed in more detail below.

Calcium concentrations correlated strongly ( $r = 0.8\text{--}0.9$ ) with both alkalinity (Figure 7b and 9c) and sulfate (Figure 9d). Only a small fraction of the dissolved  $\text{Ca}^{2+}$  in the tributaries has a seawater source ( $<6\text{ mg Ca}^{2+}/\text{L}$  based on  $\text{Cl}^-$  values); instead, it seems that about 70% and 30% of the  $\text{Ca}^{2+}$  is derived from limestone weathering and calcium sulfate, respectively (slopes from Figures 9 c, d and related cation and anion balances not shown here). The calcium sulfate source is more important for SA as shown by the much higher slope for  $\text{SO}_4^{2-}$  versus  $\text{Ca}^{2+}$  and the higher  $\text{SO}_4^{2-}$  concentrations (Figure 9d). Calcium sulfate is added to citrus fields to correct Ca and S deficiencies (Zekri and Obreza, 2013); collectively, the St. Sebastian River drainage basin has 31% agricultural usage with abundant citrus-growing areas (SJRWMD, 2009).

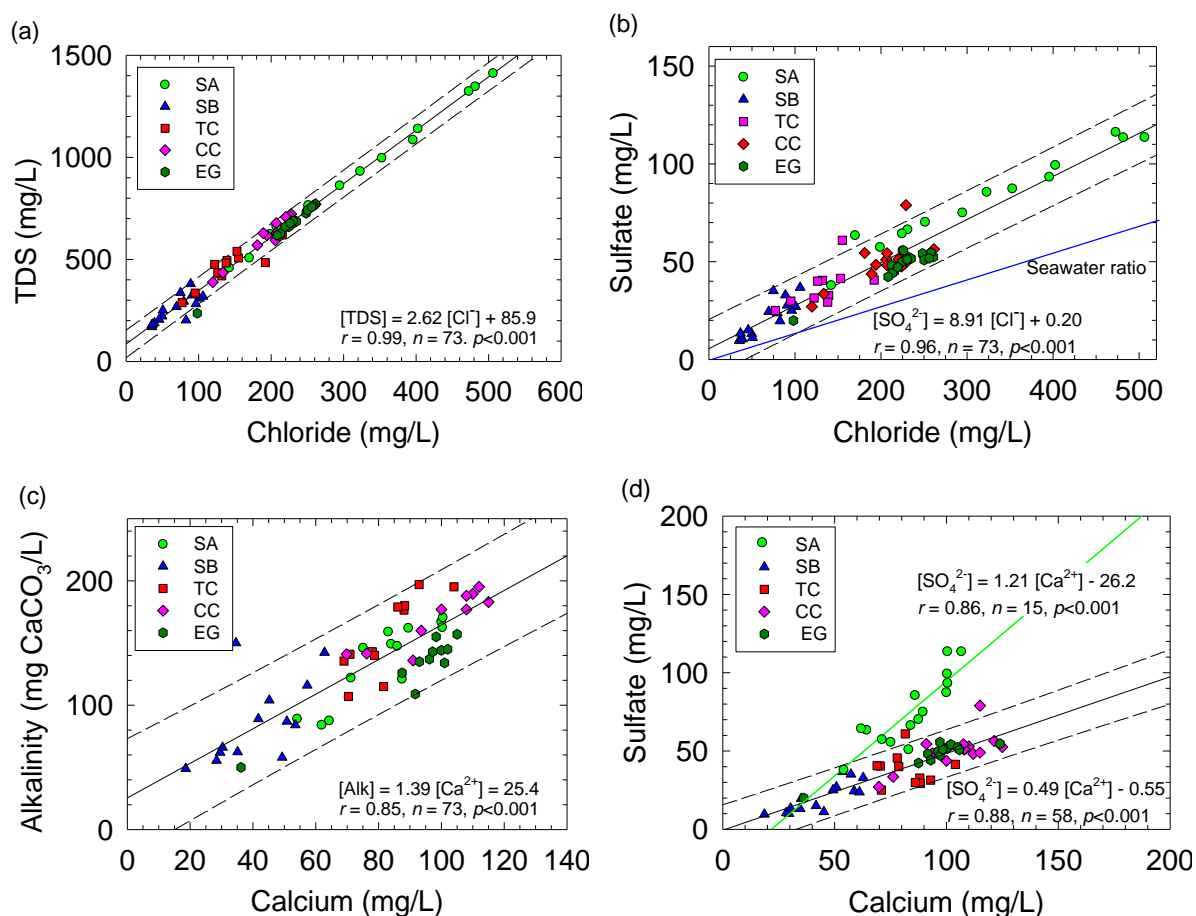


Figure 9. Concentrations of (a) total dissolved solids (TDS) versus chloride, (b) sulfate versus chloride, (c) alkalinity versus calcium, and (d) sulfate versus calcium. Solid lines are from linear regressions, dashed lines show 95% prediction intervals,  $r$  is the correlation coefficient and  $n$  is the number of data points. Two regression lines are shown on (d), one for SA and one for the other four tributaries.



Average concentrations of the various chemical forms of nitrogen were relatively uniform among the tributaries with the exception of higher DON values for SB, higher nitrate + nitrite values for CC, and higher ammonium values for the EG site (Table 5 and Figure 10a). Concentrations of DON at SB were ~50% higher than the mean of  $470 \pm 40 \mu\text{g/L}$  for the other four tributaries (Table 5 and Figure 10a). This same trend was found for DOC (Table 4, Figure 7c). Agricultural development on drained Histosols (organic soils) with high N and P content in Fellsmere and the Upper St. Johns River is certainly a reasonable source for higher DON and DOC values in runoff or irrigation water carried to SB (Morris and Gilbert, 2005).

Higher nitrate + nitrite concentrations for CC ( $280 \mu\text{g/L}$ ) may be related to runoff of reclaimed water from the nearby Crane Creek Reserve Golf Course (map in Figure 3). Reclaimed water from the irrigation system at the golf course contained  $\sim 9 \text{ mg } (\text{NO}_3^- + \text{NO}_2^-)/\text{L}$ ; a value that is  $\sim 30$  times higher than the mean value for our CC sampling site located  $\sim 400 \text{ m}$  from the eastern side of the golf course. Regulations for applied reclaimed water are set at  $12 \text{ mg nitrate-N/L}$  (Florida Department of State, 2010); the samples we collected had an average TDN value of  $11.7 \text{ mg/L}$ . Mean concentrations of ammonium at EG ( $140 \pm 64 \mu\text{g N/L}$ ) were about three times greater than for the other four tributaries ( $45 \pm 9 \mu\text{g N/L}$ ); EG has the highest urban land use (71%, SJRWMD, 2009) combined with a wide, slow-moving river that has a sizeable surface area of organic-rich sediments with the potential of greater benthic fluxes of ammonium.

Average phosphate concentrations ranged from  $20 \mu\text{g P/L}$  (TC) to  $140 \mu\text{g P/L}$  (EG) (Table 5 and Figure 10b) and made up more than half the total P in each tributary (Table 5). Mean concentrations of DOP were very low at  $1\text{--}14 \mu\text{g P/L}$  (Table 5). Concentrations DOP have been shown to be very low in freshwater ( $3\text{--}6 \mu\text{g P/L}$ ; Lin and Guo, 2012).

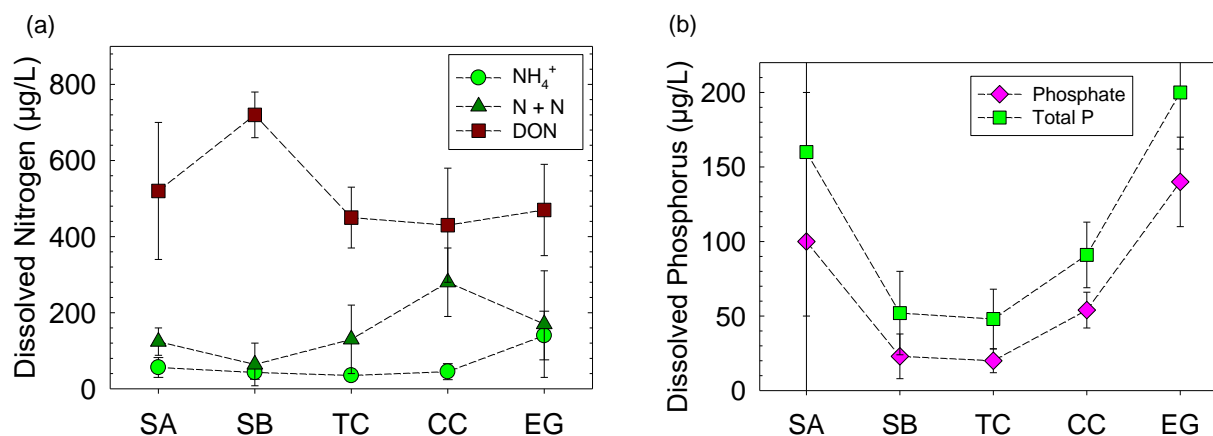


Figure 10. Mean values ( $\pm$  standard deviation) for dissolved (a) ammonium ( $\text{NH}_4^+$ ), nitrate + nitrite (N + N) and dissolved organic nitrogen (DON) and (b) total phosphorus and phosphate for the tributaries during monthly surveys from December 2015 to February 2017. Dashed lines added to help show differences in values among tributaries.

Table 5. Summary data (means  $\pm$  standard deviations) for flow and nutrients in tributaries for monthly (non-storm) samples from December 2015 through February 2017 (15 months).

Tributary	St. Sebastian (A)	St. Sebastian (B)	Turkey Creek	Crane Creek	Eau Gallie River
Median Flow <sup>1</sup> (30 yr) (CFS)	59 $\pm$ 27	64 $\pm$ 22	107 $\pm$ 52	12.6 $\pm$ 4.8	8.6 $\pm$ 3.6
Median Flow (2016) <sup>1</sup> (CFS)	65	68	115	24	7.4
TSS (mg/L)	8.5 $\pm$ 4.8	2.3 $\pm$ 1.5	3.3 $\pm$ 1.3	2.8 $\pm$ 1.0	5.7 $\pm$ 1.8
TN (dis + part) ( $\mu$ g N/L)	890 $\pm$ 240	980 $\pm$ 90	740 $\pm$ 160	870 $\pm$ 190	1050 $\pm$ 220
NH <sub>4</sub> <sup>+</sup> ( $\mu$ g N/L)	56 $\pm$ 26	43 $\pm$ 18	35 $\pm$ 11	45 $\pm$ 21	140 $\pm$ 64
NO <sub>3</sub> <sup>-</sup> +NO <sub>2</sub> <sup>-</sup> ( $\mu$ g N/L)	124 $\pm$ 36	64 $\pm$ 56	130 $\pm$ 90	280 $\pm$ 90	170 $\pm$ 140
DON ( $\mu$ g N/L)	520 $\pm$ 180	720 $\pm$ 60	450 $\pm$ 80	430 $\pm$ 150	470 $\pm$ 120
Partic. N ( $\mu$ g N/L)	190 $\pm$ 70	150 $\pm$ 60	130 $\pm$ 40	120 $\pm$ 50	270 $\pm$ 100
TP (Dis + Part) ( $\mu$ g P/L)	160 $\pm$ 110	52 $\pm$ 28	48 $\pm$ 20	91 $\pm$ 22	200 $\pm$ 38
PO <sub>4</sub> <sup>3-</sup> ( $\mu$ g P/L)	100 $\pm$ 100	23 $\pm$ 15	20 $\pm$ 8	54 $\pm$ 12	140 $\pm$ 30
DOP ( $\mu$ g P/L)	7 $\pm$ 19	14 $\pm$ 26	10 $\pm$ 25	7 $\pm$ 21	1 $\pm$ 2
Part P ( $\mu$ g P/L)	50 $\pm$ 19	17 $\pm$ 16	19 $\pm$ 9	33 $\pm$ 11	60 $\pm$ 16

<sup>1</sup>USGS (2017).

We also determined the relative amounts of the different chemical species of N and P for each creek. Collectively for all tributary samples ( $n = 73$ ), DON was the dominant chemical form of nitrogen (Figure 11a). Some differences were observed among the tributaries. For example, SB an average of 77% of TN as DON whereas EG carried an average of 49% of TN as DON (Table 5). In addition, a large difference in the % of TN in the form of nitrate + nitrite was found for the two creeks with 32% for CC and 6% for TC (Table 5). The distributions in chemical forms of N for Turkey Creek from this study are similar to those reported for TC by Dierberg (1991).

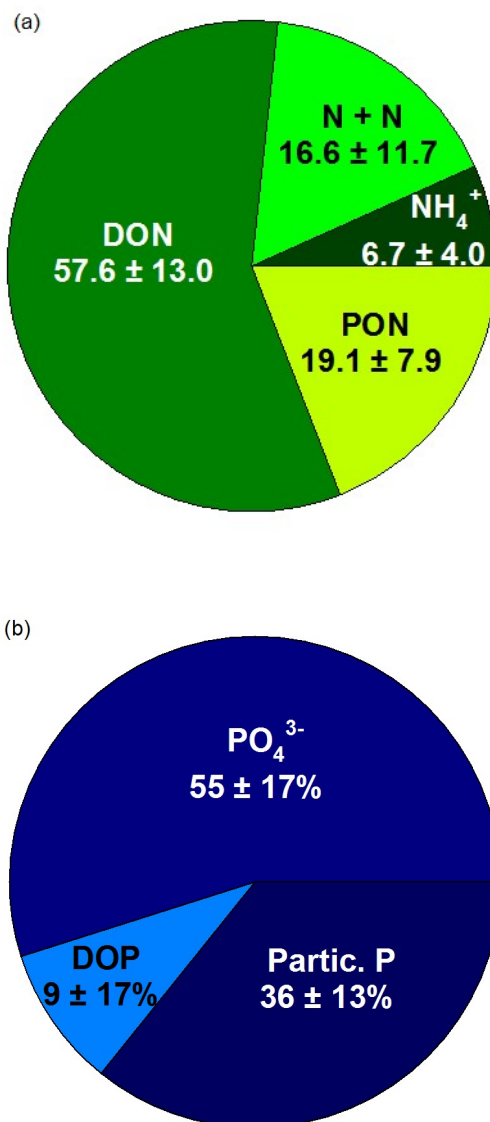


Figure 11. Chemical forms of (a) nitrogen where: DON = dissolved organic nitrogen, N + N = nitrate + nitrite, NH<sub>4</sub><sup>+</sup> = ammonium, and PON = particulate organic nitrogen and (b) phosphorus where PO<sub>4</sub><sup>3-</sup> = phosphate, DOP = dissolved organic phosphorus, and Partic. P = particulate phosphorus for all samples from all tributaries ( $n = 73$ ).

In contrast with N, the ionic form of P (phosphate) accounted for an average of 55% of the total P relative to only 23% of the total N present in an ionic form (nitrate + nitrite + ammonium; Figure 11). Therefore, the N/P ratio (molar) for the ionic forms of N:P is ~4:1 relative to 16:1 for the classic ratio of Redfield (1934). This observation will be investigated in more detail during 2017-2018 by comparing dissolved N and P forms and concentrations in Turkey Creek and the adjacent IRL. Another difference between the chemical forms of N and P is that DON accounted for a six-fold higher percent of the total N than DOP did for P (Figure 11).

Terrestrial clay minerals and other inorganic particles are an important component of muck because these silts and clays from upland soil and sod typically make up 50–60% of muck deposits (Trefry et al., 1990). Concentrations of TSS during non-storm flow were low with an overall average of  $4.5 \pm 3.4$  mg/L (Table 6 and Figure 12a) and a range of 0.9–22 mg/L. The ratio of TDS/TSS for all non-storm samples averaged ~180 and shows the dominance of dissolved versus suspended solids in the IRL tributaries during non-storm flow.

As a percent of TSS, POC has the highest values with an average range of 16.3–32.8% (Table 6 and Figure 12b); therefore organic matter makes up ~50 to >90% of the suspended matter (based on [% organic matter = ~3 x %POC]; Trefry et al., 2007). This amount of organic matter is much greater than the 10–30% organic matter in muck sediments because these organic-rich, fine-grained particles carried during non-storm flow represent a small fraction (<30%) of the solids found in muck. In agreement with the OC content of the suspended sediment, the Si (7–12%) and Al (2–4%) content of the suspended matter were much lower than in muck (Si =  $19 \pm 2\%$  and Al =  $4.0 \pm 0.7\%$ ) because the POC-rich particles dilute the inorganic component. Therefore, either a large fraction of the organic matter is decomposed in the lagoon and/or storm flow carries a different and larger mass of particles to the IRL as discussed below.

The tributary particles were highly enriched in Fe with mean values of 4.2% (EG) to 11.6% (TC, Table 6 and Figure 12c) relative to muck with Fe concentrations that typically range from 3–4% (Table 6 and Figure 12c). The likely source for this is dissolved Fe in groundwater water that adsorbs to particles.

Table 6. Summary data (means  $\pm$  standard deviations) for suspended particles in tributaries for monthly (non-storm) samples from December 2015 through February 2017 (15 months).

Tributary	St. Sebastian (A)	St. Sebastian (B)	Turkey Creek	Crane Creek	Eau Gallie River
Median Flow <sup>1</sup> (30 yr) (CFS)	59 $\pm$ 27	64 $\pm$ 22	107 $\pm$ 52	12.6 $\pm$ 4.8	8.6 $\pm$ 3.6
Median Flow (2016) (CFS)	65	68	115	24	7.8
TSS (mg/L)	8.5 $\pm$ 4.8	2.3 $\pm$ 1.5	3.3 $\pm$ 1.3	2.8 $\pm$ 1.0	5.7 $\pm$ 1.8
POC (mg/L)	1.31 $\pm$ 0.53	0.69 $\pm$ 0.46	0.58 $\pm$ 0.21	0.54 $\pm$ 0.14	1.57 $\pm$ 0.35
POC (% of TSS)	16.3 $\pm$ 2.6	32.8 $\pm$ 9.1	18.7 $\pm$ 4.5	19.6 $\pm$ 3.8	29.5 $\pm$ 9.5
PON ( $\mu$ g N/L)	190 $\pm$ 70	150 $\pm$ 60	130 $\pm$ 40	120 $\pm$ 50	270 $\pm$ 100
PON (% of TSS)	2.7 $\pm$ 1.3	8.1 $\pm$ 2.8	4.6 $\pm$ 1.8	4.4 $\pm$ 1.5	5.1 $\pm$ 1.8
Partic. P ( $\mu$ g P/L)	50 $\pm$ 19	17 $\pm$ 16	19 $\pm$ 9	33 $\pm$ 11	60 $\pm$ 16
Partic. P (% of TSS)	0.60 $\pm$ 0.12	0.8 $\pm$ 0.4	0.58 $\pm$ 0.10	1.18 $\pm$ 0.18	1.1 $\pm$ 0.2
Partic. Si (mg Si/L)	1.0 $\pm$ 0.8	0.16 $\pm$ 0.24	0.31 $\pm$ 0.14	0.27 $\pm$ 0.14	0.50 $\pm$ 0.27
Partic. Si (% of TSS)	12.0 $\pm$ 1.7	7.3 $\pm$ 5.2	9.8 $\pm$ 2.3	10.4 $\pm$ 7.8	8.6 $\pm$ 2.1
Partic. Al (mg Al/L)	0.36 $\pm$ 0.29	0.038 $\pm$ 0.053	0.094 $\pm$ 0.048	0.067 $\pm$ 0.042	0.14 $\pm$ 0.11
Partic. Al (% of TSS)	4.1 $\pm$ 1.0	2.0 $\pm$ 1.9	2.8 $\pm$ 0.7	2.2 $\pm$ 0.8	2.2 $\pm$ 1.0
Partic. Fe (mg Fe/L)	0.50 $\pm$ 0.24	0.15 $\pm$ 0.15	0.35 $\pm$ 0.20	0.32 $\pm$ 0.12	0.24 $\pm$ 0.09
Partic. Fe (% of TSS)	6.6 $\pm$ 1.5	6.3 $\pm$ 4.2	10.0 $\pm$ 3.0	11.6 $\pm$ 1,9	4.2 $\pm$ 0.8

<sup>1</sup>USGS (2017).

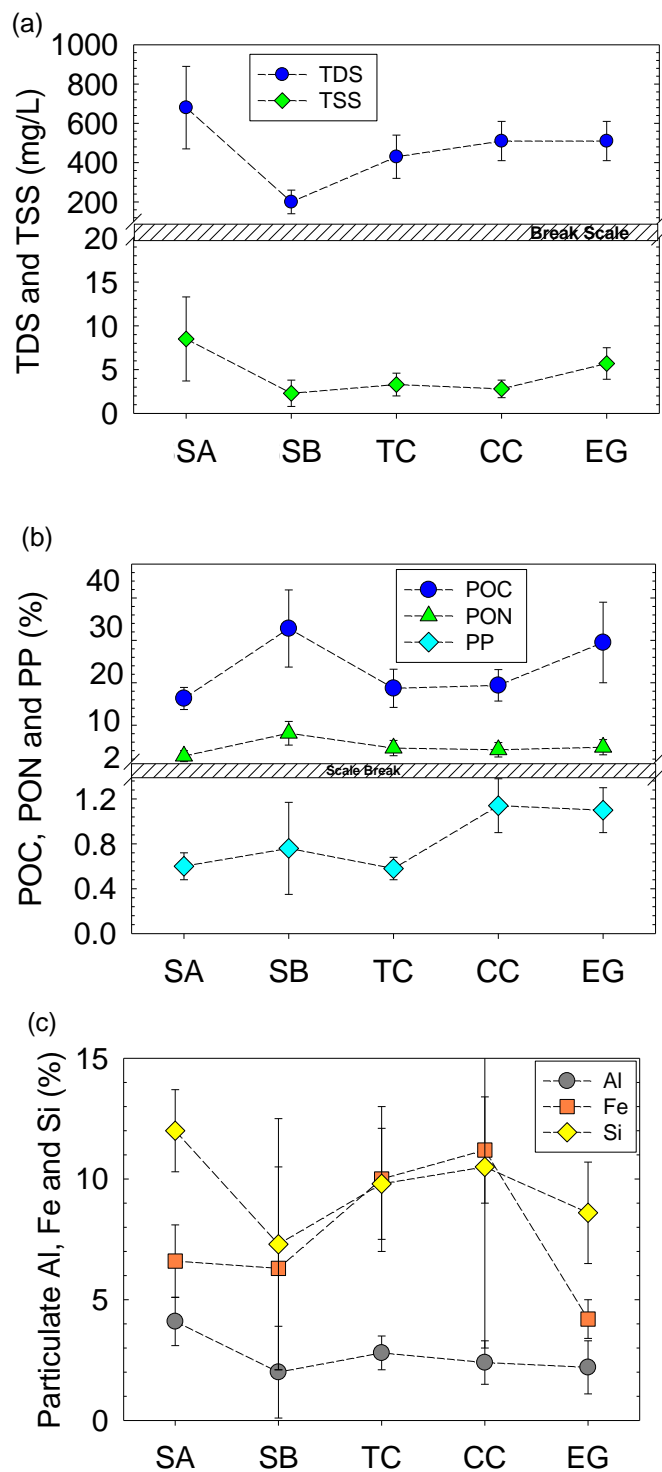


Figure 12. Mean values ( $\pm$  standard deviation) for (a) total dissolved solids (TDS) and total suspended solids (TSS), (b) particulate carbon (POC), nitrogen (PON) and phosphorus (PP) and (c) particulate aluminum (Al), iron (Fe) and silicon (Si) for the tributaries during monthly surveys from December 2015 to February 2017. Dashed lines added to help show differences in values among tributaries.

Mean values for pH, DO, turbidity, phosphate, DOC and total N for the same location in Turkey Creek in 1989 (Dierberg, 1991) were within 10% of our 2016 values (Table 7). Although concentrations of nitrate + nitrite were quite variable in each study, the mean value in 2016 was 85% greater than in 1989 (Table 7). In addition, PON values were three times greater in 2016 (Table 7). Concentrations of DOP were low in both 1989 and 2016 (Table 7).

Two of the shifts in concentrations from 1989 to present (a 40% decrease in TDS and a 30% decrease in DON) may reflect the large growth and development in Palm Bay and the Turkey Creek drainage basin. The population of Palm Bay has increased by 78% from 63,000 in 1989 to 112,000 in 2016. Along with the increase in population, increases in housing, commercial properties and impervious surface area also occurred. These changes lead to increased runoff of freshwater, a decrease in the relative amount of groundwater in TC and thus a decrease in TDS. Similarly, the decrease in DON concentrations also reflects the decrease in natural land area as previously discussed.

Table 7. Comparison of results from the same Turkey Creek site during this study in 2016 and in 1989 (Dierberg, 1991).

Parameter or Chemical	2016	1989
Conductivity ( $\mu\text{S}/\text{cm}$ )	$770 \pm 90$	$1100 \pm 200$
pH	$7.52 \pm 0.17$	$7.58 \pm 0.25$
DO <sub>2</sub> (mg/L)	$7.2 \pm 1.4$	$6.6 \pm 1.3$
Turbidity (NTU)	$4.0 \pm 1.2$	$3.7 \pm 2.0$
Total Suspended Solids (TSS in mg/L)	$3.3 \pm 1.3$	$4.3 \pm 4.0$
Ammonium ( $\mu\text{g N}/\text{L}$ )	$35 \pm 11$	$26 \pm 16$
Nitrate + Nitrite ( $\mu\text{g N}/\text{L}$ )	$120 \pm 92$	$65 \pm 67$
Dissolved Organic N (DON, $\mu\text{g}/\text{L}$ )	$450 \pm 80$	$660 \pm 150$
Particulate Organic N (PON, $\mu\text{g}/\text{L}$ )	$130 \pm 40$	$40 \pm 30$
Total N (dissolved + particulate) ( $\mu\text{g}/\text{L}$ )	$720 \pm 170$	$750 \pm 180$
Phosphate ( $\mu\text{g P}/\text{L}$ )	$20 \pm 8$	$20 \pm 11$
Dissolved Organic P ( $\mu\text{g P}/\text{L}$ )	$8 \pm 5$	$5 \pm 5$
Particulate P ( $\mu\text{g}/\text{L}$ )	$19 \pm 8$	$13 \pm 10$
Total P (dissolved + particulate) ( $\mu\text{g}/\text{L}$ )	$48 \pm 20$	$35 \pm 16$
Dissolved Organic Carbon (mg C/L)	$11.5 \pm 3.4$	$10.1 \pm 3.9$

Monthly Trends in Non-Storm Tributary Flow and Composition

Summary data for each tributary (Tables 4, 5 and 6) show that relative standard deviations (RSD =  $[\text{SD}/\text{mean}] \times 100\%$ ) for selected nutrient species can be  $<20\%$  in a few cases (e.g., DON in SB) to more than 100% in others (e.g., nitrate + nitrite in SB and EG, and phosphate in SA). Therefore, monthly trends during non-storm flow may provide one means for identifying processes that regulate concentrations and fluxes of nutrients. During this first year of the tributaries study, we set out to sample storm events where peak flow was expected to be ten-fold higher than the 30-year median; a point that will be addressed in the next section. Here, we use all data ( $n = 15$  months) for water flow at each tributary on non-storm days when samples were collected. Within our limited data sets, a negative relationship between non-storm flow and TDS was observed for SA, TC and CC; no clear relationship was observed for SB (Figure 13) where water is retained behind a weir and flow occurs in response to rainfall and agricultural water releases or storage upstream. If these processes at SB were to occur at different times, some confusion in the relationship between TDS and flow could occur.

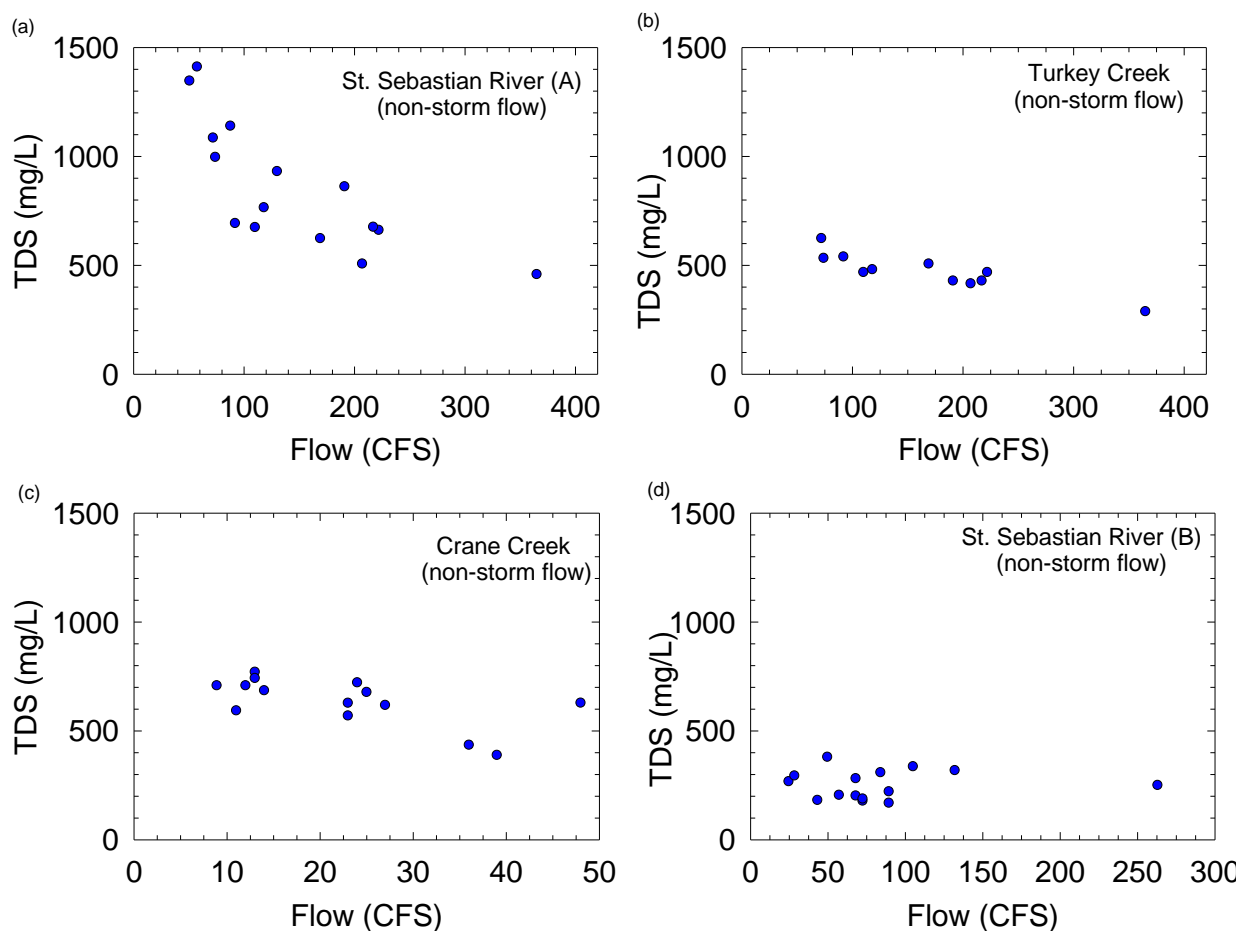


Figure 13. Total dissolved solids (TDS) versus water flow for (a) St. Sebastian River A, (b) Turkey Creek, (c) Crane Creek and (d) St. Sebastian River B. Water flow data from USGS (2017).



Water flow is, of course, highly variable in all the tributaries due to variations in rainfall and the sizes of the drainage basins. The full data set for water flow from December 2015 to February 2017 for SA shows a >30-fold range in flow (Figure 14a). Even during non-storm conditions, a 5- to 8-fold range in flow was observed at SA (Figure 14b), a range that may be conducive to tracking changes in concentrations of various chemical parameters as a function of water flow. During the second year of the tributary project, we will pursue these relationships to look for trends during the extended period of baseflow that we experienced from December 2015 to June 2017.

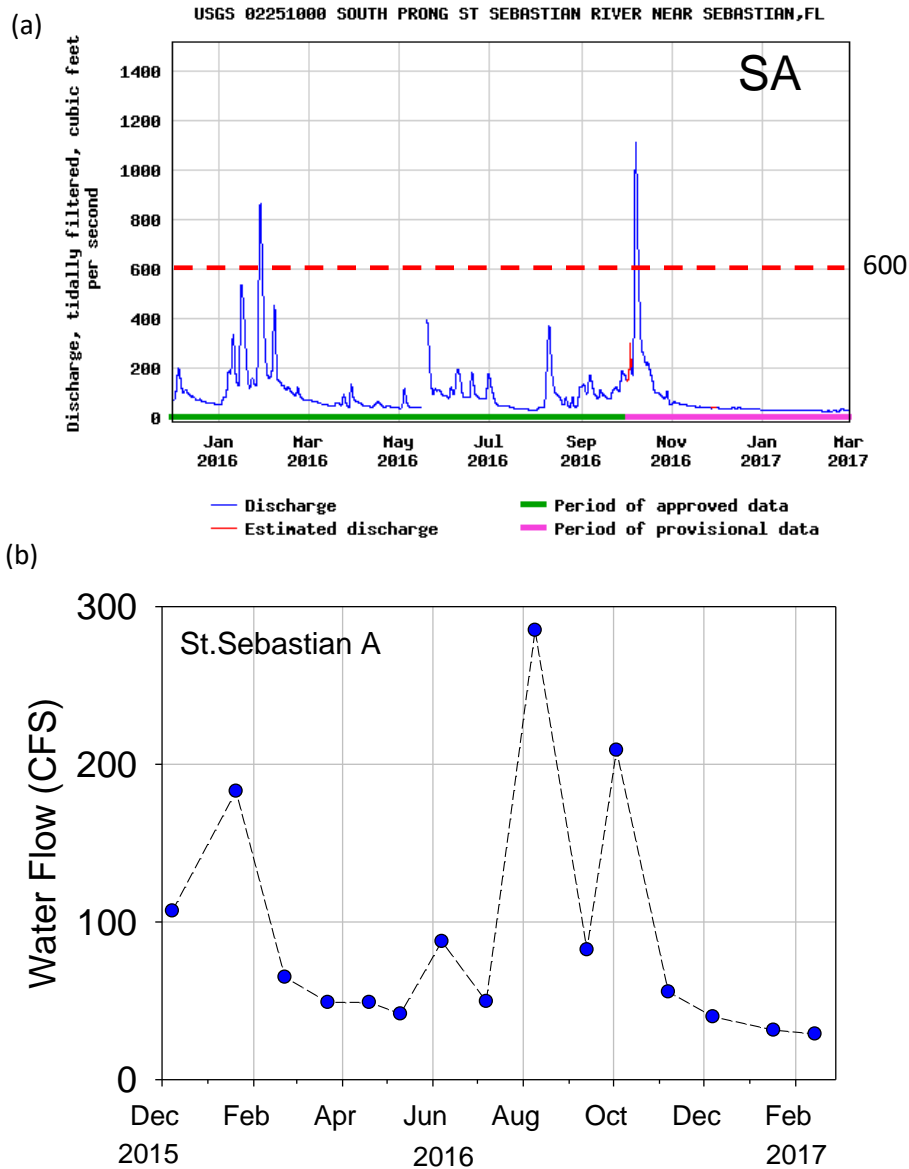


Figure 14. Water flow at St. Sebastian River South Prong (SA) from (a) continuous data for December 2015 to February 2017 and (b) for dates that were sampled monthly during this project. Water flow data from USGS (2017). Note: scales for flow on (a) and (b) are different. Dashed red line on (a) at ~10 times the 30-year, median flow. Dashed line on (b) added to help show changes over time.

The trend for TDS versus flow for SA (Figure 13a) also can be seen in the time series plot for TDS and flow (Figure 15a); water flow and TDS show a reasonably good mirror image. In contrast, values for TSS follow water flow more positively with only minor exceptions (Figure 15b). No consistent trends for flow and values for DON, nitrate + nitrite, ammonium or phosphate at SA were observed during non-storm flow (Figure 16). However, higher flow during the sampling day in August 2016 coincided with lower concentrations of nitrate + nitrite; and, higher flow during the October 2016 sampling day corresponded with increased values for DON, ammonium and phosphate. A single day's sampling does not always seem to show flow-related changes; the storm event data do, however, give insight to flow-related trends as described in the next section.

The complete USGS water flow data for SB during our study show at least 15 periods of increased flow (Figure 17a); however, only about two of these periods had >10-fold increases in flow relative

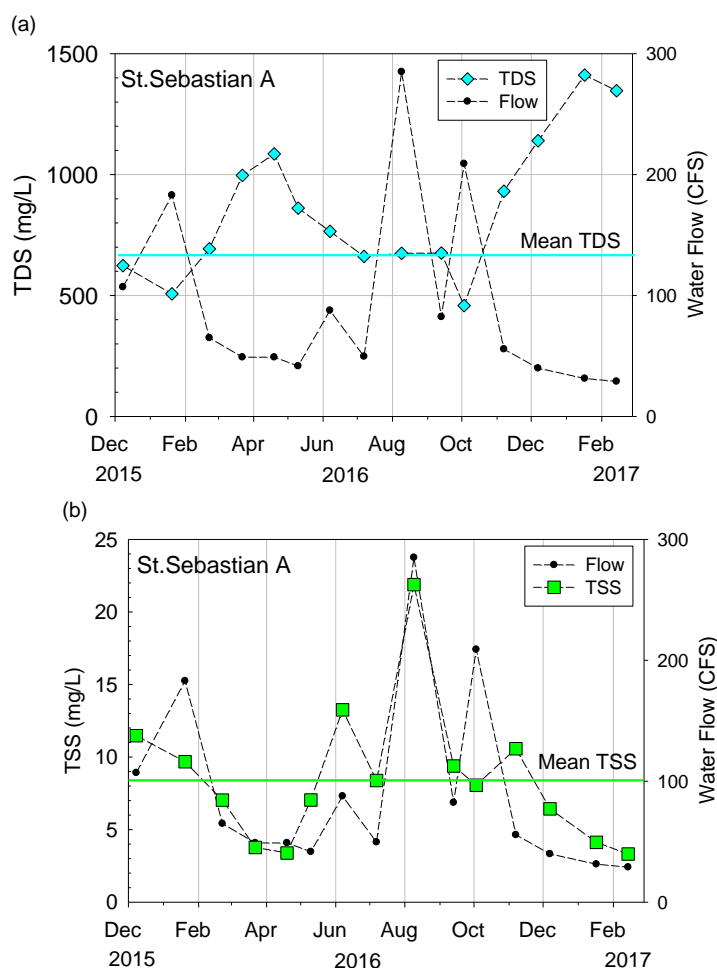


Figure 15. Water flow and (a) total dissolved solids (TDS) and (b) total suspended solids (TSS) for the St. Sebastian River A (South Prong) for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

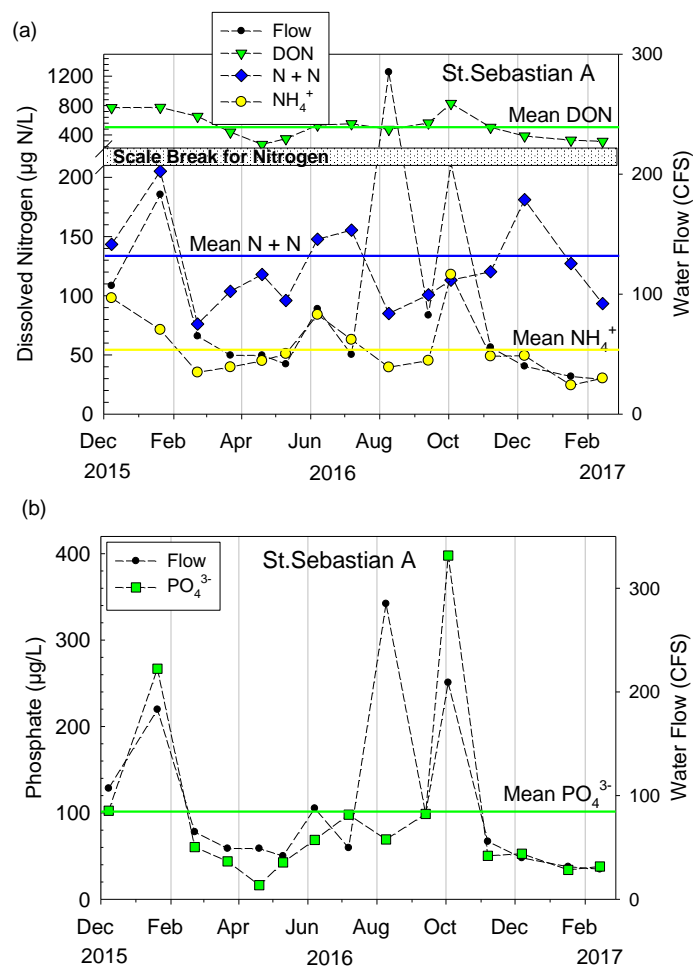


Figure 16. Water flow and (a) dissolved organic nitrogen (DON), nitrate + nitrite (N + N) and ammonium (NH<sub>4</sub><sup>+</sup>) and (b) phosphate (PO<sub>4</sub><sup>3-</sup>) for the St. Sebastian River South Prong (SA) for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

to the long-term median of 59 CFS. Therefore, considerable variability in flow occurs within a range of 3–4 times the average median flow (Figure 17). During our monthly surveys, we sampled SB over a 7- to 8-fold range in flow. Concentrations of TDS appear to increase during lower water flow on the time-series graph (Figure 18a), but not on the x-y plot (Figure 13d). Again, this may be related to the greater control of flow at SB by the weir and upland irrigation processes. Both views of the trend (Figures 13d and 18a) may be valuable when used together. TSS tracks flow relatively well in the monthly samples with one large spike during the one sample day with higher flow (Figure 18b). Values for DON were uniform (RSD = 8%) whereas concentrations of ammonium (RSD = 41%), phosphate (RSD = 65%) and nitrate + nitrite (RSD = 88%) were quite variable during non-storm periods (Figure 18c for DON, N + N and NH<sub>4</sub><sup>+</sup>) with no significant relationships between nitrate + nitrite and phosphate ( $p = 0.95$ ) or ammonium ( $p = 0.94$ ). The complex storage and mixing of water in SB greatly complicate trends for dissolved nutrients.

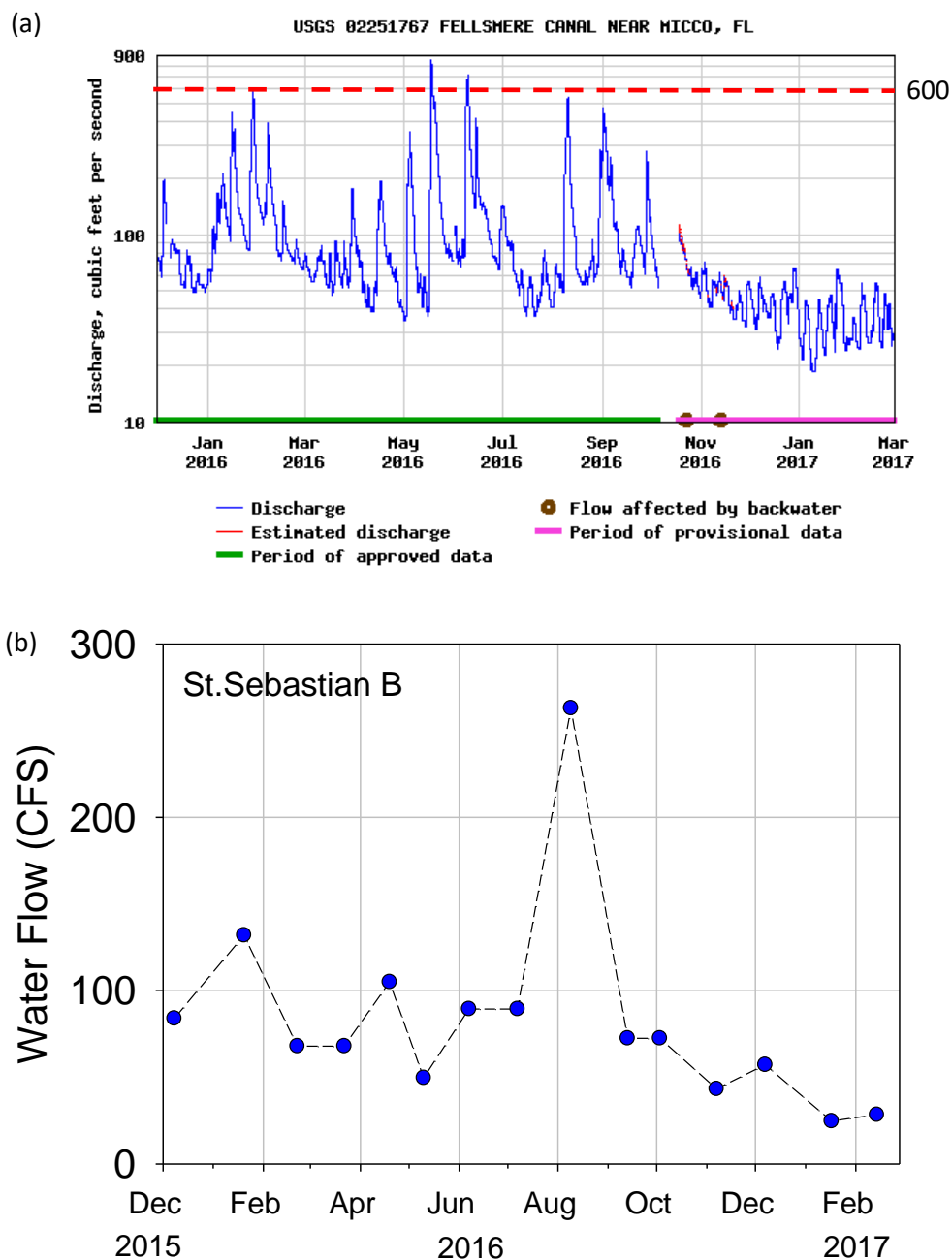


Figure 17. Water flow at St. Sebastian River, Fellsmere Canal (SB) from (a) continuous data (log scale) for December 2015 to February 2017 and (b) for dates that were sampled monthly for this project. Water flow data from USGS (2017). Note: scales for flow on (a) and (b) are different. Dashed red line on (a) ~10 times the 30-year, median flow. Dashed line on (b) added to help show changes over time.

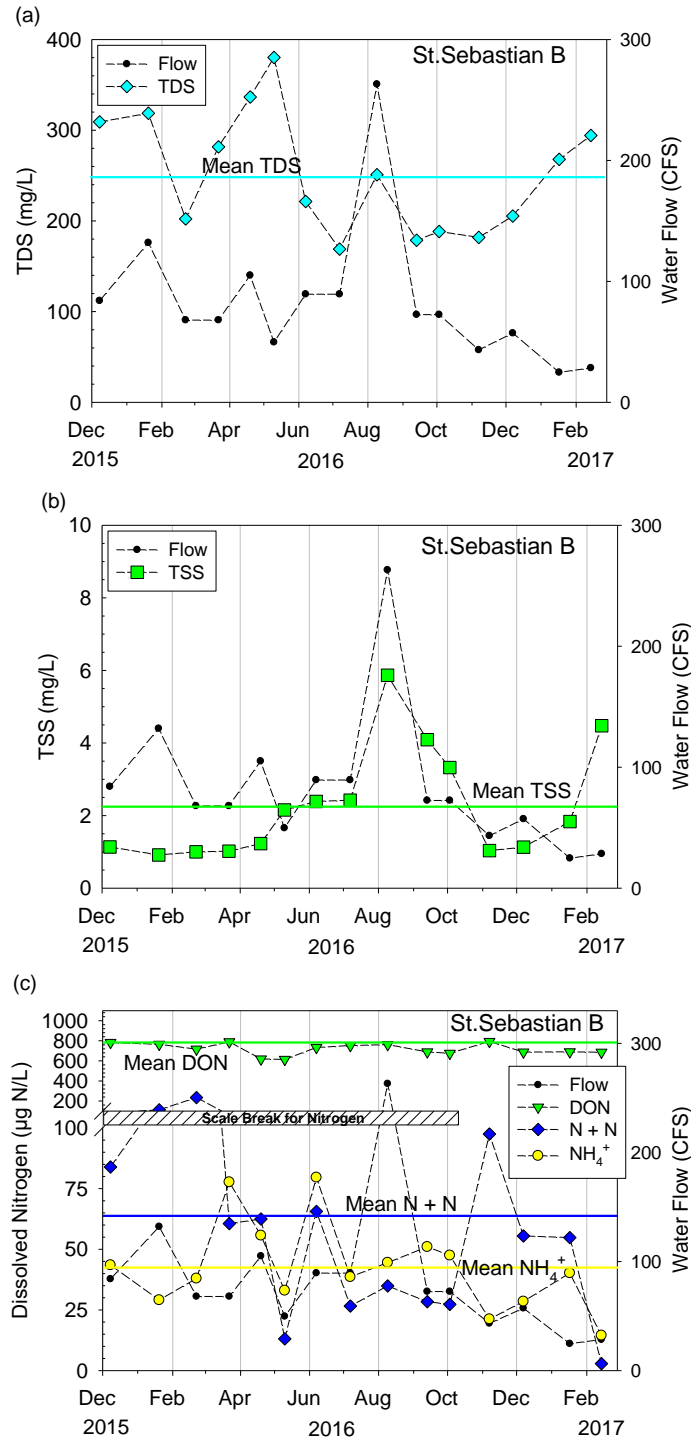


Figure 18. Water flow and (a) total dissolved solids (TDS), (b) total suspended solids (TSS) and (c) dissolved organic nitrogen (DON), nitrate + nitrite (N + N) and ammonium (NH<sub>4</sub><sup>+</sup>) for the St. Sebastian River, Fellsmere Canal (SB) for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

Flow variations of only 3–4 fold were observed during monthly sampling in TC (Figure 19); however, we did sample an extended storm event during May 2016; this event will be discussed in the next section. Again, TDS values seem to mirror water flow, showing a dilution effect at high flow (Figure 20a). Salt intrusion upstream to our sampling site was observed from November 2016 through February 2017 with TDS values of ~1000 mg/L in surface water and >15,000 mg/L in water at 2–3 m. Concentrations of TSS tracked flow directly with the exception of the October 3 sample, most likely due to the effect of following a peak flow by 2–3 days (Figure 19a) during which TSS values typically decrease considerably. Concentrations of DON and ammonium do not seem to track flow at TC with the relatively small changes in flow. Nitrate + nitrite seems to show some positive responses to volume changes during non-storm flow (Figure 20c). What you do you think happened during the May 2016 storm?

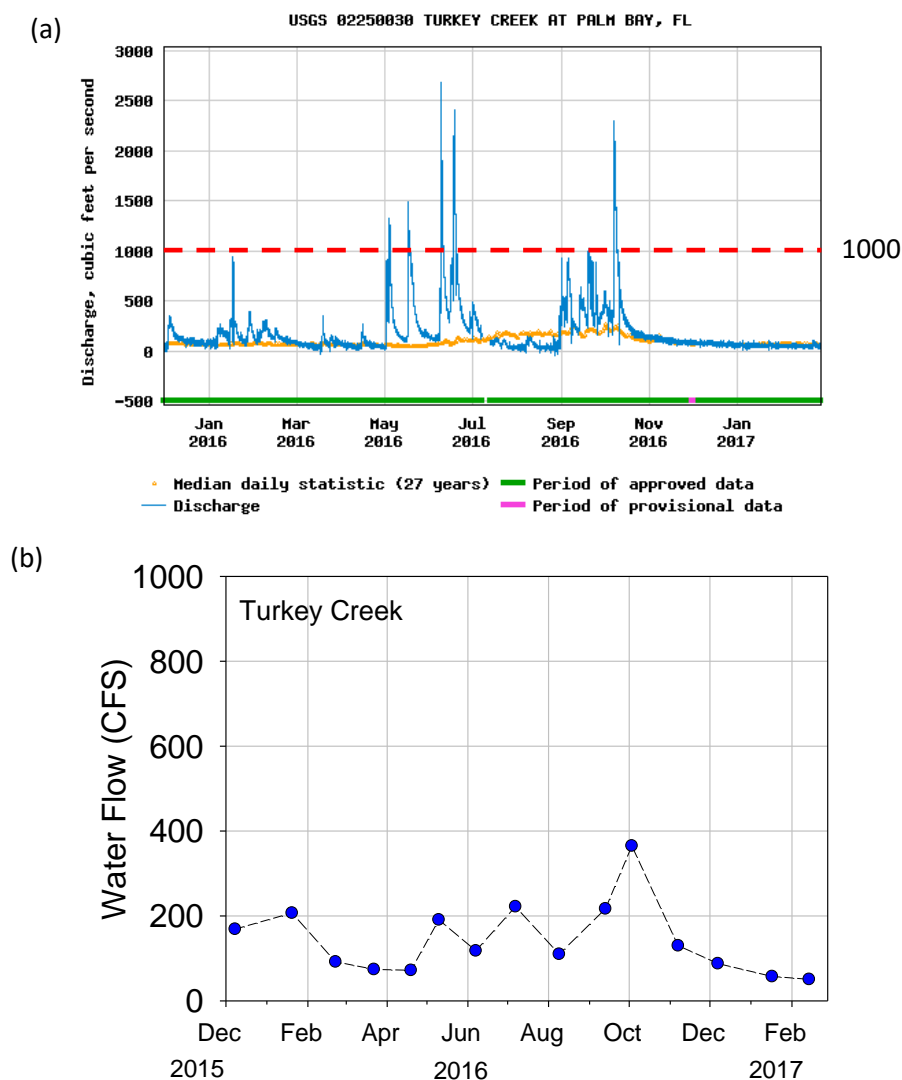


Figure 19. Water flow at Turkey Creek from (a) continuous data (log scale) for December 2015 to February 2017 and (b) for dates sampled monthly for this project. Water flow data from USGS (2017). Dashed red line on (a) at ~10 times the 30-year, median flow. Dashed line on (b) added to help show changes over time.

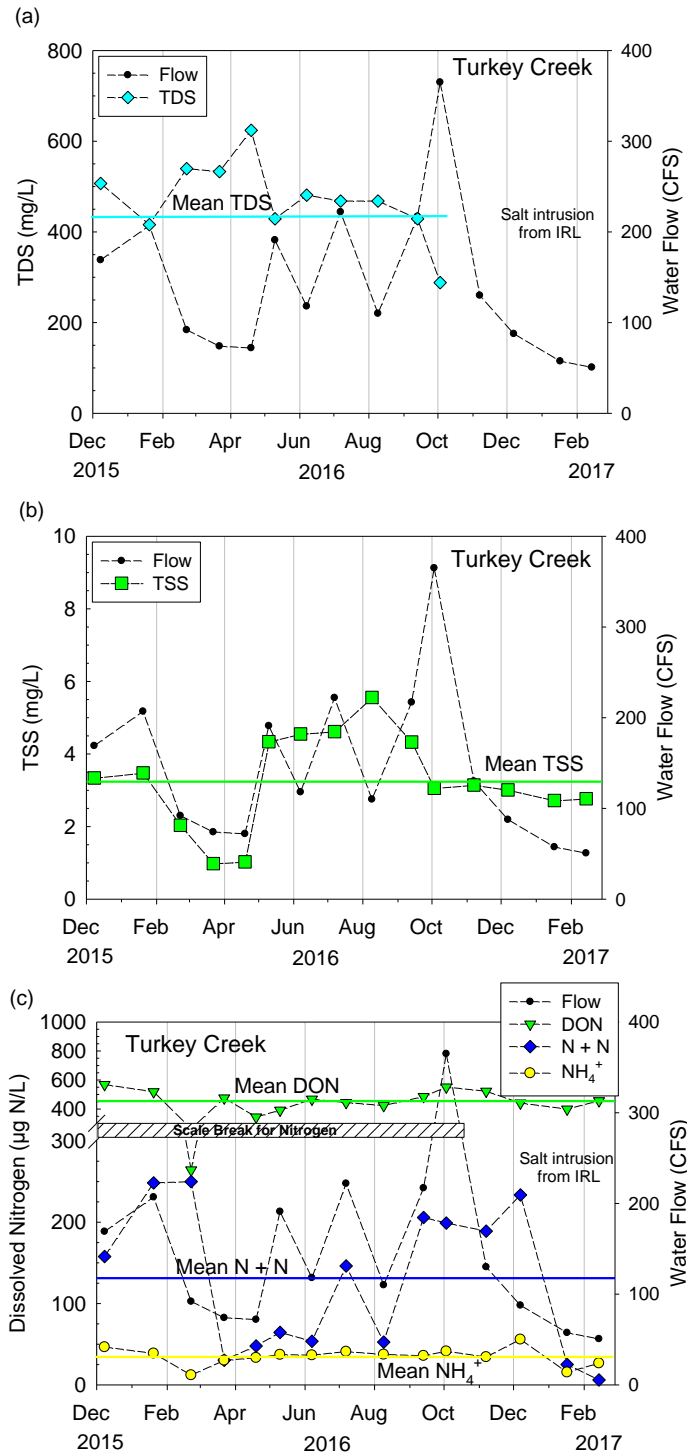


Figure 20. Water flow and (a) total dissolved solids (TDS), (b) total suspended solids (TSS) and (c) dissolved organic nitrogen (DON), nitrate + nitrite (N + N) and ammonium (NH<sub>4</sub><sup>+</sup>) for Turkey Creek for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

The USGS installed continuous nitrate + nitrite samplers at TC and CC; results for TC show all values to be <0.4 mg N/L (<400 µg N/L) with what appear to be relatively abrupt shifts (Figure 21a); the median daily values vary by about 2–3 fold. Our discrete samples also show large deviations (range of 10–250 µg/L, Figure 21b). Overall, concentrations of nitrate + nitrite track flow during the non-storm period. During January and February 2017, concentrations of the nitrate + nitrite approached zero because a high salinity (S = 25) wedge of low-oxygen (<20% saturation) water had encroached into the sampling site.

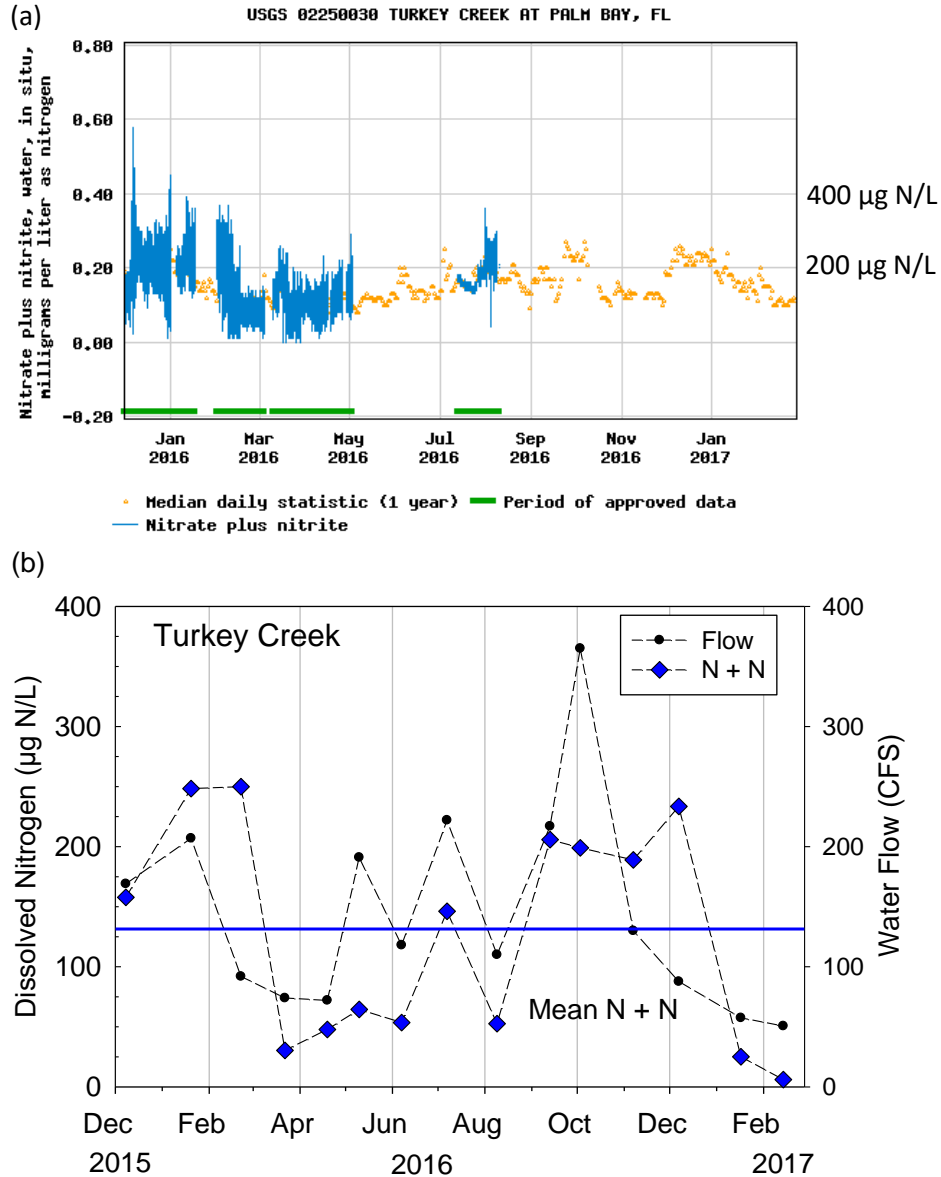


Figure 21. (a) Concentrations of nitrate + nitrite for Turkey Creek from USGS continuous monitoring and (b) water flow and nitrate + nitrite (N + N) for monthly samples for Turkey Creek (December 2015–February 2017) with mean values of N + N for the study period as a horizontal line on the figure. Water flow data from USGS (2017). Dashed lines on (b) added to help show changes over time.



The more dense urban land use in the Crane Creek drainage basin (66% urban, SJRWMD, 2009) seems to foster large swings in flow (Figure 22a) that certainly reflect the high degree of runoff into a well channelized creek. Our monthly sampling extended over a five-fold range in flow (Figure 22b).

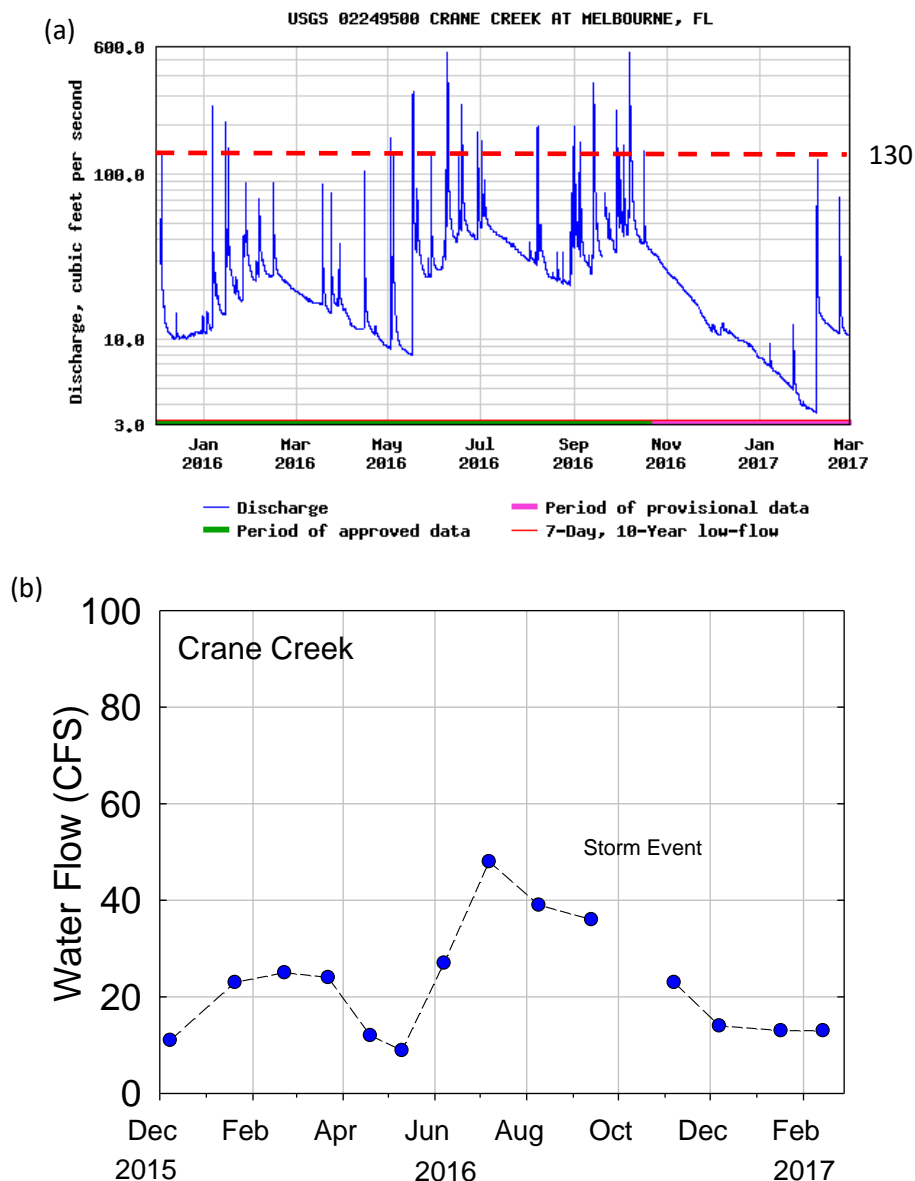


Figure 22. Water flow at Crane Creek from (a) continuous data (log scale) from December 2015 to February 2017 and (b) for dates that were sampled monthly for this project. Water flow data from USGS (2017). Dashed red line on (a) ~10 times the 30-year, median flow. Dashed line on (b) added to help show changes over time.

Variability in values for TDS for Crane Creek was relatively low (RSD = 20%); however, some opposite responses to increased flow were observed (Figure 23a). Concentrations of TSS showed direct changes relative to water flow (Figure 23b). Nutrient values did not vary with flow in any clear pattern (Figure 23c). A larger data base is needed to better understand how the low and transient flow in Crane Creek influences chemical composition of the water. Absolute values for nitrate + nitrite from the USGS continuous sampler match our results for discrete samples relatively well (Figure 24). More, high temporal resolution data are needed to directly compare agreement between data from the USGS and us.

The USGS continuous flow data were not available at this time for the Eau Gallie River; however, we did record flow values for our discrete samples (Figure 25). Despite the small flow of EG, both TDS and TSS showed negative and positive responses, respectively, to flow (Figure 25 a, b). Both nitrate + nitrite and DON showed large swings in concentration that do not appear to influence by flow (Figure 26). We certainly have quite a bit more data analysis to carry out in the year to come.

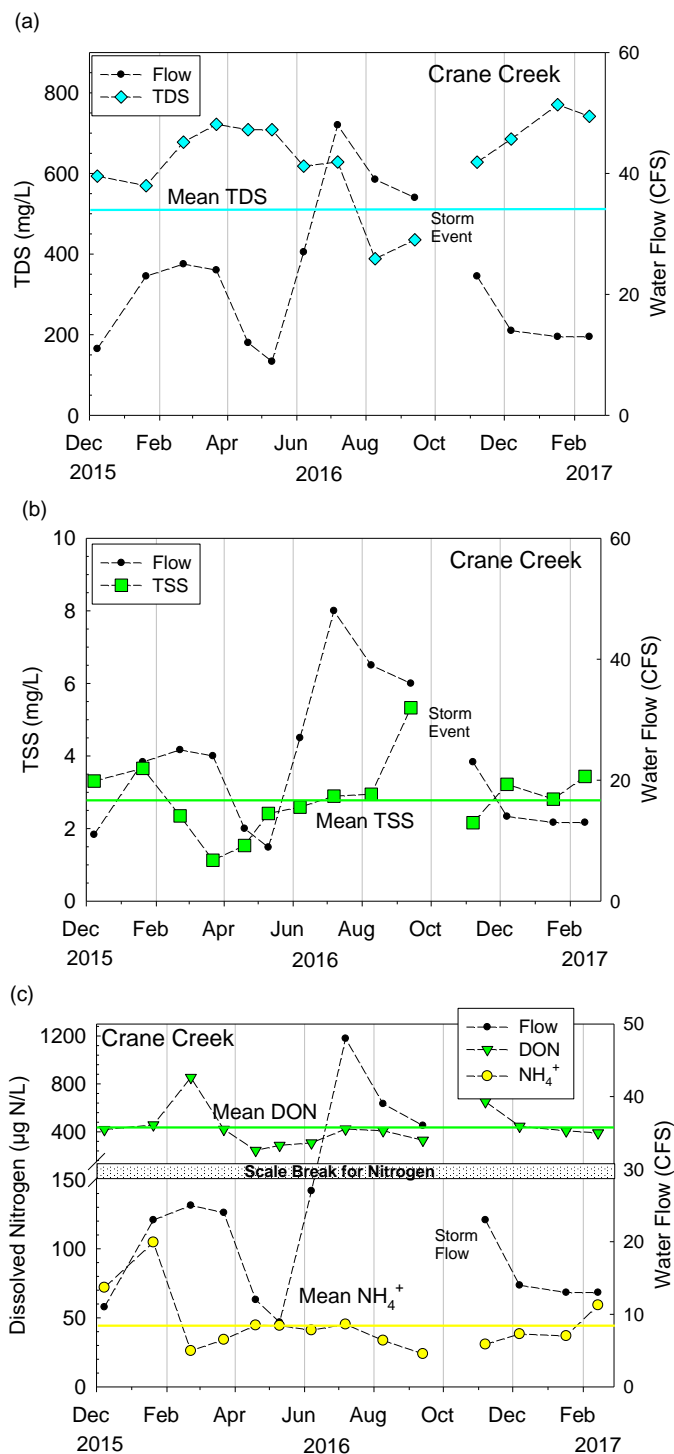


Figure 23. Water flow and (a) total dissolved solids (TDS), (b) total suspended solids (TSS) and (c) dissolved organic nitrogen (DON) and ammonium (NH<sub>4</sub><sup>+</sup>) for Crane Creek for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

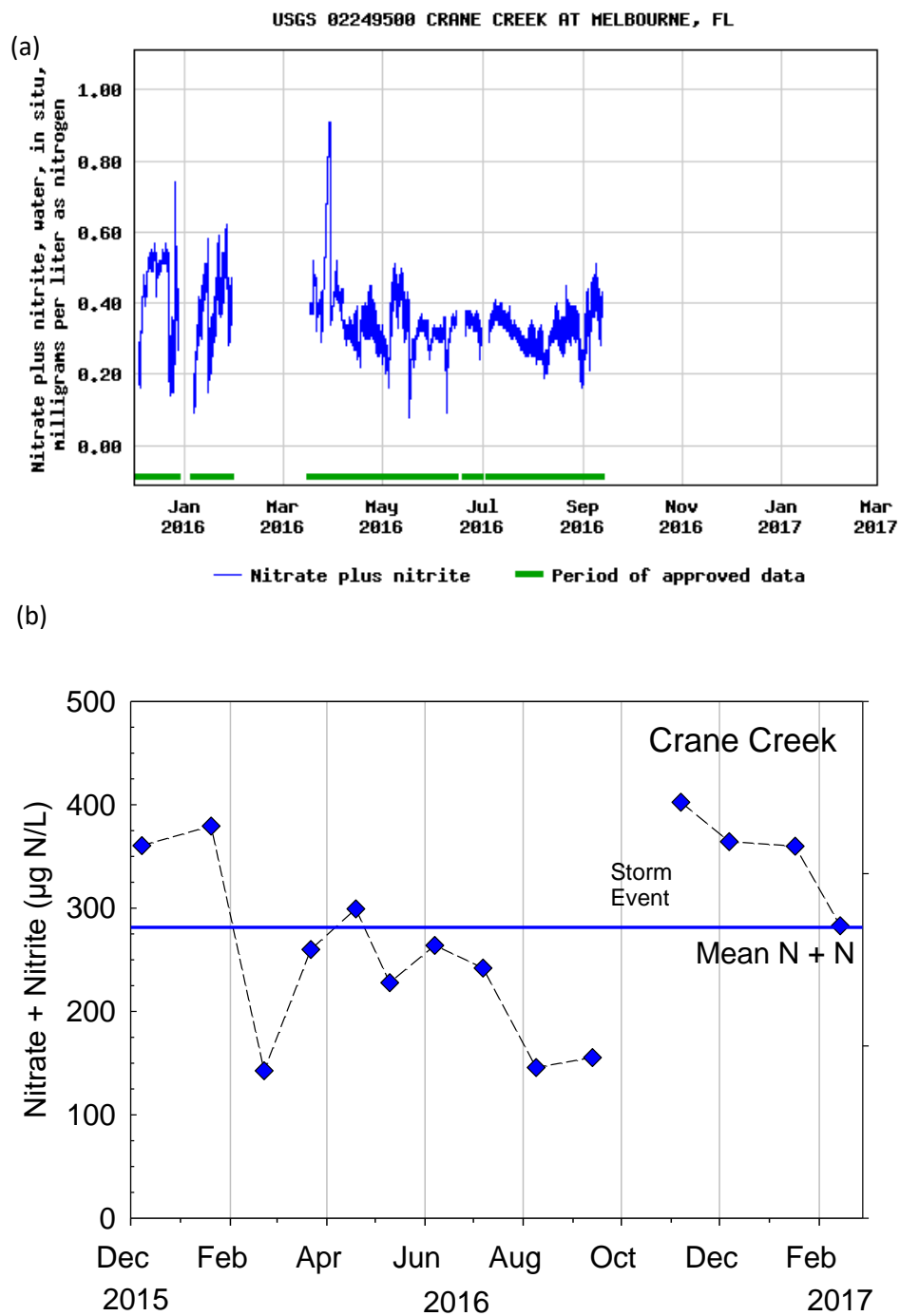


Figure 24. Concentrations of nitrate + nitrite from (a) USGS continuous monitoring and (b) our data from discrete samples for Crane Creek (December 2015–February 2017) with mean values for the 15-month study period as a horizontal, solid line across (b). Dashed line on (b) added to help show changes over time.

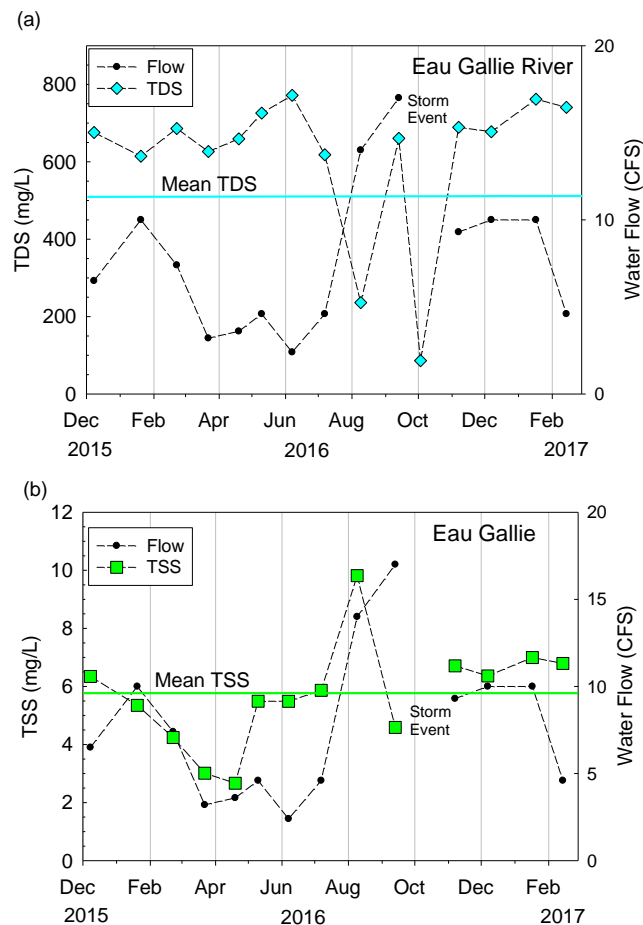


Figure 25. Water flow and (a) total dissolved solids (TDS) and (b) total suspended solids (TSS) for the Eau Gallie River for monthly samples (December 2015–February 2017) with mean values for the study period as horizontal lines on each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

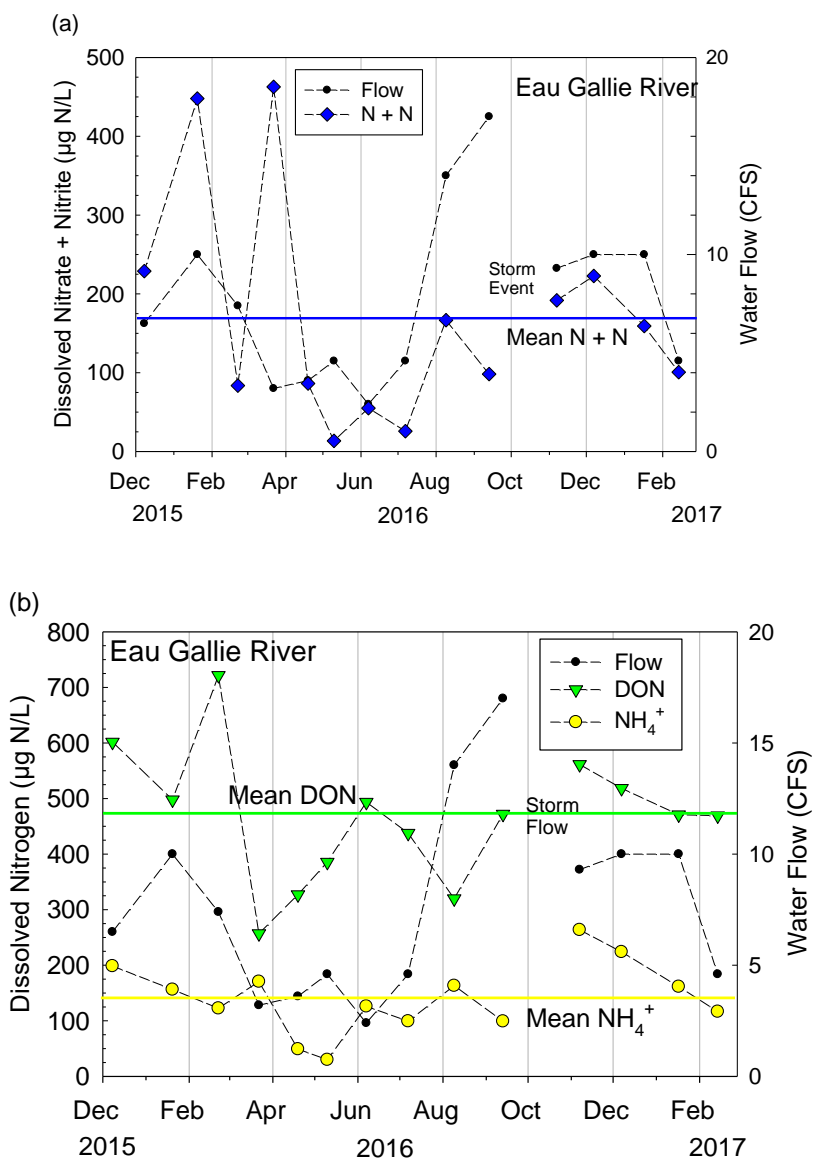


Figure 26. Water flow and (a) concentrations of nitrate + nitrite (N + N) and (b) dissolved organic nitrogen (DON) and ammonium (NH<sub>4</sub><sup>+</sup>) for monthly samples from the Eau Gallie River (December 2015–February 2017) with mean values for the study period as horizontal lines across each figure. Water flow data from USGS (2017). Dashed lines added to help show changes over time.

*Trends in Concentrations of Chemicals during Storm Flow*

Results from storm event sampling on nine occasions have given us some valuable insight into sources of the various chemicals from groundwater water versus surface water runoff. We have just begun the process of interpreting this large database for storm flow. As previously mentioned, we planned to sample storm events where we predicted that peak flow would be ten-fold higher than the 30-year median. It is, of course, difficult to predict peak flow in advance of the storm; therefore, we did not always obtain storm flow data that was as high as set during planning (Table 8). As we obtain more data, the use of a continuum of flow scenarios, rather than clear-cut non-storm and storm flow seems likely. The 2016–2017 year included a very dry winter. Therefore, as we assemble data not included in this annual report (i.e., March to June, 2017), we foresee its value for contributing to our knowledge about the composition of baseflow water in the tributaries and for improving our perspective on storm and non-storm flow.

This section will focus on a multi-day event during May 17-24, 2016 in both Turkey Creek and Crane Creek. We recently captured a very nice event during May 2017 that will be included in the 2017–2018 report. We hope for a wetter and more predictable 2017–2018. Based on past experience (Trefry et al., 1989), high-resolution sampling of even one very good storm is quite valuable.

Table 8. Summary of pertinent data for storm events sampled. Samples include peak flow and the rising and falling limbs of the hydrograph.

Tributary	Dates	Median Flow (30 yr., CFS)	Peak of Storm Flow (CFS)	Number of Samples
Turkey Creek	May 4–5, 2016	107	896	2
	May 17–24, 2016		1380	15
	Jun 9–11, 2016		2640	3
Crane Creek	May 4–5, 2106	12.6	27	2
	May 17–24, 2106		119	15
	Jun 9–11, 2016		553	3
	Feb 7, 2017		123	4
	Feb 22–23, 2017		79	6
Eau Gallie River	Feb 22–23, 2017	8.6	131	6

During the May 17–24, 2016, event, water flow in Turkey Creek increased from ~100 CFS (close to the 30-yr median flow of 107 CFS) to ~1500 CFS in <12 hours (Figure 27a). Flow decreased slowly over the following few days while being punctuated with slight new peaks in flow almost every day (Figure 27). Concentrations of TDS decreased to about half the mean value for 2016 in <1 day and then slowly increased back to near mean values over the ensuing 5–6 days (Figure 28a). We were fortunate to catch the often observed initial peak in TSS that was almost 10 times higher than mean TSS values for the year (Figure 28b). Concentrations of DON and ammonium stayed relatively unchanged during the event; however, concentrations of nitrate + nitrite decreased by 50% and then slowly increased to mean values for 2016 (Figure 28, c, d, e). The data suggest that sources of nitrate + nitrite, like TDS, may be similar and related to groundwater inputs that are diluted during the rain event. In contrast, concentrations of DON and ammonium seem less influenced by flow. Indeed, the net flux of these two forms of nitrogen (DON and  $\text{NH}_4^+$ ) requires a large input from surface runoff. We will continue this line of investigation with all our storm data. Concentrations of phosphate increased from 18  $\mu\text{g P/L}$  on May 10 (a monthly sampling, 7 days prior to the storm) to 40  $\mu\text{g P/L}$  early in the storm, peaked at ~60  $\mu\text{g P/L}$  and then stayed above the 2016 mean value for the remainder of the event. When we returned on June 7 for a monthly sample, the phosphate concentration was back to 19  $\mu\text{g P/L}$ . This certainly supports a large pulse of phosphorus with the storm.

The composition of the particles during the storm event became more clay-rich and less organic-C rich as the storm ramped up (Figure 29). The impact on Fe was quite dramatic as particles with typically 10% Fe were diluted by more than two fold within 24 hours. The normal source of Fe is likely groundwater plus well water used for irrigation that would be greatly diluted by rain.



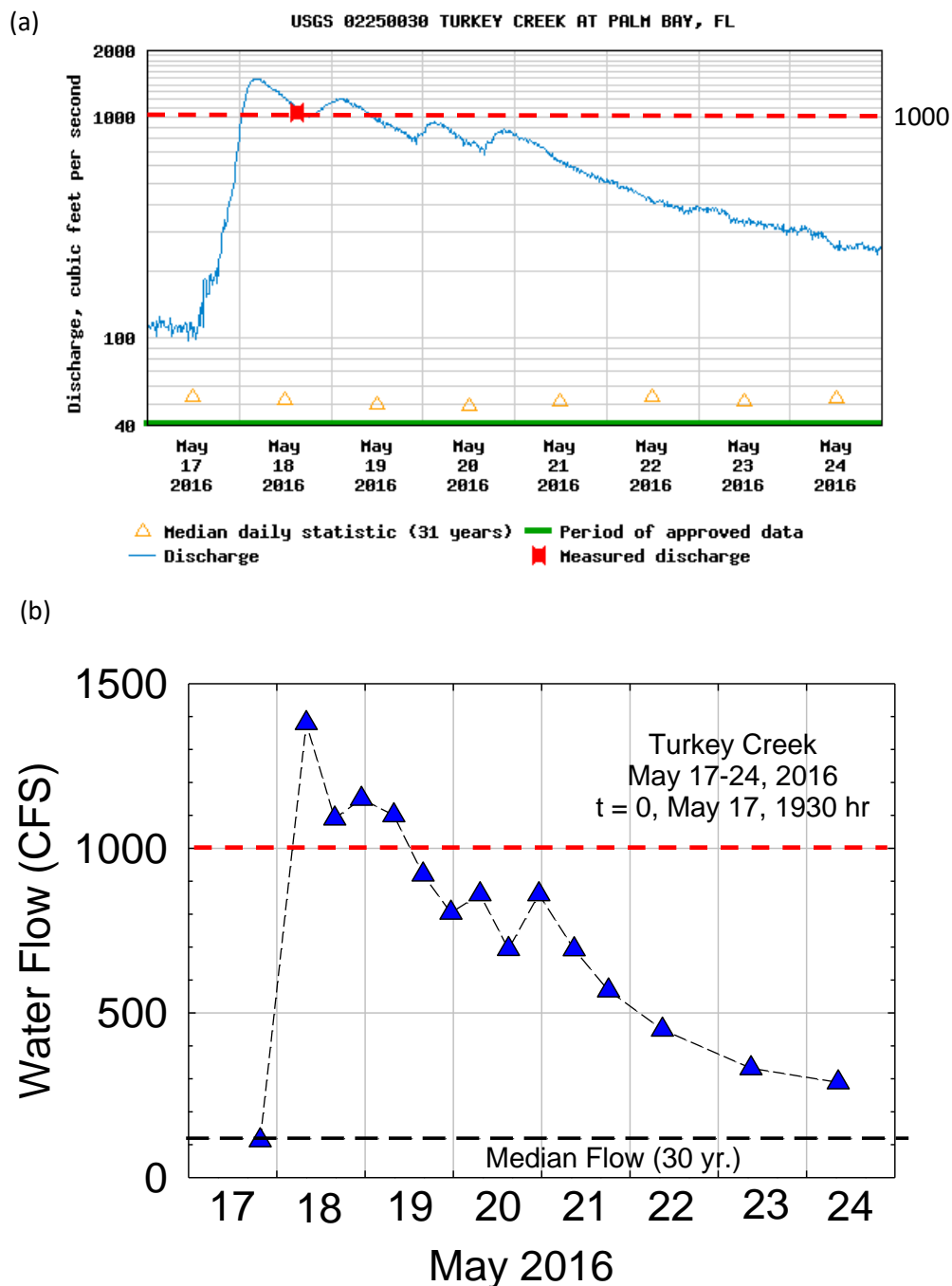


Figure 27. Water flow at Turkey Creek from (a) continuous data (log scale) from May 17–24, 2016 and (b) dates and times when discrete water samples were collected for this project. Water flow data from USGS (2017). Dashed red line on (a) and (b) at ~10 times the 30-year, median flow. Dashed line connecting markers on (b) added to help show changes over time.

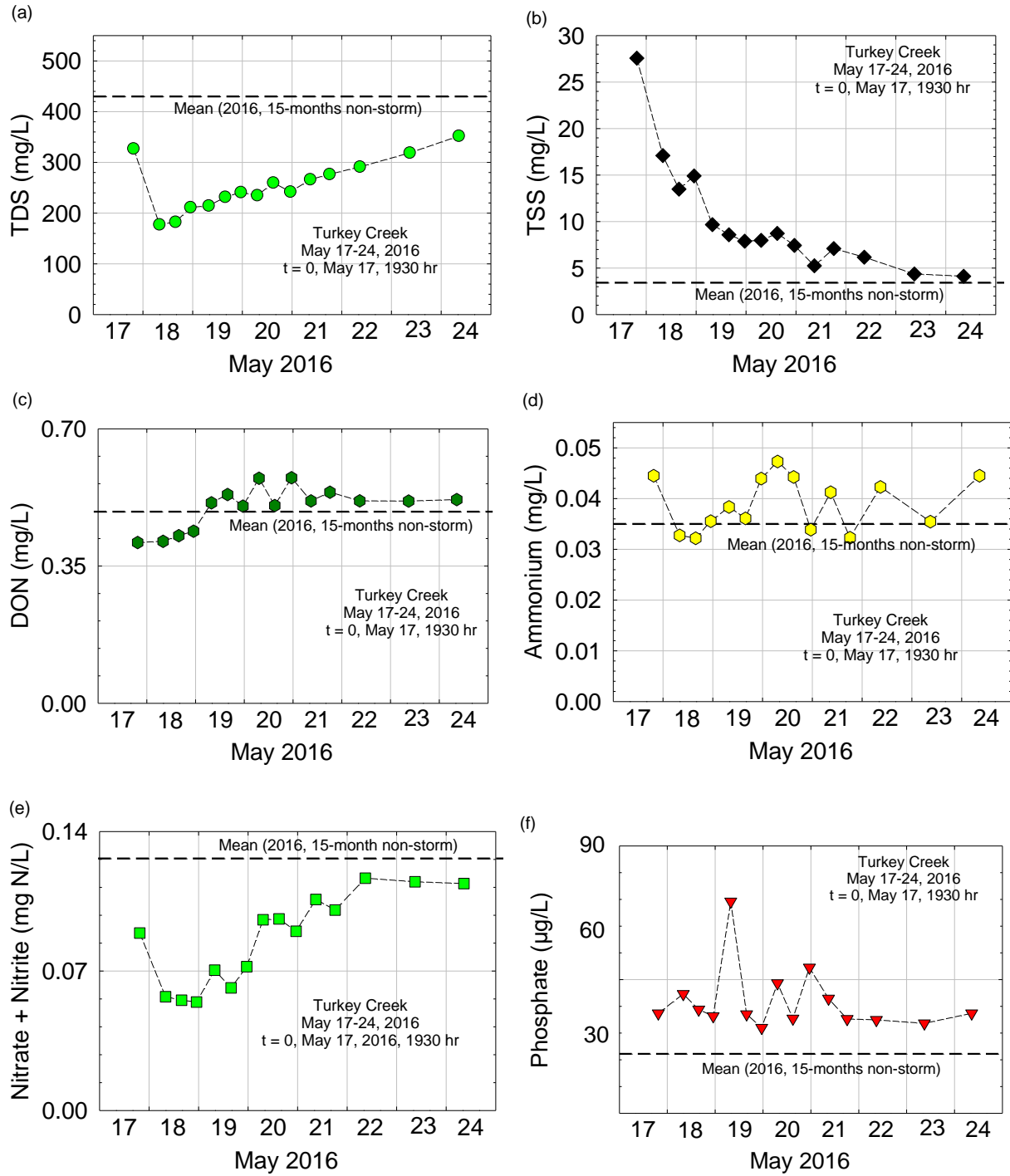


Figure 28. Time series trends for concentrations of (a) total dissolved solids (TDS), (b) total suspended solids (TSS), (c) dissolved organic nitrogen (DON), (d) ammonium, (e) nitrate + nitrite and (f) phosphate for Turkey Creek from data during May 17–24, 2016, when discrete water samples were collected for this project. Dashed lines connecting markers added to help show changes over time.

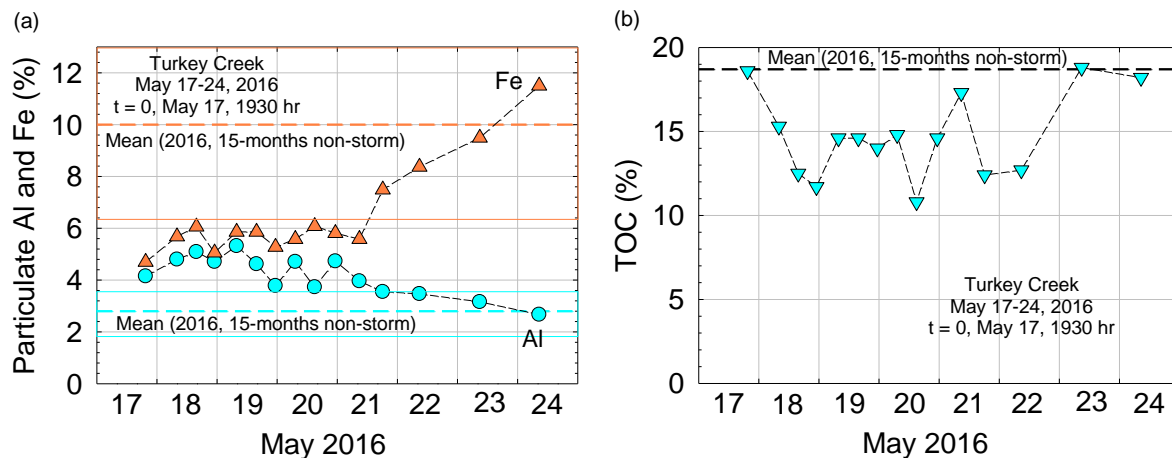


Figure 29. Time series trends for concentrations of (a) particulate aluminum and iron and (b) total organic carbon (TOC) for Turkey Creek from data during May 17–24, 2016, when discrete water samples were collected for this project. Dashed lines connecting markers added to help show changes over time.

The May 2016 rain event gave us an interesting opportunity to study two nearby tributaries with different flow and composition regimes. On May 17, 2016, flow in Crane Creek increased from only 6 CFS to 80 CFS within 1-2 hours (Figure 30); we have seen this trend in Crane Creek several times now. We sampled at a peak of ~120 CFS; the momentary peak recorded by the USGS seems to have been ~300 CFS (Figure 30a). One of the more interesting observations during this storm was the effect of an additional small storm (May 20) on flow in Crane Creek (Figure 30). As with Turkey Creek, concentrations of TDS in Crane Creek decreased to almost half of the mean value. In this instance, the decreases in TDS occurred twice in quick succession with each event (May 17 and 20, 2016); then, TDS values increased as post-storm flows in Crane Creek decreased (Figure 31a). Values for TSS did not increase greatly; most likely because we missed the short, first flush of particles. Thus far in the project, we were able to sample CC at peak flow on one occasion (February 22, 2017) when we obtained a TSS of 110 mg/L relative to <10 mg/L in May 2016. Concentrations of nitrate + nitrite showed the most interesting behavior of the nutrients with two minima caught by the USGS and us (Figure 32). Trends for the other nutrients, plus particulate Fe and Al were similar to that observed in Turkey Creek; however, the organic C content of the particles stayed high in this heavily vegetated, narrow and channelized creek.

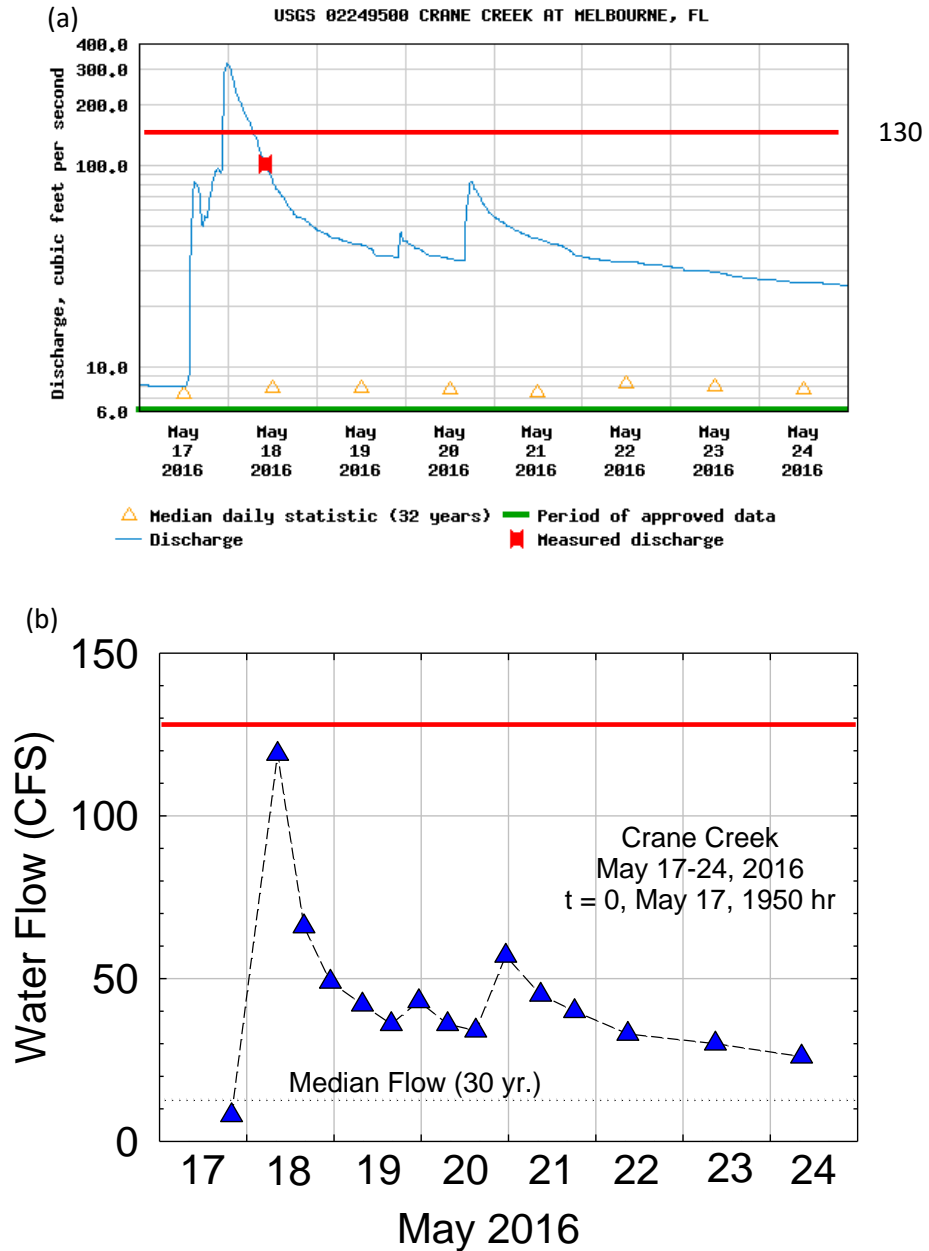


Figure 30. Water flow at Crane Creek from (a) continuous data (log scale) and (b) for dates and times when discrete samples were collected for this storm event. Water flow data from USGS (2017). Solid red lines on (a) and (b) at ~10 times the 30-year, median flow. Dashed line connecting markers on (b) added to help show changes over time.

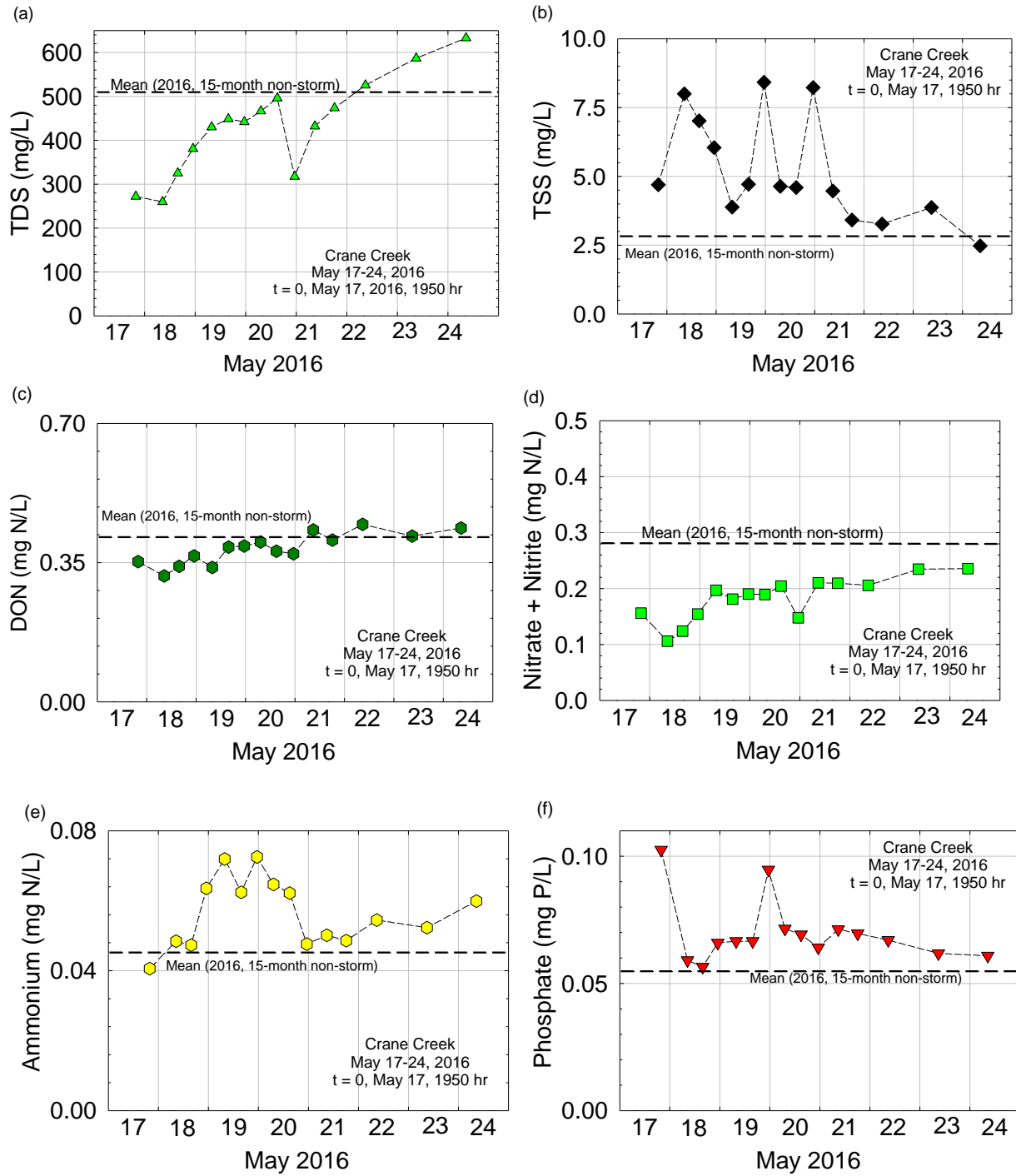


Figure 31. Time series trends for concentrations of (a) total dissolved solids (TDS), (b) total suspended solids (TSS), (c) dissolved organic nitrogen (DON), (d) ammonium, (e) nitrate + nitrite and (f) phosphate for Crane Creek from data during May 17–24, 2016, when discrete water samples were collected for this project. Dashed line connecting markers added to help show changes over time.

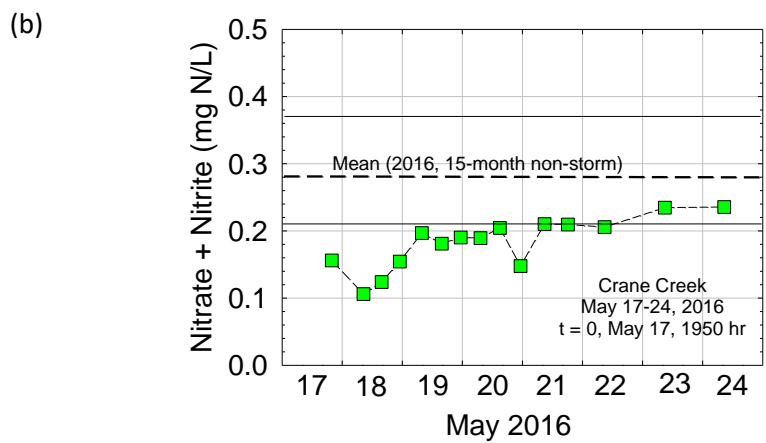
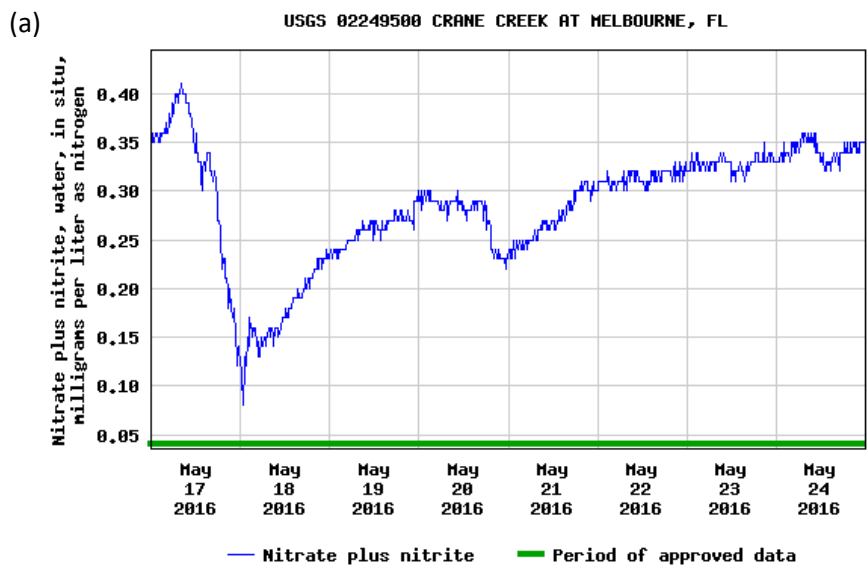


Figure 32. Concentrations of nitrate + nitrite from (a) USGS continuous monitoring and (b) from our discrete water samples for Crane Creek from May 17–24, 2016. Dashed line connecting markers on (b) added to help show changes over time.

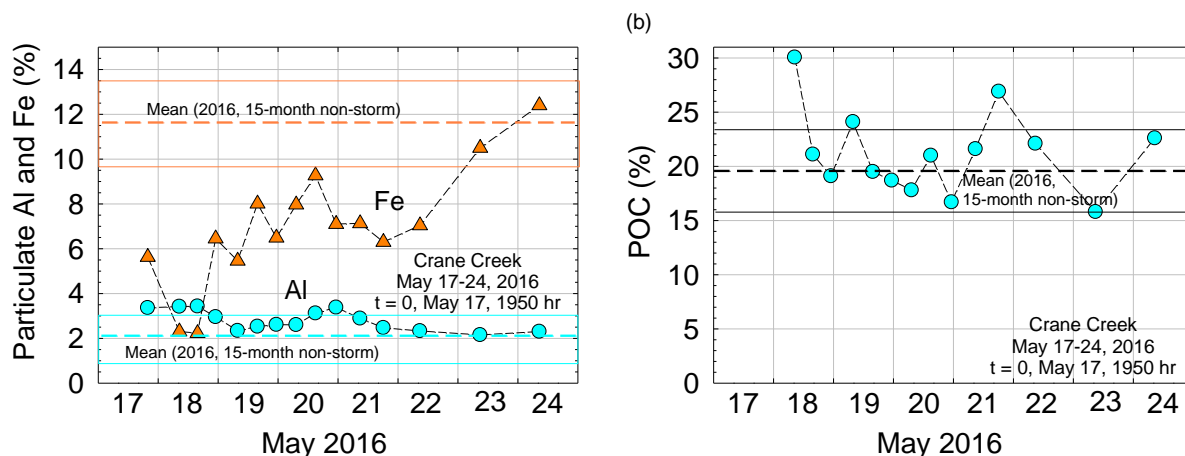


Figure 33. Time series trends for concentrations of (a) particulate aluminum and iron and (b) particulate organic carbon (POC) for Crane Creek from data during May 17–24, 2016, when discrete water samples were collected for this project. Dashed lines connecting markers added to help show changes over time.

## Conclusions

This first year of study yielded a wealth of data and some preliminary interpretations and conclusions. These conclusions are presented below as a series of bulleted items:

- Concentrations of total N and P (dissolved + particulate) averaged  $890 \pm 120 \mu\text{g/L}$  and  $110 \pm 60 \mu\text{g/L}$ , respectively, for all non-storm data for the tributaries relative to Florida water quality criteria for rivers and streams of  $1540 \mu\text{g total N/L}$  and  $120 \mu\text{g total P/L}$  (USEPA, 2017).
- The forms of total nitrogen (dissolved plus particulate) for all monthly samples ( $n = 73$ ) from all tributaries averaged  $57 \pm 13\%$  dissolved organic N (DON),  $19 \pm 8\%$  particulate N,  $17 \pm 12\%$  nitrate + nitrite and  $7 \pm 4\%$  ammonium.
- The forms of total phosphorus (dissolved plus particulate) for all tributaries averaged  $55 \pm 17\%$  dissolved phosphate,  $36 \pm 13\%$  particulate phosphorus, and  $9 \pm 17\%$  dissolved organic phosphorus (DOP).
- Lower fractions of nitrate + nitrite and higher fractions of DOP were found in less urban tributaries such as the Fellsmere Canal. The opposite trends (higher nitrate + nitrite and lower DOP) were found in more urban areas including Crane Creek and the Eau Gallie River.

- Concentrations of TDS (in mg/L) inversely tracked flow during storm events (i.e., decreased TDS during increased flow). Values for TSS (in mg/L) showed an opposite (positive) trend. Phosphate values also tended to be higher during storm flow. Concentrations of nitrate + nitrite tended to decrease below mean values during peak flow and then slowly returned to mean values as storm flow decreased. The other forms of dissolved nitrogen were less influenced during storm flow. These differences may be linked to the relative importance of groundwater versus surface runoff as sources of the various ions to tributary waters.
- Fluxes of all ions and solids were higher during storm flow. Particulate Fe values (as a percent of the mass of TSS) decreased significantly at the beginning of a storm event, again most likely due to a groundwater/irrigation water source for the Fe; the Fe content of the particles returned to mean values as flow decreased.
- Calculated annual fluxes of total nitrogen and phosphorus for the various tributaries, based simply on total flow and average concentrations was as follows:

Tributary	Total N (tons/yr)	Total P (tons/yr)
Eau Gallie River	10	1
Crane Creek	20	2
Turkey Creek	80	5
St. Sebastian B	60	3
St. Sebastian A	60	9
Total	230	20

- Estimated inputs of nitrogen and phosphorus from the sum of the tributaries are close to estimated benthic fluxes of nitrogen (280 tons) and phosphorus (40 tons) from muck sediments in the North Indian River Lagoon; however, the tributary fluxes are much larger than the muck fluxes from the Central IRL of ~80 and 10 tons/km<sup>2</sup>/yr for N and P (Tetra Tech, 2016).
- Recommendations for future study include (1) continued study of major tributaries, (2) sampling and analysis of minor tributaries and outfalls plus (3) continued assessment of the relative importance of baseflow versus stormwater inputs for major ions and the various forms of nutrients.



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