

Trends for Inputs of Muck Components from Rivers, Creeks and Outfalls to the Indian River Lagoon (Subtask 3)



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Impacts of Environmental Muck Dredging 2017-2018

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Executive Summary

Successful management plans for controlling muck in the Indian River Lagoon (IRL) require continuing assessment of external and internal inputs of nutrients and other substances that are precursors to algal blooms and muck deposits. Runoff from tributaries to the IRL provide one major pathway for external inputs. Atmospheric deposition, direct runoff from hundreds of outfalls and groundwater seepage also are important external sources. Benthic fluxes from IRL muck are the main internal source of nutrients. This study focused on runoff to the IRL from large tributaries by obtaining and interpreting data for concentrations and chemical forms of dissolved and particulate nitrogen (N) and phosphorus (P) as well as calculating nutrient fluxes to the IRL. Surveys were carried out monthly, as well as episodically during rain events, from December 2015 to March 2018. Sampling locations, all with U.S. Geological Survey (USGS) flow gauges, included St. Sebastian River, Turkey Creek, Crane Creek and Eau Gallie River.

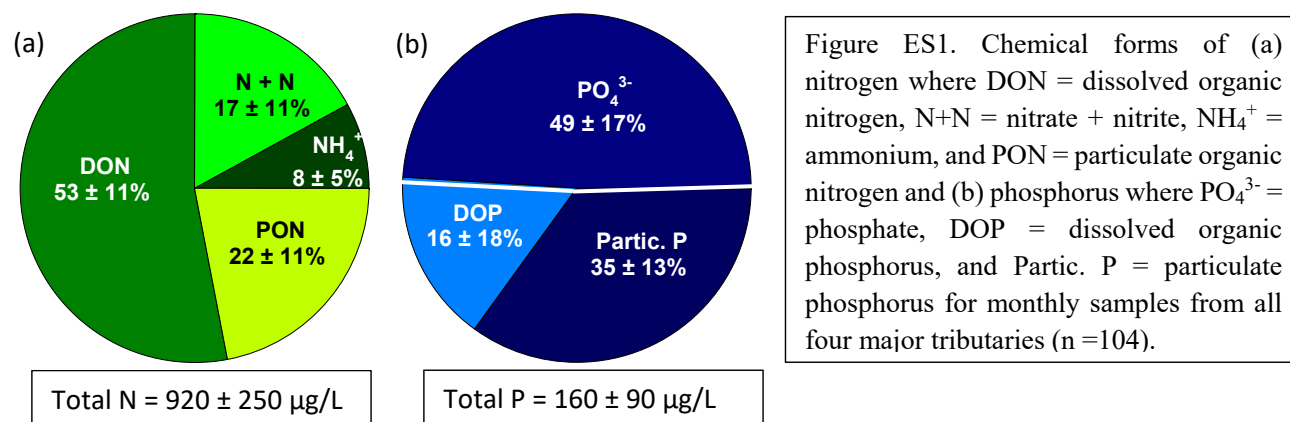
Vertical profiles for conductivity, temperature, dissolved oxygen and pH, along with discrete water samples, were obtained from each tributary. Water samples were analyzed for total dissolved and suspended solids, total nitrogen, ammonium, nitrate + nitrite, dissolved and particulate organic nitrogen, total phosphorus, phosphate, dissolved organic phosphorus, particulate phosphorus, dissolved iron, sulfate, calcium, chloride, silica, alkalinity, plus particulate organic carbon, iron, aluminum and silicon. The two-year study yielded a wealth of data and interpretations that are presented in the four sections of *Results and Discussion* summarized below.

The first section, ***Overview of Water Flow and Chemical Composition***, takes a big-picture look at the four tributaries. The largest tributary, Turkey Creek, has an average water flow of 158 ft³/sec (CFS; 0.13 km³/y) and an area of 254 km² relative to 20 million CFS (16,500 km³/y) and 3.3 million km² for the Mississippi River. Yet, despite their small sizes and water flow, the four IRL tributaries have annual water runoff (water flow/basin area) that is greater than mean estimated values for all continents except South America. This above-average runoff flows into a poorly flushed IRL that is vulnerable to rapid inputs of freshwater and nutrients which can promote extensive algal blooms. Management solutions for reducing nutrient inputs to the IRL depend on robust and continuous data for all nutrient sources, including major tributaries.

Concentrations of total dissolved solids (TDS) for all four tributaries (n = 104) averaged 740 mg/L,

relative to 110 mg/L for world rivers. TDS inversely tracked flow with highest values during low flow. Chloride and sodium from seawater intrusion into groundwater made up 75% of the TDS. Average values for total nitrogen (TN) in all four tributaries ($920 \pm 250 \mu\text{g/L}$) were 30–50% lower than the U.S. Environmental Protection Agency (USEPA) standard for Florida (1540 $\mu\text{g/L}$). In contrast, three tributaries had mean values for total phosphorus (TP) that were higher than the Florida criteria (120 $\mu\text{g/L}$); the highest mean value was 244 $\mu\text{g/L}$ for the Eau Gallie River. Only Turkey Creek had mean TP values (63 $\mu\text{g/L}$) below the USEPA standard.

Concentrations of the various forms of N and P also were determined (Figure ES1). Such information is important because each form of N and P is used at a different rate and biological efficiency during the onset and sustained growth of large algal blooms. Dissolved organic nitrogen (DON) made up more than half of the TN for all four tributaries (Figure ES1). Phosphate, the more biologically available and only inorganic form of P, comprised about half of the TP for the four tributaries. In contrast, more biologically available N (NH_4^+ and N+N) made up only ~25% of TN.



In the second section, *Trends in Concentrations of Chemicals as a Function of Water Flow*, one hypothesis was tested regarding the significance of water flow in controlling concentrations of TDS, total suspended solids (TSS), as well as the various chemical forms of N and P. Equations for each chemical parameter versus log water flow were written, where possible, for each tributary to calculate fluxes to the IRL (e.g., Figure ES2a, b). Our data for IRL tributaries yielded acceptable equations for calculating fluxes (i.e., $r \geq 0.6$ and $p < 0.05$) for 9 of 13 chemical parameters in the St. Sebastian River. However, flux equations for only 3–5 chemical parameters versus flow met our criteria in the other three tributaries. In these other cases, median values, rather than equations, were used to calculate chemical fluxes. Equations and medians were less successful in adequately calculating fluxes when chemical concentrations followed complex patterns versus water flow. These complexities included (i) large enrichment or dilution of chemicals during high flow, (ii) low values for NH_4^+ and N+N during the June–September fertilizer ban and (iii) increased concentrations of NH_4^+ and N+N after the ban (e.g., Figure ES2c, d). Recycling of ~8 million liters (2.2 million gallons) of reclaimed wastewater per day in the Melbourne area was another example of human activity that was identified in Crane Creek.

Phosphate concentrations tended to be greater during very high flow, including instances of 10–40 times higher PO_4^{3-} concentrations following Hurricanes Matthew (October 2016) and Irma (September 2017). Very low ratios for $[(\text{N}+\text{N}) + (\text{NH}_4^+)] / (\text{PO}_4^{3-})$ during higher flow indicated release of phosphate from soil minerals. In contrast, concentrations of $\text{N}+\text{N}$ were often diluted below median values during peak flow, then slowly returned to median values as flow decreased.

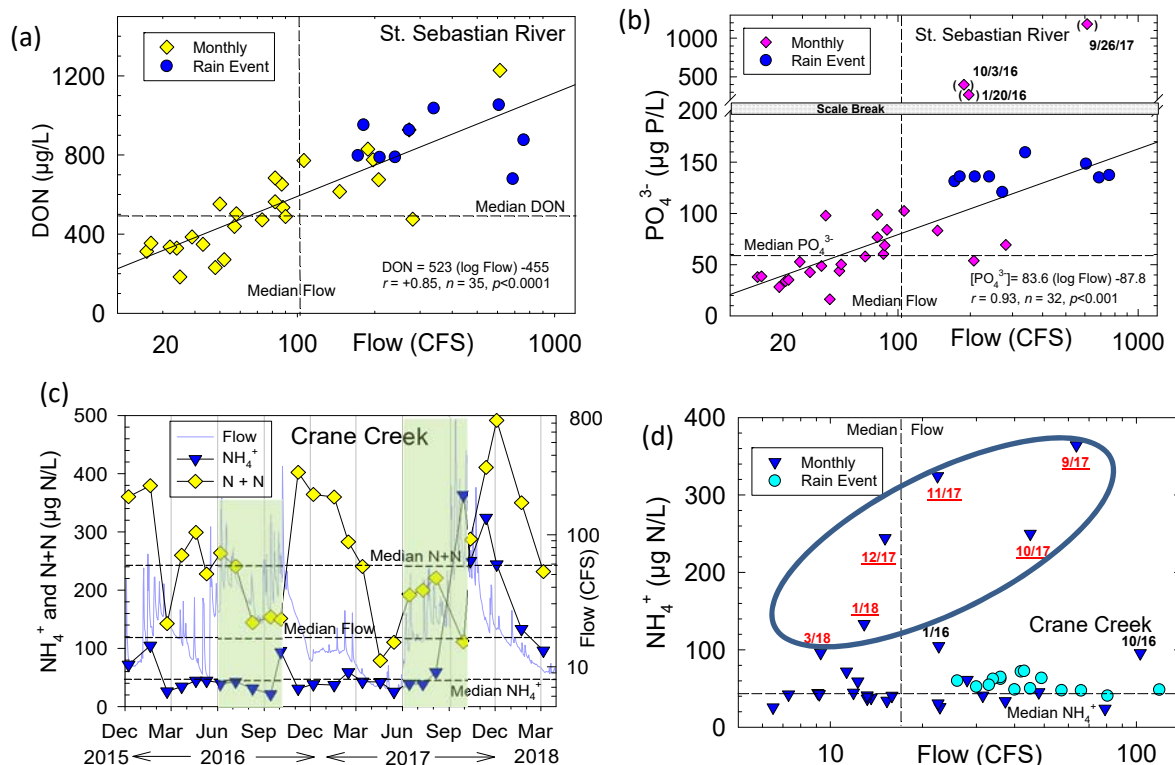


Figure ES2. Concentrations of (a) dissolved organic N (DON) and (b) phosphate (PO_4^{3-}) versus water flow at St. Sebastian River; (c) ammonium (NH_4^+), nitrate + nitrite (N+N) and water flow and (d) NH_4^+ versus water flow at Crane Creek. Green shading on (c) shows period of fertilizer restriction in Brevard and Indian River Counties. Oval on (d) shows NH_4^+ from September 2017–March 2018. Details in full report.

In the third section, *Tributary Fluxes of Dissolved and Particulate Chemicals to the Indian River Lagoon*, annual fluxes of total N and P for the four major tributaries for 2016 and 2017 were calculated based on daily flows and tributary-specific equations or medians (Table ES1).

Table ES1. Fluxes of total nitrogen (N) and total phosphorus (P) from major tributaries of the Indian River Lagoon.

Tributary	Total N (tons/y)		Total P (tons/y)		Mean Flow (CFS)		Drainage Area (km ²)
	2016	2017	2016	2017	2016	2017	
Eau Gallie River (EG)	10	14	2.5	3.7	11	17	24
Crane Creek (CC)	24	27	3.4	3.8	32	35	48
Turkey Creek (TC)	164	162	11	11	211	210	254
St. Sebastian River So. Prong (SR)	108	184	19	57	111	165	91
Total	306	387	36	76	365	427	417

Mean annual inputs of total N and P (2016, 2017) from the four major tributaries were within 25% of estimated benthic fluxes of N (300 tons) and P (45 tons) from muck sediments in the North IRL (north of Melbourne Causeway, State Road 192). Very high PO_4^{3-} fluxes, concurrent with low $\text{N}+\text{N}$ and NH_4^+ fluxes, were observed in the St. Sebastian River (South Prong) during large rain events when pH was < 7 ; this observation is likely due to remobilization of phosphate minerals. In most cases, $>70\%$ of the TN and TP were delivered to the IRL during above-median flow that occurred on ~ 120 days per year. These results confirm the importance of continuing a fertilizer ban during the June–September period of higher water flow and nutrient transport. To further improve estimates of nutrient loading, continuous data for nutrients are needed to match available continuous water flow data.

Turkey Creek: Then (1988–89) and Now (2016–2017) uses data from the present study and an earlier Florida Institute of Technology study to test the hypothesis that concentrations and fluxes of N and P have increased over a three-decade period in Turkey Creek (TC) due to increased urban development. We estimate that urban land use increased from 36% in 1988–89 to 64% in 2016–17. Accompanying that change were several increases in nutrient concentrations in TC including an 82% increase in total P plus 400% and 500% increases in PON and $\text{N}+\text{N}$, respectively (Table ES2). Decreased Al and Si in Turkey Creek particles (as a % of TSS) for 2016–17 relative to 1988–89 (Table ES2) suggested that erosion and transport of soil inorganic minerals (i.e., Si and Al) may have decreased due to improvements in soil retention in upland basins of TC. In contrast, an increased organic matter (OM) fraction may yield future muck deposits that are more organic rich.

Table ES2. Changes in concentrations of chemical parameters for Turkey Creek from 1988–89 to 2016–17.

Chemical Parameter	Significant Change from 1988-89 to 2016-17 ^a
Particulate Organic C (mg C/L)	76% increase, $p < 0.0001$
Dissolved Organic N ($\mu\text{g N/L}$)	25% decrease, $p = 0.0018$
Nitrate + Nitrite ($\mu\text{g N/L}$)	500% increase, $p < 0.0001$
Particulate Organic N ($\mu\text{g N/L}$)	400% increase, $p = 0.0024$
Total P ($\mu\text{g P/L}$)	82% increase, $p = 0.0100$
Particulate P ($\mu\text{g P/L}$)	90% increase, $p = 0.0125$
Particulate Al (as % of TSS)	37% decrease, $p = 0.0012$
Particulate Si (as % of TSS)	24% decrease, $p = 0.0051$
TDS, TSS, DOC, TN, NH_4^+ , PO_4^{3-} , DOP;	No significant change, $p > 0.05$

^at-test, two-tailed, equal variance; mean values were statistically different when $p \leq 0.05$.

Our data for the IRL, along with results from this and other studies, support renewed focus on studies of P, and continuing assessment of N, including their various chemical forms. Recent studies globally project increased river flow during extreme events at mid-latitudes. Data from Hurricanes Matthew (2016) and Irma (2017) along the IRL support that projection and encourage enhanced evaluation of phosphate and other chemical releases during these large-scale events. Once again, we confirm previous conclusions that the main fuel for enhanced algal blooms is large, rapid inputs of nutrients to areas of the IRL where lagoon water has a long residence time.

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1.0. Introduction

Excess inputs of nutrients have led to a worldwide crisis of eutrophication in the coastal ocean (Diaz and Rosenberg, 2008). Sources for global overloading of nutrients include, but are not limited to, the following: (i) animal and human waste, (ii) inadequate or improper wastewater treatment, (iii) excess fertilizer application and runoff, and (iv) organic matter (OM) inputs from stormwater flow through urban and agricultural land. Nutrients also are released directly to the overlying water when OM decomposes in estuarine sediments. The impacts of this crisis include degraded water quality, harmful algal blooms and fish kills. Ongoing climate change enhances the eutrophication process because increased evaporation and precipitation, spurred by solar heating, intensify runoff and transport of nutrients and OM from land to tributaries, estuaries and oceans (Trenberth and Asrar, 2014). Therefore, the quality of water carried by tributaries has become an important component for predicting the health of the coastal ocean.

Flow rates for water in rivers and streams play an important role in controlling both concentrations and fluxes of selected chemicals to estuaries and the coastal ocean (e.g., Seitzinger et al., 2010; Bowes et al., 2015). For example, increased concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and phosphate (PO_4^{3-}) have been reported for rivers during high flow due to enhanced desorption and remineralization of OM and nutrients in soils and greater water flow through the upper, organic-rich soil horizon during rain events (e.g., Morel et al., 2009; Jeanneau et al., 2015). Significant fractions of river-borne DOC and DON have been shown to be biologically available (e.g., Martin and Harrison, 2011). Furthermore, loading of suspended sediments bearing N and P typically increases during high water flow, especially after land clearing (e.g., Li et al., 2015; Chen et al., 2015). Increased water flow during rain events also can decrease concentrations of some chemicals, especially N+N, via dilution (e.g., Bowes et al., 2015).

Human-induced changes in land use also have been shown to increase runoff and transport of nutrients from river basins to coastal estuaries and bays (e.g., Bowes et al., 2015; Bussi et al., 2017). For example, increased agricultural and urban development have been linked to higher concentrations and fluxes of ammonium (NH_4^+), nitrate + nitrite (N+N) and PO_4^{3-} (e.g., Jickells et al., 2014; Chen et al., 2015).

The Indian River Lagoon (IRL) spans 250 km along the central east coast of Florida and is presently experiencing its own environmental crisis in the form of poor water quality, intense algal blooms, a 50% decline in seagrass area, and fish kills (e.g., Steward et al., 2006, Philips et al., 2014; Kang et al., 2015). These impacts are now transforming the lagoon from a macrophyte-based system to an algae-based system (Philips et al., 2015). Specific sources of nutrients to the IRL include runoff (baseflow and rain) and benthic fluxes from muck sediments, each of which contributes ~20–40% of the total (dissolved + particulate) N and P added annually to the IRL system (Tetra Tech, 2019). Atmospheric deposition adds ~20% and ~4% of the N and P, respectively, to the IRL annually (Tetra Tech, 2019).

The following four major tributaries were the focus of this study: St. Sebastian River South Prong (SR), Turkey Creek (TC), Crane Creek (CC) and the Eau Gallie River (EG) (Figure 1). USGS flow gauges were present at each location. Nutrients transported from SR to the IRL have an increased likelihood of being exported to the coastal Atlantic Ocean because of its close proximity to Sebastian Inlet. Releases from the other three tributaries are to areas with poor circulation that are separated from inlets to the ocean. Therefore, rapid inputs of freshwater and nutrients from TC, CC and EG are more likely to stay in the IRL and promote algae blooms. Among the four IRL tributaries, SR has a 4-fold lower percentage of urban land use than TC, CC and EG (Table 1).

Data for the different chemical forms of N and P for tributaries are important because biological availability and uptake rates of N and P during photosynthesis are directly linked to the chemical form of a nutrient (e.g., Kang et al., 2015). For example, the brown tide alga *Aureoumbra lagunensis* takes up NH_4^+ very rapidly, but cannot thrive when NO_3^- is the only form of N available (Kang et al., 2015). A study of P uptake by cyanobacteria showed that they were able to take up ATP, one of many components of dissolved organic P (DOP); however, they took up PO_4^{3-} at a 3–4 times greater rate (Michelou et al., 2011). Inorganic reactions of N and P in coastal waters (e.g., solubility, sorption and precipitation) also depend on the chemical forms present (e.g., Louis et al., 2011). Therefore, the importance of knowing the chemical forms of N and P that make up TN and TP, respectively, cannot be overemphasized.

The primary goal of this study was to obtain a detailed data set for the concentrations and fluxes of the various forms of nitrogen (N), phosphorus (P) and other chemicals to the IRL from major tributaries. Such information is needed to help environmental managers determine the effectiveness of upland controls and water diversion projects on nutrient and soil runoff and thereby assess the success of decreasing inputs of new muck-forming components. Samples for this study were collected monthly from December 2015 to March 2018 and episodically during 1–to 7–day rain events. The rainy period for the IRL is commonly specified as May–October; the dry season is identified as November–April. This study is in line with ongoing emphasis on nutrient inputs to estuaries and coasts from small streams as well as restoration of coastal waterways via better management of rural and suburban land (e.g., Schlesinger et al., 2006).

Table 1. Urban and agricultural land use, plus population statistics for upland basins of four major tributaries to the Indian River Lagoon.

Tributary	Urban Land Use (2009) ^a	Agricultural Land Use (2009) ^a	Population (2009) ^b	Population (2016) ^b	Urban Land Use (2016, est.) ^c
St. Sebastian River (SR)	15%	31%	21,000	25,000	18%
Turkey Creek (TC)	59%	14%	103,000	112,000	64%
Crane Creek (CC)	66%	1.4%	76,000	81,000	70%
Eau Gallie River (EG)	71%	1.6%	76,000	81,000	76%

^aSJRWMD (2009); complete land use data in Appendix A.

^bWPU (2019).

^cEstimate assumes growth in urban land use was proportional to population increase.

2.0. Approach

2.1. Sampling Locations

Our two-year study of major tributaries began in December 2015 as a complement to the Environmental Muck Dredging (EMD) projects for 2016–17. This report presents and interprets results for water chemistry obtained from December 2015 to March 2018 at the following major tributaries: Eau Gallie River (EG), Crane Creek (CC), Turkey Creek (TC), and St. Sebastian River (SR) at the South Prong (Table 2, Figures 1–5). All sampling stations were located near USGS gauging stations that were sited sufficiently upstream in each tributary to avoid collecting admixed seawater.

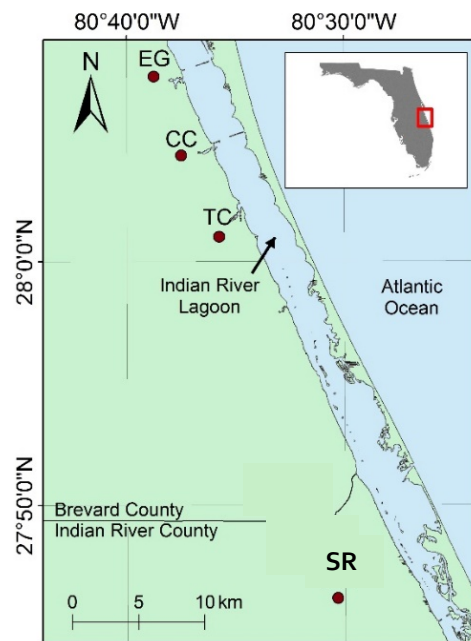


Figure 1. Locations of tributaries sampled [Eau Gallie River (EG), Crane Creek (CC), Turkey Creek (TC) and St. Sebastian River, South Prong (SR)]. Inset map shows study area along central east coast of Florida.

Table 2. Major tributaries, identifications (ID), location names, coordinates, U.S. Geological Survey (USGS) numbers for sampling sites and median water depths at the sampling locations.

Tributary	ID	Name of Sampling Site	Coordinates	USGS #	Median Depth (m)
Eau Gallie River	EG	N. Apollo Boulevard Bridge	28° 7.608' N, 80° 38.762' W	02249007	1.3
Crane Creek	CC	Country Club Road	28° 4.364' N, 80° 37.501' W	02249500	0.3
Turkey Creek	TC	Port Malabar Boulevard	28° 1.021' N, 80° 35.764' W	02250030	4.5
St. Sebastian River	SR	South Prong, SR 512	27° 46.168' N, 80° 30.345' W	02251767	0.9



Figure 2. Location of sampling site at the Eau Gallie River (EG) on North Apollo Boulevard (within red circle). USGS website at https://waterdata.usgs.gov/nwis/dv?referred_module=sw&site_no=02249007. Land usage includes 71% urban and 13% transportation, communication and utilities (SJRWMD, 2009, complete land use table in Appendix A)



Figure 3. Location of sampling site at Crane Creek (CC) on Country Club Road (within red circle). USGS website at https://waterdata.usgs.gov/nwis/uv/?site_no=02249500. Land usage includes 66% urban and 7% transportation, communication and utilities (SJRWMD, 2009, complete land use table in Appendix A).



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. Land use includes 59% urban, 14% agriculture and 7% forest (SJRWMD, 2009, complete land use table in Appendix A).

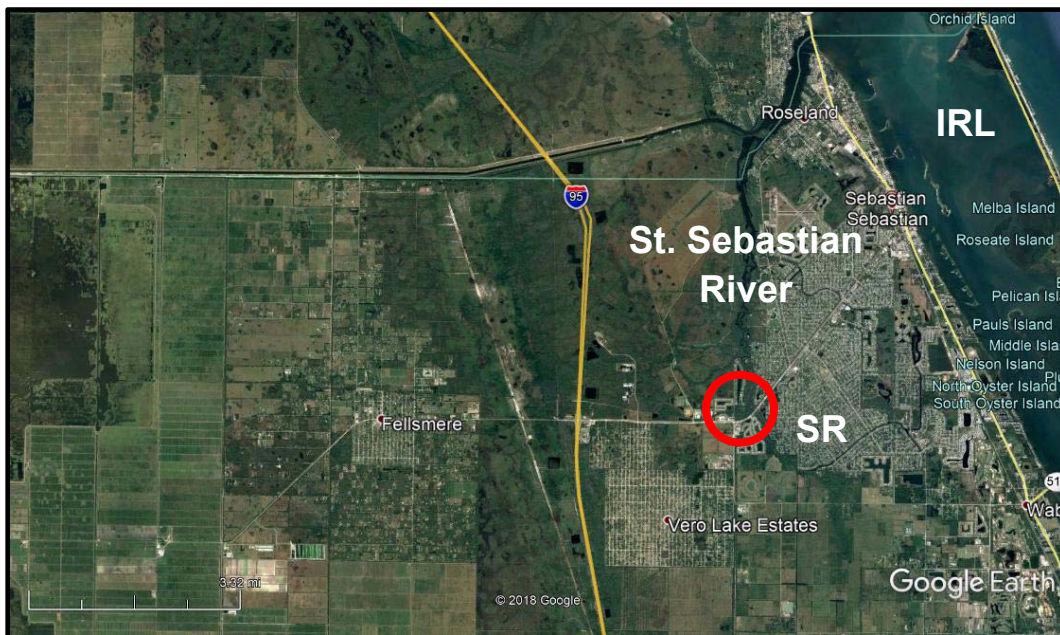


Figure 5. Location of sampling site at the St. Sebastian River (SR), South Prong, on State Road 512 (within red circle). USGS website at https://waterdata.usgs.gov/nwis/uv/?site_no=02251000. Land use includes 15% urban, 31% agriculture, 18% non-forested upland, 15% forested land and 15% wetland (SJRWMD, 2009, complete land use table in Appendix A).

2.2. Field Sampling

Surveys of the major tributaries were carried out monthly from December 2015 to March 2018. Vertical profiles for conductivity, temperature, pH and dissolved oxygen were obtained first at each site using a YSI 6600 V2 (Yellow Springs Instruments, Figure 6a). The sonde was calibrated at the beginning of each day following manufacturer's specifications and intercalibrated with the YSI ProDSS when it replaced the 6600 V2 in 2017. During each survey, water samples were collected in acid-washed, low-density polyethylene bottles. The open bottles were placed in a weighted holder (Figure 6b) and lowered from a bridge to the surface of the water and then quickly (1–2 seconds) lowered to a water depth of 0.5 m, based on a marked rope that supported the sampler. A bottom water sample was collected at TC if a salt wedge was identified during the Sonde cast. Upstream intrusions of saline water were observed in surface water at TC from March to August 2017 plus January and March 2018; data for TC during these months is archived, but not used in this report. Due to difficulties with periodic upstream migration of saline water, we recommend that the USGS consider moving the gauge for TC farther west. Sampling locations for the other tributaries were upstream of their respective salt wedges. These locations contained well-mixed freshwater, as determined by uniform conductivity profiles; thus, no bottom water was collected. 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- μm pore size polycarbonate filters (for particulate Fe, Al, Si, P and dissolved forms of N, P and C) and 47-mm diameter, 0.7- μm pore size, glass-fiber filters (for particulate C and N).

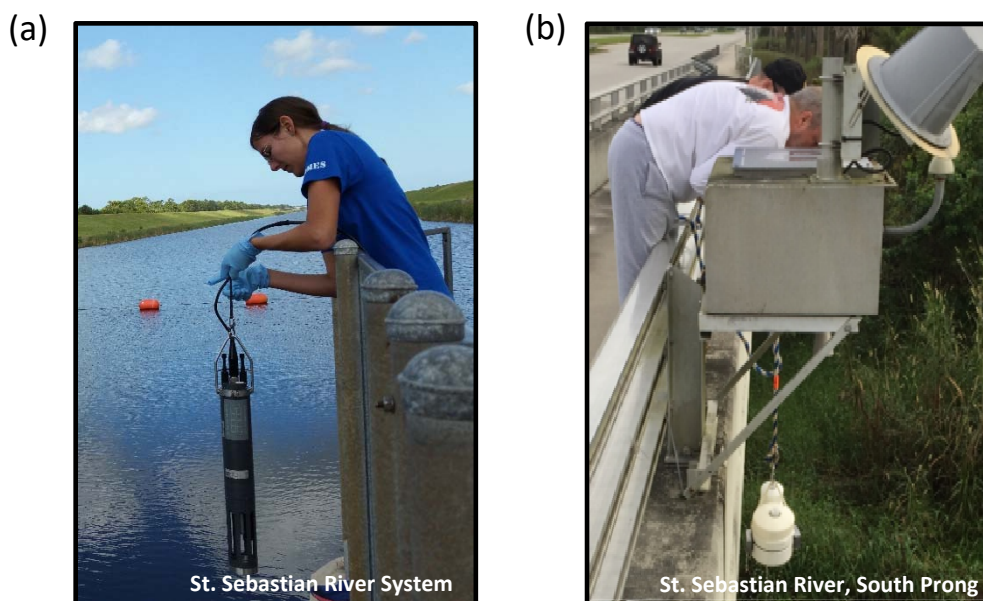


Figure 6. Lowering (a) YSI Sonde 6600 for vertical profile of conductivity, temperature, dissolved oxygen and pH and (b) weighted sampler for collecting water samples.

2.3. Laboratory Analyses: Dissolved Chemicals

Filtered water samples and suspended particles were analyzed for a variety of dissolved and particulate chemicals (Table 3). Samples for nutrient analysis were vacuum filtered through polycarbonate filters (Poretics, 47-mm diameter, and 0.4- μm pore size) in a laminar-flow hood. Concentrations of (i) nitrate + nitrite (N+N), (ii) total dissolved nitrogen (TDN), (iii) ortho-phosphate (PO_4^{3-}), (iv) total dissolved phosphorus (TDP) and (v) dissolved silica (SiO_2) were determined using a SEAL AA3 HR Continuous Segmented Flow AutoAnalyzer following manufacturer's method G-218-98. For TDN, organic and inorganic N compounds were converted to nitrate using UV irradiation and persulfate digestion. Nitrate was then reduced to nitrite using a cadmium column; analysis followed by UV-visible spectrometry. For TDP, UV and persulfate digestion were used to free organically-bound P for analysis by UV-visible spectrometry. 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.

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. Alkalinity analysis followed 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_3/L is directly proportional to the volume of acid added to reach the pK_a . Standard seawater solution (Ocean Scientific International Limited, UK) was analyzed as a reference standard.

Table 3. Chemical parameters included in this study.

Parameter	Dissolved	Particulate
<i>In situ</i> water column	conductivity (total dissolved solids, TDS), temperature (T), pH, dissolved oxygen (DO)	-
Nitrogen (N)	ammonium (NH_4^+), nitrate + nitrite (N+N), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON)	particulate organic N (PON)
Phosphorus (P)	phosphate (PO_4^{3-}), total dissolved phosphorus (TDP), dissolved organic phosphorus (DOP)	total particulate P (PP)
Dissolved and particulate solids	conductivity, total dissolved solids (TDS)	total suspended solids (TSS), turbidity (in NTU)
Major elements	chloride (Cl^-), calcium (Ca^{2+}), alkalinity (Alk), sulfate (SO_4^{2-}), (sodium, magnesium and potassium on a subset)	silicon (Si), aluminum (Al), iron (Fe), Particulate organic carbon (POC)
Trace elements	Iron (Fe), silica (SiO_2)	-

2.4. Laboratory Analyses: Particulate Chemicals

Samples of suspended matter were collected by vacuum filtering water through polycarbonate filters (Poretics, 47-mm diameter, 0.4- μm pore size) in a Class-100 laminar-flow hood in an FIT clean room with controlled temperature and relative humidity. 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 μg . Each filter was weighed twice in random order, with a minimum of 5% of the filters being weighed in triplicate as described in Trefry and Trocine (1991). Samples for particulate organic carbon (POC) were filtered in a Class-100 laminar flow hood through pre-combusted Gelman Type A/E glass fiber filters mounted on acid-washed filtration glassware. Particle-bearing filters were sealed in separate, acid-washed petri dishes, labeled, double-bagged in plastic and stored until dried and re-weighed.

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 HNO₃ and HF as described by Trefry and Trocine (1991). Concentrations of Al, Fe and Si were determined by flame atomic absorption spectrometry using a Perkin-Elmer 4000 instrument and concentrations of P were determined by inductively-coupled plasma mass spectrometry (ICP-MS) using a Varian 820 instrument.

Concentrations of POC and particulate organic N (PON) were determined by first treating particles on the glass-fiber filter with 10% (v/v) hydrochloric acid to remove any inorganic carbon, then dried. Organic N was not lost during this process. Filters with 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. Quantification of the resultant CO₂ gas (for POC) was via an infrared detection cell and N₂ gas (for PON) via a thermal conductivity detector. Concentrations of C and N in the sediment Standard Reference Material #2704 and LECO reference samples 502-309 were within the 95% confidence intervals for certified values.

2.5. Calculations and Data Interpretation

Data and graphical analyses were carried out using Systat 12 and SigmaPlot 10 (Systat Software, Inc.), Excel 2016 (Microsoft) and ArcGIS (Version 10.2.2.3552, Esri, Redlands, CA). An alpha value to define statistical significance was set at 0.05 for statistical tests and regressions. Least squares linear regressions were calculated to determine relationships between individual pairs of parameters (e.g., DON versus water flow). Equations, 95% prediction intervals, correlation coefficients (r) and p values were determined for each relationship. Correlation coefficients are sometimes described in this report using the following terms and intervals: very strong (≥ 0.90), strong (0.80–0.89), moderately strong (0.60–0.79), moderate (0.40–0.59), mild (0.2–0.39) and weak (< 0.2). All correlation coefficients are presented with a corresponding p value. Comparisons

of two independent groups of data were carried out using two-tailed t-tests assuming equal variance. Independent groups of data with p -values >0.05 were considered not significantly different from one another. Analysis of variance (ANOVA) was used to determine differences for a given parameter among the four tributaries; p values >0.05 showed that population means were not significantly different. If a significant difference was determined via ANOVA (i.e., $p < 0.05$), a post-hoc Tukey’s test was carried out to identify pairs of data that had significantly different means. Statistics for 2016–17 were calculated for data from monthly samples to keep the sampling days the same for all four tributaries. Sampling for rain events took place on a variety of different days for each tributary with some overlap.

Fluxes of nutrients and other chemicals from each of the four major tributaries during 2016 and 2017 were calculated using several approaches. When a significant correlation ($r \geq 0.06$, $p < 0.05$) was obtained for concentration of a chemical versus log water flow, the pertinent equation was used to calculate the concentration for each day using the USGS (2019) flow data. Total transport was determined from the sum of the daily transport (Equation 1). Log flow was used in Eq. 1 because non-linear changes in concentration versus water flow were observed and $\log[\text{flow}]$ was successfully used to model TDS versus flow by O’Connor (1976) and Sinyukovich (2003).

$$M = \sum_{i=1}^{365} [(a * \log \text{Flow}(i) + b) * \text{Flow}(i)] \quad \text{Equation 1.}$$

where: M = total mass of nutrient or other parameter per year (365 days) = tons/y.
 $(a * \log \text{Flow} + b)$ = equation for concentration versus flow and concentration of a particular chemical on each day (i).

When no significant correlation between a chemical and average daily water flow was obtained and the data grouped around the median for the chemical, Equation 2 was used.

$$M = \sum_{i=1}^{365} [\text{Median} * \text{Flow}(i)] \quad \text{Equation 2.}$$

In a few instances where very high concentrations of a chemical were found at high water flow (e.g., PO_4^{3-} and TP at SR), Equation 1 was used plus high concentrations were used on a day-by-day basis for flows with $>200 \text{ ft}^3/\text{sec}$ (CFS; $1 \text{ ft}^3/\text{sec} = 0.028 \text{ m}^3$). All equations or medians, as appropriate, for each chemical at each location are summarized in Appendix B. We used water flow at the time of sampling on graphs and in calculations of chemical transport for consistency and because the impact of flow prior to sampling was generally minor. Median values for annual flows were within 1% of mean values for SR and EG and within 6-8% for TC and CC. Therefore, median and mean water flows are essentially interchangeable. This was not always true for concentrations of chemicals. Outlying data points were omitted in calculating chemical versus flow equations when they were outside the mean by two standard deviations and/or had a clear explanation for the anomaly (e.g., “first flush” during a rain event).

The alphabet soup of abbreviations and chemical terms used in the report are summarized below in Table 4.

Table 4. Key to selected abbreviations used in this report.

Abbreviations	Complete Description
EG	Eau Gallie River
CC	Crane Creek
TC	Turkey Creek
SR	St. Sebastian River (South Prong)
TN	Total Nitrogen (dissolved + particulate nitrogen, all the nitrogen)
DON	Dissolved Organic Nitrogen (includes urea and more complex molecules)
NH ₄ ⁺	Ammonium, the reduced form of dissolved inorganic N
N+N	Nitrate + Nitrate, the oxidized forms of dissolved inorganic N
DIN	Dissolved Inorganic Nitrogen ([NH ₄ ⁺] + [N+N])
TDN	Total Dissolved Nitrogen (NH ₄ ⁺ + [N+N] + DON)
PON	Particulate Organic Nitrogen
TP	Total Phosphorus (dissolved + particulate phosphorus, all the phosphorus)
PO ₄ ³⁻	Phosphate
DOP	Dissolved Organic Phosphorus (includes ATP and other molecules)
TDP	Total Dissolved Phosphorus (PO ₄ ³⁻ + DOP)
DIP	Dissolved Inorganic Phosphorus (same as phosphate)
PP	Particulate Phosphorus (inorganic + organic; forms not differentiated here)
DOC	Dissolved Organic Carbon
POC	Particulate Organic Carbon
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
OM	Organic Matter

2.6. Quality Assurance Plan

A revised and detailed Quality Assurance plan (QAP) with responses to comments for the second year of this study was submitted during January 2017. This plan meets the minimum requirements for description of Research Field and Laboratory Procedures according to Rule 62-160.600, Florida Administrative Codes (F.A.C.). The 33-page document, plus a long list of Statements of Work (SOW) covers all project plans, objectives and analyses for this component of the EMD study. As a continuation project, the January 2017 QA Plan covered the activities and analyses for 2017–2018.

The QAP used in the Marine & Environmental Chemistry Laboratories at FIT was reviewed without comment by the Florida Department of Environmental Protection (DEP). Water collection and analyses followed the guidelines listed below.

- (i) *Sample handling.* 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 spikes, field replicates, duplicate samples, standard reference materials, procedural blanks 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 5.
- (iii) *Matrix spike analysis.* One matrix spike sample (method of additions analysis) was analyzed with every batch of 20 samples. Results from the method of additions analysis provided 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. For example, milligram quantities of a river bottom sediment from the NIST (#2704, Buffalo River Sediment) were analyzed with every batch of particle 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 elemental 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. Continuing calibration consisted of complete three- to five-point calibrations or single standard checks after every eight samples until all analyses were complete. The relative standard deviation ($RSD = [\text{mean}/SD] \times 100\%$) between complete calibration and standard checks was required to be $<10\%$ or recalibration and reanalysis of the previous samples were performed.

Table 5. Data quality objectives for this study.

Element or Sample Type Criteria	Minimum Frequency	Data Quality Objective/Acceptance
Initial Calibration	Standard curve prior to every batch of samples	3–5 point curve depending on the element plus a blank Correlation coefficient $r \geq 0.999$ required 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 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

3.0. Results and Discussion

3.1. Introduction

Data for concentrations and inputs of nutrients to the IRL from all sources are needed on a continuing basis to help guide a wide variety of management decisions and to evaluate the success of remediation activities. This two-year study was designed to obtain and interpret data for the concentrations, chemical forms and fluxes of dissolved and particulate nitrogen (N) and phosphorus (P) for major tributaries to the IRL. Nutrient concentrations and fluxes were investigated primarily from the perspective of water flow and land usage. Where relevant, the IRL tributaries are viewed within the context of global rivers and climate change.

Results and Discussion for IRL tributaries are presented in the following four sections:

- 3.2. Overview of Water Flow and Chemical Composition introduces the data set and presents a big picture of water flow and chemical composition for the IRL tributaries.
- 3.3. Trends in Concentrations of Chemicals as a Function of Water Flow investigates the significance of water flow on concentrations of TDS, TSS and the chemical forms of C, N and P in the tributaries. This section presents and assesses, where possible, mathematical relationships between water flow and concentrations of the forms of N and P.

- 3.4. Tributary Fluxes of Dissolved and Particulate Chemicals to the Indian River Lagoon presents results for fluxes of the chemical forms of N and P, as well as organic carbon, dissolved solids and suspended solids, to the IRL based on water flow data for 2016 and 2017.
- 3.5. Turkey Creek: Then (1988–89) and Now (2016–17) uses data from a previous FIT study to identify and explain significant changes in the chemical composition and fluxes of the various chemical forms of N and P from Turkey Creek to the IRL over the past three decades.

3.2. Overview of Water Flow and Chemical Composition

Concentrations and fluxes of dissolved and particulate chemicals in all tributaries globally are controlled by water flow, land use and the size and mineral composition of the drainage basin (Berner and Berner, 2012). Among the four IRL tributaries studied, median annual water flow for the past 2–3 decades ranged from 12 CFS in the Eau Gallie River to 158 CFS in Turkey Creek (Table 6, Figure 7). These flows are, of course, much lower than 20 million CFS for the Mississippi River, the largest river in North America and sixth largest river in the world (Dai et al., 2009). The upland basins of the IRL tributaries also are small, ranging in area from 24 km² for the Eau Gallie River to 254 km² for Turkey Creek (Table 6), relative to 3.3 million km² for the Mississippi River (Syvitski and Milliman, 2007). In contrast, these subtropical, IRL tributaries have values for water runoff (water flow /drainage basin area) that are greater than means estimated for all continents except South America (Table 6, especially footnote c) based on water balance and transport models (WBM/WTM) from Syvitski et al. (2005). Therefore, the major IRL tributaries are sizeable sources of freshwater and nutrients as a function of basin area relative to most rivers worldwide. This factor increases the likelihood that they carry large loadings of nutrients to the IRL per km² of catchment basin. Furthermore, restricted flushing renders the IRL vulnerable to rapid influxes of nutrients during large rain events. Such events have promoted large algal blooms and fish kills (IRL Consortium, 2015). Sensitivity to rapid shifts in temperature, salinity, light penetration (turbidity) and nutrient concentrations also has been a key factor in establishing the present degraded condition of the IRL system (e.g., Philips et al., 2015).

Table 6. Summary data for water flow and drainage basin area for tributaries in this study,

Parameter	St. Sebastian River (SR)	Turkey Creek (TC)	Crane Creek (CC)	Eau Gallie River (EG)
Median Annual Daily Flow ^a (CFS)	100	158	17	12
Mean Annual Flow ± SD (CFS) ^a	102 ± 29	157 ± 56	21 ± 7	12 ± 3
Mean Flow on Sampling Day ^a (CFS)	110 ± 104	191 ± 158	26 ± 24	10 ± 12
Median Annual Flow ^a (m ³ /sec)	2.9	4.1	0.48	0.34
Median Annual Flow (km ³ /y)	0.092	0.13	0.015	0.011
Drainage Basin Area ^b (km ²)	91	254	48	24
Flow from drainage basin ^c (m/y) [i.e., water runoff]	1.0	0.51	0.31	0.46
Maximum Mean Annual Flow (CFS) With [Year]	177 [1994]	260 [1995]	35 [2017]	20 [2008]
Minimum Mean Annual Flow (CFS) With [Year]	55 [2000]	76 [2013]	13.3 [2003]	7.3 [1993]
(Max/Min) Annual Flow	3.2	3.4	2.6	2.7

^aUSGS (2019). SR (n = 24 y, 1994–2017), TC (n = 28 y, 1990–2017), CC (n = 15 y, 2003–2017), EG (n = 27 y, 1991–2017).

^bSJRWMD (2009) where 1 km² = 247.1 acres.

^cFlow from drainage basin = [Flow/Basin Area] = [(km³/y)/km²] = (km/y) * 1000 m/km = m/y (as m/y: North America = 0.28, Europe = 0.27, Asia = 0.31, Africa = 0.19, South America = 0.68; Berner and Berner, 2012). Mean for four IRL tributaries is 0.57.

Mean water flows in the four IRL tributaries studied during 2016 and 2017 (both hurricane years) were among the highest reported during the past two to three decades (Figure 7). The first and third highest values recorded in 17 years of data for Crane Creek were during 2016 and 2017 (Figure 7). Likewise, annual mean flows for 2017 were the second highest observed for SR and third highest for EG. Despite these very recent increases, water flows in the IRL tributaries show no significant trends over the past two decades (Figure 7). A similar lack of decades-long trends was observed for 745 (81%) of the world’s 916 rivers; only 120 (13%) and 51 (6%) rivers, respectively, showed significant increases and decreases (Su et al., 2018). When changes were

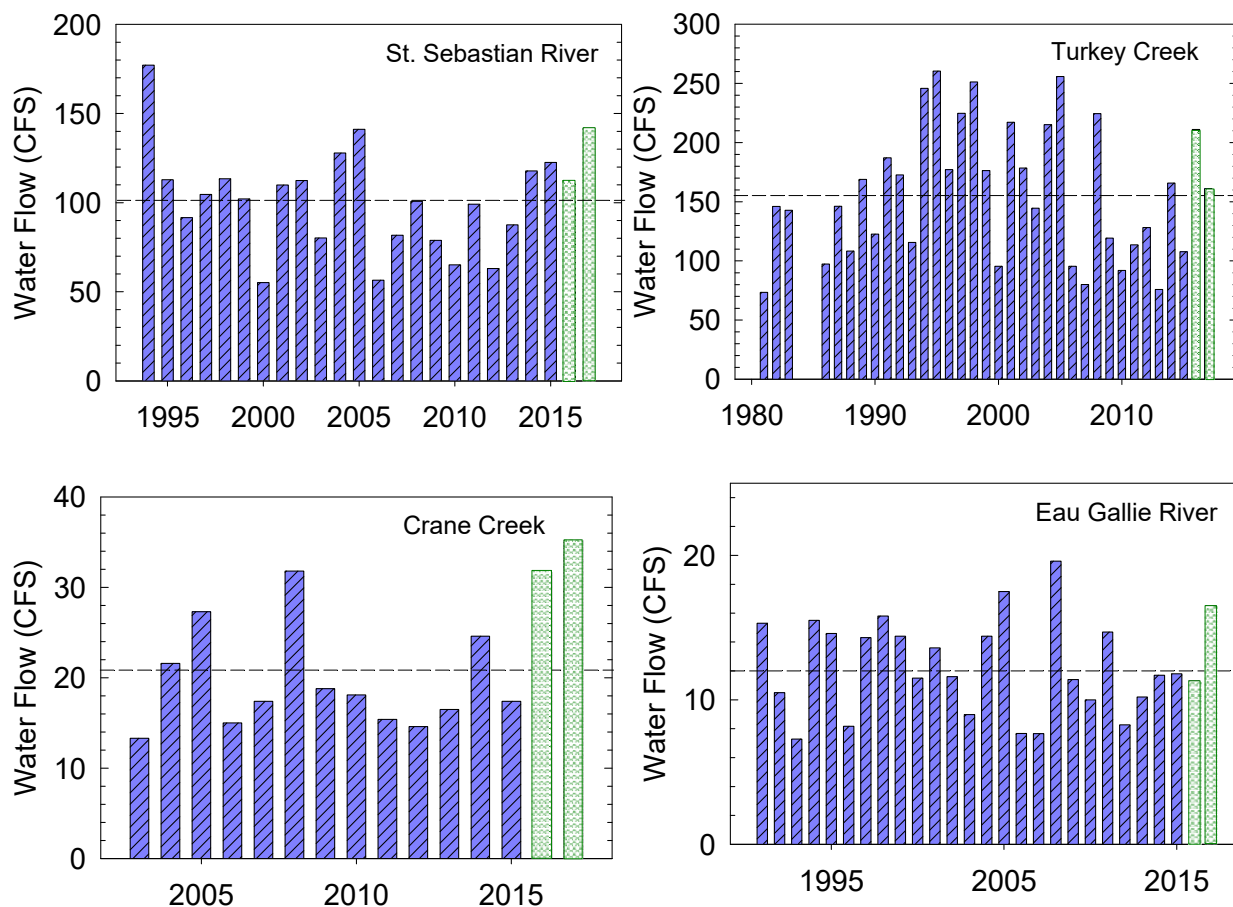


Figure 7. Average mean daily water flow by year for major tributaries of the Indian River Lagoon in this study. Bars for 2016 and 2017, the period of this study, are shown with green, cross-hatched patterns (Data from USGS, 2019). Dashed horizontal lines show mean annual flow (1 CFS = 1 ft³/sec = 0.0283 m³/sec).

observed, construction of dams, other large-scale human activities and the onset of global climate change were the primary causes.

Total dissolved solids (TDS) specifies the total concentration of major cations and anions in solution. Concentrations and relative abundances of these dissolved solids in IRL tributaries are the product of rainfall, runoff, salt intrusion, groundwater seepage plus dissolution of soil and rock minerals. TDS values provide a general frame of reference for the relative contributions of groundwater (baseflow) versus stormwater to water flow. Seasonal maxima in TDS corresponded with low water flow and a higher fraction of groundwater (baseflow). TDS minima were observed during high-flow rain events.

Mean concentrations of TDS for the four IRL tributaries ranged from 670 mg/L (TC) to 870 mg/L (SR) with a grand mean of 740 ± 220 mg/L (Figure 8, Table 7). Within each tributary, the range for TDS values was large (e.g., 360–1690 mg/L for TC). TDS values for the IRL tributaries were

well above the global average for river water of ~110 mg/L (Berner and Berner, 2012), yet below values of 35,000 mg/L for seawater and 2600 mg/L for rivers that flow through ancient salt tributaries were consistent with salt intrusion into the surface aquifer of coastal basins along the deposits such as the Pecos River (Berner and Berner, 2012). High TDS values for these IRL central east coast of Florida. Artesian wells and the upper Floridan Aquifer in Brevard County have TDS values of ~1,000–4,000 mg/L (Kroening, 2004).

Results from an ANOVA for TDS in the four IRL tributaries showed that mean values for one or more creeks was different from the others (Table 7). However, a post-hoc Tukey’s test showed no significant differences among the creeks; this is not unusual because the ANOVA and Tukey’s test are asking different questions (Tukey, 1949). Nevertheless, the mean TDS value for SR was ~30% greater than for TC, CC and EG, an observation consistent with slightly higher conductivity for groundwater in northern Indian River County than southern Brevard County (Schiner et al., 1988).

Concentrations of TSS during monthly surveys in 2016–17 were low with a grand mean of 6.6 ± 5.4 mg/L (Table 7 and Figure 8a) and range of 1–31 mg/L. Results from the ANOVA for TSS also showed that one or more tributaries had a statistically different mean (Table 7). The post-test identified SR as having a higher mean TSS than TC or CC; likely because SR has less channelization and upstream water control structures plus more soil disturbance due to agriculture than TC, CC or EG. The ratio of TDS/TSS for all monthly samples averaged ~112 and shows a dominance of dissolved (99%) versus suspended solids (1%) in the tributaries (Table 7). Globally, TDS/TSS ratios for rivers are <1 and much lower than found for the IRL (Berner and Berner, 2012). Details about the composition of TSS, an important precursor to muck deposits, are presented later in this section.

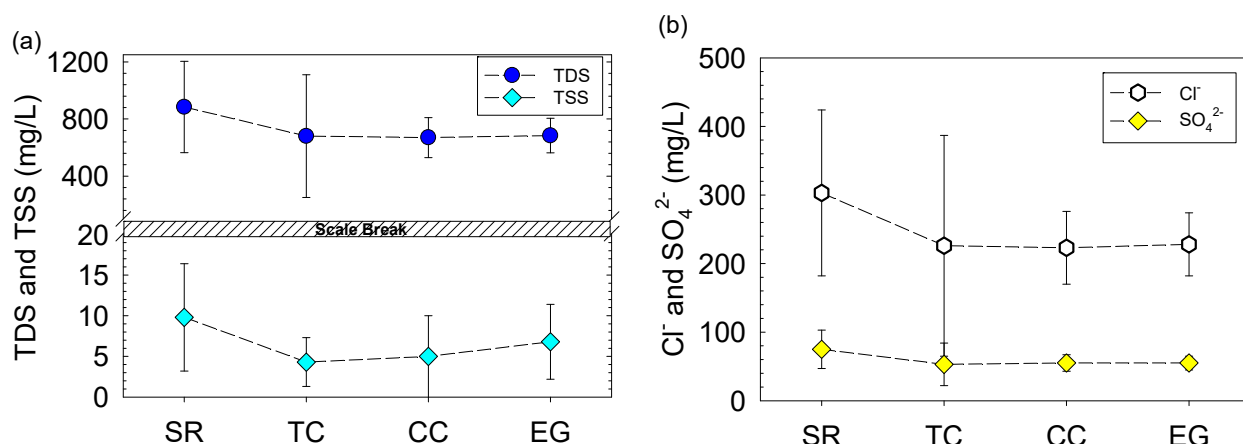


Figure 8. Means (\pm standard deviations) for (a) total dissolved solids (TDS) and total suspended solids (TSS) and (b) chloride (Cl^-) and sulfate (SO_4^{2-}) for monthly surveys from December 2015 to March 2018. Dashed lines added to help show differences in values among tributaries [St. Sebastian River (SR), Turkey Creek (TC), Crane Creek (CC) and Eau Gallie River (EG)].

Table 7. Means ± standard deviations (SD) and {medians} for concentrations of selected chemical parameters from monthly surveys, December 2015–March 2018. Values for *p* and *F* from the ANOVA are in bold font and underlined when means not significantly different (*p*>0.05). Means and SDs for chemical parameters are listed in bold font and underlined when post-hoc test showed value to be significantly greater.

Parameter	St. Sebastian River (n = 26)	Turkey Creek (n = 19)	Crane Creek (n = 27)	Eau Gallie River (n = 27)	ANOVA ^a <i>p</i> and [<i>F</i>] Values
Total Dissolved Solids (TDS) (mg/L)	870 ± 340 {857}	680 ± 430 {490}	670 ± 140 {690}	680 ± 120 {685}	0.034 ^b [2.8]
Total Suspended Solids (TSS) (mg/L)	<u>9.8 ± 6.6</u> ^c {8.2}	4.3 ± 3.0 {3.5}	5.0 ± 5.0 {3.1}	6.8 ± 4.6 {5.9}	0.0014 [5.6] SR>TC, CC
Dissolved Organic Carbon (DOC, mg C/L)	13.5 ± 7.1 {13.7}	12.1 ± 3.4 {12.6}	10.5 ± 3.7 {11.1}	13.2 ± 3.2 {13.1}	<u>0.063</u> <u>17.5</u>
Particulate Organic Carbon (POC, mg C/L)	<u>1.4 ± 0.9</u> {1.2}	0.67 ± 0.31 {0.63}	0.80 ± 0.66 {0.60}	<u>1.7 ± 0.6</u> {1.6}	<0.0001 [12.8] SR>TC, CC EG>TC, CC
% of (TDS + TSS) that is TDS	98.5 ± 1.4	99.1 ± 0.9	99.2 ± 0.9	99.1 ± 0.7	<u>0.062</u> <u>12.5</u>
pH	<u>7.63 ± 0.47</u> {7.56}	7.47 ± 0.20 {7.51}	7.19 ± 0.45 {7.19}	7.34 ± 0.35 {7.27}	0.0026 [5.1] SR>CC
Chloride (Cl ⁻) (mg/L)	<u>303 ± 121</u> {293}	226 ± 161 {153}	223 ± 53 {230}	228 ± 46 {228}	0.017 [3.6] SR>CC, EG
Sulfate (SO ₄ ²⁻) (mg/L)	<u>75 ± 28</u> {73}	53 ± 31 {41}	55 ± 12 {56}	55 ± 10 {56}	0.0044 [4.7] SR>CC, EG
HCO ₃ ⁻ (mg/L)	172 ± 37 {180}	<u>208 ± 46</u> {217}	<u>221 ± 46</u> {229}	173 ± 38 {175}	<0.0001 [9.5] CC>EG SR<TC, CC
Ca (mg/L)	85 ± 21 {89}	90 ± 19 {88}	<u>103 ± 22</u> {109}	96 ± 22 {98}	0.011 [3.9] CC>SR
SiO ₂ (mg/L)	<u>11.6 ± 2.5</u> {11.1}	9.7 ± 3.0 {9.8}	<u>10.2 ± 2.4</u> {10.0}	7.8 ± 2.1 {7.6}	<0.0001 [10.2] SR>EG CC>EG
Fe (µg/L)	195 ± 173 {137}	205 ± 182 {118}	134 ± 145 {74}	115 ± 79 {82}	<u>0.16</u> <u>1.8</u>

^aANOVA, one-way, unpaired, means statistically not different if *p*>0.05; one or more means is different if *p*<0.05.

^bPost-hoc test showed no significant differences.

^cThe following outlying values for extreme flow during monthly sampling, have been omitted: SR (9/17); TC (9/17), CC (9/17, 10/17).

An average of $75 \pm 5\%$ of the TDS in IRL tributaries was Cl^- plus Na^+ with means of ~ 250 and ~ 130 mg/L, respectively (Cl^- in Figure 8b). These high concentrations are the product of salt-rich groundwater in Brevard and Indian River Counties where Cl^- and Na^+ concentrations range from ~ 700 to >1300 mg/L and 200 to >6000 mg/L, respectively (Wander and Reitz, 1950; Planert and Aucott, 1985). Clearly, the IRL tributaries have high Cl^- and Na^+ values relative to 8.3 mg/L and 7.2 mg/L, respectively, in average world river water (Berner and Berner, 2012). Significantly higher concentrations of Cl^- and SO_4^{2-} in SR than the other tributaries is consistent with higher TDS values in SR (Figure 8b, Table 7).

Concentrations of Cl^- correlated very strongly ($r \geq 0.9$) with TDS for the IRL tributaries due to the dominance of Cl^- and Na^+ from salt water intrusion into groundwater (Figure 9a; Table 7). Chloride also correlated strongly with sulfate because $\sim 55\%$ of the sulfate, and essentially all of the Cl^- and

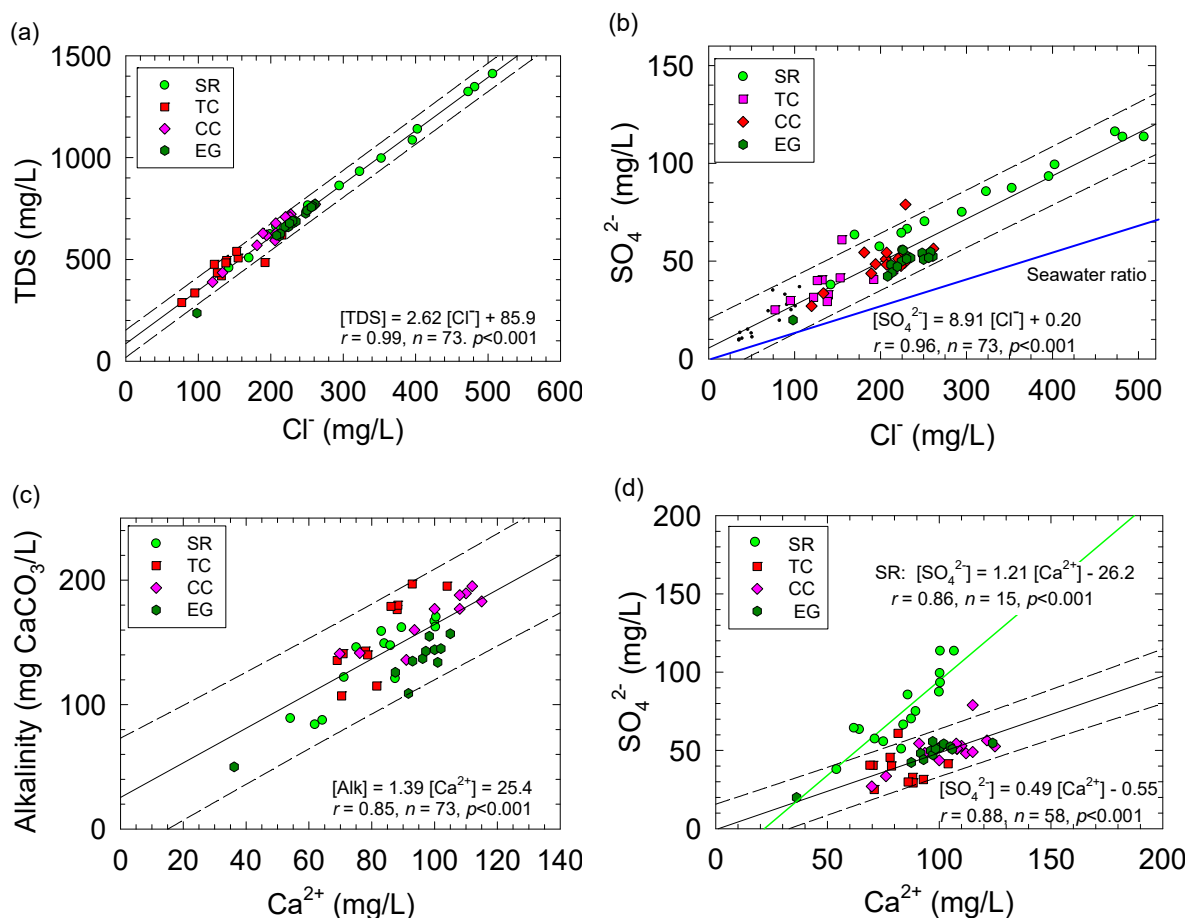


Figure 9. Concentrations of (a) total dissolved solids (TDS) versus chloride (Cl^-), (b) sulfate (SO_4^{2-}) versus Cl^- , (c) alkalinity (Alk) versus calcium (Ca^{2+}) where an alkalinity of 10 mg $\text{CaCO}_3/\text{L} \approx 8.2$ mg HCO_3^-/L , and (d) SO_4^{2-} versus Ca^{2+} . Solid lines are from linear regressions, dashed lines show 95% prediction intervals, r is the correlation coefficient, n is the number of data points and p is the p statistic. Two regression lines are shown on (d), one for St. Sebastian River (SR) and one for the other three tributaries [Turkey Creek (TC), Crane Creek (CC) and Eau Gallie River (EG)].

Na^+ , in tributary waters could be traced to an original seawater source (note that the $[\text{SO}_4^{2-}/\text{Cl}^-]$ ratio for the tributaries is greater than the ratio for seawater, Figure 9b). The source of excess SO_4^{2-} (the 45% of the SO_4^{2-} without a seawater source) is discussed in more detail below.

Average values for Ca^{2+} and HCO_3^- in the tributaries ranged from 85–103 mg/L and 172–221 mg/L, respectively (Table 7, Figure 10a). Values for IRL tributaries were greater than average world river water ($\text{Ca}^{2+} = 15$ mg/L; $\text{HCO}_3^- = 53$ mg/L; Berner and Berner, 2012). Clearly, baseflow in central east Florida has dissolved subsurface limestone (CaCO_3). Results for major elements (e.g., Cl^- and Ca^{2+}) also show the importance of groundwater to the major element composition of the tributaries. Significantly more HCO_3^- in TC and CC plus Ca^{2+} in CC suggest a greater contribution from limestone weathering than in SR and EG (Table 7), a point partly supported by the presence of limestone mines only in the catchment basins of TC and CC (US-Mining, 2019).

Calcium concentrations correlated strongly with both alkalinity and sulfate (Figure 9c, d). Only a small fraction of the 80–100 mg/L of dissolved Ca^{2+} in the tributaries had a seawater source (<6 mg Ca^{2+} /L based on Cl^- values and a seawater ($\text{Ca}^{2+}/\text{Cl}^-$) ratio = 0.021) because 70% and 30% of the excess Ca^{2+} (non-seawater source), respectively, were derived from chemical weathering of limestone and dissolution of calcium sulfate. The calcium sulfate source is more prominent for SR as shown by the higher slope for SO_4^{2-} versus Ca^{2+} as well as higher SO_4^{2-} concentrations (Figure 9d). Calcium sulfate has been added to citrus fields to correct Ca and S deficiencies (Zekri and Obreza, 2013). Although the St. Sebastian River drainage basin had 31% agricultural usage and abundant citrus-growing areas during the early 2000s (SJRWMD, 2009), a 45% decline in citrus acreage from ~35,000 acres in 2011 to ~19,000 in 2017 has occurred (FL Dep Ag, 2012, 2019); yet, a large amount of agricultural land with a potential for disturbance and erosion is still present. We are unsure about current practices for applications of Ca^{2+} and SO_4^{2-} .

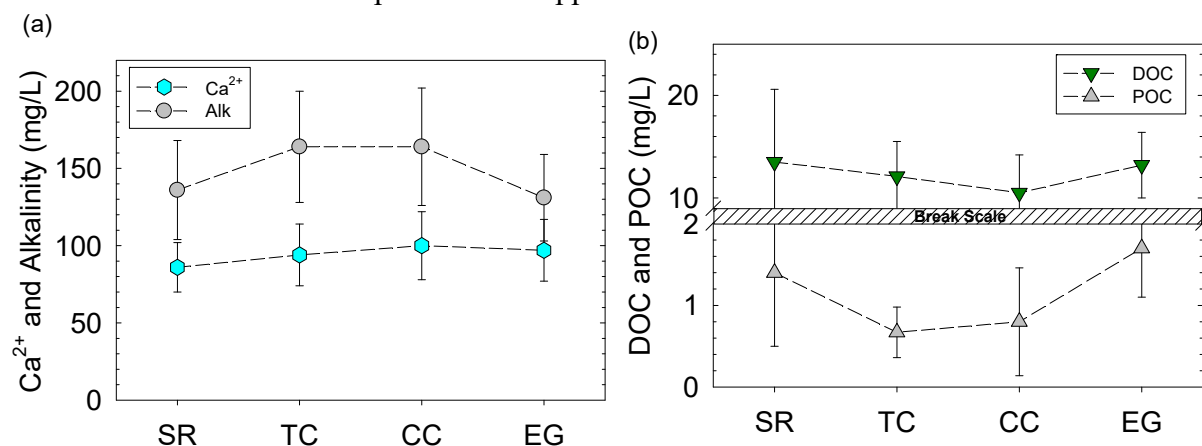


Figure 10. Means (\pm standard deviations) during monthly surveys from December 2015 to March 2018 for (a) calcium (Ca^{2+}) and alkalinity (Alk) and (b) dissolved organic carbon (DOC) and particulate organic carbon (POC). Dashed lines added to help show differences in values among tributaries [St. Sebastian River (SR), Turkey Creek (TC), Crane Creek (CC) and Eau Gallie River (EG)]. An alkalinity of 10 mg $\text{CaCO}_3/\text{L} \approx 8.2$ mg HCO_3^-/L , assuming all dissolved carbonate is HCO_3^- ($>99\%$ HCO_3^- at average pH of 7.3 in IRL tributaries).

Concentrations of dissolved silica in the IRL tributaries averaged $\sim 10 \pm 3$ mg SiO₂/L, close to the global mean of 10.4 mg SiO₂/L (Berner and Berner, 2012). Dissolution of silica in IRL tributaries is enhanced by warm temperatures that promote dissolution (Jennerjahn et al., 2005). Even though natural sources of aluminosilicates (silt and clay) in tributary soils are minor ($3.8 \pm 3.7\%$; Huckle et al., 1974), they are enhanced by releases from sod (St. Augustine) in central Florida that contains a mean of $7.5 \pm 1.6\%$ silt + clay (Trefry et al., 2009). Sod is widely used in Brevard County. Silt + clay comprise more than half the dry solids in IRL muck (Trefry et al., 1990).

The close similarity in relative ion compositions for IRL tributaries can be further demonstrated using an anion ternary diagram (Figure 11). Data for anions from the IRL tributaries and the upland St. Johns River plot closest to the Cl⁻ + SO₄²⁻ vertex (i.e., 100% [Cl⁻ + SO₄²⁻]) on the diagram (Figure 11), in support of the previous discussion. The impact of limestone weathering also is displayed on the ternary diagram as the plot shows ~ 20 to 35% HCO₃⁻ for IRL tributaries (Figure 11). The IRL tributaries have a distinctly different anion composition than average world river water (Figure 11). Although the ternary diagram describes river composition and suggests sources of ions, it does not show the high concentrations of Cl⁻, HCO₃⁻ and SO₄²⁻. Indeed, the IRL tributaries have 7- to 30-fold higher values for these anions than average global rivers due to the importance of groundwater inputs.

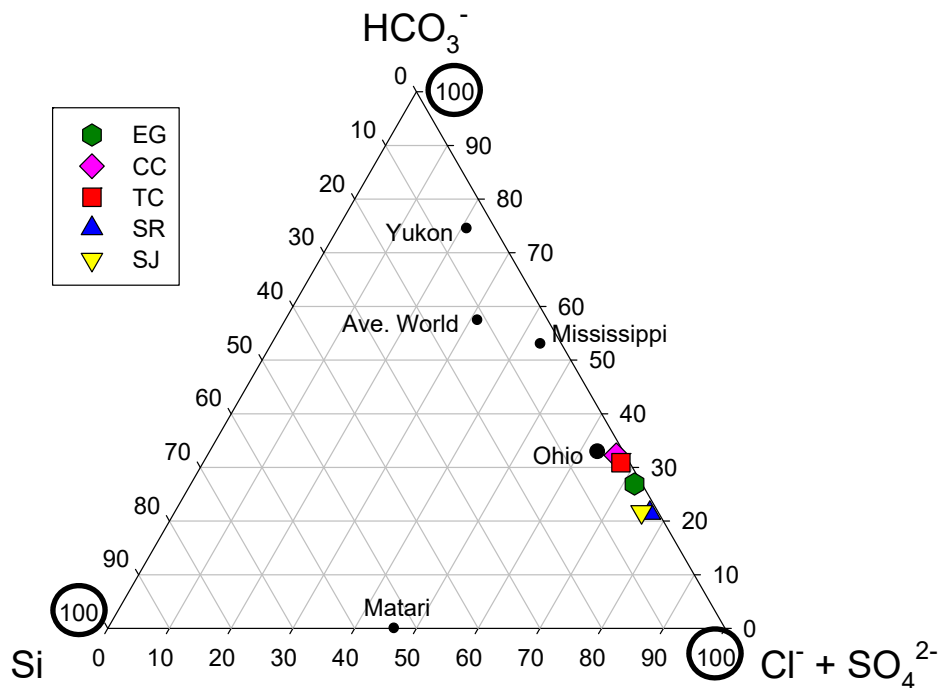


Figure 11. Ternary diagram showing relative chemical compositions of IRL tributaries (December 2015–March 2018), the St. Johns River near Cocoa, FL (SJ) and selected world rivers. The data point for the Eau Gallie River (EG), for example, shows the following distribution: 1.3% Si, 72.7% Cl⁻ + SO₄²⁻, and 26.0% HCO₃⁻. Units are as follows: Si (μmol/L), Cl⁻ + SO₄²⁻, and HCO₃⁻ (μeq/L). Data for St. Johns River from Wendy Tweedale (SJRWMD, written communication). [St. Sebastian River (SR), Turkey Creek (TC), Crane Creek (CC)].

Mean concentrations of DOC were not significantly different among the four IRL tributaries (Table 7). The grand mean for DOC (12 ± 6 mg/L) was 2.3–2.9 times greater than estimated global mean values for rivers (5.3 mg/L, Meybeck, 1993; 4.2 mg/L, Seitzinger et al., 2010) as well as humid, tropical rivers (4.9 mg/L). Rivers in China and India with DOC values of 12–14 mg/L, similar to DOC concentrations in IRL tributaries, have been reported to have an anthropogenic component (Ludwig et al., 1996). Although the IRL tributaries may contain anthropogenic inputs from human and agricultural activities in the drainage basin, the uniformity of these higher mean values is more consistent with higher runoff (water flow/basin area) and subtropical weather than anthropogenic inputs. Future studies of the chemical and isotopic makeup of the DOC would be needed to confirm any anthropogenic contributions.

Concentrations of TN and TP provide an overview of nutrient conditions in lakes and rivers and are frequently included in management plans such as total maximum daily loads for the IRL (e.g., USEPA, 2007; Gao, 2009). Mean concentrations of TN were not significantly different among the four tributaries (Table 8). When results for IRL tributaries were compared with water quality criteria for TN in Florida rivers and streams (USEPA, 2017, Florida peninsula), average values for TN in all four tributaries were 30–50% lower than the Florida standard (Table 9). In contrast, mean values for TP in SR and EG were significantly ~3.7- and 1.8-fold higher than in TC and CC, respectively (Table 8). SR and EG had mean TP values that were 80% and 100% higher, respectively, than the EPA criteria (Table 9). Only TC had a mean value for TP that was lower than the Florida criteria (Table 9). These results prompt us to increase our focus on P while maintaining a steady effort with N when evaluating water quality in the IRL.

We also determined concentrations of the different chemical forms of N and P for each tributary (Figure 12, Table 10) because biological availability and uptake rates of N and P during photosynthesis in the IRL were directly linked to the chemical form of the nutrient (e.g., Kang et al., 2015). DON was the dominant chemical form of nitrogen for all four tributaries (Figure 12, Table 8). Mean values for DON, like DOC, were not significantly different among the IRL tributaries (Table 8). However, the range of DON concentrations in IRL tributaries (180–930 μ g/L) was greater than the range of concentrations reported for east coast U.S. rivers (DON = 118–485 μ g/L; Wiegner et al., 2006). High runoff values and subtropical climate likely promote higher DON and DOC concentrations. Laboratory incubation experiments for east coast U.S. rivers have shown that 20–70% of the river-borne DON can be biologically available (e.g., Wiegner et al., 2006). This is certainly an important point as we consider the fate of DON in the IRL because DON is such a large fraction of TN in the four tributaries ($53 \pm 11\%$) and the IRL ($61 \pm 11\%$). Furthermore, samples of *Aureoumbra lagunensis* from the IRL were shown to take up urea (that makes up <10% of the DON) more rapidly than NH_4^+ (Kang et al., 2015). Urea can be introduced to the environment externally from livestock waste and fertilizer and internally from metabolic waste products from lagoon biota.

Table 8. Means ± standard deviations and {medians} for concentrations of selected chemical parameters and dissolved and particulate forms of nitrogen (N) and phosphorus (P) during monthly surveys, December 2015–March 2018. Values for *p* and *F* from the ANOVA are in bold font and underlined when means not significantly different (*p*>0.05). Means and SDs for chemical parameters are listed in bold font and underlined when post-hoc test showed value to be significantly greater.

Parameter	St. Sebastian River (n = 26)	Turkey Creek (n = 19)	Crane Creek (n = 27)	Eau Gallie River (n = 27)	ANOVA ^a <i>p</i> and [<i>F</i>] Values
Total N (TN as µg N/L)	934 ± 363 {906}	834 ± 270 {866}	934 ± 289 {861}	1020 ± 180 {975}	0.21 [1.55]
Dissolved Organic N (DON as µg N/L)	536 ± 239 {496}	495 ± 122 {476}	444 ± 135 {420}	496 ± 117 {504}	0.24 [1.42]
Nitrate + Nitrite (NO ₃ ⁻ + NO ₂ ⁻ as µg N/L)	113 ± 39 {108}	129 ± 82 {146}	258 ± 106 {242}	138 ± 118 {123}	<0.0001 [13.6] CC>SR,TC,EG
Ammonium (NH ₄ ⁺ as µg N/L)	50 ± 25 {49}	48 ± 32 {37}	89 ± 94 {44}	131 ± 72 {126}	<0.0001 [9.1] EG>SR and TC
Particulate Organic N (PON as µg N/L) ^c	200 ± 71 {191}	139 ± 77 {129}	120 ± 56 {121}	268 ± 115 {290}	<0.0001 [14.8] EG>SR,TC,TC SR>CC
DOC/DON	24.9 ± 8.9	25.5 ± 9.4	25.7 ± 11.9	27.9 ± 10.2	0.69 [0.49]
Total P (TP as µg P/L)	224 ± 308 {143}	63 ± 34 {48}	132 ± 54 {121}	244 ± 66 {248}	0.0019 [5.4] SR&EG>TC
Phosphate (PO ₄ ³⁻ as µg P/L)	70 ± 50 {56}	22 ± 9 {22}	58 ± 13 {57}	149 ± 47 {134}	<0.0001 [54] EG>SR,TC, CC SR>TC
Dissolved Organic P (DOP as µg P/L)	51 ± 34 {41}	18 ± 24 {5}	29 ± 32 {47}	36 ± 31 {39}	0.034 [3.1] SR>TC
Particulate P (PP as µg P/L)	54 ± 30 {51}	25 ± 14 {21}	47 ± 28 {36}	69 ± 22 {72}	<0.0001 [11.3] SR, CC, EG>TC EG>CC

^aANOVA, one-way, unpaired, means statistically not different if *p*>0.05; one or means is different if *p*<0.05.

^bPost-hoc test showed no significant differences.

^cThe following outlying values for extreme flow during monthly sampling, have been omitted: SR (9/17); TC (9/17), CC (9/17, 10/17).

Table 9. Means ± standard deviations for total nitrogen (TN) and total phosphorus (TP) for monthly samples from IRL tributaries relative to USEPA Florida Water Quality Criteria.

	St. Sebastian River	Turkey Creek	Crane Creek	Eau Gallie River	Florida Water Quality Criteria ^a
12/15 to 3/18 TN ^b (µg N/L)	930 ±360	830 ±270	930 ±290	1020 ±180	<u>1540</u>
12/15 to 3/18 TP ^b (µg P/L)	220 ±300	63 ±34	130 ±54	244 ±66	<u>120</u>

^aUSEPA, 2017. ^bTotal N (TN) and Total P (TP) include both dissolved and particulate N and P.

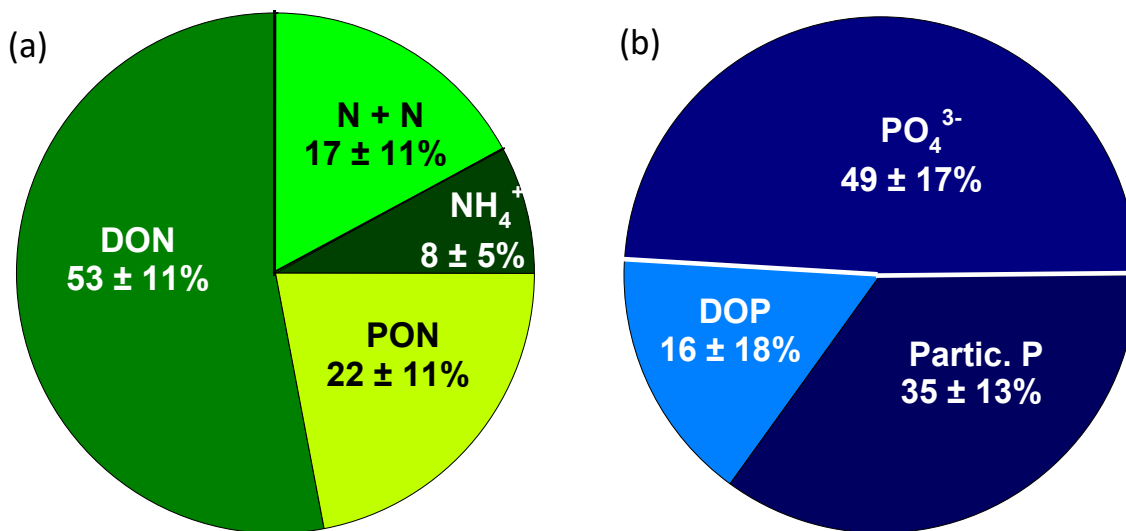


Figure 12. Percentages of the chemical forms of (a) nitrogen where DON = dissolved organic nitrogen, N+N = nitrate + nitrite, NH₄⁺ = ammonium, and PON = particulate organic nitrogen and (b) phosphorus where PO₄³⁻ = phosphate, DOP = dissolved organic phosphorus, and Partic. P = particulate phosphorus for all samples from all four major tributaries (n =104).

Table 10. Means \pm standard deviations for chemical forms of nitrogen and phosphorus (as % of total) in IRL tributaries. Values for p and F from ANOVA are in bold font and underlined when means are not significantly different ($p > 0.05$). Means and SDs for chemical parameters are listed in bold font and underlined when post-hoc test showed value to be significantly greater.

Chemical Form	Sebastian River	Turkey Creek	Crane Creek	Eau Gallie River	ANOVA ^a p and $[F]$ Values
TN ($\mu\text{g N/L}$)	934 \pm 363	834 \pm 270	934 \pm 289	1020 \pm 180	<u>0.21</u> [1.6]
DON (%)	<u>56.3 \pm 9.3</u>	<u>60.8 \pm 9.2</u>	47.9 \pm 10.8	48.3 \pm 9.6	<0.0001 [10.6] SR>CC,EG TC>CC,EG
NH ₄ ⁺ (%)	6.0 \pm 2.0	5.4 \pm 1.9	7.9 \pm 5.1	<u>12.1 \pm 5.8</u>	<0.0001 [12.5] EG>SR,TC,CC
N+N (%)	13.3 \pm 4.7	15.4 \pm 10.0	<u>28.7 \pm 9.7</u>	12.6 \pm 10.5	<0.0001 [17.4] CC>SR,TC,CC
PON (%)	<u>24.4 \pm 9.1</u>	18.3 \pm 7.6	15.5 \pm 8.0	<u>27.0 \pm 12.4</u>	0.0002 [7.4] SR>CC; EG>TC, CC
TP ($\mu\text{g P/L}$)	<u>224 \pm 308</u>	64 \pm 34	131 \pm 54	<u>244 \pm 66</u>	0.0019 [5.4] SR>TC; EG>TC
PO ₄ ³⁻ (%)	48.0 \pm 17.3	41.5 \pm 15.6	48.0 \pm 14.4	<u>62.0 \pm 12.4</u>	0.0001 [7.8] EG>SR, TC, CC
DOP (%)	17.1 \pm 20.5	16.8 \pm 20.8	17.3 \pm 18.0	9.2 \pm 10.0	<u>0.26</u> [1.4]
PP (%)	34.9 \pm 13.3	<u>41.7 \pm 12.8</u>	34.7 \pm 12.4	28.8 \pm 8.6	0.007 [4.3] TC>EG

^a ANOVA, one-way, unpaired, means statistically not different if $p > 0.05$.

Mean values for ratios of DOC/DON also were not significantly different among the four tributaries (Table 8). The grand mean for DOC/DON was 26 by mass and 30 by atom (e.g., SR in Figure 13a), higher than the classic Redfield ratio of 16 (Redfield, 1934). Yet, this average molar DOC/DON ratio was not significantly different than the mean of 29 ± 3 (by atom) for the Delaware, Hudson, Savannah and Peconic Rivers. These high values for DOC/DON in these east coast, U.S. rivers were reported to be the product of readily-consumed DON (Wiegner et al., 2006). As in other rivers (e.g., Wiegner et al., 2006) higher DON in SR and TC relative to CC and EG was likely linked to inputs from greater percentages of natural and agricultural land area in SR and TC (Table 1).

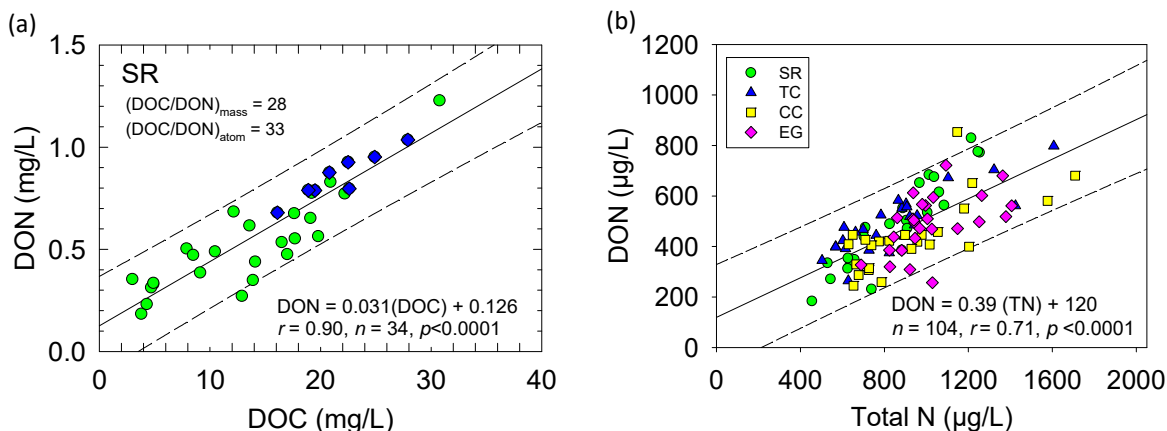


Figure 13. Results for (a) concentrations of dissolved organic nitrogen (DON) versus dissolved organic carbon (DOC) for St. Sebastian River (SR) and (b) DON versus total N (TN) for all four tributaries.

Mean values for N+N in CC were significantly higher (~2-fold) than in the other three tributaries (Table 8, Figure 14). High N+N concentrations for CC (258 µg/L) may be partly explained by runoff of reclaimed water from nearby Crane Creek Reserve Golf Course (map, Figure 3, page 4). Reclaimed water that we collected from the irrigation system at the golf course contained ~9 mg N+N/L. Regulations for applied reclaimed water are set at 12 mg nitrate-N/L (Florida Department of State, 2010); the samples we collected had an average TDN value of 11.7 mg/L. The high values for N+N that we found at sampling site CC, ~400 m from the eastern side of the golf course, were about a 35-fold dilution of values for reclaimed water. The City of Melbourne Florida recycles ~8.3 million liters of reclaimed water per day (2.2 million gallons per day; City of Melbourne, FL, 2019). At a dissolved N content of 12 mg/L, annual recycling would yield ~36 tons of N/year. A very large fraction of the reclaimed water is certainly taken up by plants; the amount that enters the IRL has not been determined. Assuming a release of ~3% of the N+N (i.e., a 35-fold dilution), the annual transport to the IRL could be ≥ 1 ton N/y. Present goals are to reduce the dissolved N content of the reclaimed water from ~12 mg/L to 6 mg/L.

The mean concentration of NH_4^+ and the percentage of TN that was NH_4^+ at EG were both ~2-fold higher than at the other three tributaries (Tables 8 and 10). This is similar to the trend for N+N at CC (Tables 8 and 10). Sources of NH_4^+ and N+N to tributary water include human and animal waste, some fertilizers and in the case of N+N, industrial inputs. In addition to NH_4^+ , EG also carried high concentrations of PON, TP, PO_4^{3-} and PP; such was not the case for CC as concentrations of the same four chemical species were significantly lower than in EG. The distinction between concentrations and fluxes of N and P for CC and EG will be sorted out in Section 3.4 on fluxes to the IRL.

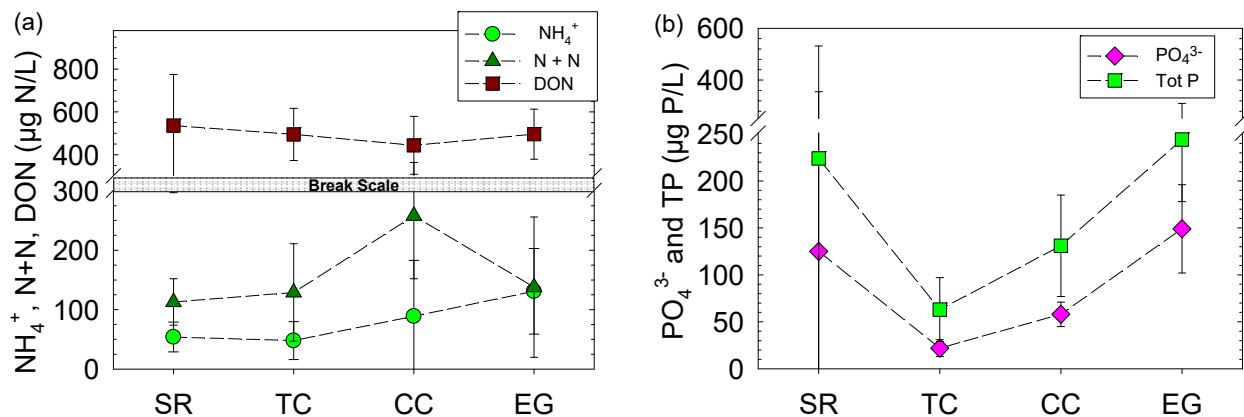


Figure 14. Mean values (± standard deviations) for dissolved (a) ammonium (NH₄⁺), nitrate + nitrite (N+N) and dissolved organic nitrogen (DON) and (b) phosphate (PO₄³⁻) and total phosphorus (TP) for tributaries during monthly surveys from December 2015 to March 2018. Dashed lines added to help show differences in values among tributaries [St. Sebastian River (SR), Turkey Creek (TC), Crane Creek (CC) and Eau Gallie River (EG)].

Mean concentrations of TP in SR and EG were ~3.7-fold and 1.8-fold higher, respectively, than in TC and CC (Table 8, Figure 14). Similar significant differences were obtained for PO₄³⁻ and PP with markedly lower values at TC than the other three tributaries (Table 8 and Figure 14). Lower concentrations for all forms of phosphorus were found in TC.

Suspended particles borne by IRL tributaries are an important precursor to muck deposits. Organic matter (OM) typically makes up 10 to >20% of the dry weight of IRL muck sediments with inputs from tributaries and upland sources as well as OM from decomposing seagrass, drift algae and other biological detritus (Trefry et al., 1990). Inorganic silts and clays comprise more than half the dry weight of IRL muck (Trefry et al., 1990). The main source of inorganic material is from land with transport to the IRL via tributaries, storm drains and direct discharge from erosion along the banks of the lagoon. The amounts and composition of incoming TSS from major tributaries can provide some insight regarding trends for future muck deposits as discussed in Section 3.5 when TSS concentrations for TC from 1988–89 are compared with 2016–17.

Mean concentrations of POC in the four tributaries ranged from 15.5–26.7% of the TSS (Table 11). Based on a carbon content of ~40% for OM in suspended sediments from the IRL (Trefry et al., 1990), the incoming TSS carries 39% (15.5/0.4) to 67% (26.7/0.4) OM. These OM values are significantly greater than the 10–30% OM in present-day IRL muck.

Table 11. Means ± standard deviations (SD) for concentrations as a percent of total suspended solids (TSS), for particulate organic carbon (POC), particulate organic nitrogen (PON), particulate phosphorus (PP), particulate iron (Fe), particulate aluminum (Al) and particulate silicon (Si) plus various ratios for elements bound to suspended particles for Indian River Lagoon tributaries (December 2015–March 2018). Values for *p* and *F* from the ANOVA are in bold font and underlined when means not significantly different (*p*>0.05). Means and SDs for chemical parameters are listed in bold font and underlined when post-hoc test showed value to be significantly greater.

Parameter (% of TSS, by mass)	St. Sebastian River ^a (n = 26)	Turkey Creek ^a (n = 19)	Crane Creek ^a (n = 27)	Eau Gallie River (n = 27)	ANOVA ^b <i>p</i> and [<i>F</i>] Values
POC	15.5 ± 2.6 {15.5}	17.5 ± 4.7 {16.7}	17.9 ± 4.2 {18.6}	<u>26.7 ± 8.1</u> {24.9}	<0.0001 [22.7] EG>SR, TC,CC
PON	2.9 ± 1.5 {2.6}	4.2 ± 1.9 {4.2}	3.7 ± 1.8 {4.0}	<u>4.4 ± 2.0</u> {4.7}	0.018 [3.5] EG>SR
PP	0.69 ± 0.41 {0.62}	0.58 ± 0.11 {0.60}	<u>1.1 ± 0.3</u> {1.2}	<u>1.1 ± 0.2</u> {1.1}	<0.0001 [20.0] CC>SR,TC EG>SR,TC
POC/PON	<u>7.1 ± 4.3</u> {6.7}	4.2 ± 1.1 {4.1}	5.4 ± 2.73 {4.8}	<u>6.6 ± 2.5</u> {6.3}	0.015 [5.6] SR>TC; EG>TC
POC/PP	26 ± 6 {26}	31 ± 9 {30}	17 ± 5 {16.6}	25 ± 8 {24.2}	<0.0001 [15.2] CC<SR,TC,EG; TC>EG
POP/PP	4.3 ± 2.0 {4.2}	<u>8.1 ± 3.4</u> {7.2}	3.5 ± 1.4 {3.5}	4.0 ± 1.7 {4.3}	<0.0001 [13.2] TC>SR, CC, EG
Particulate Fe	6.6 ± 1.4 {6.7}	<u>10.6 ± 3.1</u> {10.4}	<u>10.7 ± 2.6</u> {11.1}	4.2 ± 1.1 {4.0}	<0.0001 [63] CC>SR,EG TC>SR,EG
Particulate Al	<u>4.3 ± 1.4</u> {4.3}	2.7 ± 0.6 {2.7}	2.8 ± 1.0 {2.5}	2.5 ± 0.9 {2.3}	<0.0001 [16.8] SR>TC,CC,EG
Particulate Si	<u>13.3 ± 5.8</u> {12.6}	9.2 ± 2.3 {9.4}	11.1 ± 7.7 {8.6}	8.8 ± 2.6 {8.3}	0.017 [3.6] SR>EG
Particulate Fe/Al	2.0 ± 2.1 {1.6}	<u>4.1 ± 1.7</u> {3.6}	<u>4.6 ± 2.3</u> {4.5}	1.9 ± 0.7 {1.8}	<0.0001 [15.2] TC>SR,EG; CC>SR,EG
Particulate Si/Al	3.1 ± 1.1 {2.9}	3.4 ± 0.8 {3.3}	3.9 ± 1.8 {3.6}	3.8 ± 1.2 {3.6}	<u>0.14</u> <u>[1.8]</u>

^aThe following outlying values for extreme flow during monthly sampling, have been omitted: SR (9/17); TC (9/17), CC (9/17, 10/17).

^bANOVA, one-way, unpaired, means statistically not different if *p*>0.05; one or means is different if *p*<0.05.

Al is a good proxy for soil minerals carried with TSS (i.e., aluminosilicates present as silts and clays). Concentrations of Al were significantly higher (as % of TSS) in SR (4.3%) than in the other three tributaries (2.7%; Table 11). Trefry et al. (1990) determined that the aluminosilicate content of suspended or bottom sediments in the IRL was equal to 12 times the Al concentration. Therefore, the aluminosilicate (inorganic silt + clay) content was ~50% for SR and 30% for the other tributaries relative to >60% for IRL muck. No significant differences were found for the Si/Al ratio (grand mean 3.4 ± 1.0) among the four tributaries (Table 11, Figure 15a regression line), likely because the aluminosilicate minerals are relatively similar across the study area (Huckle et al., 1974). Therefore, the relative amounts of OM (40–70%) versus silt + clay (30–50% aluminosilicates) carried by suspended matter in each tributary give some insight toward future muck deposits. The three tributaries with higher urban land usage (TC, CC, EG) have higher OM content relative to SR or IRL muck. One explanation for the observed difference between SR and the other creeks is a reduction in soil erosion from drainage basins with more residential (urban) land usage. Residential yards are not frequently undergoing soil disturbance relative to agricultural land. This is positive news. However, increased transport of particulate OM in urban (residential) land is a potential concern because the OM eventually decomposes to release N and P into the IRL.

Particulate Fe concentrations and the Fe/Al ratios (as % of TSS) were significantly higher for TC and CC (Table 11). Furthermore, the mean Fe concentration (8.0%) and Fe/Al ratios (3.2) for all tributaries were high relative averages of $2.6 \pm 1.0\%$ and 0.6 for IRL sediments (Trefry and Trocine, 2011). Two possible sources of increased Fe on suspended particles (relative to Al) were added releases of Fe-rich irrigation water and/or releases from Fe- and P-rich minerals in soils. The reason for this trend is uncertain at present. However, a freshly precipitated Fe-oxide coating of riverine suspended matter would take up PO_4^{3-} , thereby enhancing concentration of PP.

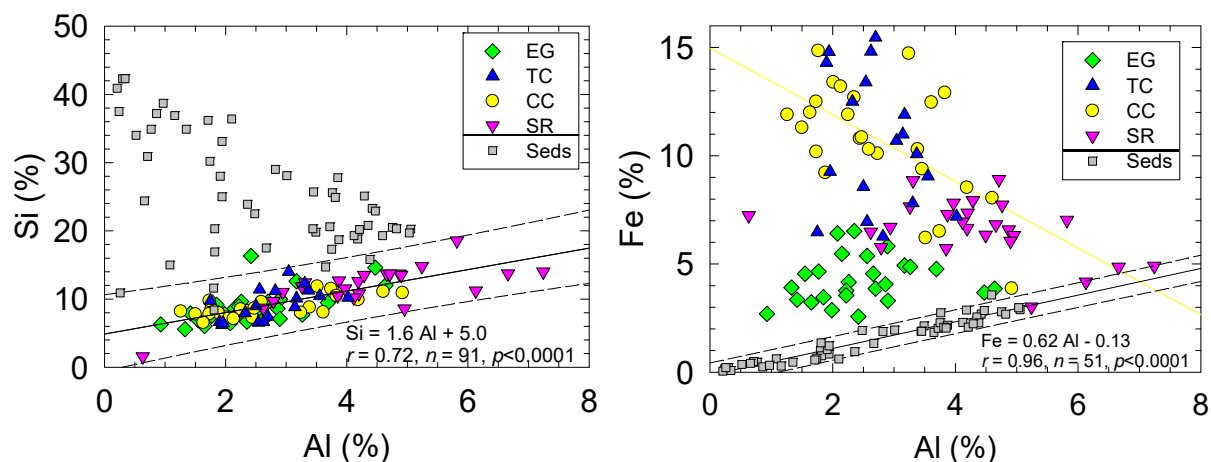


Figure 15. Concentrations of aluminum (Al) in bottom sediments from the Indian River Lagoon and suspended particles from the Eau Gallie River (EG), Turkey Creek (TC), Crane Creek (CC) and St. Sebastian River (SR) versus (a) silicon (Si) and (b) iron (Fe). Solid lines are from linear regressions for (a) suspended particles and (b) sediments; dashed lines show 95% prediction intervals, r is the correlation coefficient, n is the number of data points and p is the p statistic.

3.3. Trends in Concentrations of Chemicals as a Function of Water Flow

To further advance and test our ability to model and predict relationships between water flow and nutrient concentrations in tributaries, we collected data for the IRL that enabled us to write equations and test the following hypothesis:

H₁: Concentrations of total dissolved solids (TDS), total suspended solids (TSS), dissolved organic carbon (DOC) and chemical forms of N (NH₄⁺, N+N, DON, PON and TN) and P (PO₄³⁻, DOP, PP and TP) in IRL tributaries are correlated moderately strongly to very strongly with water flow ($r \geq 0.6$, $p < 0.05$).

Concentrations of TDS in the four IRL tributaries increased as water flow decreased and vice versa (Figure 16a, c, e, g). High concentrations of TDS occurred when salt-rich groundwater became more abundant during low water flow. Highest TDS values were observed from December 2016 through May 2017, a 6-month period of very low flow (Figure 16a, c, e, g). For example, during low waterflow at SR (32 ± 5 CFS), TDS increased sharply and then stabilized at 1300 ± 80 mg/L, ~50% higher than the 26-month mean of 860 mg/L (Figure 16a).

The lowest TDS values in the IRL tributaries ranged from 232 mg/L at EG to 370 mg/L at CC and were observed during high flow after Hurricanes Matthew (October 2016) and Irma (September 2017; Figure 16a, c, e, g). During rain events, TDS commonly decreased by 50% or more during the first 12 hours via dilution with rain water, followed by a gradual return to median values (Figure 17 a, c, e, g). During a concurrent rain event, TDS decreased by 55–60% in both CC and EG (Figure 17e, g). After the rain stopped, TDS increased to near median values within one day at CC while the approach to median values at EG took several more days (Figure 17e, g). In this case, the shorter recovery time at CC was likely due to higher median water flow, and a narrower, deeper channel that accelerated flushing of freshwater to the IRL (i.e., lower TDS).

Strong negative correlation coefficients (r) of -0.86 and -0.90 were calculated for TDS versus log flow for SR and CC, respectively (Figure 18a, e). Exponential flow has previously been shown to be successfully used to model TDS in rivers (e.g., O'Connor, 1976, Sinyukovich, 2003). At TC, a very strong correlation also was observed at water flows of 100–1,000 CFS ($r = -0.90$); however, four anomalously high TDS values were obtained at low water flow (>100 mg/L) from December 2016 to March 2017 (Figure 18c). These anomalies were likely related to detectable, but minor upstream migration and mixing of saline lagoon water that was not confirmed during routine field testing for the presence of a distinct salt wedge in the bottom water. Therefore, these four data points were not used to develop an equation for TDS versus log flow. Trends for EG were less well constrained, but acceptable ($r = -0.69$, Figure 18g). The lower value for r was likely due to the small watershed and large range in flows between 2–100 CFS (Figure 18g). Equations for TDS versus flow (e.g., Figure 16a, c, e, g) were used in *Section 3.4* to calculate fluxes of TDS for all four tributaries because the regressions were significant ($p < 0.05$) with r values ≥ 0.6 .

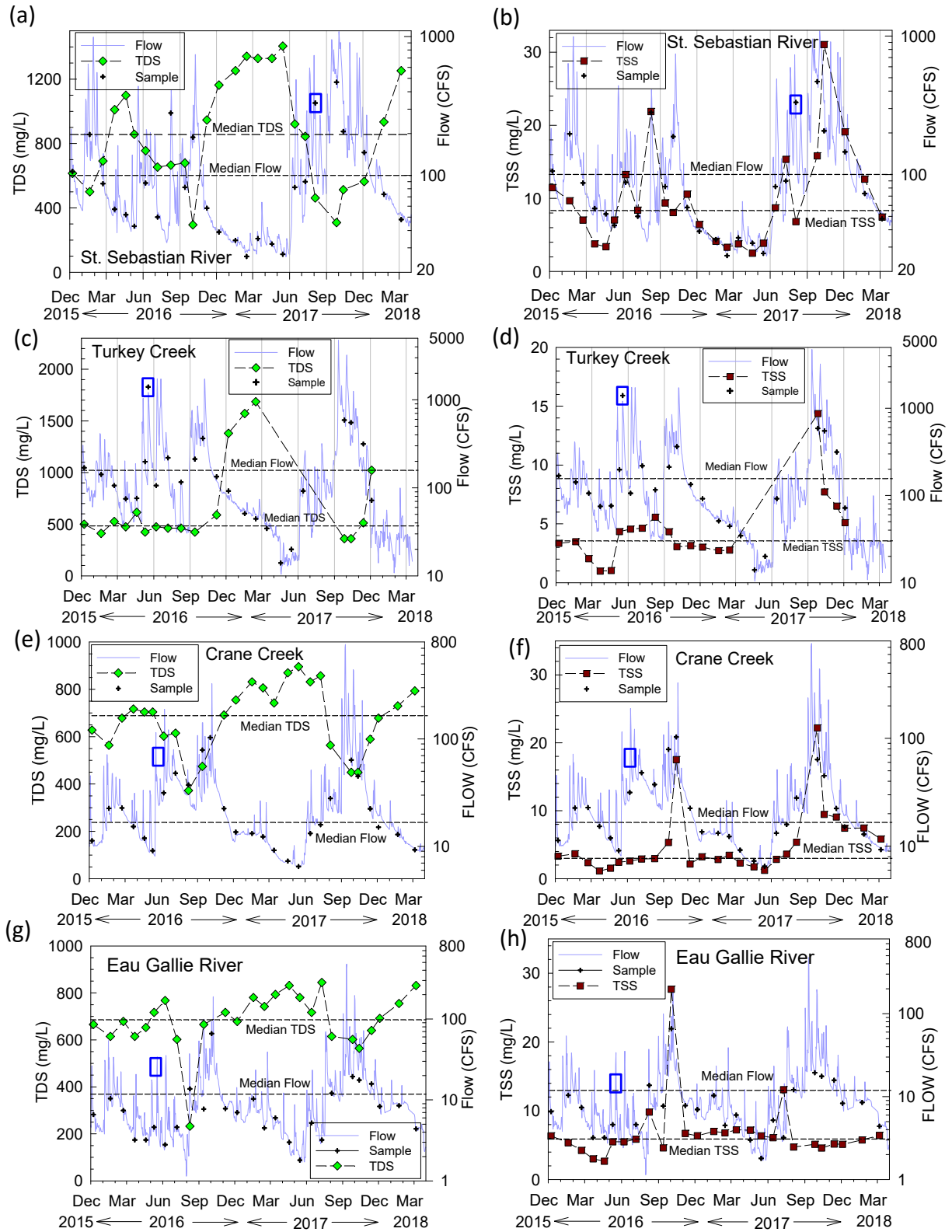


Figure 16. Results from major tributaries for (a, c, e, g) water flow and total dissolved solids (TDS) and (b, d, f, h) water flow and total suspended solids (TSS). Blue rectangles identify one rain event studied. Median annual daily flow from Table 5. Dashed lines connecting markers added to help show changes over time.

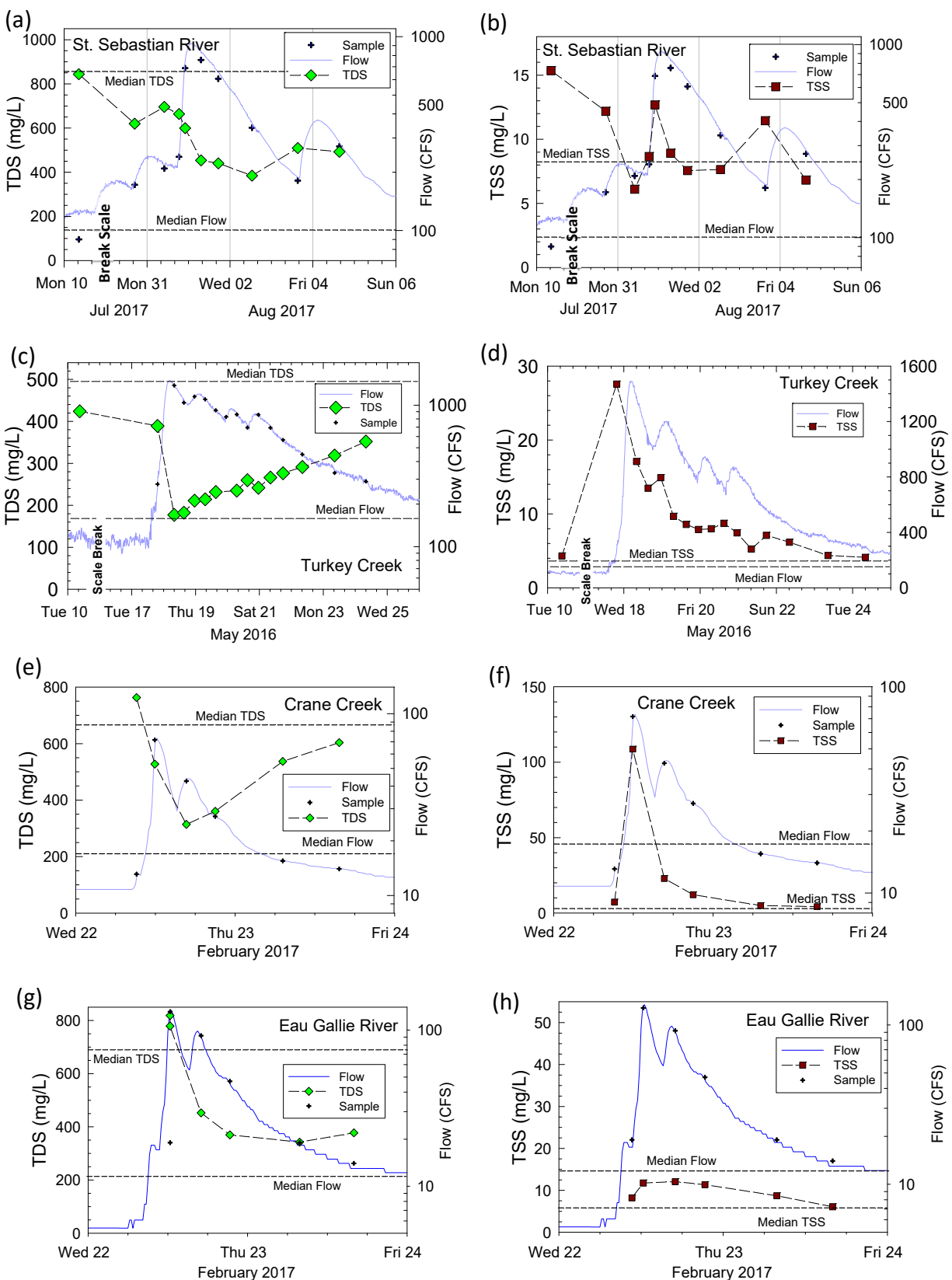


Figure 17. Results from major tributaries for selected rain events for (a, c, e, g) water flow and total dissolved solids (TDS) and (b, d, f, h) water flow and total suspended solids (TSS). Dashed lines connecting markers added to help show changes over time.

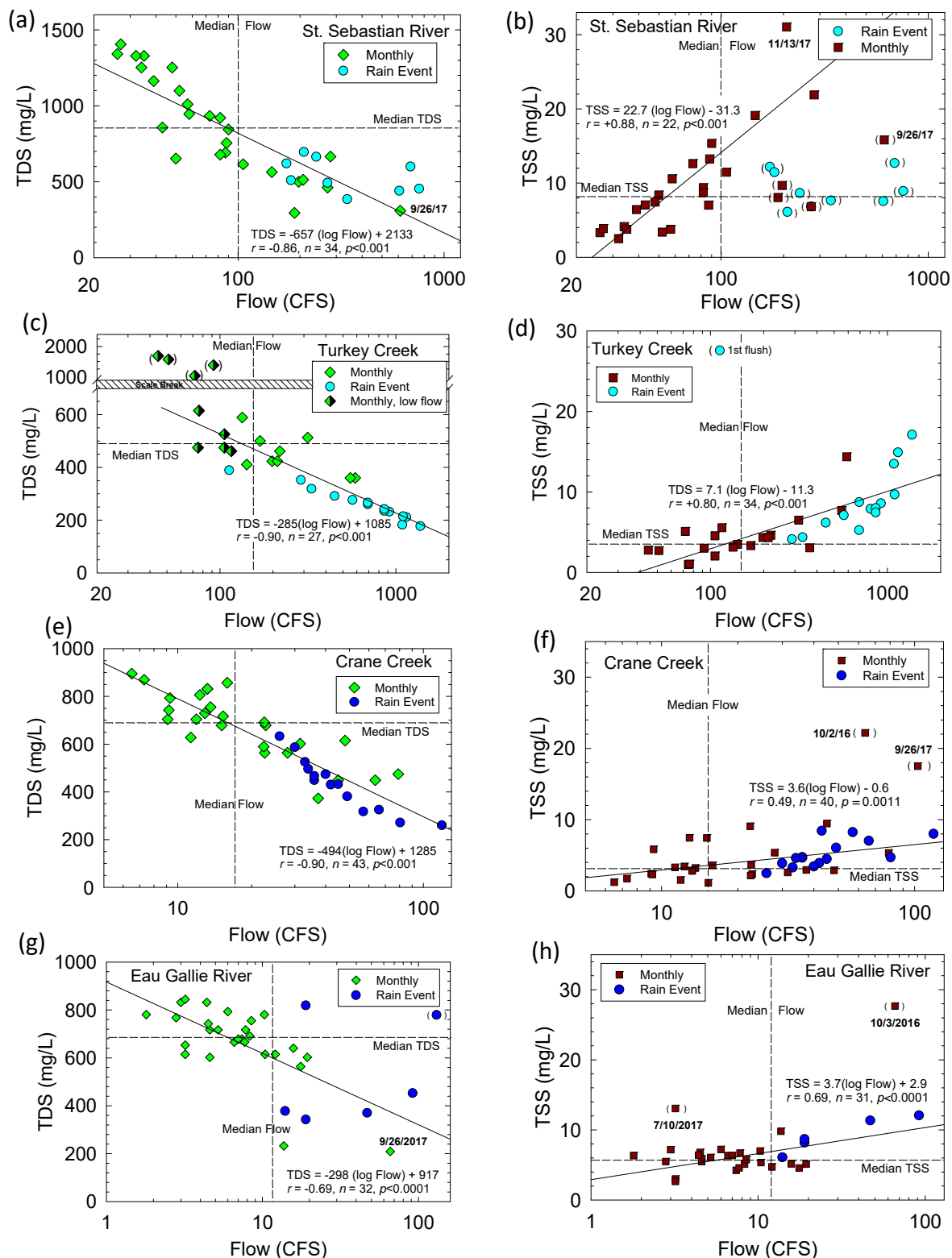


Figure 18. Results from major tributaries for (a, c, e, g) total dissolved solids (TDS) versus water flow and (b, d, f, h) total suspended solids (TSS) versus water flow for monthly and rain event data. Equations and lines from linear regression, with correlation coefficient (r), number of samples (n) and p statistic. Sampling dates added for noteworthy values; data not used in regressions identified by () on the figures.

Mean concentrations of TSS during monthly surveys were low (<10 mg/L) in all four tributaries; but, typically increased to 20–30 mg/L during increased flow (Figures 16–18). One sharp increase in TSS from 7 to 109 mg/L was observed in CC as flow increased from ~10 to 80 CFS (Figure 17f). However, only minor increases of ~5 mg/L were found at EG during the same event (Figure 17h). Concentrations of TSS during a rain event at SR in July–August 2017 also showed only minor variations (9.1 ± 2.4 mg/L, Figure 17b).

High TSS values (100s of mg/L) are common in rivers during the onset of a large rain or meltwater events (i.e., the classic “first flush”) because particles at the soil surface are easily mobilized (e.g., Meybeck et al., 2003; Rember and Trefry, 2004; Walling, 2006). Such turbidity events are sustained by abundant fine-grained particles in the catchment basin plus steep changes in elevation along the course of the tributary (e.g., Gibbs, 1967); however, both factors are not relevant for the four IRL tributaries as demonstrated with our TSS data.

Scatter plots showed increased TSS with increased log flow, an opposite and more complex trend than found for TDS (Figure 18b, d, f, h). Some higher TSS values were found during very high flow (e.g., after Hurricanes Matthew and Irma, Figure 18). In contrast, TSS values for SR at water flows >200 CFS during a prolonged rain event in July–August 2017 were near median values and distinctly lower than predicted from the trend for the monthly data (Figure 17b). Such trends are common because inputs decrease after readily erodible soil is flushed away near the beginning of the storm event. Acceptable equations for TSS versus log flow were obtained for SR, TC and EG (Figure 18 b, d, h), after omitting 2–3 outliers. The median value for TSS was used in flux calculations for CC because a weaker r was obtained for TSS versus log (or linear) water flow (Figure 18h).

Concentrations of DOC and DON increased with increasing water flow in the IRL tributaries (Figure 19) as observed in many other rivers globally (e.g., Wiegner et al., 2006; Martin and Harrison, 2011). This trend is sustained by enhanced release of soil OM during flushing of the upper soil horizon. The highest monthly values for DOC and DON in each tributary occurred on September 26, 2017, following Hurricane Irma (Figure 19). The lowest concentrations of DOC and DON were found during the low-flow period of December 2016–May 2017 (Figure 19).

Concentrations of DOC and DON increased above median values during rain events at SR and TC, reaching maxima within 1–2 days after peak flow (Figure 20a–d). Peak values for DOC during rain events at SR (~30 mg/L) were high by global standards for tropical rivers (5.4 mg/L, Huang et al., 2012) and sub-tropical rivers (21 ± 5 mg/L, Moyer et al., 2015). In contrast with SR and TC, trends for DOC and DON during rain events at CC and EG showed decreased values to less than the median with minor changes during the event, and then subsequent increases to median values after the event (Figure 20 e–h). The two small drainage basins were in largely urban areas with

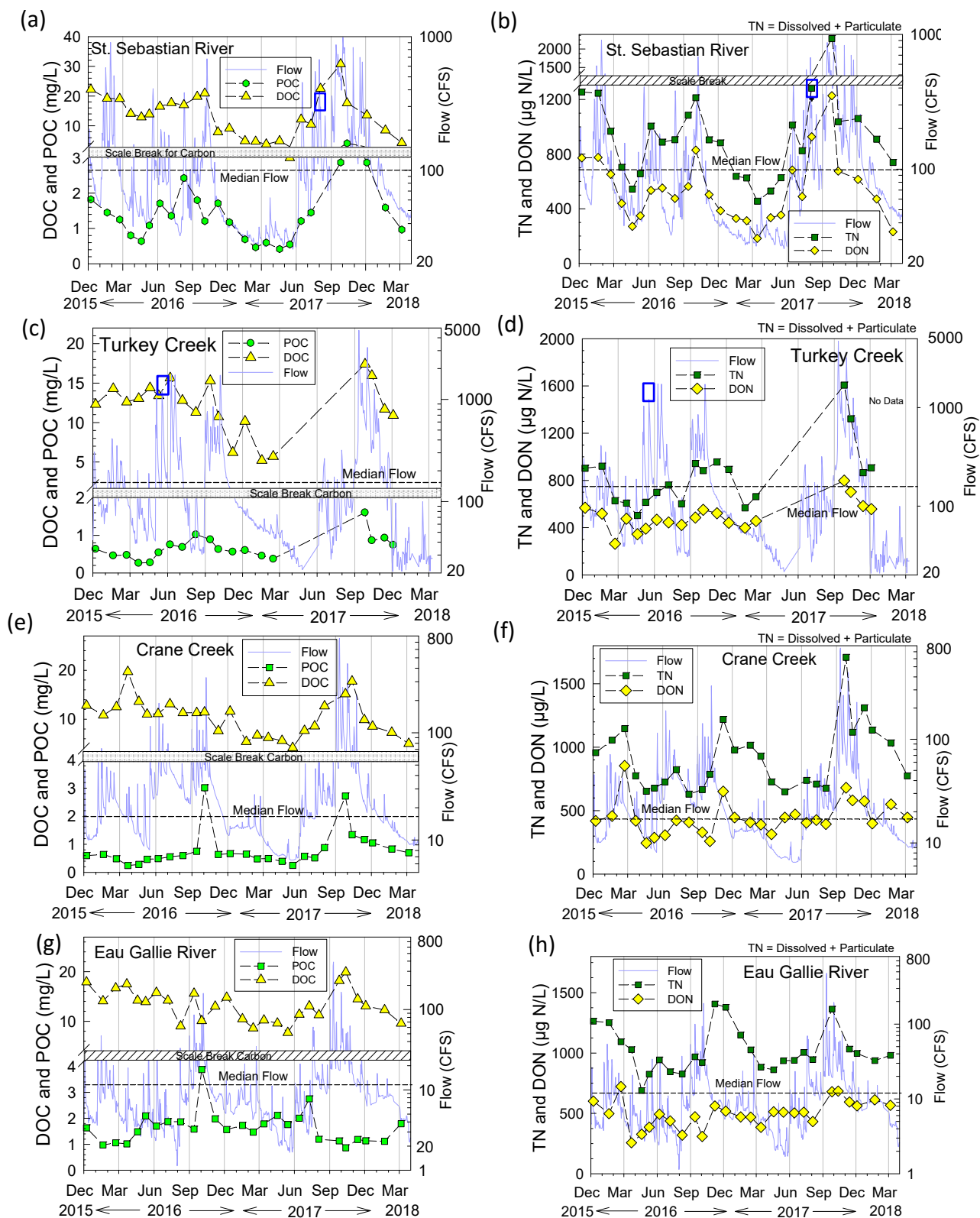


Figure 19. Results from major tributaries for (a, c, e, g) water flow, particulate organic carbon (POC) and dissolved organic carbon (DOC) and (b, d, f, h) water flow, total nitrogen (TN) and dissolved organic nitrogen (DON) for monthly samples. Dashed lines connecting markers added to help show changes over time.

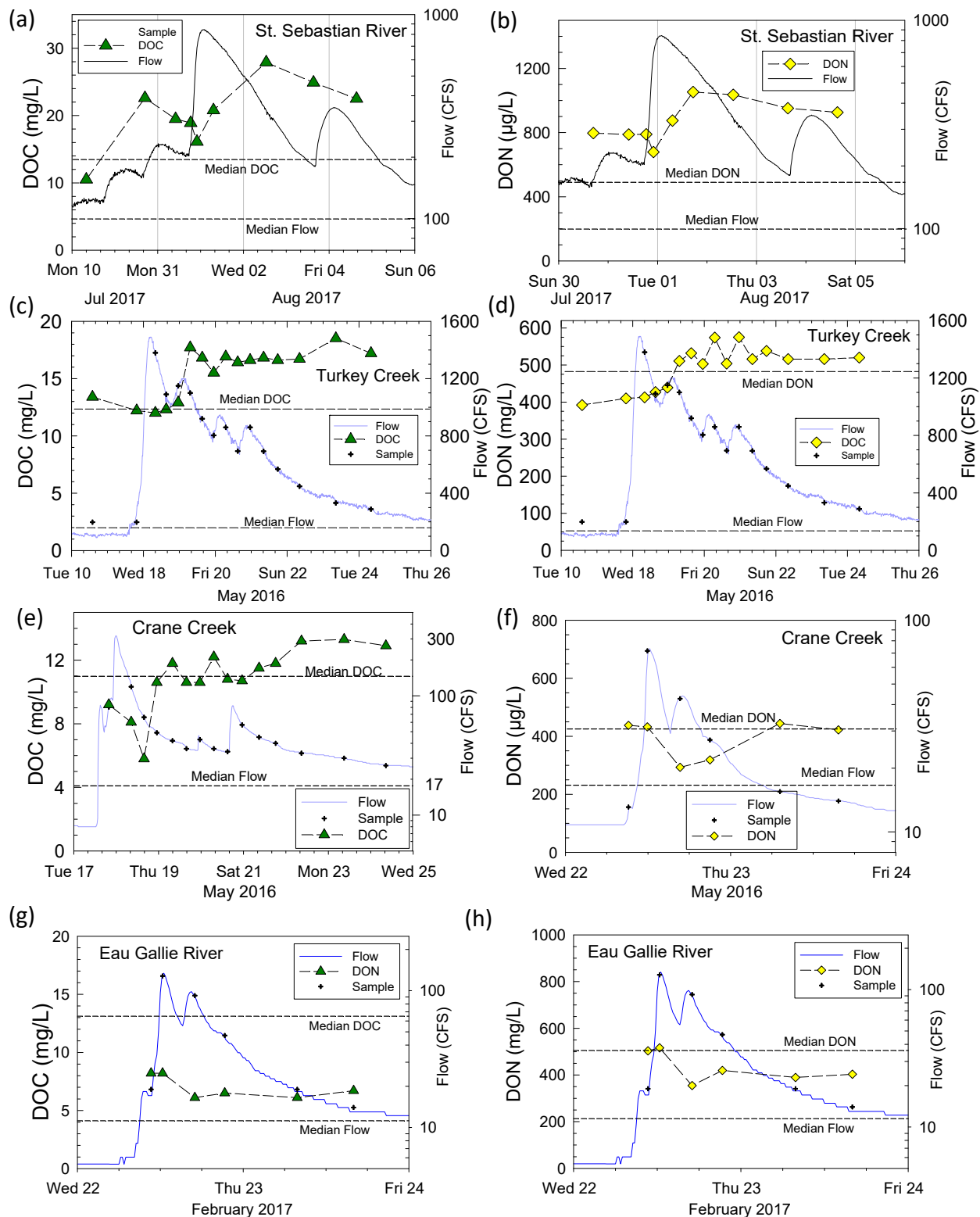


Figure 20. Results from selected rain events for (a, c, e, g) water flow and dissolved organic carbon (DOC) and (b, d, f, h) water flow and dissolved organic nitrogen (DON). Dashed lines connecting markers added to help show changes over time.

extensive impervious surfaces that showed little evidence of significant mobilization and flushing of DOC and DON from sod or soil during rain events, even hurricanes. This trend is very different from results for larger tributaries in this study (SR and TC) that have greater fractions of non-urban land usage.

Concentrations of both DOC and DON at SR and TC showed strong correlations with flow (Figure 21). Therefore, acceptable equations were fit to data for DOC and DON versus log flow for SR and TC; an equation for DOC, but not DON, versus log flow was acceptable for CC (Figure 21a–d; Table 12). Much weaker correlations were found for DOC (EG) and DON (CC and EG) versus log flow in the two smaller tributaries that had 70–76% urban land use. The urban character of the drainage basins (CC and EG) restricted releases of DOC and DON at increased flow to concentrations less than those of undeveloped or agricultural areas. Therefore, median values were used to calculate fluxes of DOC for EG and DON for CC and EG (Table 12).

In the IRL tributaries, when concentrations of DON increased with increased flow due to enhanced release from soils, the other forms of N (e.g., N+N) decreased (Figure 22). Therefore, the % of TN that was DON increased. Increases in %DON are less common in rivers with a source of fine-grained sediment because PON values increase significantly with flow (e.g., Seitzinger et al., 2010). The percent of N+N in IRL tributaries, especially SR (Figure 20c), decreased by factors of 2 to >4 with increased flow. The observed shift was significant because the tributaries were delivering less biologically active DIN during rain events. Therefore, unless water flow increases by >5 to 10 times over median flow during the rain event, the net transport of DIN actually decreased in the IRL tributaries.

Concentrations of TN generally tracked DON because DON accounted for more than half of the TN (Figure 19b, d, f, h). However, an acceptable equation for TN versus log flow was only obtained for SR (Table 12). Large shifts in the % of TN that was DON were found because concentrations of N+N, NH_4^+ and PON varied, especially at high flow, with an opposite trend relative to DON (Figure 22).

Indeed, concentrations of N+N and NH_4^+ in each tributary followed more complex patterns versus water flow than described for TDS, DOC or DON. (Figure 23). During June–September, when the fertilizer ban was in effect, lower concentrations of N+N were observed at CC, EG and to a lesser extent at TC (Figure 23c, e, g). Highest concentrations of N+N, and in some cases NH_4^+ , were found from October to February during each year, a period of lower flow (Figure 23a, c, e, f). Juxtaposed to the June–September period of higher flow and lower concentrations of N+N and NH_4^+ , higher values were observed during the lower flow period of October to March (Figure 23a, c, e, g). This observation was especially distinct for N+N and NH_4^+ during September 2016–March 2017 (Figure 23). Thus, there was a possibility that new applications of fertilizer could be rapidly washed into the tributaries along with nutrients from septic systems and reclaimed water.

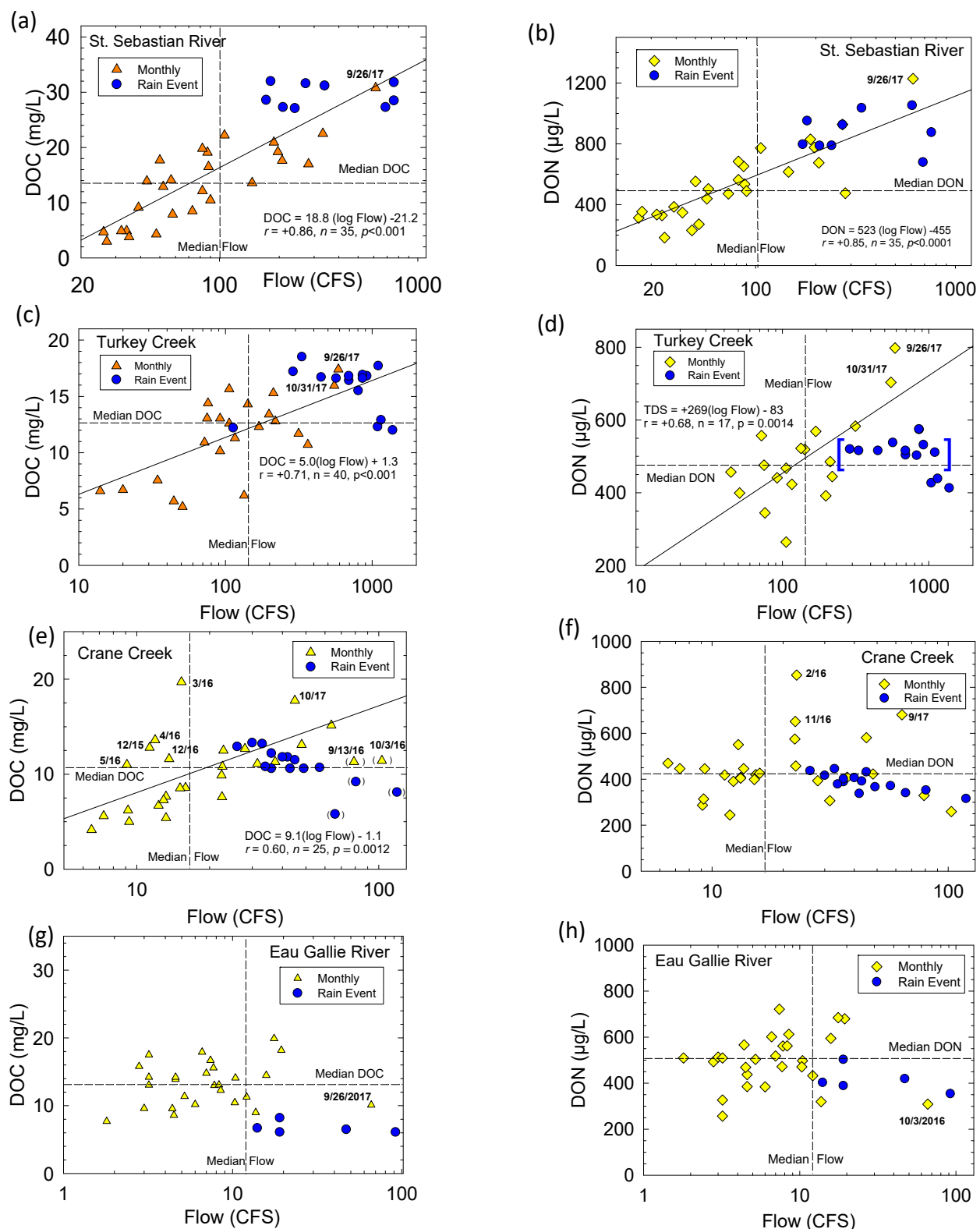


Figure 21. Results from major tributaries for (a, c, e, g) dissolved organic carbon (DOC) versus water flow and (b, d, f, h) dissolved organic nitrogen (DON) versus water flow for monthly and rain event data. Equations and lines from linear regression, with correlation coefficient (r), number of samples (n) and p statistic. Sampling dates added for noteworthy values; data not used in regressions identified by () or [] on figures.

Table 12. Summary of results for acceptability of equations for thirteen chemical parameters versus log water flow. All correlation coefficients (r) were significant at $p < 0.05$. In cases where an equation was not acceptable ($r < 0.6$, $p > 0.05$) the median value was used to calculate fluxes. Additional detail and full equations listed in Appendix B.

Parameter	SR	TC	CC	EG
TDS	$r = -0.86$	$r = -0.90$	$r = -0.90$	$r = -0.69$
TSS	$r = +0.88$ excluded large rain events	$r = +0.80$ excluded 1 st flush	median	$r = +0.69$ exclude
DOC	$r = +0.86$	$r = +0.71$	$r = +0.60$	median
POC	$r = +0.84$	median	median	median
TN	$r = +0.88$	median	median	median
N+N	20–100CFS, $r = +0.71$ >100CFS, $r = -0.98$	≥ 200 CFS, $r = -0.83$ <200 CFS, $r = +0.58$	median	+0.72
NH ₄ ⁺	median	median	median	median
DON	$r = +0.85$	$r = +0.68$	median	median
PON	median	median	+0.63	median
TP	$r = +0.72$	median	median	median
PO ₄ ³⁻	$r = +0.93$ excludes 3 hurricane samples	median	median	median
DOP	median	median	median	median
PP	median	median	median	median
Equations/Medians	9/4	5/8	3/10	3/10

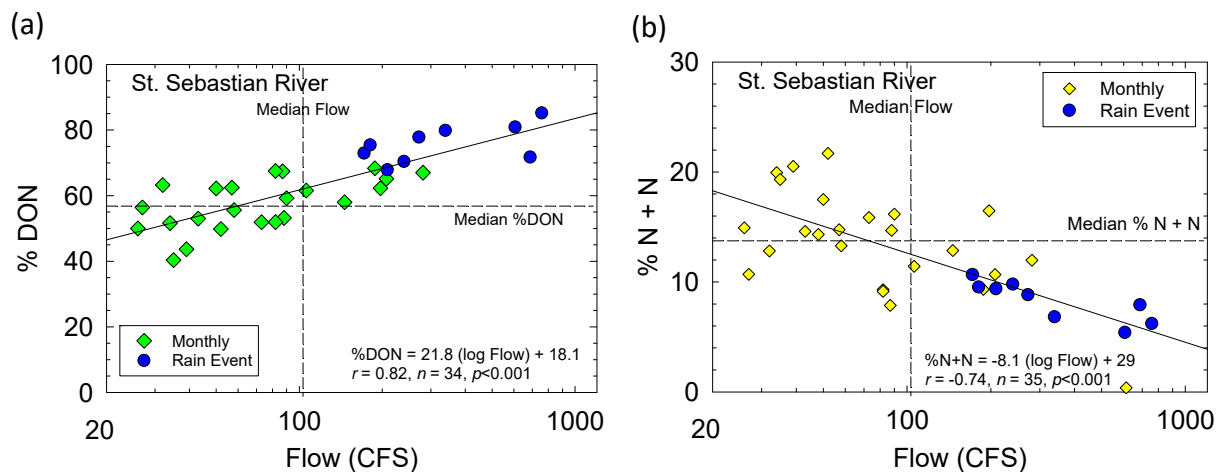


Figure 22. Results for (a) % dissolved organic nitrogen (DON as a % of TN) versus water flow and (b) % nitrate + nitrite (N+N as a % of TN) versus water flow for St. Sebastian River. Equations and lines from linear regression, with correlation coefficient (r), number of samples (n) and p statistic.

Some lower values at high flow may be due to dilution of N+N and NH_4^+ during rain events. Higher concentrations during low (e.g., <10 CFS) or moderate (10–30 CFS) water flow may be related to human activities such as application of fertilizer. These trends complicated calculation of fluxes. In most cases, median values were used for N+N and NH_4^+ because we had insufficient data (26 monthly plus 30–40 rain event samples relative to 731 days) to adequately track complex changes in concentration of these two forms of N with flow. Continuous nutrient data are needed to more reliably track fluxes.

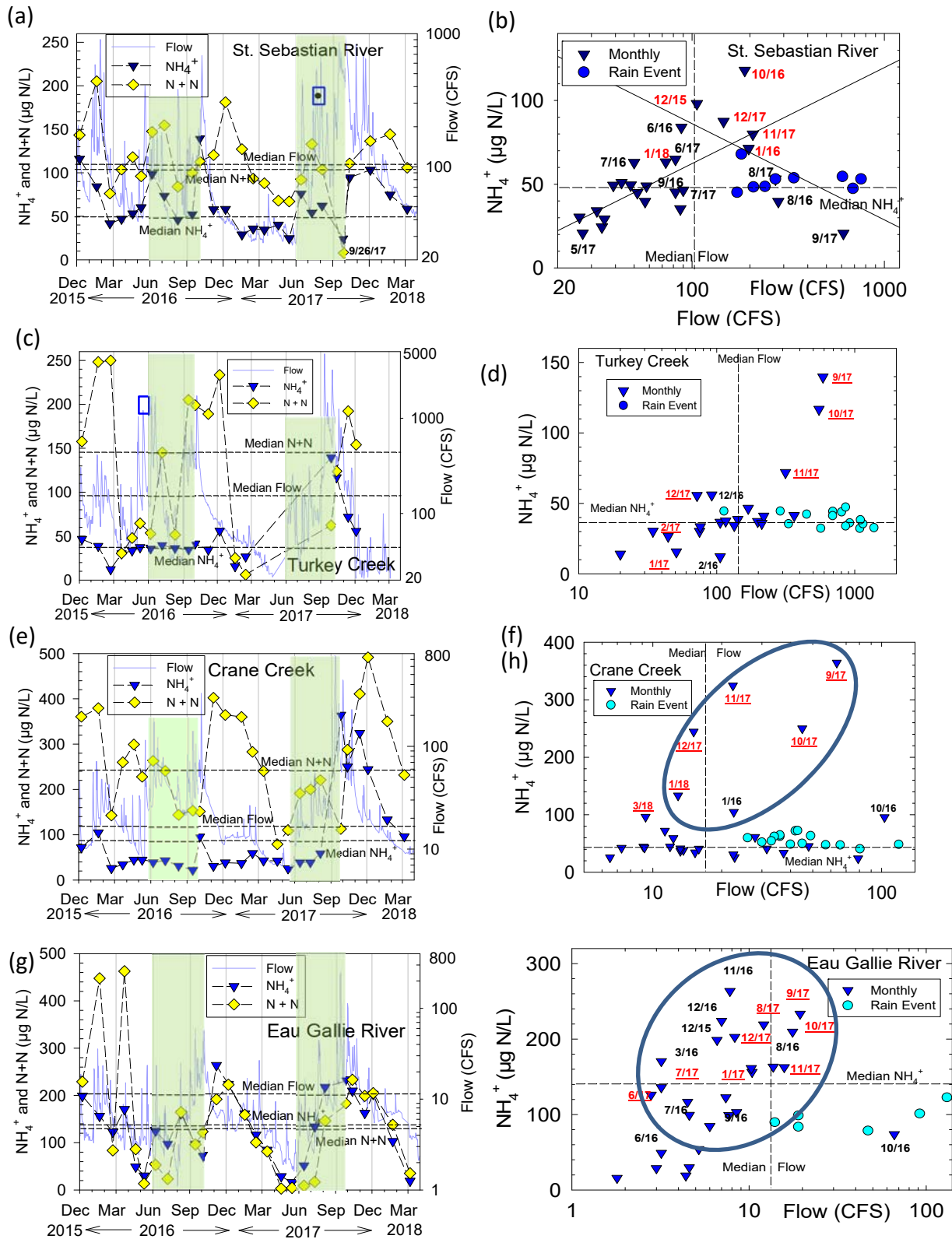


Figure 23. Results for major tributaries for (a, c, e, g) water flow, ammonium (NH_4^+) and nitrite + nitrate (N+N) for monthly samples and (b, d, f, h) NH_4^+ versus water flow. Dashed lines connecting markers added to help show trends. Green shading on a, c, e and g shows periods during fertilizer ban in Brevard County (June–September). Ovals highlight NH_4^+ enrichment during fall and winter at Crane Creek and Eau Gallie River.

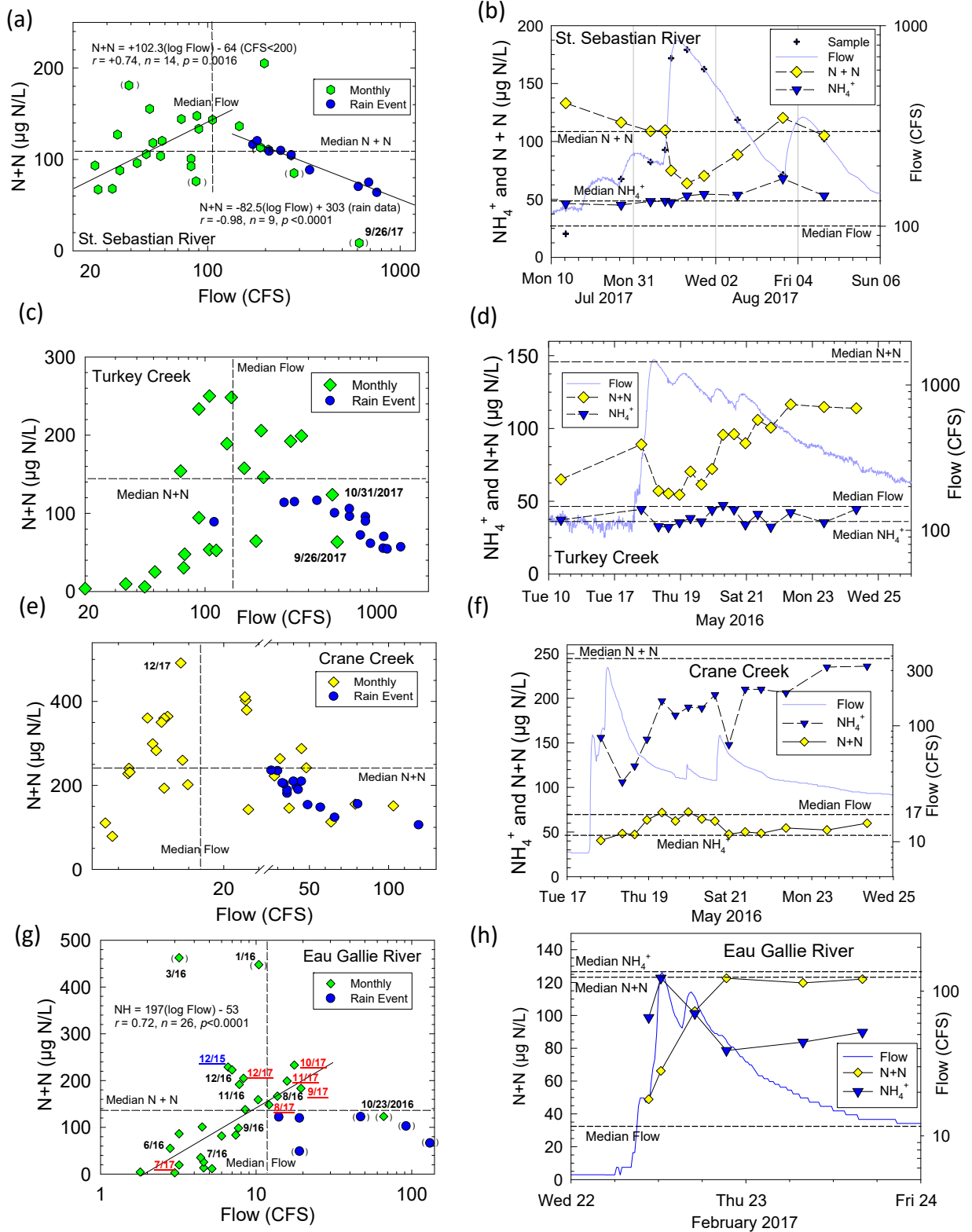


Figure 24. Results for major tributaries for (a, c, e, g) nitrate + nitrite (N+N) versus water flow and (b, d, f, h) ammonium (NH_4^+) and N+N versus water flow during storm events.

Concentrations of TP and PO_4^{3-} followed parallel patterns versus flow with varying differences in concentrations of the two forms of P. This gap on the graphs was greater during some higher flows when concentrations of PP increased, especially at TC and CC during high flow in September and October 2017 (Figure 25a, c, e, g). During a rain event in TC, for example, a >3-fold increase in PO_4^{3-} occurred when flows increased by 8-fold above the median (Figure 26b).

During Hurricanes Matthew (October 2016) and Irma (September 2017) concentrations of PO_4^{3-} at SR increased above 400 and 1000 $\mu\text{g P/L}$, respectively (Figure 25a). This trend was consistent with results for the St. Johns River where high PO_4^{3-} concentrations were explained by fertilizer runoff or mineralization of livestock manure or organic soils (Kroening, 2004). At high flow in SR, including hurricanes, PO_4^{3-} concentrations increased greatly (Figure 25a for September 2017) while concentrations of N+N and NH_4^+ became very low (Figure 23a for September 2017). Therefore, a graph of $\text{DIN}/\text{PO}_4^{3-}$ (in molar units) shows a decrease in the ratio from 8–10 N/P at low flow to <3 N/P at high flow (Figure 27a). The trend for PON/PP (molar units) is similar to a large and significant decrease from 18–20 N/P at low flow to 1–6 N/P at high flow (Figure 27b). These trends support release of inorganic P during high water flow, likely from desorption or dissolution of P from solids. Collectively, the data also do not show trends for PO_4^{3-} that could be linked to concentrations during the fertilizer ban as was the case for N+N and NH_4^+ . Phosphate-free fertilizers are generally used in catchment basins of the study area.

Except for SR, concentrations of phosphate were not significantly correlated with log flow (Figure 25b, d, f, h). Concentrations of phosphate during the low-flow period were about half of the monthly average value and support the importance of surface runoff versus groundwater flow to phosphate input to the SR tributary (Figure 25a). The trend of lower or no change in PO_4^{3-} concentrations at low flow also was observed at TC and CC (Figure 25d, f). In contrast, some higher PO_4^{3-} concentrations were observed at low flow in EG (Figure 25h). However, high concentrations during the fertilizer ban at EG occurred during a May–July period of low flow (Figure 25g, h). Phosphate clearly follows different patterns with flow that support likely inputs of inorganic P from soils (Figure 27).

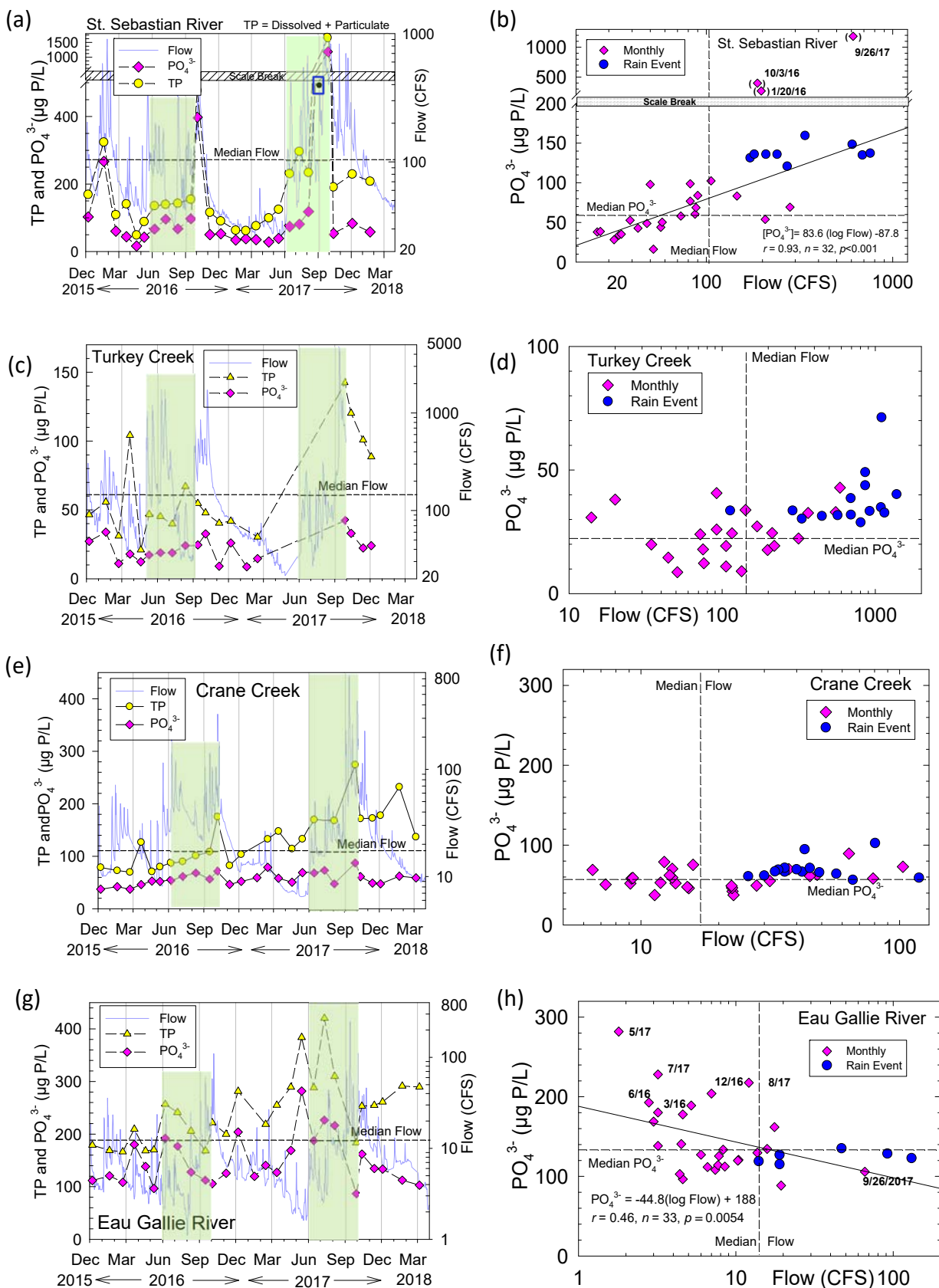


Figure 25. Results for major tributaries for (a, c, e, g) water flow, total phosphorus (TP) and phosphate (PO_4^{3-}) and (b, d, f, h) PO_4^{3-} versus water flow. Dashed lines connecting markers added to help show changes over time.

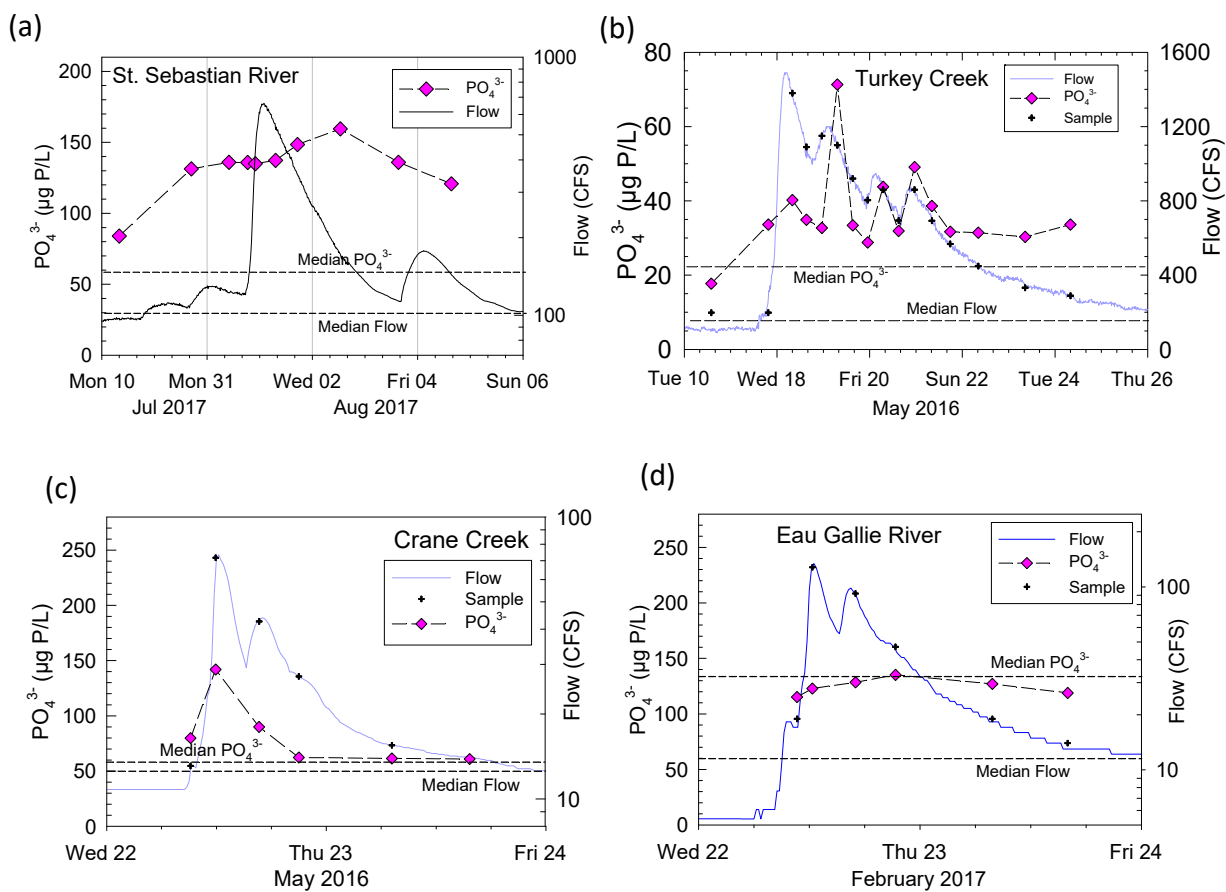


Figure 26. Results from tributaries for water flow and phosphate (PO_4^{3-}) during selected rain events. Dashed lines connecting markers added to help show changes over time.

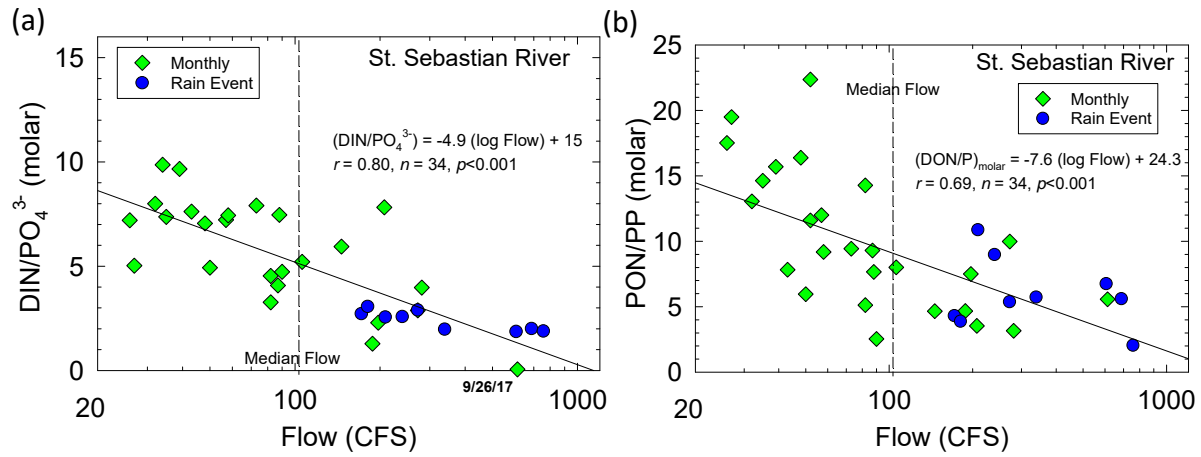


Figure 27. Results for (a) ratio of dissolved inorganic nitrogen (DIN) to phosphate versus flow at St. Sebastian River South Prong (SR), and (b) ratio of particulate organic nitrogen (PON) to particulate phosphorus (PP) versus flow at SR.

3.4. Tributary Fluxes of Dissolved and Particulate Chemicals to the Indian River Lagoon

Fluxes of TDS, TSS, DOC, POC and the chemical forms of N (NH_4^+ , $\text{N}+\text{N}$, DON, PON) and P (PO_4^{3-} , DOP, PP) to the IRL from each tributary were determined using daily water flow with either (i) concentrations from specific equations obtained via regression analysis (e.g., Equation 3) or (ii) median values (e.g., Equation. 4). Equations were used when the correlation coefficient (r) was ≥ 0.6 with $p < 0.05$. The equations used are listed in Appendix B. Fluxes were calculated for 2016 (366 days) and 2017 (365 days) using site-specific chemical data from this study and daily water flows from the USGS (USGS, 2019) for each tributary.

As an example, fluxes of TN for 2017 from SR were calculated using the same daily flows with both Equations 3 and 4.

$$M_{\text{TN,SR,eq}} = \sum_{i=1}^{365} [(595 * \log \text{Flow}(i) - 234) * \text{Flow}(i)] = 184 \text{ TN/y} \quad (\text{Equation 3})$$

where:

$M_{\text{TN,SR,eq}}$ = total mass of TN for SR per year (365 days) = tons/y using linear regression equation from Figure 28 where $r = +0.86$ and $p < 0.001$.

$(595 * \log \text{Flow} - 234)$ = equation for concentration versus flow and concentration [TN = $595 (\log \text{Flow}) - 234$] from Figure 28 on each day (i).

When no significant correlation between a chemical and average daily flow was found, and the data grouped around the median, Equation 4 was used. However, Equation 3 was acceptable for

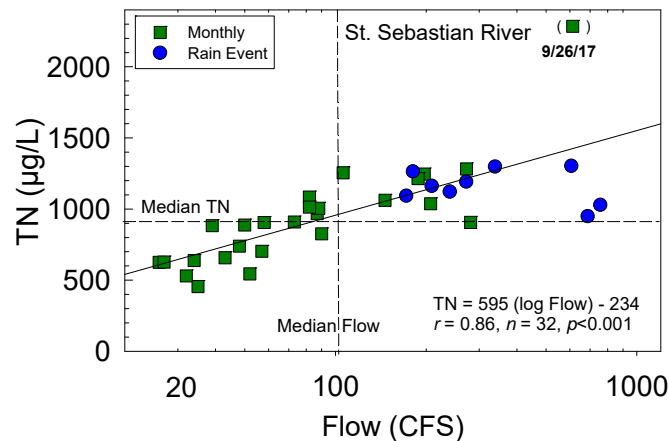


Figure 28. Total nitrogen (TN) for St. Sebastian River (SR) versus water flow. Equation and line from linear regression, with correlation coefficient (r), number of samples (n) and p statistic. Sampling dates added for noteworthy values; data not used in regression identified by ().

TN in SR for 2017 (Figure 28). To compare the two approaches, Equation 4 with a median value for TN in SR of 906 mg N/L was used here.

$$M_{\text{TN,SR,median}} = \sum_{i=1}^{365} [(906 \text{ mg N/L} * \text{Flow} (i))] = 137 \text{ T N/y} \quad (\text{Equation 4})$$

This example for TN at SR shows that the flux via the equation method was 34% higher than when the median approach was used. This difference seems reasonable for 2017 because there were a larger number of days with higher flow that weighted the equation format (Eq. 4) with a larger number of higher values because concentrations of TN increased with flow. When an acceptable equation was available, use of that equation was more likely to provide a better value for the flux of a given chemical.

Table 13. Fluxes of total nitrogen, dissolved organic nitrogen (DON), nitrate + nitrite (N+N) ammonium (NH₄⁺) and particulate organic nitrogen (PON) plus the sum of the fluxes for each parameter in all four tributaries.

Parameter	Year	Water Flow (CFS)				
		SR	TC	CC	EG	TOTAL ^b
Water Flow ^a	2016	111	211	32	11	365
	2017	165	210	35	17	427
Chemical	Year	Mass Transport (metric tons N/y)				
Total Nitrogen	2016	108	164	24	10	306
	2017	184	162	27	14	387
DON	2016	70	90	11.9	5.0	177
	2017	125	92	13.2	7.3	234
N+N	2016	10.7	20.7	8.1	2.0	41.5
	2017	15.9	14.0	9.1	3.8	42.8
NH ₄ ⁺	2016	4.9	7.0	1.2	1.3	14.4
	2017	7.2	6.9	1.4	1.9	17.4
PON	2016	19.0	24.4	5.0	2.9	51.3
	2017	28.2	24.2	6.9	4.3	63.6
Σ (DON + (N+N) + NH ₄ ⁺ + PON) ^b	2016	105	142	26.2	11.2	284
	2017	176	137	30.6	17.3	358

^aAverage daily flow (USGS, 2019) CFS = ft³/second where 35.34 CFS = 1 m³/sec.

^bTotals shown with 3-significant figures.

Fluxes of TN and the various forms of N, show large and expected variations among tributaries and, in some cases, between years (Table 13). The sums of the four separate forms of N agree with the flux calculated for TN within 4% (SR) to ~18% (EG). Because of the complex relationships for N+N and NH₄⁺ versus water flow, we tried substituting available concentrations for one day per month, plus all rain event data, and interpolating between resulting data points for 2016. The results for N+N in Crane Creek yielded the following: June 1–Sep 30 (2.8 tons N), Oct 1–Dec 31 (1.4 tons N), Jan 1–Mar 31 (1.6 tons N) and Apr 1–May 31 (0.7 tons N) for a total of 6.6 tons N/y relative to 8.1 tons per year using the median. Despite limitations in available concentration data, the results showed that ~40% of the annual flux of N+N (2.8/6.6) was carried during June 1 to September 30 because the flow was higher during the summer when concentrations of N+N were lower due to the fertilizer ban. Furthermore, even though higher concentrations of N+N were obtained after October 1, the end of the fertilizer ban, a lower flux was calculated because water flows were generally lower from October through March (Figure 23e).

Fluxes for TP and the various forms of P also showed large variations among tributaries and, in some cases, between years (Table 14). The sums of the three separate forms of P agreed well for

Table 14. Fluxes of total phosphorus, phosphate (PO₄³⁻), dissolved organic phosphorus (DOP) and particulate phosphorus (PP) plus the sum of the fluxes for each parameter in all four tributaries.

Parameter	Year	Water Flow (CFS)				
		SR	TC	CC	EG	TOTAL ^b
Water Flow ^a	2016	111	211	32	11	365
	2017	165	210	35	17	427
Chemical	Year	Mass Transport (metric tons P/y)				
Total Phosphorous	2016	19	11	3.4	2.5	36
	2017	57	11	3.8	3.7	76
PO ₄ ³⁻	2016	19	5.7	1.6	1.4	27.7
	2017	55	5.6	1.8	2.0	64.4
DOP	2016	3.4	2.6	0.8	0.3	7.1
	2017	4.6	2.6	0.9	0.4	8.5
PP	2016	5.1	4.7	1.0	0.7	11.5
	2017	7.5	4.7	1.1	1.1	14.4
Σ (PO ₄ ³⁻) + (DOP) +(PP)	2016	27	13	3.4	2.4	45.8
	2017	67	13	3.8	3.5	87.3

^aAverage daily flow (USGS, 2019), CFS = ft³/second where 35.34 CFS = 1 m³/sec).

^bTotals shown with 3-significant figures.

CC and EG (<6%) and less well for TC (~18%) or SR (30%). Although concentrations of PO₄³⁻ and PP were significantly greater in EG (Table 10, page 24), the total fluxes for these two forms of P were lower in EG relative to CC due to 2- to 3-fold higher flow in CC. Water flow matters.

Fluxes for TDS, TSS and DOC (Table 15) are likely more accurate than for the other chemical parameters because of the strong correlation coefficients for concentrations versus water flow (Table 12). Fluxes for TSS, DOC, POC and TDS mirror the discussion of differences in concentrations among tributaries very well (Table 15). To help put the TSS into perspective with muck deposits, an average of 1500 tons of dry suspended sediment is carried by TC each year (Table 15). The deposition sites for this material range from just downstream of Port Malabar Boulevard to well out in the IRL. When hydrated, 1500 tons (10⁶ g/ton) of dry suspended material would yield ~8,000 yd³ of wet muck with a porosity of 0.9 $\{[(1500 \times 10^6 \text{ g/y}/2.5 \text{ g/cm}^3)/0.1] \times [1 \text{ m}^3/10^6 \text{ cm}^3] \times (1.3 \text{ yd}^3/\text{m}^3)\}$. This volume of wet muck equates to ~10% of the muck dredged from the lowermost area of TC in 2016 (Fox and Trefry, 2018). However, the suspended particles carried by TC contained 2- to 3-fold more OM than sediment muck deposits (see page 26) and we really do not know how much or where suspended matter is deposited within TC or the IRL. Therefore, any estimate of time to reintroduce muck to lower TC is difficult; it is clearly on the order of decades.

Table 15. Fluxes of total suspended solids (TSS), dissolved organic carbon (DOC), particulate organic carbon (POC) and total dissolved solids (TDS) for each of the four tributaries plus the sum of fluxes for each parameter in all four tributaries.

Parameter	Year	Water Flow (CFS)				
		SR	TC	CC	EG	TOTAL
Water Flow ^a	2016	111	211	32	11	365
	2017	165	210	35	17	427
Chemical	Year	Mass Transport (metric tons/y)				
TSS	2016	810	1270	147	76	2300
	2017	1200	1600	195	128	3120
DOC	2016	2000	2640	312	133	5080
	2017	1600	2850	346	194	4990
POC	2016	230	190	17	16	453
	2017	170	190	19	24	403
TDS	2016	68,000	79,000	14,000	5500	166,000
	2017	73,000	65,000	12,000	6600	157,000

^aAverage daily flow (USGS, 2019) CFS = ft³/second where 35.34 CFS = 1 m³/sec).

^bTotals shown with 3-significant figures.

Fluxes also were divided in two periods, days with flow greater than median flow and days with flow below median flow (Table 16). The results showed that $77 \pm 10\%$ of the water flow was on the $35 \pm 9\%$ of the days when water flow was greater than the median. These results and the data used to obtain them can be used to address a variety of questions related to seasonal fluxes. For example, $>70\%$ of the TN and TP transported by the four tributaries per year was delivered to the IRL during days with above median water flow.

Table 16. Fluxes of chemical forms of nitrogen and phosphorus during water flows at greater and less than median values (TN = total nitrogen, TP = total phosphorus, TSS = total dissolved solids, DOC = dissolved organic carbon, POC = particulate organic carbon, TDS = total dissolved solids).

Parameter	Year	SR	TC	CC	EG
Water Flow ^a (CFS)	2016	111	211	32	11
	2017	165	210	35	17
# Wet Days ^b	2016	123	129	119	110
# Dry Days ^c	2016	242	236	247	256
# Wet Days ^b	2017	156	76	175	127
# Dry Days ^c	2017	210	290	190	239
Chemical	Year	Mass Transport (metric tons/y)			
TN	2016 wet	80	124	18	6.4
	2016 dry	28	40	7	3.5
	2017 wet	167	125	23	11.8
	2017 dry	18	38	5	2.6
TP	2016 wet	14	7.0	2.5	1.4
	2016 dry	5	2.1	0.9	1.1
	2017 wet	54	7.5	2.7	2.8
	2017 dry	3	1.5	1.1	0.9
TSS	2016	810	1270	147	76
	2017	1200	1600	195	128
DOC	2016	2000	2640	312	133
	2017	1600	2850	346	194
POC	2016	230	190	17	16
	2017	170	190	19	24
TDS	2016	68,000	79,000	14,000	5500
	2017	73,000	65,000	12,000	6600

^aAverage daily flow (USGS, 2019) CFS = ft³/second where 35.34 CFS = 1 m³/sec.

^bWet days are days with above median water flow. ^cDry days are days with below median water flow.

Fluxes also were calculated as kg/km² (Table 17). Then, global river fluxes flux were compared with the fluxes for each IRL tributary. All TN and TP values (as kg/km²) for SR were greater than global values, whereas ratios for the other tributaries to global fluxes were close to or <1 (Table 16). Overall, these data suggest that inputs of TN and TP from three of the four IRL tributaries (TC, CC and EG) are on par with the global average. These trends for SR versus TC, CC and EG are consistent with data for flow (m/y) from each drainage basins (Table 6, page 14). The negative impact at TC, CC and EG in the IRL seems to be more a factor of high nutrient transport during a limited number of days, combined with restricted mixing of these nutrients due to confinement of the barrier island along most of the IRL in Brevard County.

Table 17. Fluxes of total nitrogen (TN) and total phosphorus (TP) to the Indian River Lagoon during 2016 and 2017 from major tributaries as a function of basin area plus comparison with average global rivers with fluxes as kg/km²/y. (SR = St. Sebastian River, South Prong; TC = Turkey Creek; CC = Crane Creek; EG = Eau Gallie River.

Parameter	Year	SR	TC	CC	EG
Drainage Area (km ²)	-	91	254	48	24
Flow (CFS)	2016	111	211	32	11
	2017	165	210	35	17
Flow (m ³ /sec)	2016	3.14	5.97	0.91	0.31
	2017	4.67	5.94	0.99	0.48
TN (metric tons/y)	2016	108	164	24.4	9.9
	2017	184	162	27.1	14.4
TN (kg/km ² /y)	2016	1190	646	508	413
	2017	2020	638	565	600
TN _{Tribs} /TN _{Global} (kg/km ² /y)	2016	2.5	1.3	1.1	0.9
	2017	2.3	1.3	1.2	1.2
TP (metric tons/y)	2016	19	9.1	3.4	3.7
	2017	57	9.0	3.8	1.4
TP (kg/km ² /y)	2016	209	36	71	154
	2017	626	35	79	58
TP _{Tribs} /TP _{Global} (kg/km ² /y)	2016	2.2	0.4	0.7	1.6
	2017	6.5	0.4	0.8	0.6

3.5. Turkey Creek: Then (1988–89) and Now (2016–2017)

Enroute to the IRL, water flow from the 254-km² watershed of Turkey Creek (TC) passes through >300 km of canals and a 2017 population of ~112,000 in the sprawling city of Palm Bay (WPU, 2019). The present population of Palm Bay has grown by ~80% since the late 1980s (pop. ~62,000) and 40-fold since 1960 (pop. 2,808). Such extensive human development in the upland basin of TC has increased the likelihood that concentrations, forms and fluxes of nutrients have changed over time. Our present study, along with research from 1988–89 (Trefry et al., 1989, Iricanin, 1990; Dierberg, 1991), provided an opportunity to test the following hypothesis:

H₂: Concentrations and fluxes of the various chemical forms of N (NH₄⁺, N+N, DON, PON) and P (PO₄³⁻, DOP, PP) from Turkey Creek to the IRL have increased from 1988–89 to 2016–2017.

The mean TDS concentration of 690 ± 130 mg/L in TC during 1988–89 was not significantly different from the mean of 680 ± 430 mg/L in 2016–2017 (Table 18). All samples were collected from the same location, the Port Malabar Boulevard Bridge (Figure 4, page 5). The larger standard deviation for TDS in 2016–2017 was likely due to six months of very low flow and a maximum TDS of 1690 mg/L relative to no prolonged dry period and peak values of ~1100 mg/L in 1988–89 (Trefry et al., 1989). These results suggest that a similar annual mix of groundwater and runoff has likely persisted in TC over a span of decades.

The average TSS in TC of 4.4 ± 4.0 mg/L for March 1988 to March 1989 was not significantly different from the value of 4.3 ± 3.0 mg/L for monthly samples during 2016–17 (Table 18). A maximum TSS of 23 mg/L during non-storm periods in 1988–89 was ~60% greater than the maximum of 14.4 mg/L obtained in 2016–17. Values for water flow and TSS during rain events in May 2016 and January 1988 showed a classic shape with maximum TSS at the start of each event and values that decreased toward background after peak rainfall (Figure 29). Despite similar trends and higher flow during some 2016-17 rain events, maximum TSS values were 4-fold greater at 107 mg/L during a rain event in 1988–89 (Figure 29 and Iricanin, 1990). Such differences in TSS values during rain events are likely due to (i) runoff from extreme clearing of >2.5 km² of land in the western basin by General Development, Inc., during the late 1980s and (ii) regular openings of the upstream control structure in TC at the bottom during the 1980s to help flush sediment out of the C-1 canal. Neither of these factors is applicable today. Nonetheless, TSS concentrations during rain events in 1988–89 were greater than in 2016–17, whereas non-storm values for TSS were unchanged.

The mean concentration of DOC at TC was ~20% higher in 2016–17 than in 1988–89; however, the means were not significantly different (Table 18). In contrast, the mean DON value was about

Table 18. Concentrations of dissolved and particulate forms of nitrogen (N), phosphorus (P) and other chemicals in Turkey Creek (TC) at Port Malabar Boulevard during 1988–89 and 2016–2017. Significantly higher values are listed in bold font and underlined; corresponding *p* values are shaded.

Parameter	1988-89 ^a (n = 12)	2016-17 ^b (n = 19)	<i>p</i> value ^c (t-test)
Total Dissolved Solids (TDS) (mg/L)	690 ± 130 ^d	680 ± 430	0.94
Total Suspended Solids (TSS) (mg/L)	4.4 ± 4.0 ^d	4.3 ± 3.0	0.94
Dissolved Organic Carbon (DOC as mg C/L)	10.1 ± 3.9	12.1 ± 3.4	0.13
Particulate Organic Carbon (POC as mg C/L)	0.38 ± 0.23 ^e	<u>0.67 ± 0.13</u>	0.0001
Total N (TN as µg N/L)	750 ± 180	834 ± 270	0.35
Dissolved Organic N (DON as µg N/L)	<u>660 ± 150</u>	495 ± 122	0.002
Nitrate + Nitrite (NO ₃ ⁻ + NO ₂ ⁻ as µg N/L)	26 ± 16	<u>129 ± 82</u>	0.0001
DOC/DON	15 ± 6	<u>26 ± 9</u>	0.0008
Particulate Organic N (PON as µg N/L)	40 ± 30	<u>163 ± 131</u>	0.002
Ammonium (NH ₄ ⁺ as µg N/L)	65 ± 67	48 ± 32	0.34
Total P (TP as µg P/L)	35 ± 16	<u>63 ± 34</u>	0.010
Phosphate (PO ₄ ³⁻ as µg P/L)	20 ± 11	22 ± 9	0.58
Dissolved Organic Phosphate (DOP as µg P/L)	(5 ± 5) ^f	14 ± 23	0.18
Particulate P (PP as µg P/L)	13 ± 10	<u>25 ± 14</u>	0.012
Particulate Si (µg Si/L)	500 ± 330	380 ± 200	0.22
Particulate Al (µg Al/L)	200 ± 220	120 ± 70	0.15
Particulate Fe (µg Fe/L)	460 ± 300	490 ± 340	0.80

^aDierberg (1991) unless otherwise noted.

^bThis study.

^ct-test, two-tailed, equal variance; mean values are not statistically different if *p* ≥ 0.05.

^dTrefry et al. (1989).

^eIricanin (1990).

^fDOP_{Dierberg} = Total Soluble P – Soluble Reactive P.

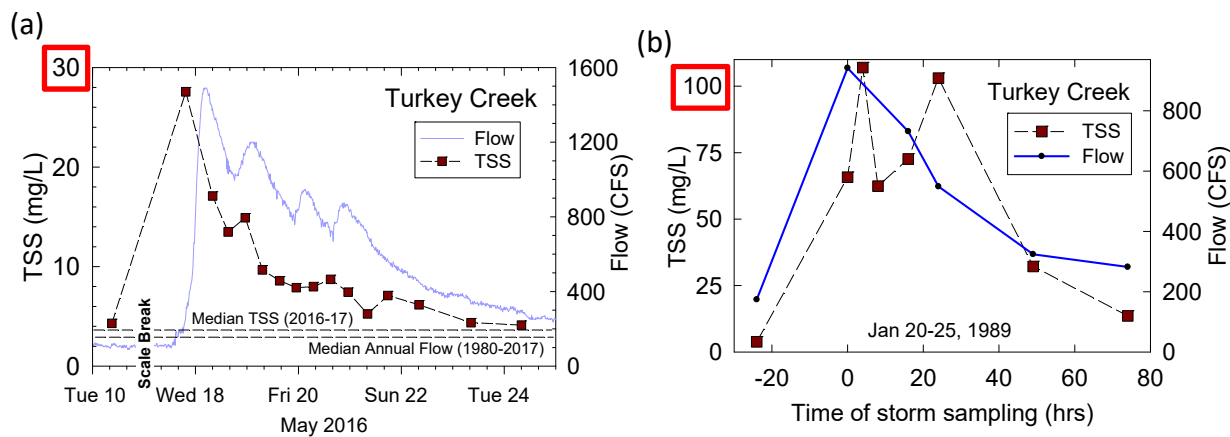


Figure 29. Concentrations of total suspended solids (TSS) and water flow during rain events in Turkey Creek for (a) May 2016 and (b) January 1989. Dashed lines connecting markers added to help show changes over time.

25% lower in 2016–17 and statistically different from 1988–89 (Table 18). A significantly lower concentration for DON at TC during 2016–17 was consistent with studies from other areas where decreases in DON, but not DOC, coincided with a lower fraction of forested and natural land, in the absence of increased agricultural land usage (e.g., Wiegner et al., 2006; Osburn et al., 2016). Based on the premise stated for Table 1 (page 2), we estimated 36% urban land use in TC during 1988–89 relative to 64% in 2016 (Table 1, 2); plus, agricultural land area decreased between studies. A significant increase in the DOC/DON ratio from 15 ± 6 in 1988–89 to 26 ± 9 in 2016–17 (Table 18) was consistent with decreased DON in TC that likely resulted from (i) decreased natural and agricultural land area and/or (ii) an increase in the fraction of the DON, relative to DOC, that was bioavailable and consumed during river transport. Wiegner et al. (2006), for example, found that $23 \pm 4\%$ of the DON and only $4 \pm 1\%$ of the DOC in East Coast U.S. Rivers were consumed by bacteria during laboratory incubation experiments.

A large and significant increase in mean values for N+N (400% ; $+103 \mu\text{g N/L}$) from 1988–89 to 2016–17 (Table 18) was a strong indicator of increased human activity, expanded use of reclaimed water and inputs of fertilizer runoff and/or human sewage (e.g., Bowes et al., 2015). The 300% ($+123 \mu\text{g N/L}$) increase in PON 2016–17 (Table 18) was likely related to increased inputs of OM from sod and other vegetation, the result of increased residential property. Additional discussion of PON follows below with results for suspended sediments. Overall, increases in the number of septic systems plus residential lawns and fertilizer use in Palm Bay that accompanied the large population growth from 1988–89 to 2016–17 help explain the increased N+N and PON found in TC.

Concentrations of TN and NH_4^+ were 11% higher ($+84 \mu\text{g N/L}$) and 26% lower ($-17 \mu\text{g N/L}$), respectively, for 2016–2017 relative to 1988–89, but not significant between studies (Table 18). Consequently, the significant decrease in DON by $165 \mu\text{g N/L}$ from 1988–89 to present, in the absence of statistically significant changes in TN and NH_4^+ , was offset by increases of $>200 \mu\text{g N/L}$ (N+N, $+103 \mu\text{g N/L}$; PON, $+123 \mu\text{g N/L}$; Table 14). If only data for TN were available, the significant changes in the chemical forms of N, especially the large increase in the more bioavailable N+N, would not have been observed.

Average concentrations of TP in 2016–2017 were $\sim 80\%$ higher than in 1988–89 (Table 18) and consistent with observations for phosphorus increases in rivers globally when non-point sources are dominant (Berner and Berner, 2012). Non-point sources of anthropogenic nutrients are certainly important in TC and throughout the IRL (Tetra Tech, 2019). In sharp contrast with TP, concentrations of PO_4^{3-} in TC during 2016–17 were not significantly different from those in 1988–89 (Table 18). Therefore, the increase in TP is explained by concurrent and significant increases in PP plus large, but not significant, increases in DOP (Table 18). Adsorption/desorption of PO_4^{3-} by particles in rivers is an important component of the P cycle globally (e.g., Nguyen et al., 2019), and undoubtedly in the IRL. Perhaps PO_4^{3-} concentrations in TC have increased over time and

PO₄³⁻ has been taking up on particles rich in positively charged, freshly precipitated Fe oxides. More discussion of this topic also follows below when data for suspended particles are introduced.

Large and significant increases in both POC (as mg/L) and PON (as µg/L) were observed from 1988–89 to 2016–17 (Table 18). Because no significant differences in mean TSS values were observed from 1988–89 to 2016–17, increases in POC and PON (as mass/volume) were linked to significant increases in the % of the TSS that was organic carbon and nitrogen (Table 19). Overall, concentrations of POC and PON (as a % of TSS) increased from 1988–89 to 2016–17 by 72% and 91%, respectively (Table 19). Despite these increases, no significant change in the average POC/PON ratio was found (Table 19). Therefore, the chemical character of the particulate OM has likely not changed significantly.

Table 19. Concentrations, as percent of total suspended solids (TSS), for particulate organic carbon (POC), particulate organic nitrogen (PON), particulate phosphorus (PP), particulate iron (Fe), particulate aluminum (Al) and particulate silicon (Si) plus various ratios for elements bound to suspended particles in Turkey Creek during 1988-89 and 2016–17. Means that are statistically higher are listed in bold font and underlined; corresponding *p* values are shaded.

Parameter (as % of TSS, by mass)	1988-89 ^a (n = 12)	This Study (2016-17) (n = 19)	<i>p</i> value ^b (t-test)
POC	10.2 ± 4.9	<u>17.5 ± 4.7</u>	0.0003
PON	2.2 ± 1.2	<u>4.2 ± 1.9</u>	0.003
PP	0.16 ± 0.07	<u>0.58 ± 0.11</u>	<0.0001
POC/PON	5.0 ± 1.2	4.2 ± 1.1	0.48
POC/PP	<u>50 ± 5</u>	31 ± 9	<0.0001
PON/PP	<u>10.7 ± 3.4</u>	8.1 ± 3.4	0.047
Particulate Fe	10.6 ± 2.5	10.6 ± 3.1	1.0
Particulate Al	<u>4.3 ± 1.8</u>	2.7 ± 0.6	0.0012
Particulate Si	<u>11.9 ± 2.6</u>	9.2 ± 2.3	0.0051
Particulate Si/Particulate Al	3.0 ± 0.7	3.4 ± 0.8	0.17
Particulate Fe/Particulate Al	3.0 ± 0.7	<u>3.9 ± 1.9</u>	0.042

^aTricanin (1990).

^bt-test, two-tailed, equal variance; mean values are not statistically different if *p* ≥ 0.05.

Increased concentrations of POC in 2016–2017 corresponded with ~20% and ~40% decreases in particulate Si and Al, respectively (as mg/L and as % of TSS; Tables 18 and 19). Silicon and Al are proxies for soil minerals in suspended solids carried by TC (i.e., aluminosilicates present as silts and clays). However, ratios of Si/Al in TC particles were not significantly different between the two studies, likely because the aluminosilicate minerals have remained essentially the same (Huckle et al., 1974; Iricanin 1990; this study), there is just less of them in 2016–17 (Table 18 and 19). This is positive news for the IRL because silts and clays make up >60% of the muck in the IRL. Such improvement may have resulted from better retention of mineral particles in soils in the TC basin or at the C-1 control structure. In contrast, increased transport of particulate OM by TC is a potential concern because the OM can decompose to release N and P into the IRL.

Particulate Fe concentrations (as both $\mu\text{g/L}$ and as % of TSS) did not change significantly from 1989–1990 to 2016–2017 (Tables 18 and 19). However, the Fe/Al ratio for suspended particles increased significantly by 30% from 1989–1990 (Table 19). As previously mentioned, two possible sources of increased Fe on TC particles (relative to Al) were added releases of Fe-rich irrigation water and/or releases from Fe- and P-rich minerals in soils. Furthermore, Fe/Al ratios for suspended sediment in TC (3.0–3.9) were high relative to averages of 0.8 and 0.6 for TC and IRL sediments, respectively (Trefry and Trocine, 2011; Fox and Trefry, 2018). The reason for this trend is uncertain at present. However, a freshly precipitated Fe-oxide coating on riverine suspended matter would take up PO_4^{3-} , thereby enhancing concentration of PP. If 5 $\mu\text{g PO}_4^{3-}$ -P were taken up by 4 mg of TSS, PP values would increase by 12 $\mu\text{g P/L}$, which is the observed increase from 1988–89 to 2016–17 (Table 18). Considerably more study of chemical reactions involving P and Fe in TC and the IRL are needed.

Even though no significant changes in the POC/PON ratio of the TSS were found, the POC/PP and PON/PP ratios decreased significantly by 38% and 24%, respectively, from 1988–89 to 2016–17. This shift was supported by a larger increase in PP than POC and PON (as % of TSS) over time (Table 19). Clearly, more particulate P is being carried by TC; however, it is not clear from presently available data whether the increased P is associated with P-rich OM or Fe oxides. We also do not know whether uptake of P by particles is obscuring increased loading of PO_4^{3-} in the upper reaches of TC.

Data also were available from 1988–99 to 2016–17 to compare relative changes in the chemical forms of N and P (Table 20). Although concentrations of TN did not change significantly between studies, significant differences in all four chemical forms of N were observed (Table 20). The fraction of TN that was DON decreased by 27% from 1988–89 to 2016–17 whereas the other three chemical forms of N increased by 64% (NH_4^+), 88% (N+N) and 260% (PON) from 1988–89 to 2016–17 (Table 20). This shift led to an 81% increase in the concentration of bioavailable, dissolved inorganic nitrogen ($\text{DIN} = \text{NH}_4^+ + \text{N+N}$) from 91 $\mu\text{g/L}$ in 1988–99 to 177 $\mu\text{g/L}$ in 2016–

Table 20. Means ± standard deviations for chemical forms (as % of total) for dissolved nitrogen and phosphorus in Turkey Creek (TC) during 1988–89 and 2016–2017. [Ammonium (NH₄⁺), nitrate + nitrite (N+N), dissolved organic nitrogen (DON), particulate organic nitrogen (PON), phosphate (PO₄³⁻) dissolved organic phosphorus (DOP), particulate phosphorus (PP)] Means that are statistically higher listed in bold font and underlined; corresponding *p* values are shaded.

Chemical	% of TN or TP		<i>p</i> value TC vs IRL (t-test) ^b
	TC (1988–89) (n = 12)	TC (2016–17) (n = 19)	
NH ₄ ⁺	3.3 ± 1.2	<u>5.4 ± 1.9</u>	0.0019
N+N	8.2 ± 5.3	<u>15.4 ± 10.0</u>	0.0295
DON	<u>83.4 ± 12.6</u>	60.9 ± 9.2	0.0001
PON	5.1 ± 2.1	<u>18.3 ± 7.6</u>	0.0001
PO ₄ ³⁻	52.6 ± 19.8	41.5 ± 15.6	0.093
DOP	13.2 ± 16.3	16.8 ± 20.8	0.62
PP	34.2 ± 10.5	41.7 ± 12.8	0.10
TN	100% N 100% P	100% N 100% P	1.0
TP	100% N 100% P	100% N 100% P	1.0

^aDierberg (1991). Sum of chemical forms used to calculate percentages because TN and TP values obtained did not equal the sum of the chemical forms.

^bt-test, two-tailed, equal variance; mean values not statistically different if *p* ≥ 0.05.

17 (Table 20). Such an increase is important because DIN is more rapidly taken up by algae from the IRL than DON or PON, leading to higher growth rates and increased support of more intense algal blooms (e.g., Kang et al., 2015).

In contrast with TN, TP increased in TC by 83% from 1988–99 to 2016–17 (Table 20). Yet, despite this increase in TP, no significant differences were found for percentages of TP that was PO₄³⁻, DOP or PP (Table 20). The apparent uniformity in percentages of the forms of P was linked to large standard deviations for concentrations of TP and all chemical forms of P in both the 1988–99 to 2016–17 data sets (Table 20). Furthermore, the large decrease in the POC/PP supports uptake of inorganic P (i.e., PO₄³⁻) by suspended particles in TC.

Samples of IRL water were collected monthly from April 2015 to April 2017 at one site located ~1 km east of the mouth of TC, as part of a study of dredging in TC (Fox and Trefry, 2018). Table

21. Means \pm standard deviations for concentrations and chemical forms (as % of total) for dissolved nitrogen and phosphorus in Turkey Creek (TC) and the IRL during 2016–2017. [Ammonium (NH₄⁺), nitrate + nitrite (N+N), dissolved organic nitrogen (DON), particulate organic nitrogen (PON), phosphate (PO₄³⁻) dissolved organic phosphorus (DOP), particulate phosphorus (PP)]. Means that are statistically different listed in bold font and underlined; corresponding *p* values are shaded.

Chemical	Concentration		<i>p</i> value TC vs IRL (t-test) ^b	% of TN or TP		<i>p</i> value TC vs IRL (t-test) ^b
	TC (2016–17) (n = 19)	IRL ^a (2016–17) (n = 72)		TC (2016–17) (n = 19)	IRL ^a (2016–17) (n = 72)	
NH ₄ ⁺	48 \pm 32 (μ g N/L)	78 \pm 69 (μ g N/L)	0.069	5.4 \pm 1.9	8.2 \pm 6.3	0.060
N+N	<u>129</u> \pm 82 (μ g N/L)	21 \pm 35 (μ g N/L)	<0.0001	<u>15.4 \pm 10.0</u>	1.8 \pm 2.6	0.0001
DON	495 \pm 122 (μ g N/L)	<u>640 \pm 270</u> (μ g N/L)	0.025	60.9 \pm 9.2	61.1 \pm 11.0	0.94
PON	163 \pm 131 (μ g N/L)	<u>319 \pm 240</u> (μ g N/L)	0.0078	18.3 \pm 7.6	<u>28.9 \pm 12.7</u>	0.0008
PO ₄ ³⁻	<u>22 \pm 9</u> (μ g P/L)	16 \pm 12 (μ g P/L)	0.045	<u>41.5 \pm 15.6</u>	26.1 \pm 17.8	0.0009
DOP	14 \pm 23 (μ g P/L)	17 \pm 13 (μ g P/L)	0.46	16.8 \pm 20.8	26.2 \pm 17.9	0.052
PP	25 \pm 14 (μ g P/L)	32 \pm 21 (μ g P/L)	0.17	41.7 \pm 12.8	47.7 \pm 17.8	0.172
TN	834 \pm 270 (μ g N/L)	<u>1050 \pm 440</u> (μ g N/L)	0.045	100% N 100% P	100% N 100% P	1.0
TP	63 \pm 34 (μ g N/L)	65 \pm 29 (μ g N/L)	0.80	100% N 100% P	100% N 100% P	1.0
TSS	4.3 \pm 3.0 (mg/L)	<u>7.9 \pm 6.2</u> (mg/L)	0.016	100% TSS	100% TSS	1.0
Salinity (‰)	0.69 \pm 0.13	<u>22 \pm 4</u>	<0.0001	100% TDS	100% TDS	1.0

^aTrefry et al. (2016) for Indian River Lagoon, Palm Bay, FL at 28° 2.419'N, 80° 35.574'W.

^bt-test two-tailed, equal variance; mean values not statistically different if $p \geq 0.05$; results from TC for 2016–17 versus IRL 2016–17.

Concentrations of TN were significantly greater by 26% at the IRL site than in TC (Table 21). Yet, the mean concentration of N+N and mean fraction of TN that was N+N were 6.1- and 8.6-fold lower, respectively, in the IRL site than in TC (Table 21). This observation supports efficient biological uptake of incoming N+N from TC by phytoplankton and algae in the IRL.

DON values were significantly higher (29%) in the IRL than TC; however, no significant difference in the fraction of TN that was DON was found between TC and IRL (Table 21). TSS,

PON and the fraction of TN that was PON were significantly higher in the IRL (Table 21). Total P concentrations in the IRL were not significantly different from TC; however, phosphate concentrations were significantly lower by 27% in the IRL than TC (Table 22).

Overall, the main differences between TC and the adjacent IRL were 26% higher TN in the IRL and 6.1-fold lower concentrations of N+N (Table 21). Perhaps the most striking difference was in salinity at 22‰ for the IRL and 0.7‰ for TC. Clearly, salt is accumulating as water evaporates or ocean water is added while N and P are being removed from the water column by biological processes to maintain smaller differences in nutrient concentrations between freshwater in the tributaries relative to ~30-fold saltier water in the lagoon than the tributaries.

Comparisons of fluxes of TN and TP from TC to the IRL from 1988–89 to 2016–17 were complicated because flow in the present study was about double that of the earlier study. Fluxes for 2016 and 2017 are compared with the 1988 results from Dierberg (1991) who expressed fluxes in kg/km²/y (Table 22). We also used TN and TP concentrations from Dierberg (1991) to calculate fluxes for 1988–89 and found them to be within 10–20% of the values obtained by Dierberg. The present and previous fluxes were compared by dividing the mean values for 2016 and 2017 by the fluxes for 1988 (Table 22). Only four parameters (PON, PO₄³⁻, DOP and DOC) had fluxes in 2016–2017 that were greater by 2:1; this is the projected difference in flow between 1988–89 to 2016–17 if water flow doubled and concentrations did not change.

Table 22. Fluxes of various chemical forms of nitrogen and phosphorus from Turkey Creek to the Indian River Lagoon using data for 2016 and 2017 from this study and from March 1988–March 1989 using data from Dierberg (1991). Units of kg N or P/km²/y used for all parameters except flow that is in CFS (units used by Dierberg, 1991). [DON = dissolved organic nitrogen, N+N = nitrate + nitrite, NH₄⁺ = ammonium, PON = particulate organic nitrogen, PO₄³⁻ = phosphate, DOP = dissolved organic phosphorus, and Partic. P = particulate phosphorus].

Parameter	2016 (kg/km ² /y)	2017 (kg/km ² /y)	Mar 1988 – Mar 1989 (kg/km ² /y) ^a	<u>Mean 2016 & 2017</u> <u>Mar 88 to Mar 89</u>
Flow (CFS)	211	210 (161)	104	2.02
TN	646	638	382	1.69
N+N	83	55	44	1.57
NH ₄ ⁺ -N	28	27	23	1.20
DON	354	527	282	1.56
PON	94	94	34	2.76
TP	36	35	22	1.61
PO ₄ ³⁻ -P	22	22	10	2.20
DOP	10	10	2	5.00
PP	18	18	9	2.00
DOC	10,000	11,000	4000	2.62

^aDierberg (1991).

Based on concentrations of the various chemicals, five increased (POC, N+N, PON, TP and PP) from 1988–89 to 2016–17 and one decreased (DON). The chemicals that showed increased concentrations could all be explained by increased population and urbanization. These increases may be decreased by diversion of water from the C-1 Canal for as many days as practical, considering other factors such as flood potential and the impact of the St. Johns River. The decrease in DON is also consistent with increased urbanization and decreased natural and agricultural land, as previously explained.

Table 23. Summary of changes in concentrations of chemical parameters for Turkey Creek between 1998–89 and 2016–17.

Chemical Parameter	Significant Changes in Concentrations from 1988-89 to 2016-17^a
Particulate Organic C (mg C/L)	76% increase
Dissolved Organic N (µg N/L)	25% decrease
Nitrate + Nitrite (µg N/L)	400% increase
Particulate Organic N (µg N/L)	300% increase
Total P (µg P/L)	82% increase
Particulate P (µg P/L)	90% increase
TDS, TSS, DOC, TN, NH ₄ ⁺ , PO ₄ ³⁻ , DOP; Particulate Al, Si and Fe	No significant change

^at-test, two-tailed, equal variance; mean values are statistically different if $p \leq 0.05$.

4.0. Conclusions

The major tributaries of the IRL carry large volumes of water relative to the areas of their respective drainage basins. This above average runoff flows into a poorly flushed lagoon where rapid inputs of freshwater and nutrients have promoted extensive algal blooms. Mean concentrations of total nitrogen (TN) for the four tributary were 30–50% lower than the USEPA standard of 1540 $\mu\text{g N/L}$ for Florida inland waters. However, two of the four tributaries (SR and EG) had mean concentrations of total phosphorus (TP) that were 80% and 100% higher than the USEPA criteria.

Detailed data for the chemical forms of N and P showed that DON made up more than half of the TN. The more biologically available forms of N (NH_4^+ and N+N) made up ~25% of the TN. In contrast, PO_4^{3-} , the more biologically available form of P made up about half of the TP. Recent studies on nutrient uptake in the IRL (Kang et al., 2015) can now be applied to the forms that are actually present rather than TN or TP.

Within the scope of our first hypothesis, mathematical relationships for TDS, TSS, DON and DOC versus water flow met our criteria of $r \geq 0.6$ and $p < 0.05$. However, only a few of the other parameters for SR (TN, TP and P) met the criteria for using equations to calculate fluxes due to complexities in concentration versus flow during both high and low flow and likely periodicity for inputs of fertilizer and other sources of nutrients. Continuous nutrient data for tributaries would greatly improve flux calculations.

Phosphate concentrations were very high during Hurricanes Matthew (October 2016) and Irma (September 2017). At the same time, the ratio of dissolved inorganic N to dissolved inorganic P (DIN/DIP) was extremely low during this high flow, most likely due to transport of inorganic P that was desorbed from aluminosilicates and/or dissolved from inorganic P minerals. This observation may be a sign of future trends if water flows from major tributaries to the IRL increase.

Lower concentrations of NH_4^+ and N+N were found during the June 1 to September 30 period when the local fertilizer ordinance prohibiting use of N-fertilizers was in effect. Significantly higher concentrations of NH_4^+ and N+N were found during fall and winter after the fertilizer ban was lifted. However, the observed spike in concentrations during the fall season was significantly decreased water flow. As much as 40% of the NH_4^+ and N+N added to the lagoon each year was from June 1 to September 30, a point that certainly supports maintaining the fertilizer ordinance.

Estimated fluxes of TN (306–387 metric tons of N/y) and TP (36–76 metric tons of P/y) were at the same order-of-magnitude found for muck fluxes from the north IRL (300 metric tons N/y and 45 metric tons P/y). Overall, >70% of the TN and TP were carried during the ~120 days with above median flow in the tributaries.

A test of our second hypothesis found that concentrations of TDS, TSS, DOC, TN, NH_4^+ , PO_4^{3-} , DOP, plus particulate Al, Fe Si were not significantly different in water samples collected Turkey Creek during 2016–17 relative to 1988–89. In contrast, the following parameters showed significant increases of the three decade period: POC (+76%), TP (+82%), PP (+90%), PON (+300%) and N+N (+400%). Only DON showed a significant 25% decrease. Increased urbanization and residential property, plus decreased natural lands, support the trends observed.

Nutrient inputs from major tributaries are still an important aspect of the eutrophication issue in the IRL. Overall, the overarching issue is still enhanced nutrient transport to the IRL during a limited number of days with high water flow, combined with trapping of this nutrient-rich water in a poorly-flushed lagoon. Continuous chemical data for tributaries and the IRL are needed to better assess nutrient inputs, especially during extreme water flows that accompany hurricanes. The fertilizer ban is certainly worth continuing. A decrease in the N and P content of reclaimed water also would be a positive step forward. More data are needed to identify the specific components that make up DON and DOP. Furthermore, wherever possible, isotope data for specific chemical forms of N are needed to help better identify nutrient sources. But, most of all, we need to work to restrict nutrient runoff during brief periods of extreme water flow.

5.0. References

- Berner, E.K., Berner, R.A. 2012. *Global Environment: Water, Air, and Geochemical Cycles*. Princeton University Press, 444 pp.
- Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Loewenthal, M., Gozzard, E., Newman, J.R., Palmer-Felgate, E.J. 2015. Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration–flow relationships. *Science of the Total Environment* 511:608–620.
- Bussi, G., Janes, V., Whitehead, P.G., Dadson, S.J., Holman, I.P. 2017. Dynamic response of land use and river nutrient concentration to long-term climatic changes. *Science of the Total Environment* 590–591:818–831.
- Chen, N., Wu, Y., Chen, Z., Hong, H. 2015. Phosphorus export during storm events from a human perturbed watershed, southeast China: Implications for coastal ecology. *Estuarine, Coastal and Science* 166:178–188.
- City of Melbourne, Florida. 2019. Melbourne reclaimed water. Department of Public Works. <https://www.melbourneflorida.org/departments/public-works-utilities/reclaimed-water> .
- Dai, A., Qian, T., Trenberth, K.E., Milliman, J.D. 2009. Changes in continental freshwater discharge from 1948 to 2004. *Journal of Climate* 22:2773-92.
- Diaz, R.J., Rosenberg, R. 2008. Spreading dead zones and consequences for marine ecosystems. *Science* 321:926–929.
- Dierberg, F.E. 1991. Non-point source loadings of nutrients and dissolved organic carbon from an agricultural-suburban watershed in east central Florida. *Water Research* 25:363–374.
- [FL Dept. Ag] Florida Department of Agriculture and Consumer Services. 2012. Florida Citrus Statistics, 2010–2011.
- [FL Dept. Ag] Florida Department of Agriculture and Consumer Services. 2019. Florida Citrus Statistics, 2017–2018.
- Florida Department of State. 2010. Florida Administrative Code and Florida Administrative Register. Reuse of Reclaimed Water and Land Application. Rule Chapter 62-610.510.

- Fox, A.L., Trefry, J.H. 2018. Environmental dredging to remove fine-grained, organic-rich sediments and reduce inputs of nitrogen and phosphorus to a subtropical estuary. *Marine Technology Society Journal* 52:42–57.
- Gao, X. 2009. Nutrient and dissolved oxygen TMDLs for the Indian River Lagoon and Banana River Lagoon. Florida Department of Environmental Protection, Division of Environmental Assessment and Restoration, 71 pp.
- Gibbs, R.J. 1967. Amazon River: Environmental factors that control its suspended load. *Science* 156:1734–1737.
- Huang, T-H., Fu, Y-H., Pan, P.Y., Chen, C-T. 2012. Fluvial carbon fluxes in tropical rivers. *Current Opinion in Environmental Sustainability* 2012, 4:162–169.
- Huckle, H.F., Dollar, H.D., Pendleton, R.F. 1974. Soil survey of Brevard County, Florida. U.S. Department of Agriculture in cooperation with University of Florida Agricultural Experiment Stations, 123 pp.
- Iricanin, N. 1990. The role of storms in the transport and composition of particulate matter in a central Florida creek. Ph.D. Dissertation, Florida Institute of Technology, 137 pp.
- [IRL Consortium] Indian River Lagoon 2011 Consortium. 2015. 2011 Superbloom Report: Evaluating effects and possible causes with available data. St. Johns River Water Management District, Palatka, FL, 56 pp.
- Jeanneau, L., Denis, M., Pierson-Wickmann, A-C., Grau, G., Lambert, T., Petitjean, P. 2015. Sources of organic matter during storm and inter-storm conditions in a lowland headwater catchment: constraints from high-frequency molecular data. *Biogeosciences* 12:4333-4343.
- Jennerjahn, T.C., Knoppers, B.A., Souza, W., Brunskill, G.J., Silva, I.L, Adi, S. 2006. Factors controlling dissolved silica in tropical rivers. In: V. Ittekkot, D. Unger, C. Humborg, N.T. An (eds.) *The Silica Cycle*. Island Press, Washington, DC, pp. 29–51.
- Jickells, T.D., Andrews, J.E., Parkes, D.J., Suratman, S., Aziz, A.A., Hee, Y.Y. 2014. Nutrient transport through estuaries: The importance of estuarine geography. *Estuarine, Coastal and Shelf Science* 150:215–229.
- Kang, Y., Koch, F., Gobler, C.J. 2015. The interactive roles of nutrient loading and zooplankton grazing in facilitating the expansion of harmful algal blooms caused by the pelagophyte, *Aureoumbra lagunensis*, to the Indian River Lagoon, FL, USA. *Harmful Algae* 49:162-173.

- Kroening, S.E. 2004. Streamflow and water-quality characteristics at selected sites of the St. Johns River in central Florida, 1933 to 2002. Scientific Investigations Report 2004-5177, U.S.G.S., 102 pp.
- Li, L., He, Z., Li, Z., Zhang, S., Li, S., Yongshan, W., Stoffella, P.J. 2015. Spatial and temporal variation of nitrogen concentration and speciation in runoff and storm water in the Indian River watershed, South Florida. *Environmental Science and Pollution Research* 23:19,561–19,569.
- Louis, J., Bressac, M., Pedrotti, M.L., Guieu, C. 2015. Dissolved inorganic nitrogen and phosphorus dynamics in seawater following an artificial Saharan dust deposition event. *Frontiers in Marine Science* 2:Article 27.
- Ludwig, W., Probst, J.L., Kempe, S. 1996. Predicting the oceanic input of organic C by continental erosion. *Global Biogeochemical Cycles* 10:23–41.
- Martin, R.A., Harrison, J.A. 2011. Effect of high flow events on in-stream dissolved organic nitrogen concentration. *Ecosystems* 2011:1328–1338.
- Meybeck, M. 1993. C, N, P and S in rivers: From sources to global inputs. In: Interactions of C, N, P and S in Biogeochemical Cycles and Global Change. R. Wollast, F.T. Mackenzie, L. Chou (eds.). Berlin, Heidelberg, Springer-Verlag, pp. 163-192.
- Meybeck, M., Laroche, L., Durr, H.H., Syvitski, J.P.M. 2003. Global variability of daily total suspended solids and their fluxes in rivers. *Global and Planetary Change* 39:65–93.
- Michelou, V.K., Lomas, M.W., Kirchman, D.L. 2011. Phosphate and adenosine-59-triphosphate uptake by cyanobacteria and heterotrophic bacteria in the Sargasso Sea. *Limnology and Oceanography* 56:323–332.
- Morel, B., Durand, P., Jaffrezic, A., Grau, G., Molenat, J. 2009. Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment. *Hydrological Processes* 23:2888–2901.
- Moyer, R.P., Powell, C.E., Gordon, D.J., Long, J.S. 2015. Abundance, distribution, and fluxes of dissolved organic carbon (DOC) in four small sub-tropical rivers of the Tampa Bay Estuary (Florida, USA). *Applied Geochemistry* 63:550-562.
- Nguyen, Tuyet N.T., Némery, J., Gratiota, N., Garnier, J., Strady, E., Tran, V.Q., Nguyen, A.T., Nguyen, Thi N.T., Golliet, C., Aiméd, J. 2019. Phosphorus adsorption/desorption processes in the tropical Saigon River estuary (Southern Vietnam) impacted by a megacity. *Estuarine, Coastal and Shelf Science* 227:106321.

- O'Connor, D.J. 1976. The concentration of dissolved solids and river flow. *Water Resources Research* 12:279–294.
- Osburn, C.L., Handsel, L.T., Peierls, B.L., Paerl, H.W. 2016. Predicting sources of dissolved organic nitrogen to an estuary from an agro-urban coastal watershed. *Environmental Science & Technology* 50:8473–8484.
- Phlips, E.J., Badylak, S., Lasi, M.A., Chamberlain, R., Green, W.C., Hall, L.M., Hart, J.A., Lockwood, J.C., Miller, J.D., Morris, L.J., Steward, J.S. 2015. From red tides to green and brown tides: Bloom dynamics in a restricted subtropical lagoon under shifting climatic conditions. *Estuaries and Coasts* 38:886–904.
- Planert, M., Aucott, W.R. 1985. Water-supply potential of the Floridan Aquifer in Osceola, eastern Orange, and southwestern Brevard Counties, Florida. U.S. Geological Survey, Water-Resources Investigations Report 84-4135, 76 pp.
- Redfield, A.C. 1934. On the proportions of organic derivatives in sea water and their relation to the consumption of plankton. *James Johnstone Memorial Volume*: 176.
- Rember, R.D., Trefry, J.H. 2004. Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic. *Geochimica et Cosmochimica Acta* 68:477–489.
- Rice, E.W., Baird, R.B., Eaton, A.D., Clesceri, L.S. 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association, American Water Works Association, Water Environment Federation, 1496 pp.
- Schiner, G.P., Laughlin, C.P., Toth, D.J. 1988. Geohydrology of Indian River County, Florida. USGS Water Resources Investigation 88-4073. Tallahassee, FL.
- Schlesinger, W.H., Reckhow, K.H., Bernhardt, E.S. 2006. Global change: The nitrogen cycle and rivers. *Water Resources Research* 42, W03S06, doi:10.1029/2005WR004300, 2006.
- Seitzinger, S.P., Mayorga, E., Bouwman, A.F., Kroeze, C., Beusen, A.H.W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B.M., Garnier, J., Harrison, J.A. 2010. Global river nutrient export: A scenario analysis of past and future trends. *Global Biogeochemical Cycles* 24, doi10.1029/2009GB003587, 2010.
- Sinyukovich, V.N. 2003. Relationships between water flow and dissolved solids discharge in the major tributaries of Lake Baikal. *Water Resources* 30:186–190.

- [SJRWMD] St. Johns River Water Management District. 2009. Land Cover/Land Use Maps for Sub-basins of the Indian River Lagoon. St. Johns River Water Management District, Palatka, FL.
- Steward, J.S., Virnstein, R.W., Lasi, M.A., Morris, L.J., Miller, J.D., Hall, L.M., Tweedale, W.A. 2006. The impacts of the 2004 hurricanes on hydrology, water quality, and seagrass in the Central Indian River Lagoon, Florida. *Estuaries and Coasts* 29:954–965.
- Su, L., Miao, C., Kong, D., Duan, Q., Lei, X., Hou, Q., Li, H. 2018. Long-term trends in global river flow and casual relationships between river flow and ocean signals. *Journal of Hydrology* 563:818–833.
- Syvitski, J.P., Vösömarty, C.J., Kettner, A.J., Green, P. 2005. Impact of humans on the flux of terrestrial sediment to the global coastal ocean. *Science* 308:376–380.
- Syvitski, J., Milliman, J.D. 2007. Geology, geography, and humans battle for dominance over the delivery of fluvial sediment to the coastal ocean. *Journal of Geology* 115:1–19.
- Tetra Tech, Inc. and Close Waters, LLC. 2019. Save our Lagoon Project Plan for Brevard County, Florida. Report to Brevard County Natural Resources Management Department. <http://www.brevardfl.gov/SaveOurLagoon/Home>
- Trefry, J.H., Trocine, R.P., Metz, S., Iricanin, N., Chen, N-C. 1989. Particulate nutrient and metal investigations in the Turkey Creek watershed. Final Report to the St. Johns River Water Management District, 74 pp.
- Trefry, J.H., Metz, S., Trocine, R.P., Iricanin, N., Burnside, D., Chen, N., Webb, B. 1990. Design and operation of a muck sediment survey. Special Report to the St. Johns River Water Management District. Palatka, FL. SJ90-SP3, 62 pp.
- Trefry J.H., Trocine R.P. 1991. Collection and analysis of marine particles for trace elements. *In*: D.C. Hurd, D.W. Spencer (eds.). *Marine Particles: Analysis and Characterization*. Geophysical Monograph 63, pp. 311–315 American Geophysical Union, Washington, DC.
- Trefry, J.H., Trocine, R.P., Woodall, D.W. 2007. Composition and sources of suspended matter in the Indian River Lagoon, Florida. *Florida Scientist* 70:363–382.
- Trefry, J.H., Trocine, R.P., Bennett, H. 2009. Sediment sourcing study of Lake Worth Lagoon and C-51 basin, Palm Beach County. Final Report to Palm Beach County and the South Florida Water Management District for Contract R2008-0985.

- Trefry, J.H., Trocine, R.P. 2011. Metals in sediments and clams from the Indian River Lagoon, Florida: 2006-7 versus 1992. *Florida Scientist* 74:43–62.
- Trenberth, K.E., Asrar, G.R. 2014. Challenges and opportunities in water cycle research: WCRP contributions. *Surveys in Geophysics* 35:515–532.
- Tukey, J.W. 1949. Comparing individual means in the analysis of variance. *Biometrics* 5:99–114.
- Tweedale, W. 2017. St. Johns River Water Management District, written communication.
- [USEPA] U.S. Environmental Protection Agency. 2007. Total Maximum Daily Loads for the northern and central Indian River Lagoon and Banana River Lagoon, Florida: Nutrients and dissolved oxygen. Atlanta, GA: Region 4.
- [USEPA] U.S. Environmental Protection Agency. 2017. State Progress toward Developing Numeric Nutrient Water Quality Criteria for Nitrogen and Phosphorus. <https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality-criteria>.
- [USGS] U.S. Geological Survey. 2019. Water resources of the United States. <https://www2.usgs.gov/water/> and various specific websites listed in Figures 2–5.
- US-Mining.com. 2019. Florida limestone mines. <http://www.us-mining.com/florida/limestone-mines>
- Walling, D.E. 2006. Human impact on land-ocean sediment transfer by the world's rivers. *Geomorphology* 79:192–216.
- Wander, I.W., Reitz, H.J. 1950. The chemical composition of irrigation water used in Florida citrus groves. Florida State Horticultural Society, pp. 11–16.
- Wiegner, T.N., Seitzinger, S.P., Gilbert, P.M., Bronk, D.A. 2006. Bioavailability of dissolved organic nitrogen and carbon from nine rivers in the eastern United States. *Aquatic Microbial Ecology* 43:277–287.
- [WPU] World Population Review. 2019. Palm Bay, Florida. <http://worldpopulationreview.com/us-cities/palm-bay-fl-population/>
- Zekri, M., Obreza, T. 2013. Calcium (Ca) and sulfur (S) for citrus trees. Document SL382, Department of Soil and Water Sciences; University of Florida, Institute of Food and Agricultural Sciences Extension, 5 pp.

Appendix A. Land Use Data Tables for the drainage basins of St. Sebastian River, Turkey Creek, Crane Creek and the Eau Gallie River (SJRWMD, 2009)

St. Sebastian River Basin

Land Use Type	Area (km ²)	% of Total Area
Urban	63.85	15.3
Agriculture	131.05	31.4
Upland Non-forested	74.30	17.8
Forest	61.94	14.8
Water	10.81	2.5
Wetland	63.51	15.2
Barren Land	5.66	1.4
Transportation, Communication, Utilities	6.90	1.6
Total	418.04	100

Turkey Creek

Land Use Type	Area (km ²)	% of Total Area
Urban	149.32	58.9
Agriculture	34.48	13.6
Upland Non-forested	12.08	4.8
Forest	17.86	7.0
Water	6.96	2.8
Wetland	19.68	7.8
Barren Land	4.81	1.9
Transportation, Communication, Utilities	8.46	3.3
Total	253.65	100

Crane Creek

Land Use Type	Area (km ²)	% of Total Area
Urban	31.76	66.2
Agriculture	0.66	1.4
Upland Non-forested	3.69	7.7
Forest	2.86	6.0
Water	1.54	3.2
Wetland	1.70	3.5
Barren Land	0.07	0.1
Transportation, Communication, Utilities	5.72	7.4
Total	48.00	100

Eau Gallie River

Land Use Type	Area (km ²)	% of Total Area
Urban	16.83	70.9
Agriculture	0.37	1.6
Upland Non-forested	0.68	2.9
Forest	1.31	5.5
Water	0.65	2.7
Wetland	0.82	3.4
Barren Land	0.02	0.1
Transportation, Communication, Utilities	3.06	12.9
Total	23.74	100

Appendix B: Supporting Data and Information for Flux Calculations

St. Sebastian River, South Prong (SR)

Chemical	Equation and/or Concentration from Flow	Comment	<i>r</i>	<i>n</i>	<i>p</i>
TN	TN = 595(log Flow) -234	-	+0.88	32	<0.001
DON	DON = 523(log Flow) -455	-	+0.85	35	<0.001
N+N	N+N = -82.5(log Flow) + 303	>200 CFS	-0.98	9	<0.001
	N+N = 102.3(log Flow) - 64	<200 CFS	+0.74	14	0.0016
NH ₄ ⁺	Median = 49 µg N/L	-	-	-	-
PON	Median = 191 µg N/L	-	-	-	-
TP	TP = 130(log Flow) -84	-	+0.72	33	<0.001
PO ₄ ³⁻	PO ₄ ³⁻ = 83.6(log Flow) - 87.8	-	+0.93	32	<0.001
	1100@>700 CFS; 200@300-699 CFS	-	-	-	-
DOP	Median = 31 µg P/L	-	-	35	-
PP	Median = 51 µg P/L	-	-	35	-
TSS	TSS = 22.7 (log Flow) - 31.3	n = 22	+0.88		<0.001
	(Median = 8.2 mg/L)	-	-	35	-
DOC	DOC = 18.8(log Flow) -21.2	-	+0.86	35	<0.001
POC	POC = 2.3(log Flow) - 2.8	-	+0.84	22	<0.001
TDS	TDS = -657(log Flow) + 2133/		+0.86	34	<0.001

n = 13

n_{eq} = 9

n_{median} = 4

Turkey Creek (TC)

Chemical	Equation and/or Concentration from Flow	Comment	<i>r</i>	<i>n</i>	<i>P</i>
TN	Median = 866 µg N/L	-	-	-	-
DON	DON = +269 (Log Flow) – 83 [µg N/L]		+0.68	17	0.0814
	Median = 476 µg N/L	-	-	-	-
N+N	N+N = -160 (log Flow) + 549 [µg N/L]	≥200 CFS	-0.83	20	<0.001
	N+N = 163 (log Flow) – 212 [µg N/L]	<200 CFS	+0.58	17	0.012
	Median = 146 µg N/L				
NH ₄ ⁺	Median = 37 µg N/L	-	-	-	-
PON	Median = 129 µg N/L	-	-	-	-
TP	Median = 48 µg P/L	-	-	-	-
PO ₄ ³⁻	Median = 22 µg P/L	-	-	-	-
		-	-	-	-
DOP	Median = 14 µg P/L	-	-	-	-
PP	Median = 21 µg P/L	-	-	-	-
TSS	TSS = 7.1 (log Flow) – 11.3 [mg/L]	-	+0.80	34	<0.001
DOC	DOC = 5.0 (log Flow) + 1.3 [mg/L]	-	+0.71	40	<0.001
POC	Median = 0.63 mg/L [mg/L]	-	-	-	-
TDS	TDS = -285 (log Flow) + 1085 [mg/L]	>100 CFS	-0.90	34	<0.001

n = 13

n_{eq} = 5

n_{median} = 8

Crane Creek (CC)

Chemical	Equation and/or Concentration from Flow	Comment	<i>r</i>	<i>n</i>	<i>p</i>
TN	Median = 861 µg N/L	-	-	-	-
DON	Median = 420 µg N/L	-	-	-	-
N+N	N+N = -1.8(log Flow) + 292 [µg N/L]		-0.49	42	<0.001
	Median = 242 µg N/L				
NH ₄ ⁺	Median = 44 µg N/L	-	-	-	-
PON	PON = 147 (log Flow) -59 [µg N/L]	-	+0.63	39	<0.001
TP	Median = 121 µg P/L	-	-	-	-
PO ₄ ³⁻	Median = 57 µg P/L	-	-	-	-
DOP	Median = 29 µg P/L	-	-	-	-
PP	Median = 36 µg P/L	-	-	-	-
TSS	TSS = 3.6 (log Flow) - 0.6 [mg/L]	-	+0.49	40	0.0011
DOC	DOC = 9.1 (log Flow) - 1.1 [mg/L]		+0.60	25	0.0012
	Median = 11 mg/L	-	-	-	-
POC	Median = 0.63 mg/L	-	-	-	-
TDS	TDS = -494(log Flow) + 1285 [mg/L]	-	-0.90	43	<0.001

n = 13

n_{eq} = 5

n_{median} = 8

Eau Gallie (EG)

Chemical	Equation and/or Concentration from Flow	Comment	<i>r</i>	<i>n</i>	<i>p</i>
TN	Median = 975 µg N/L	-	-	-	-
DON	Median = 504 µg N/L	-	-	-	-
N+N	$N+N = 197(\log \text{Flow}) - 53$ [µg N/L]		+0.72	26	<0.001
NH ₄ ⁺	$NH_4^+ = 116(\log \text{Flow}) + 29$ [µg N/L]		+0.48	29	0.0073
	Median = 126 µg N/L	-	-	-	-
PON	Median = 290 µg N/L	-	-	-	-
TP	Median = 121 µg P/L	-	-	-	-
PO ₄ ³⁻	Median = 134 µg P/L	-	-	-	-
		-	-	-	-
DOP	Median = 25 µg P/L	-	-	-	-
PP	Median = 72 µg P/L	-	-	-	-
TSS	$TSS = 3.7(\log \text{Flow}) + 2.9$ [mg/L]	-	+0.69	31	<0.001
DOC	Median = 13.1 mg/L	-	-	-	-
POC	Median = 1.6 mg/L	-	-	-	-
TDS	$TDS = -298(\log \text{Flow}) + 917$ [mg/L]	-	-0.69	32	<0.001

n = 13

n_{eq} = 4

n_{median} = 9