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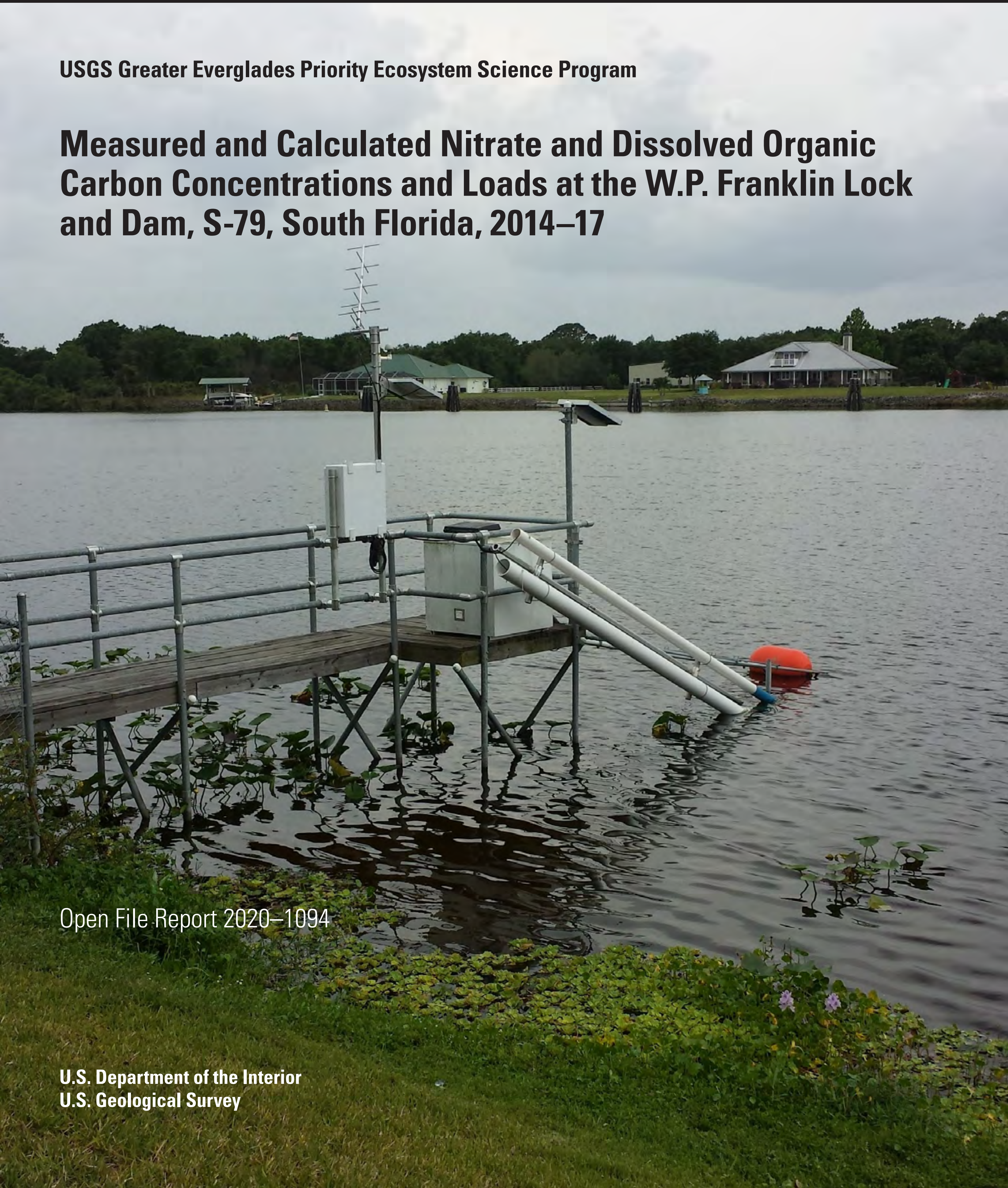
Measured and Calculated Nitrate and Dissolved Organic Carbon Concentrations and Loads at the W.P. Franklin Lock and Dam, S-79, South Florida, 2014–17



Open File Report 2020–1094

U.S. Department of the Interior
U.S. Geological Survey

Cover: U.S. Geological Survey monitoring station 02292900, on the right bank of the Caloosahatchee River, upstream of the S-79 structure, near Olga, Florida. Picture courtesy of Travis Knight, U.S. Geological Survey.

Measured and Calculated Nitrate and Dissolved Organic Carbon Concentrations and Loads at the W.P. Franklin Lock and Dam, S-79, South Florida, 2014–17

By Amanda Booth

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DAVID BERNHARDT, Secretary

U.S. Geological Survey
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Conversion Factors

Inch/Pound to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Volume	
cubic foot (ft^3)	28.32	cubic decimeter (dm^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
	Flow rate	
acre-foot per day (acre-ft/d)	0.01427	cubic meter per second (m^3/s)
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year (m^3/yr)
acre-foot per year (acre-ft/yr)	0.001233	cubic hectometer per year (hm^3/yr)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
gram	0.03527	Ounce, avoirdupois (oz)
metric ton	1.102	ton, short [2,000 lb]
metric ton	0.9842	ton, long [2.240 lb]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit

(°F) as °F = (1.8 × °C) + 32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius

(°C) as °C = (°F – 32) / 1.8.

Datum

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

CRE	Caloosahatchee River Estuary
FDEP	Florida Department of Environmental Protection
fDOM	fluorescence of chromophoric dissolved organic matter
FNU	formazin nephelometric unit
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
SC	Specific conductance
QSE	quinine sulfate equivalent
USGS	U.S. Geological Survey

Measured and Calculated Nitrate and Dissolved Organic Carbon Concentrations and Loads at the W.P. Franklin Lock and Dam, S-79, South Florida, 2014–17

By Amanda Booth

Abstract

The U.S. Geological Survey monitored dissolved nitrate plus nitrite as nitrogen (N) and dissolved organic carbon (DOC) concentrations and calculated loads of these constituents at the W.P. Franklin Lock and Dam (S-79) from April 2014 to December 2017. Flows from Lake Okeechobee controlled by S-77, S-78 and S-79 affect water quality in the downstream Caloosahatchee River Estuary, where increased nutrients and dissolved organic matter are of concern. Numerous algal blooms have occurred in the Caloosahatchee River and downstream estuaries in recent years (2005–18) and are often attributed to eutrophication. Dissolved nitrate plus nitrite as N (hereafter, referred to as nitrate) data were collected at 15-minute intervals using a submersible ultraviolet optical nitrate sensor. The instrument data were corrected for interferences, as determined by the relation between instrument measurements and 20 concurrent laboratory values. A surrogate model, based on 36 concurrent measurements of DOC, fluorescence of chromophoric dissolved organic matter, and specific conductance, was developed to calculate DOC at 15-minute intervals.

Mean and median calculated nitrate concentrations for the study period (2014–17) were both 0.21 milligram per liter (mg/L). Monthly mean nitrate concentrations ranged from 0.04 mg/L in April 2017 to 0.48 mg/L in November 2015. Monthly mean nitrate concentrations and the proportion of water that was attributed to Lake Okeechobee discharge, released through S-79, were weakly correlated and indicate that the nitrate concentrations typically decreased as the percentage of water released from the lake increased. Annual nitrate loads were 278 metric tons in 2015, 782 metric tons in 2016, and 525 metric tons in 2017. Monthly mean nitrate loads ranged from 1.2 metric tons in April 2017 to 171.3 metric tons in February 2016. Nitrate loads increased linearly with an increase in flow and typically increased during the wet season, May to October. Monthly loads of nitrate were strongly correlated with flow at S-77 and S-79.

Mean and median calculated DOC concentrations for the study period were 18.3 mg/L and 18.9 mg/L, respectively. Monthly mean DOC concentrations ranged from 12.6 mg/L in May 2017 to 21.5 mg/L in September 2015. Generally, DOC concentrations were lower during the dry season months (November to April) and higher during the wet season months. Monthly mean DOC concentrations were moderately correlated with monthly mean flow volumes at S-79. There was a strong correlation between monthly mean DOC concentrations and the proportion of water released at S-79 that can be attributed directly to Lake Okeechobee, indicating that contributions between Moore Haven Lock and Dam (S-77) and S-79 have a higher DOC concentration than water released from Lake Okeechobee. Monthly mean nitrate concentrations and monthly mean DOC concentrations were strongly correlated. Annual loads of DOC were 23,960 metric tons in 2015 and 65,610 metric tons in 2016 (2014 and 2017 data were incomplete). Monthly loads of DOC ranged from 284 metric tons in May 2017 to 15,122 metric tons in September 2017, the latter corresponding to the effects from Hurricane Irma. Monthly loads of DOC were strongly correlated with flow at S-77 and S-79.

Introduction and Background

The alteration of the Caloosahatchee River (fig. 1) and connection of the river to Lake Okeechobee (fig. 1) began in the late 1800s to mitigate flooding and provide a navigable waterway connecting eastern and western Florida (Antonini and others, 2002). Water delivery to the Caloosahatchee River (fig. 1) is managed and regulated by the U.S. Army Corps of Engineers. Flood control, public safety, navigation, water supply, and ecological health are all considered when deciding whether to retain water in the lake or release it to the Caloosahatchee River (South Florida Water Management District, 2018). Water-level elevations and flow rates between Lake Okeechobee and the Caloosahatchee Estuary are controlled by Moore Haven Lock and Dam (S-77; U.S. Geological Survey station 02292010; fig. 1), Ortona Lock and Dam (S-78; U.S. Geological Survey station 02292480; fig. 1), and W.P. Franklin Lock and Dam (S-79; U.S. Geological Survey station 02292900; figs. 1 and 2).

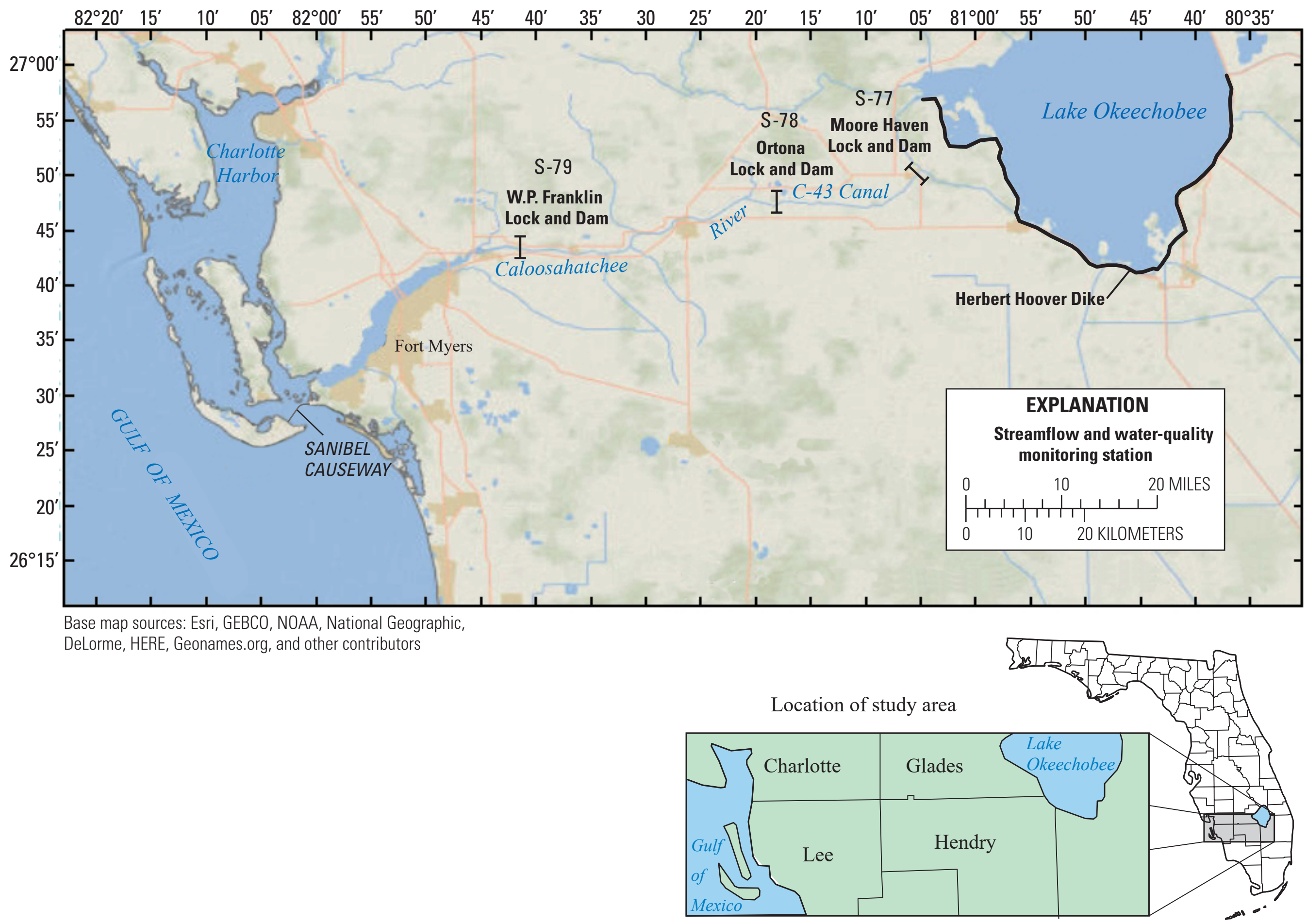

Figure 1. Lake Okeechobee, Herbert Hoover Dike, Moore Haven Lock and Dam, Ortona Lock and Dam, and W.P. Franklin Lock and Dam on Caloosahatchee River, southern Florida.

Figure 2. W.P. Franklin Lock and Dam on Caloosahatchee River, southern Florida. (Photograph by Eduardo Patino, U.S. Geological Survey.)

Changes in flow at S-79 affect water quality in the downstream Caloosahatchee River Estuary (CRE). Loads of nutrients and dissolved organic matter from Lake Okeechobee and contributions between S-77 and S-79 are of concern to downstream estuaries, owing to eutrophication. Previous research demonstrated that salinity and fluorescence of chromophoric dissolved organic matter (fDOM) concentrations within the lower portions of the estuary are affected by the release of water through S-79 (Booth and others, 2016). Lake Okeechobee has been deemed by the Florida Department of Environmental Protection (FDEP) to be impaired for phosphorous, dissolved oxygen, iron, un-ionized ammonia, coliforms, and chlorides. High phosphorous concentrations are considered the predominant impairment and the only contaminant for which a total maximum daily load (TMDL) was developed. A TMDL represents the maximum load that a waterbody can assimilate and still meet water-quality standards. FDEP set the phosphorous TMDL at 140 metric tons per year (Florida Department of Environmental Protection, 2001). The tidal Caloosahatchee River is considered impaired for excessive nutrients, low dissolved oxygen levels, and fecal coliform (Bailey and others, 2009). Total nitrogen (rather than total phosphorous) has been identified as the key contaminant of concern in the Caloosahatchee River by the FDEP (Bailey and others, 2009). The TMDL for the Caloosahatchee River is 4,121 metric tons per year of total nitrogen, which is a reduction of 23 percent compared to total nitrogen loads estimated by the FDEP in 2009 (Bailey and others, 2009).

Numerous cyanobacterial and red tide harmful algal blooms have occurred in the tidal Caloosahatchee River and downstream estuaries. *Karenia brevis* blooms were approximately 13–18 times more abundant from 1994 to 2002 than from 1954 to 1963 along the southwest coast of Florida (Brand and Compton, 2007). Cyanobacterial blooms have been documented in Lake Okeechobee and the Caloosahatchee River since the early 1980s (Havens and others, 1995a, 1995b). A state of emergency was declared in four Florida counties during June and July 2016 because a toxic cyanobacterial harmful algal bloom in the Lake Okeechobee Waterway negatively affected recreational activities, the tourism industry, and marine life (Cuevas, 2016; Rosen and others, 2017). Cyanobacterial blooms represent a major health concern for animals and humans (Pearson and others, 2016). Harmful algal bloom formation is complex; however, the rise in frequency and duration of harmful algal blooms has been documented in the Gulf of Mexico and is often attributed to eutrophication (Heisler and others, 2008).

The mean nitrate plus nitrite as nitrogen (N) annual load at S-79 from 1981 to 2003 was 435 metric tons. The mean nitrate plus nitrite as N annual loads at S-77 and S-78 were 56.8 metric tons from 1973 to 2003 and 133 metric tons from 1998 to 2003, respectively (Wetland Solutions, 2005). Nutrient concentrations and color, which can affect the light attenuation in the water column, in the CRE have been shown to increase when the inputs between S-77 and S-79 are the primary source of water released from S-79 (Doering and Chamberlain, 1999). According to calculations from the 2009 total nitrogen TMDL, 82.5 percent of the total nitrogen load in the CRE was from S-79 (Bailey and others, 2009). Nitrate plus nitrite as N concentrations decreased with distance downstream from S-79 (South Florida Water Management District, 2005; Julian and Osborne, 2018). Mean concentrations of nitrate plus nitrite as N ranged from 0.19 mg/L in the freshwater region of the CRE to 0.02 mg/L in the marine region of the CRE from 1999 to 2016 (Julian and Osborne, 2018).

Organic carbon plays a number of roles in estuarine dynamics in addition to its role in global carbon cycling. Organic carbon is a carrier of large quantities of carbon, nitrogen, and phosphorus to estuarine waters; it can affect estuaries by reducing light penetration; and is important in food web dynamics and transport of trace metals, such as mercury (Aiken and others, 2011). Dissolved organic carbon (DOC) in Lake Okeechobee basin soils has been positively correlated with nitrogen, phosphorous, and heavy metals (cobalt, chromium, nickel, and zinc; Yang and others, 2012). Organic carbon concentrations were greatest (16.69 mg/L) in the freshwater region of the CRE during 1999–2016 and decreased in the downstream direction (Julian and Osborne, 2018). Mean DOC concentrations in the CRE estuarine and marine regions were 11.89 mg/L and 7.25 mg/L, respectively, from 1999 to 2016 (Julian and Osborne, 2018).

The U.S. Geological Survey (USGS) initiated a study in April 2014 to monitor dissolved nitrate plus nitrite as N and DOC concentrations and compute nitrate plus nitrite as N and DOC loads at S-79. For simplicity, nitrate is used throughout the report to refer to dissolved nitrate plus nitrite as N data collected during the study. Nitrate and DOC concentrations were calculated in near-real time at 15-minute intervals by using the relation of water-quality monitoring measurements to measurements from discretely collected samples and by using surrogate models. The study was conducted as part of the USGS Greater Everglades Priority Ecosystem Science Program.

Purpose and Scope

The primary purpose of this report is to summarize seasonal and annual nitrate and DOC concentrations and loads entering the tidal Caloosahatchee River through the W.P. Franklin Lock and Dam (S-79). In addition, this report documents development of a site-specific surrogate model for dissolved organic carbon. Continuously measured streamflow, specific conductance (SC), temperature, turbidity, fDOM, and nitrate data were used to compute concentrations and loads. All streamflow, SC, temperature, turbidity, fDOM, and nitrate data are available for download at the USGS National Water Information System (NWIS) database (U.S. Geological Survey, 2019).

Description of the Study Area

The study area includes Lake Okeechobee, the Caloosahatchee River, and the CRE. Lake Okeechobee has a surface area of 730 square miles; is a natural habitat for fish and wildlife; supplies water for urban and agricultural uses, recharge for aquifers, and flow to the Everglades; and provides flood protection to the communities surrounding the lake (South Florida Water Management District, 2018). Lake Okeechobee has a substantial effect on the Caloosahatchee River and Estuary because of its connection to the Caloosahatchee River by means of the C-43 Canal. Water released from Lake Okeechobee enters the Caloosahatchee surface-water system at S-77 (fig. 1). Water released through S-79 can originate from Lake Okeechobee or from contributions between S-77 and S-79. The Caloosahatchee River Basin encompasses approximately 1,400 square miles and is predominantly agricultural (Wetland Solutions, 2005). S-79 is approximately 33 miles upstream from the mouth of the Caloosahatchee River; 10 miles east of Fort Myers, Florida; and 43 miles downstream from Lake Okeechobee. S-79 was constructed in 1965 for flood control and navigation, and to eliminate saltwater intrusion. The structure has a maximum discharge capability of 28,900 cubic feet per second (ft^3/s) (U.S. Army Corps of Engineers, 2017). S-79 is approximately 28 miles downstream from S-78, which was constructed in 1937 for navigation purposes; S-78 is capable of discharging 8,660 ft^3/s. S-77 is approximately 15.5 miles upstream from S-78, was built in 1935 for navigation and flood control purposes, and is capable of discharging 9,300 ft^3/s (U.S. Army Corps of Engineers, 2017). Water upstream from S-79 comes from the upstream lock structures, Lake Okeechobee, rainfall, groundwater inputs, and runoff. Mean annual total rainfall for the study area was approximately 59 inches from 1991 to 2017. Most of the rainfall (typically over 60 percent) occurs during June through September (Lee County, 2017).

Methods

Techniques and methods used in the collection, quality assurance, and analysis of data used to develop surrogate models to estimate carbon concentrations and calculate loads are described in this section of the report. Continuous (15-minute) data collected at S-79 include upstream water level, downstream water level, flow volume rate, SC, temperature, turbidity, fDOM, and nitrate concentrations. Data were transmitted on an hourly basis via the Geostationary Operational Environmental Satellite and made available to the public on a near real-time basis. Discrete water samples for nitrate and carbon laboratory analyses were collected monthly. Methods used for model development followed USGS guidance in Rasmussen and others (2009).

Continuous Monitoring

Water levels were measured at monitoring stations using shaft encoders with pulley and float systems (fig. 3). Flow at S-79 was computed using a submerged orifice equation rating and a sector gate rating. Computational methods were developed and verified using historical flow measurements. The index velocity method, which uses the relation between mean channel velocity (as measured by the acoustic Doppler current profiler), and index velocity (as measured by the acoustic Doppler velocity meter) was used to compute flow at S-77 following standard USGS methods (Levesque and Oberg, 2012). Acoustic Doppler current profiler measurements were made to verify computed flow ratings. Historical flow data are available for S-77 from May 2008 and for S-79 from April 1966 at the USGS NWIS database (U.S. Geological Survey, 2019); flow data continue to be published through NWIS for both locations.

Fixed-point in-situ water-quality data were collected at a depth of approximately 1 foot, referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29), upstream from S-79 (fig. 4) from April 2014 through December 2017. Specific conductance, in microsiemens per centimeter at 25 degrees Celsius (µS/cm); temperature, in degrees Celsius; turbidity, in formazin nephelometric units (FNU); and fDOM, in quinine sulfate equivalent (QSE) were measured with a YSI EXO2 multiparameter water-quality sonde. Nitrate concentrations were measured with a Satlantic SUNA V2 optical nitrate sensor, which measures dissolved nitrate plus nitrite as N, from April 2014 to December 2017. Water-quality sensors were inspected for fouling approximately every 4 weeks, and calibration verifications were performed every 8 weeks. Drift and fouling corrections were applied following Wagner and others (2006). Drift and fouling corrections were applied when the instrument was more than 5 percent from the standard value for fDOM.

The fDOM data were corrected for temperature, turbidity (assuming Elliot silt loam), and inner filter effects (Downing and others 2012). Serial dilutions were performed to determine the inner filter effect using filtered (<0.45 micrometer) S-79 native water that was collected on August 16, 2017.

Maintenance and field operation of nitrate sensors and data processing of nitrate data were conducted in accordance with Pellerin and others (2013). The accuracy of the SUNA used during the study was 0.06 mg/L. A correction was required for nitrate concentrations to account for interferences with the Satlantic SUNA sensor in the dark-colored water at S-79. The correction was determined on the basis of the relations of the sensor's concentrations to 20 laboratory-measured concomitant sample concentrations. The coefficient of determination was relatively high (R^2=0.93; fig. 5). Additional verification samples were collected monthly for matrix effects (fig. 5). Nitrate data are not available prior to December 2014 owing to instrument failure. Daily values were estimated via linear interpolation and were compared with additional water-quality time series data. Samples were analyzed by the USGS National Water-Quality Laboratory in Denver, Colorado. Continuously collected corrected data and discrete data are available in the USGS NWIS database (U.S. Geological Survey, 2019).

Comparison of field cross-sectional measurements collected over a range of flow conditions verified that the continuous data at the fixed location were representative of mean channel conditions. Vertical profiles of water-quality sensor data at six locations were recorded across the sampling cross section to describe vertical and horizontal stratification. Twelve cross-sectional profiles were made over the study period. Raw fDOM values were used for comparison (meaning no corrections were applied for temperature, turbidity, or inner filter effect). Water-quality sensor data collected during the six vertical profiles were averaged to represent the mean channel conditions on that date. In-situ measurements were representative of mean cross-sectional measurements; fDOM and SC profile averages were within 10 and 5 percent, respectively, of concurrent site monitor measurements. Owing to instrument availability, cross-sectional profiles with the SUNA V2 sensor were made on only eight dates and were found to be within 0.05 mg/L of concurrent SUNA V2 site monitor measurements.

Figure 3. Downstream monitoring station that contains shaft encoder at S-79, U.S. Geological Survey station 02292900, on Caloosahatchee River, southern Florida. (Photograph by Travis Knight, U.S. Geological Survey).

Figure 4. Water-quality sensor housing at S-79, U.S. Geological Survey station 02292900, on Caloosahatchee River, southern Florida. (Photograph by Travis Knight, U.S. Geological Survey).

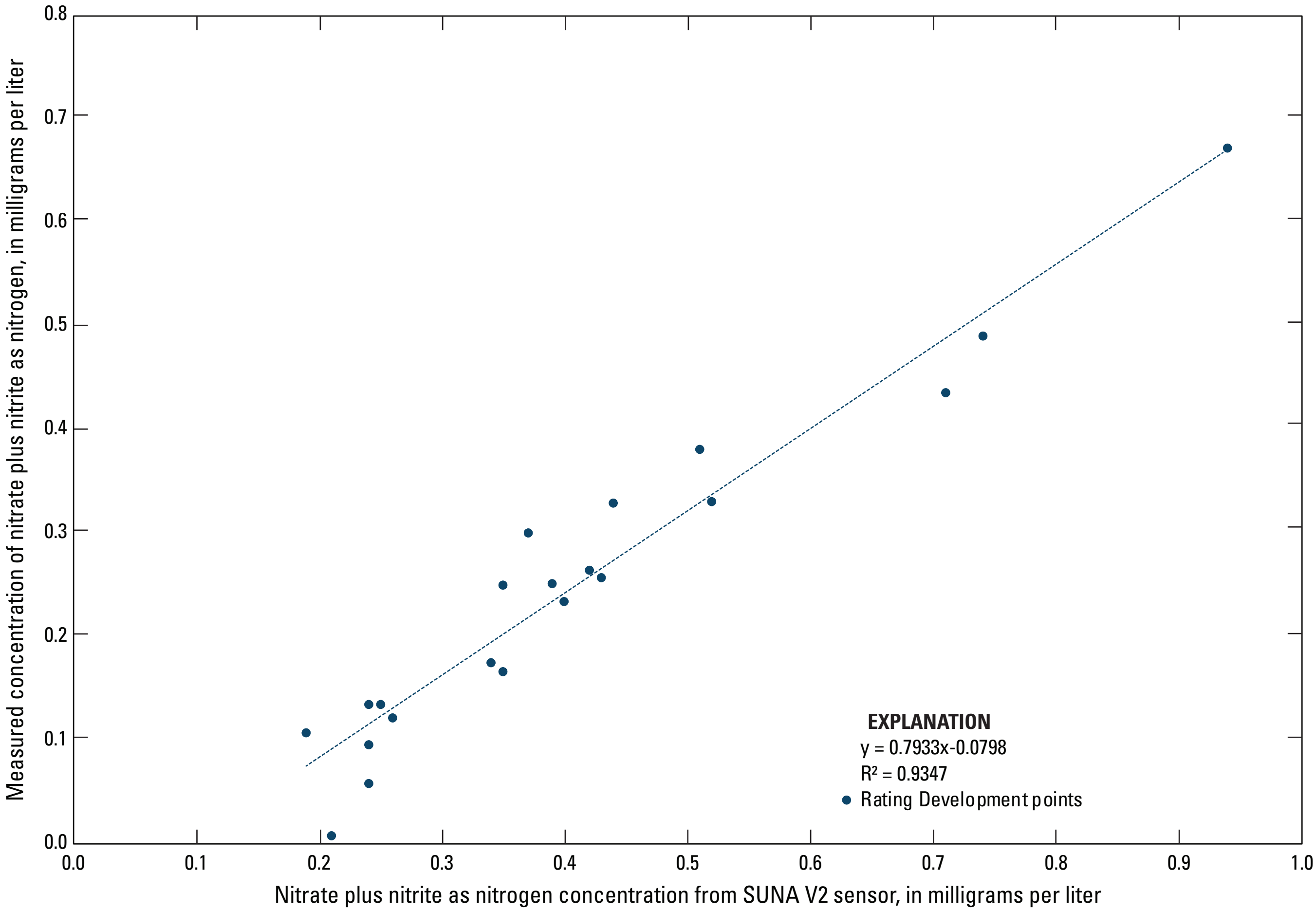

Figure 5. Correction for matrix effects on nitrate plus nitrite concentrations from the Satlantic SUNA V2 sensor.

Load Computations

Based upon comparison of field cross-sectional measurements, data collected at the station were representative of the mean channel; therefore, loads were calculated by multiplying the constituent concentration by the flow. Data were converted to metric tons of carbon or nitrate per day.

Data Analysis

The proportion of flow at S-79 that can be directly attributed to Lake Okeechobee water was estimated by dividing the monthly mean flow at S-77 by the monthly mean flow at S-79. A number greater than 0.5 indicates that Lake Okeechobee is the primary source of water, and a number less than 0.5 indicates that contributions between S-77 and S-79 are the primary sources of water released through S-79. Pearson correlation coefficients (r) and their corresponding p-value (p) were analyzed for monthly mean data. Pearson correlation coefficients measure the linear relation between two variables, and the associated p-value provides an indication of statistical significance. The strength of the correlation is described as defined in Evans (1996).

Discrete Samples

Discrete samples were collected near the sensors, filtered through a 0.45-micron capsule filter into amber glass 2-liter bottles within 15 minutes of being collected, and stored immediately on ice as described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Samples were shipped overnight to the USGS National Water-Quality Laboratory in Denver, Colorado. Samples were analyzed for DOC, total organic carbon, particulate nitrogen, absorbance at wavelength 254, absorbance at wavelength 280, nitrate plus nitrite, and nitrite. A low-level nitrate analysis was run when nitrate values were below 0.04 mg/L.

Four sequential field replicates for DOC were collected. Concentrations of DOC in replicate samples were within 0.2 mg/L of the environmental sample. Relative percent differences from the replicate samples ranged from -1 to 1 percent and averaged -0.1 percent. DOC blank samples were collected twice during the study period; in one sample, DOC was greater than the reporting level of 0.46 mg/L (sample found to contain 0.59 mg/L of DOC). Three concurrent field replicates for nitrate were collected, and replicate pair concentrations varied by 0.01 mg/L or less. Relative percent differences from the nitrate replicates ranged from -3 to 1 percent and averaged -1 percent. Four nitrate blank samples were collected, and all concentrations were less than the reporting level of 0.04 or 0.01 mg/L.

Dissolved Organic Carbon Model

The DOC linear regression model presented in Appendix 1 is based on 36 concurrent measurements of DOC, sensor-measured fDOM, and SC in samples collected from July 31, 2014, to October 4, 2017. fDOM and SC were selected as the best predictors of DOC, based on residual plots, relatively high coefficient of determination (R^2=0.65), and relatively low standard error (RMSE=1.66 mg/L). fDOM refers to the fraction of chromophoric dissolved organic matter that fluoresces and is often used as a surrogate for DOC (Spencer and others, 2007; Pellerin and others, 2012; Bergamaschi and others, 2012). The use of SC as a variable is also supported statistically and within the literature (Curtis and Adams, 1995; Monteiro and others, 2014). DOC data were calculated using the surrogate model and are available in a companion data release (Booth, 2020).

Flow Volume and Rate

Daily flow volumes at S-77 (flow from Lake Okeechobee) ranged from -898 acre-feet per day on September 10, 2017, to 15,398 acre-feet per day on October 4, 2017 (fig. 6). Flow was negative at S-77 (indicating water flowing towards Lake Okeechobee) on 117 days or 8 percent of the study period. The mean daily flow volume at S-77 during the study period was 2,883 acre-feet, and the median was 1,624 acre-feet. The mean daily flow volume at S-77 for the period of record (May 2008 to December 2017) was 2,012 acre-feet.

Daily flow volumes at S-79 ranged from 0 acre-feet on 18 dates during the study period to 50,065 acre-feet on September 11, 2017. The highest daily flow volume during the period of record (1966–2017) occurred on September 11, 2017, during Hurricane Irma. The mean daily flow volume during the study period at S-79 was 4,990 acre-feet, and the median was 3,229 acre-feet. The mean daily flow volume for the period of record (1966–2017) at S-79 was 3,311 acre-feet.

Annual flow volumes at S-77, which can be attributed primarily to Lake Okeechobee, ranged from 412,632 acre-feet in 2014 to 1,797,406 acre-feet in 2016 (fig. 7). The mean annual flow volume for the period of record (2009–2017) is 771,014 acre-feet. Annual flow volumes through S-79 ranged from 933,971 acre-feet in 2014 to 2,763,241 acre-feet in 2016. The mean annual flow volume for the period of record (1967-2017) is 1,296,875 acre-feet. In 2014, 44 percent of the water released through S-79 could be attributed to discharges from Lake Okeechobee, assuming evaporation was negligible (S-77). The highest percentage of water discharged through S-79 that could be attributed directly to discharges from Lake Okeechobee (S-77) was 65 percent in 2016. Lake Okeechobee discharges (through S-77) accounted for 54 percent and 56 percent of the water discharged through S-79 in 2015 and 2017, respectively. During years with lower flow volumes through S-79, the percentage of flow from S-77 was less than during the years with higher flow volumes.

Nitrate Concentrations and Loads

The maximum recorded instantaneous nitrate sensor concentration was 0.71 mg/L on February 2, 2016 (fig. 8). The largest daily mean value was 0.61 mg/L on February 3, 2016. The minimum recorded sensor concentration was 0.01 mg/L on July 27, 2017, and September 17, 2017. The mean and the median of the calculated nitrate concentrations for the study period were both 0.21 mg/L. Laboratory-measured data were always within 0.08 mg/L of the corrected continuous nitrate data. Owing to instrument malfunctions, daily mean nitrate concentrations were estimated based on linear interpolation and comparison with other monitored parameters on June 1, 2015, August 22–October 30, 2015, September 14–20, 2016, and August 15–16, 2017, and estimates are given in table 1.

Monthly mean nitrate concentrations ranged from 0.04 mg/L in April 2017 to 0.48 mg/L in November 2015 (fig. 9). Monthly mean concentrations in October and November 2015 were equal to or greater than 0.38 mg/L, which is two times the mean nitrate concentration found in the freshwater portion of the CRE between 1999 and 2016 as reported by Julian and Osborne (2018). October and November 2015 have the lowest flow volumes at S-79 for these months during the study period; however, correlations were not observed between monthly mean nitrate concentrations and monthly mean flow at either S-77 or S-79. There was, however, a weak correlation (r=-0.349, p=0.037) between monthly mean nitrate concentrations and the monthly mean flow at S-77 divided by the monthly mean flow at S-79. Dividing the monthly mean flow at S-77 by the monthly mean flow at S-79 provides an indication of the percentage of water that can be attributed to Lake Okeechobee. As the percentage of water at S-79 that could be directly attributed to Lake Okeechobee increased, the nitrate concentrations decreased, indicating that contributions received between S-77 and S-79 have a greater nitrate concentration than water released from Lake Okeechobee. Additional research is needed to understand variance of nitrate concentrations.

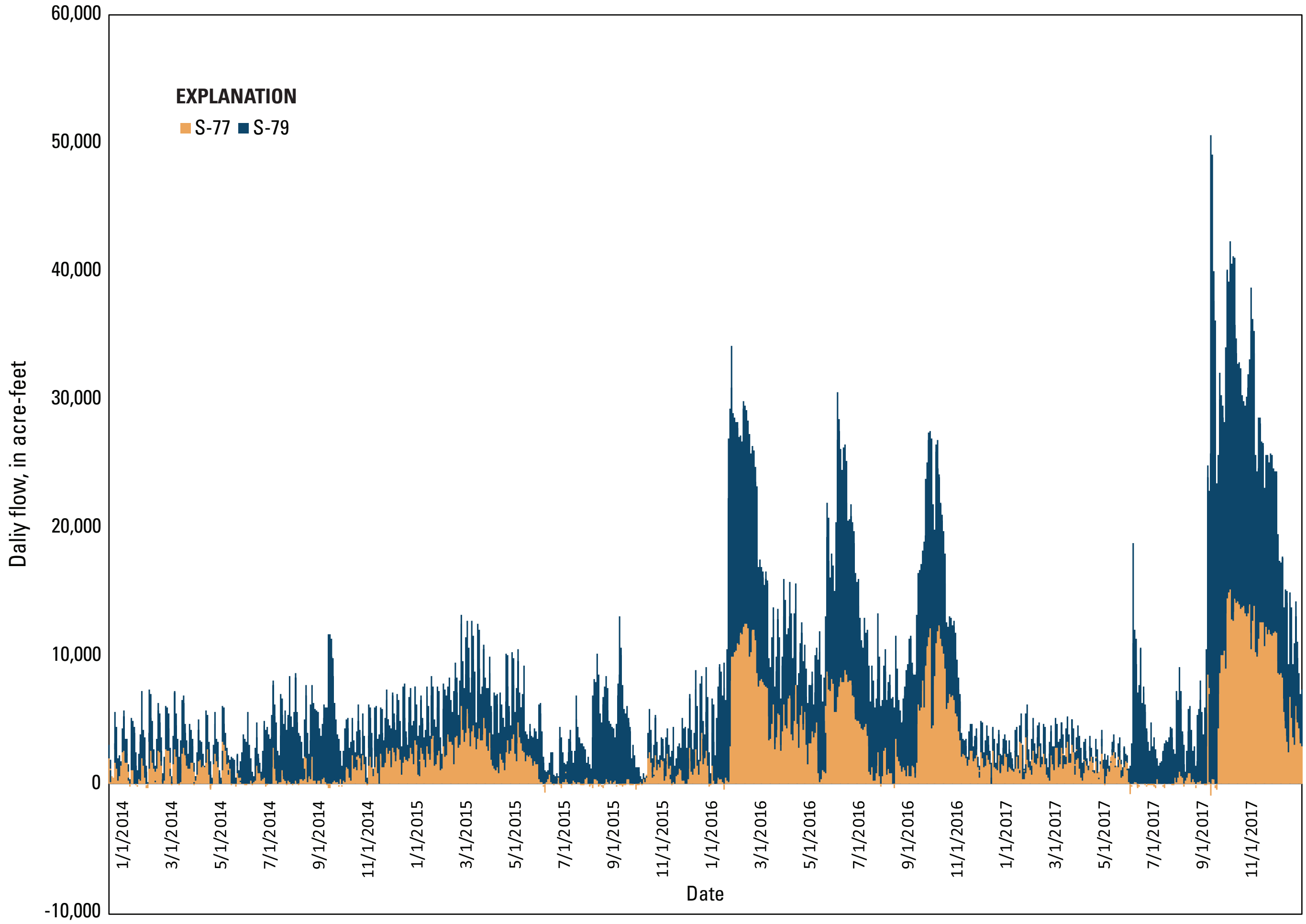

Figure 6. Daily flow volumes for locks and dams S-77 and S-79 on Caloosahatchee River, southern Florida, 2014–17.

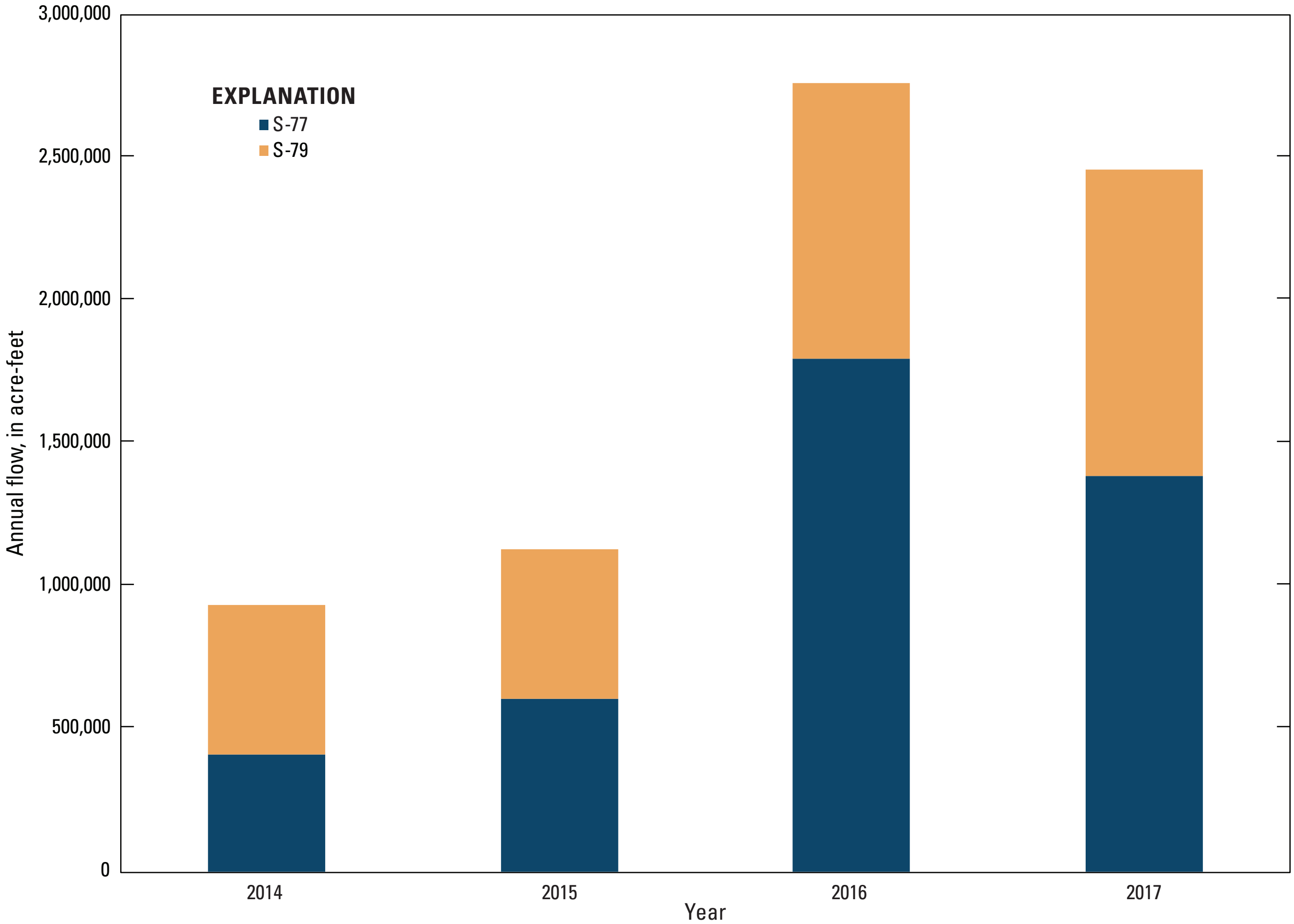

Figure 7. Annual flow volumes at locks and dams S-77 and S-79 on Caloosahatchee River, southern Florida, 2014–17. Figure depicts the total flow for S-79 and the flow that can be attributed to S-77.

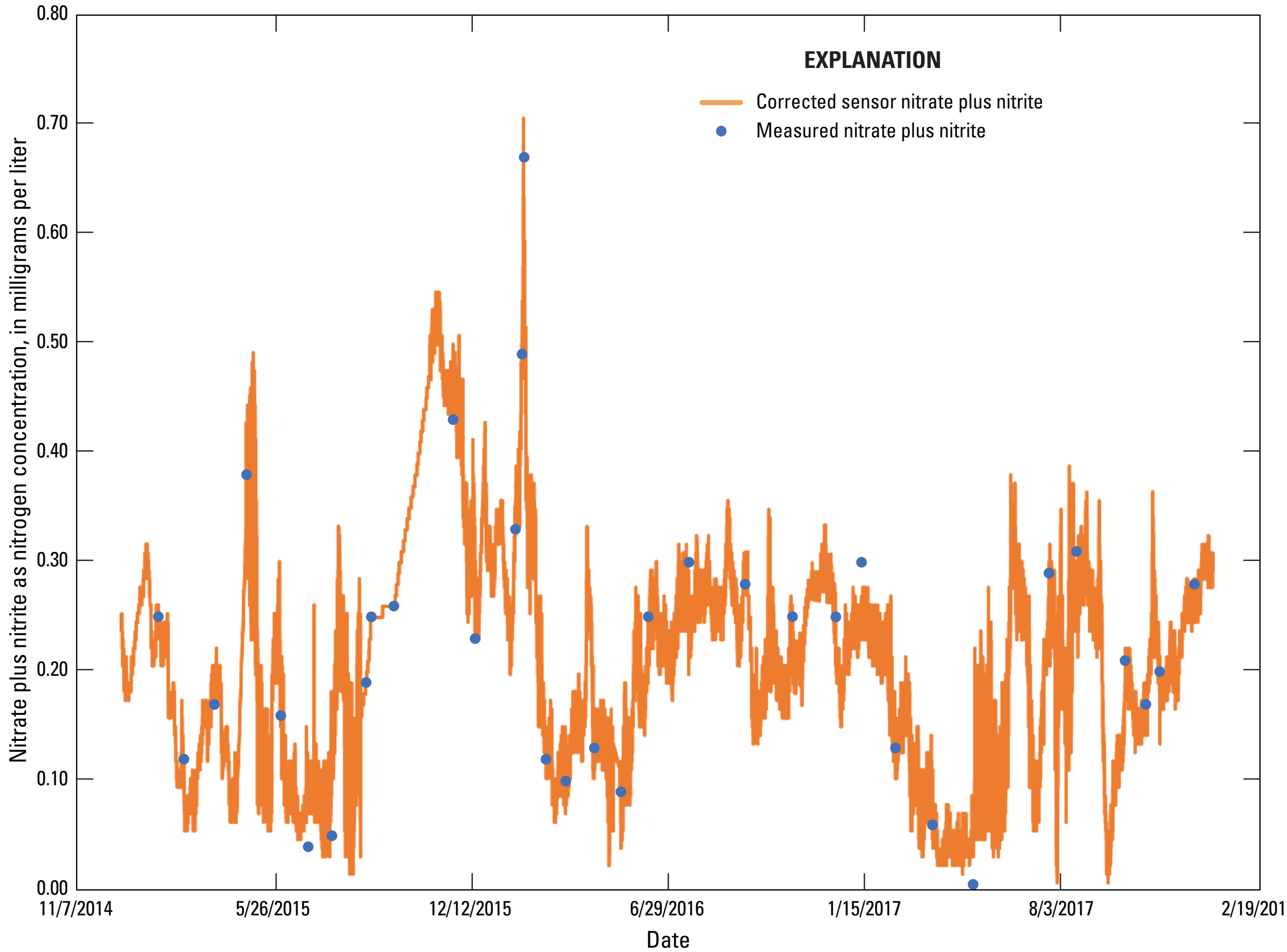

Figure 8. Corrected sensor, and measured, nitrate plus nitrite as nitrogen concentrations in samples collected from Caloosahatchee River at W.P. Franklin Lock and Dam, southern Florida, 2014–17.

Table 1. Estimated daily mean nitrate plus nitrite as nitrogen concentrations at the W.P. Franklin Lock and Dam, S-79, Caloosahatchee River, southern Florida, 2015 17.

[mg/L, milligrams per liter]

Date	Nitrate plus Nitrite as nitrogen, mg/L
6/1/2015	0.16
8/22/2015	0.16
8/23/2015	0.17
8/24/2015	0.17
8/25/2015	0.18
8/26/2015	0.18
8/27/2015	0.19
8/28/2015	0.20
8/29/2015	0.21
8/30/2015	0.22
8/31/2015	0.23
9/1/2015	0.25
9/2/2015	0.25
9/3/2015	0.25
9/4/2015	0.25
9/5/2015	0.25
9/6/2015	0.25
9/7/2015	0.25
9/8/2015	0.25
9/9/2015	0.25
9/10/2015	0.25
9/11/2015	0.25
9/12/2015	0.25
9/13/2015	0.26
9/14/2015	0.26
9/15/2015	0.26
9/16/2015	0.26
9/17/2015	0.26
9/18/2015	0.26
9/19/2015	0.26
9/20/2015	0.26
9/21/2015	0.26
9/22/2015	0.26
9/23/2015	0.26
9/24/2015	0.26
9/25/2015	0.26
9/26/2015	0.27
9/27/2015	0.28
9/28/2015	0.28
9/29/2015	0.29
9/30/2015	0.30
10/1/2015	0.30
10/2/2015	0.31
10/3/2015	0.31
10/4/2015	0.32
10/5/2015	0.32
10/6/2015	0.33
10/7/2015	0.33
10/8/2015	0.34
10/9/2015	0.34
10/10/2015	0.35
10/11/2015	0.35
10/12/2015	0.36
10/13/2015	0.36
10/14/2015	0.37
10/15/2015	0.37
10/16/2015	0.38
10/17/2015	0.38
10/18/2015	0.39
10/19/2015	0.40
10/20/2015	0.40
10/21/2015	0.41
10/22/2015	0.42
10/23/2015	0.42
10/24/2015	0.43
10/25/2015	0.44
10/26/2015	0.44
10/27/2015	0.45
10/28/2015	0.46
10/29/2015	0.46
10/30/2015	0.47
9/14/2016	0.28
9/15/2016	0.30
9/16/2016	0.31
9/17/2016	0.27
9/18/2016	0.24
9/19/2016	0.25
9/20/2016	0.21
8/15/2017	0.28
8/16/2017	0.27

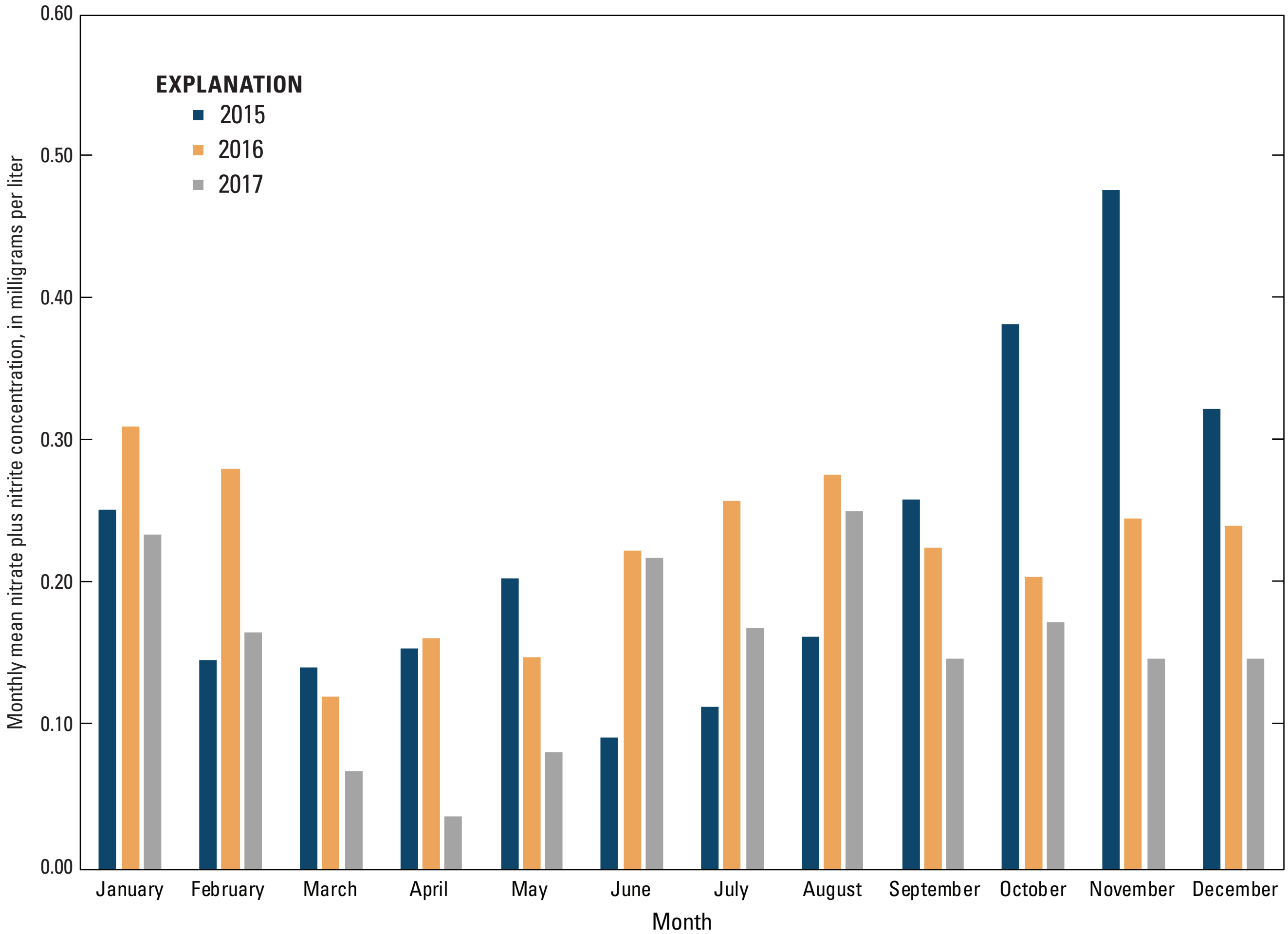

Figure 9. Monthly mean nitrate plus nitrite concentrations in samples from Caloosahatchee River at W.P. Franklin Lock and Dam, S-79, southern Florida, 2015–17.

Annual nitrate loads were 278 metric tons in 2015, 782 metric tons in 2016, and 525 metric tons in 2017 (fig. 10). The decreased annual load in 2015 can be attributed to decreased flow volume (fig. 7). Daily nitrate loads ranged from 0 on multiple dates to 15.1 metric tons on February 2, 2016. Monthly loads ranged from 1.2 metric tons in April 2017 to 171.3 metric tons in February 2016. In 2015 and 2017 the highest monthly flow volume and loads were observed in September. In 2016 the highest loads were observed in February, which corresponded with the highest flow volumes at both S-77 and S-79. Strong correlations between monthly mean flow at S-79 and monthly loads of nitrate ($r=0.889$, $p=<0.0001$), and monthly mean flow at S-77 and monthly loads of nitrate ($r=0.741$, $p=<0.0001$) were observed.

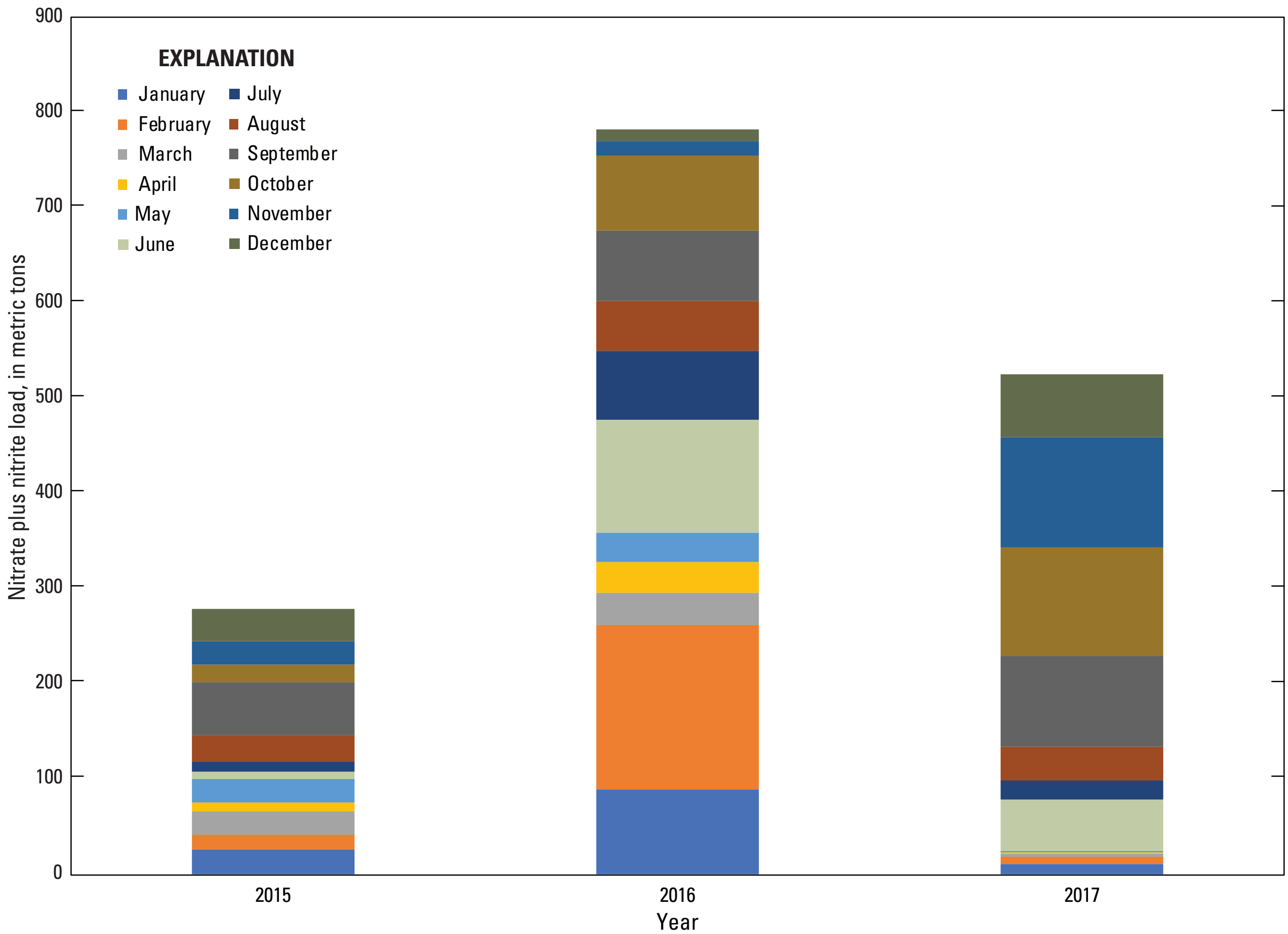

Figure 10. Annual nitrate plus nitrite loads, by month, in Caloosahatchee River, southern Florida, 2015–17.

Dissolved Organic Carbon Concentrations and Loads

Calculated concentrations of DOC ranged from 11.0 mg/L on May 6, 2017, to 22.8 mg/L on September 20, 2015 (fig. 11). The mean of the calculated DOC concentrations for the study period was 18.3 mg/L, and the median was 18.9 mg/L. All calculated concentrations were within 17 percent of laboratory-measured concentrations. DOC monthly mean concentrations ranged from 12.6 mg/L in May 2017 to 21.5 mg/L in September 2015. Generally, DOC concentrations were lower during the dry season months (November to April) and higher during the wet season (May to October). Monthly mean DOC concentrations were strongly correlated with monthly mean nitrate concentrations, ($r = 0.602$, $p=0.000$) and moderately correlated with monthly mean flow volumes at S-79 ($r=0.451$, $p=0.004$). There was a strong correlation ($r = -0.763$, $p<0.0001$) between monthly mean DOC concentrations and the monthly mean flow at S-77 divided by the monthly mean flow at S-79, which is an indicator of the percentage of water that can be directly attributed to Lake Okeechobee. As the percentage of water at S-79 that could be directly attributed to Lake Okeechobee increased, the DOC concentrations decreased, indicating that contributions received between S-77 and S-79 have a greater DOC concentration than water released from Lake Okeechobee. The annual mean DOC concentration for 2015 was 18.2 mg/L and for 2016 was 19.0 mg/L; data from 2014 and 2017 were incomplete.

Annual DOC loads were 23,960 metric tons in 2015 and 65,610 metric tons in 2016; DOC data for 2014 and 2017 were incomplete. The large difference in annual loads between 2015 and 2016 can be attributed to the difference in flow volumes (fig. 7). Daily DOC loads ranged from zero on multiple dates during the study period to 1,214 metric tons on September 11, 2017. Monthly loads of DOC ranged from 284 metric tons in May 2017 to 15,122 metric tons in September 2017, corresponding with effects from Hurricane Irma (fig. 12). The highest annual monthly loads occurred in September for 2014, 2015, and 2017, corresponding with the highest annual monthly load at S-79 (for months with DOC concentration data available). In 2016 the highest loads were observed in February, which corresponded with the highest flow volumes of the year. Strong correlations between monthly mean flow at S-79 and monthly loads of DOC ($r=0.994$, $p=<0.0001$), and monthly mean flow at S-77 and monthly loads of DOC ($r=0.656$, $p=<0.0001$) were observed.

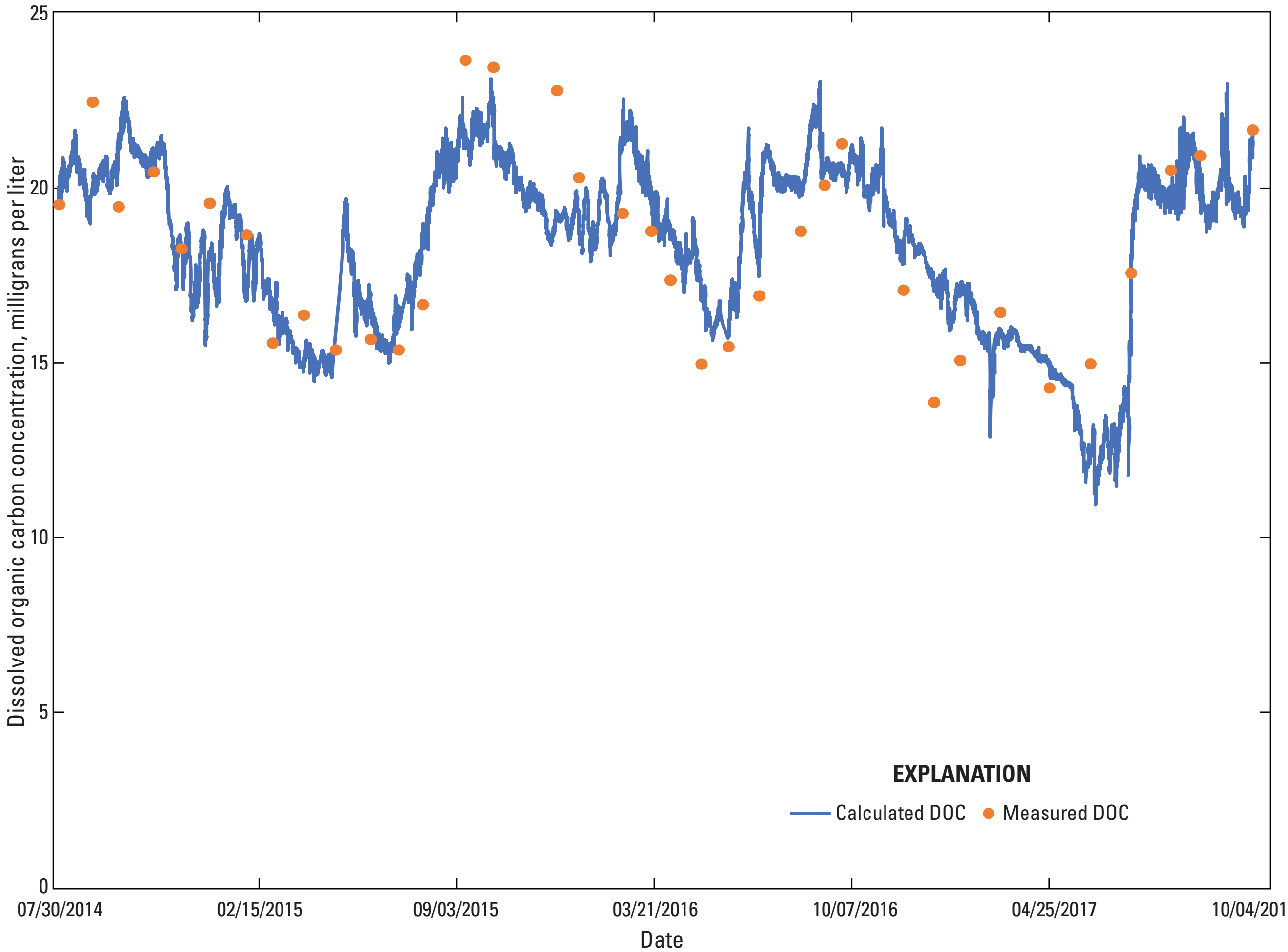

Figure 11. Calculated time series of dissolved organic carbon concentrations and measured dissolved organic carbon concentrations for Caloosahatchee River at W.P. Franklin Lock and Dam, S-79, southern Florida, 2014–17. (DOC, dissolved organic carbon)

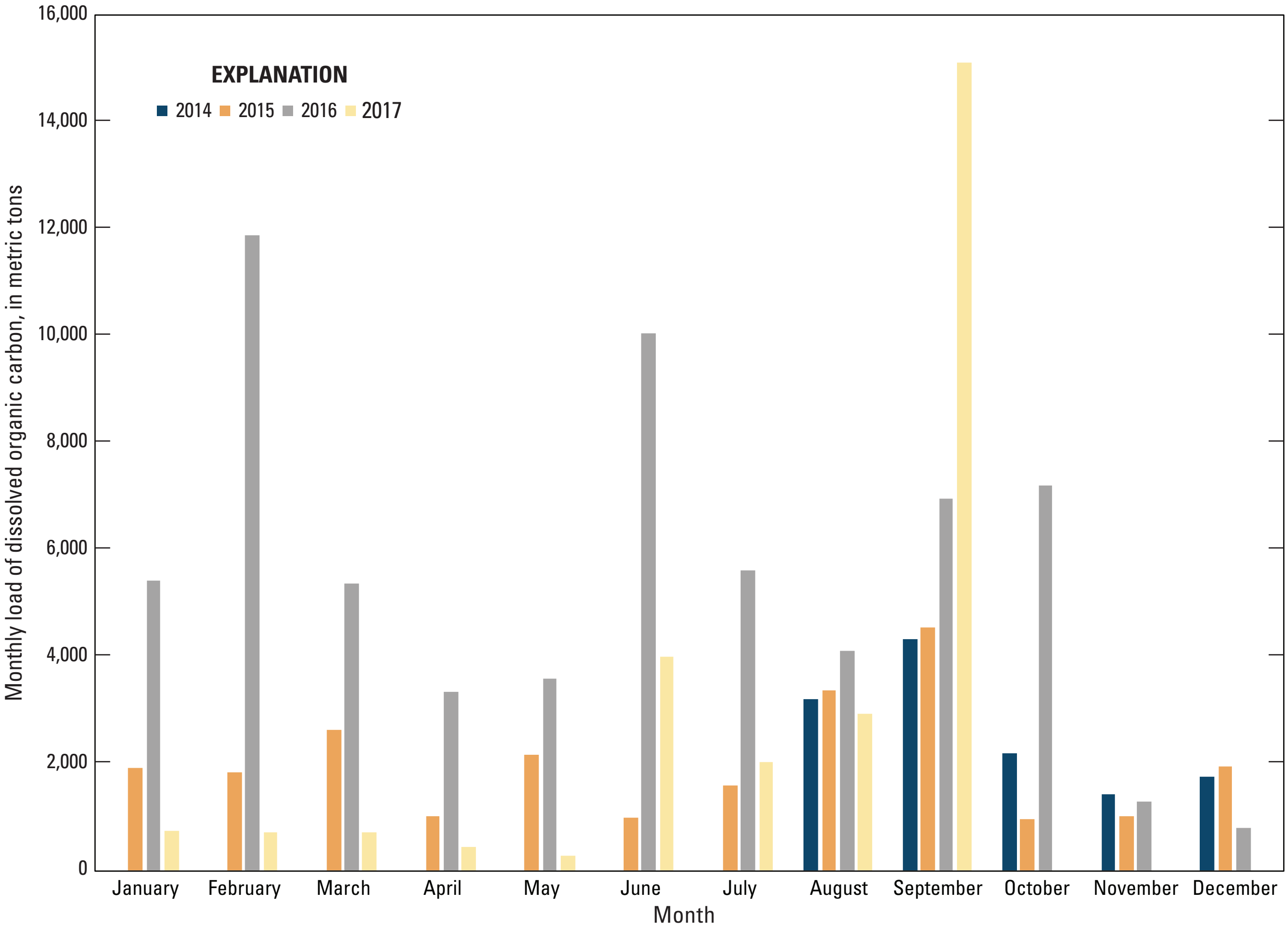

Figure 12. Monthly loads of dissolved organic carbon in Caloosahatchee River at W.P. Franklin Lock and Dam, S-79, southern Florida, 2014–17.

Summary

Lake Okeechobee has a substantial effect on the Caloosahatchee River and Estuary in southern Florida because of its connection to the Caloosahatchee River by means of the C-43 Canal. Water released from Lake Okeechobee enters the Caloosahatchee River surface-water system at Moore Haven Lock and Dam, S-77. Water released through W.P. Franklin Lock and Dam, S-79, can originate from Lake Okeechobee through S-77 or from contributions between locks S-77 and S-79. Contributions between S-77 and S-79 include rainfall, groundwater inputs, stream or canal inputs, and runoff from surrounding areas. Water-quality conditions downstream from S-79 are tidally affected. Numerous algal blooms have occurred in the tidal Caloosahatchee River and downstream estuaries in recent years. Although the causes of the blooms are complex, eutrophication is often linked to bloom formation. As such, increased nutrients and dissolved organic matter are of concern for downstream estuaries. Dissolved organic carbon (DOC) can affect estuaries by reducing light penetration, is important in food web dynamics, and is important in the transport of trace metals, such as mercury. The primary purpose of this report is to summarize seasonal and annual concentration and load data for instrument-measured nitrate plus nitrite as nitrogen (referred to as nitrate for simplicity) and DOC entering the tidal Caloosahatchee River through S-79.

Annual flow volumes at S-77 ranged from 412,632 acre-feet in 2014 to 1,797,406 acre-feet in 2016, and annual flow volumes through S-79 ranged from 933,971 acre-feet in 2014 to 2,763,241 acre-feet in 2016. Lake Okeechobee discharges (through S-77) accounted for 44 percent of the water discharged through S-79 in 2014, 54 percent in 2015, 56 percent in 2017, and 65 percent in 2016. During years with increased flow volumes at S-79, the percentage of flow from S-77 increased.

Nitrate was measured continuously (every 15 minutes) during the study period and was verified using discrete samples analyzed by the U.S. Geological Survey National Water-Quality Laboratory. Continuous nitrate concentrations ranged from 0.01 milligram per liter (mg/L) on July 27, 2017, and September 17, 2017, to 0.71 mg/L on February 2, 2016. Mean and median nitrate concentrations for the study period were 0.21 mg/L. Monthly mean nitrate concentrations ranged from 0.04 mg/L in April 2017 to 0.48 mg/L in November 2015. Correlations between monthly mean nitrate concentrations and monthly mean flow at S-77 or S-79 were not observed. A weak correlation was found between the primary source of the water (released through S-77 or from contributions between S-77 and S-79) and monthly mean nitrate concentrations, indicating that as the percentage of water that can be attributed to Lake Okeechobee increases, the nitrate concentration decreases, similar to what previous studies have documented. Annual nitrate loads were 278 metric tons in 2015, 782 metric tons in 2016, and 525 metric tons in 2017. Monthly loads ranged from 1.2 metric tons in April 2017 to 171.3 metric tons in February 2016. Correlations were strong between monthly mean flow at S-79 and monthly loads of nitrate at S-79, and monthly mean flow at S-77 and monthly loads of nitrate at S-79.

A surrogate model based on 36 concurrent measurements of DOC, fluorescence of chromophoric dissolved organic matter, and specific conductance samples collected from July 31, 2014, to October 4, 2017, was developed to calculate DOC concentrations at 15-minute intervals. Calculated concentrations of DOC ranged from 11.0 mg/L on May 6, 2017, to 22.8 mg/L on September 20, 2015. Mean and median DOC concentrations for the study period were 18.3 mg/L and 18.9 mg/L, respectively. Monthly mean concentrations of DOC ranged from 12.6 mg/L in May 2017 to 21.5 mg/L in September 2015. Generally, DOC concentrations were lower during the dry season months (November to April) and higher during the wet season (May to October). Monthly mean DOC concentrations were strongly correlated with monthly mean nitrate concentrations and moderately correlated with monthly mean flow rates at S-79. As the percentage of water that was released at S-77 increased compared to water released from S-79, the DOC concentrations decreased, indicating that contributions between S-77 and S-79 (that is, basin runoff water) had higher DOC concentrations than water released from Lake Okeechobee (strong correlation). Annual loads of DOC were 23,960 metric tons in 2015 and 65,610 metric tons in 2016; data from 2014 and 2017 were incomplete. Monthly DOC loads ranged from 284 metric tons in May 2017 to 15,122 metric tons in September 2017, corresponding with effects from Hurricane Irma. DOC loads increased linearly with an increase in flow and typically increased during the wet season. Strong correlations between monthly mean flow at S-79 and monthly loads of DOC, and monthly mean flow at S-77 and monthly loads of DOC were observed.

Acknowledgments

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References Cited

Aiken, G.R., Gilmour, C.C., Krabbenhoft, D.P., and Orem, W., 2011, Dissolved organic matter in the Florida Everglades—Implications for ecosystem restoration: Critical Reviews in Environmental Science and Technology, v. 41, p. 217–248, accessed December 1, 2018, at https://www.tandfonline.com/doi/full/10.1080/10643389.2010.530934.

Antonini, G.A., Fann, D.A., and Roat, P., 2002, A historical geography of southwest Florida waterways, volume two, Placida Harbor to Marco Island, Florida, Sea Grant SGEB56, accessed January 30, 2019, at http://www.wcind.net/wp-content/uploads/2013/05/Historical-Geography-of-SW-Florida-Vol.-Two.pdf

Bailey, N, Magley, W., Mandrup-Poulsen, J. O'Donnell, K., Peets, R., 2009, Final TMDL report, nutrient TMDL for the Caloosahatchee Estuary (WBIDS 3240A, 3240B, and 3240C): Florida Department of Environmental Protection, accessed February 24, 2020, at https://floridadep.gov/sites/default/files/tidal-caloosa-nutr-tmdl_0.pdf.

Bergamaschi, B.A., Krabbenhoft, D.P., Aiken, G.R., Patino, E., Rumbold, D.G., Orem, W.H., 2012, Tidally driven export of dissolved organic carbon, total mercury, and methylmercury from a mangrove-dominated estuary: Environmental Science and Technology, v. 46, no. 3, p. 1,371–1,378, accessed January 31, 2019, at http://pubs.acs.org/doi/abs/10.1021/es2029137.

Booth, A.C., Soderqvist, L.E., and Knight, T.M., 2016, Effects of variations in flow characteristics through W.P. Franklin Lock and Dam on downstream water quality in the Caloosahatchee River Estuary and in McIntyre Creek in the J.N. "Ding" Darling National Wildlife Refuge, southern Florida, 2010–13: U.S. Geological Survey Scientific Investigations Report 2016–5033, 33 p., accessed January 30, 2019, at http://dx.doi.org/10.3133/sir20165033.

Booth, A. 2020, Calculated carbon concentrations, Franklin Lock and Dam (S-79), southern Florida, 2014–2017: U.S. Geological Survey data release, https://doi.org/10.5066/P9V4ZGWU.

Brand, L.W., and Compton, A., 2007, Long-term increase in *Karenia brevis* abundance along the Southwest Florida Coast: Harmful Algae, v. 6, no. 2, p. 232–252, accessed January 30, 2019 at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2330169/.

Cuevas, M., 2016, Toxic algae bloom blankets Florida beaches, prompts state of emergency: Cable News Network, July 1, 2016, accessed January 31, 2019, at http://www.cnn.com/2016/07/01/us/florida-algae-pollution.

Curtis, P.J., and Adams, H.E., 1995, Dissolved organic matter quantity and quality from freshwater and saltwater lakes in east-central Alberta: Biogeochemistry, v. 30, p. 59–76, accessed January 28, 2019 at https://www.jstor.org/stable/1468929?seq=1#metadata_info_tab_contents.

Doering, P.H., and Chamberlain, R.H., 1999, Water quality and source of freshwater discharge to the Caloosahatchee Estuary, Florida: Journal of the American Water Resources Association, v. 35, no. 4, p. 793–806, accessed January 28, 2019 at https://onlinelibrary.wiley.com/doi/pdf/10.1111/j.1752-1688.1999.tb04175.x.

Downing, B.D., Pellerin, B.A., Bergamaschi, B.A., Saraceno, J.F., and Kraus, T. E., 2012, Seeing the light—The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams: Limnology and Oceanography—Methods, v. 10, no. 10, p. 767–775, accessed January 12, 2019, at https://aslopubs.onlinelibrary.wiley.com/doi/10.4319/lom.2012.10.767.

Evans, J. D., 1996, Straightforward statistics for the behavioral sciences: Pacific Grove, Calif,: Brooks/Cole Publishing.

Florida Department of Environmental Protection, 2001, Total maximum daily load for total phosphorous Lake Okeechobee, Florida, prepared by the Florida Department of Environmental Protection, accessed January 30, 2019 at https://floridadep.gov/sites/default/files/Lake_O_TMDL_Final.pdf.

Havens, K.E., Hanlon, C., and James, R.T., 1995, Seasonal and spatial variation in algal bloom frequencies in Lake Okeechobee, Florida, USA: Lake and Reservoir Management, v. 10, p. 139–148, accessed February 24, 2020 at https://www.tandfonline.com/doi/abs/10.1080/07438149409354185.

Heisler, J., Glibert, P.M., Burkholder, J.M., Anderson, D.M., and Cochlan, W., 2008, Eutrophication and harmful algal blooms—A scientific consensus: Harmful Algae, v. 8, p. 3–13, accessed February 24, 2020 at https://www.sciencedirect.com/science/article/pii/S1568988308001066.

Julian, P., and Osborne, T.Z., 2018, From lake to estuary, the tale of two waters—a study of aquatic continuum biogeochemistry: Environmental Monitoring Assessment, v. 190, p. 96, accessed May 1, 2020 at https://link.springer.com/article/10.1007/s10661-017-6455-8.

Lee County, 2017, Rain gauge data: Lee County, Florida, accessed May 2, 2017, at http://www.leegov.com/naturalresources/hydrological-monitoring/rainfall/raingaugedata.

Levesque, V.A., and Oberg, K.A., 2012, Computing discharge using the index velocity method: U.S. Geological Survey Techniques and Methods 3–A23, 148 p., accessed May 1, 2017 at https://pubs.usgs.gov/tm/3a23/.

Monteiro, M.T., Oliveira, S.M., Luizao, F.J., Candido, L.A., Ishida, F.Y., and Tomasella, J., 2014, Dissolved organic carbon concentration and its relationship to electrical conductivity in the waters of a stream in forested Amazonian blackwater catchment: Plant Ecology and Diversity, v. 7, accessed January 31, 2019, at https://doi.org/10.1080/17550874.2013.820223.

Pearson, L.A., Dittmann, E., Mazmouz, R., Ongley, S.E., D’Agostino, P.M., and Neilan, B.A., 2016, The genetics, biosynthesis and regulation of toxic specialized metabolites of cyanobacteria: Harmful Algae, v. 54, p. 98–111, accessed January 31, 2019 at https://www.sciencedirect.com/science/article/pii/S1568988315301517.

Pellerin, B.A, Saraceno J.F., Shanley, J.B, Sebestyen, S.D., Aiken, G.R., Wollheim, G.R., and Bergamaschi, B.A., 2012, Taking the pulse of snowmelt—in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream: Biogeochemistry, v. 108, p. 183–198, accessed January 31, 2019, at https://doi.org/10.1007/s10533-011-9589-8.

Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Saraceno, J.F., Garrett, J.A., and Olsen, L.D., 2013, Optical techniques for the determination of nitrate in environmental waters—Guidelines for instrument selection, operation, deployment, maintenance, quality assurance, and data reporting: U.S. Geological Survey Techniques and Methods 1–D5, 37 p, accessed October 1, 2017, at https://pubs.usgs.gov/tm/01/d5/.

Rasmussen, P.P., Gray, J.R., Glysson, G.D., and Ziegler, A.C., 2009, Guidelines and procedures for computing time-series suspended-sediment concentrations and loads from in-stream turbidity-sensor and streamflow data: U.S. Geological Survey Techniques and Methods, book 3, chap. C4, 53 p., accessed February 24, 2020, at https://doi.org/10.3133/tm3C4.

Rosen, B.H., Davis, T.W., Gobler, C.J., Kramer, B.J., and Loftin, K.A., 2017, Cyanobacteria of the 2016 Lake Okeechobee Waterway harmful algal bloom: U.S. Geological Survey Open-File Report 2017–1054, 34 p., accessed January 20, 2019, at https://doi.org/10.31333/ofr20171054.

South Florida Water Management District, 2005, The Caloosahatchee Estuary—Status and trends in water quality in the estuary and nutrient loading at the Franklin Lock and Dam, accessed May 2, 2017, at https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/2006_sfer/volume1/appendices/v1_app_12-6.pdf.

South Florida Water Management District, 2018, Lake Okeechobee Operations, accessed January 29, 2018, at https://www.sfwmd.gov/sites/default/files/documents/fyi_lakeo_responsiblities.pdf.

Spencer, R.G.M., Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Kraus, T.E.C., Smart, D.R., Dahlgren, R.A., and Hernes, P.J., 2007, Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA): Hydrological Processes, v. 21, p. 3181–3189, accessed January 28, 2109 at https://www.onlinelibrary.wiley.com/doi/abs/10.1002/hyp.6887.

U.S. Army Corps of Engineers, 2017, Background information on navigation locks, Jacksonville District: U.S. Army Corps of Engineers, accessed May 2, 2017, at http://www.saj.usace.army.mil/Missions/Civil-Works/Navigation/Navigation-Locks/.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data, Collection of Samples, vers. 2.0: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed May 2, 2017, at http://water.usgs.gov/owq/FieldManual/chapter4/html/Ch4_contents.html.

U.S. Geological Survey, 2019, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed May 8, 2019, at https://doi.org/10.5066/F7P55KJN.

Wagner, R.J., Boulger, Jr., R.W., Oblinger, C.J., and Smith, B.A., 2006, Guidelines and standard procedures for continuous water-quality monitors—Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods 1-D3, 51 p., accessed May 2, 2017, at http://pubs.usgs.gov/tm/2006/tm1D3/.

Wetland Solutions, 2005, Caloosahatchee River/Estuary nutrient issues: Gainesville, Fla., Wetland Solutions, accessed May 2, 2017, at http://crca.caloosahatchee.org/crca_docs/Caloosahatchee_Nutrient_Draft.pdf.

Yang, Y.G., He, Z.L., Wang, Y.B., Liu, Y.L., Liang, Z.B., Fan, J.H., and Stoffella, J.P., 2012, Dissolved organic carbon in association with water soluble nutrients and metals in soils from Lake Okeechobee watershed, south Florida: Water, Air, & Soil Pollution, v. 223, p. 4075–4088, accessed May 2, 2017, at https://link.springer.com/article/10.1007/s11270-012-1174-9.

Appendix 1. Model Archive Summary for Dissolved Organic Carbon Concentrations at Station 02292900: Caloosahatchee River at S-79, Nr. Olga, Florida

Water delivery to the Caloosahatchee River is highly managed and regulated by the U.S. Army Corps of Engineers through three structures S-77, S-78, and S-79. The Caloosahatchee River is directly connected to Lake Okeechobee through control structure S-77, and S-79 is the most downstream structure. Flood control, public safety, navigation, water supply, and ecological health are all important factors considered during decisions to retain water in the lake or release it to the Caloosahatchee River (South Florida Water Management District, 2018).

Increased nutrients and dissolved organic matter are of concern for downstream estuaries. Previous research demonstrated that salinity and fluorescence of chromophoric dissolved organic matter (fDOM) concentrations within the lower portions of the estuary are affected by the release of water through S-79 (Booth and others, 2016).

Dissolved organic carbon (DOC) plays many roles in estuarine dynamics in addition to its role in global carbon cycling. Organic carbon is a carrier of large quantities of carbon, nitrogen, and phosphorus to estuarine waters; it can affect estuaries by reducing light penetration and is important in food web dynamics and transport of trace metals, such as mercury (Aiken and others, 2011). DOC in Lake Okeechobee basin soils has been positively correlated with nitrogen, phosphorous, and heavy metals (cobalt, chromium, nickel, and zinc; Yang and others, 2012).

This model archive summary describes the DOC model developed to calculate 15-minute DOC concentrations from July 31, 2014, to October 4, 2017, at the Caloosahatchee River at S-79. The model data are disseminated as a data release that accompanies this report (Booth, 2020).

Site and Model Information

USGS Site number: 02292900

https://waterdata.usgs.gov/fl/nwis/inventory/?site_no=02292900&agency_cd=USGS&

Site name: Caloosahatchee River at S-79, Nr. Olga, Florida

Location: Lat 26°43’17”, long 81°41’36” referenced to North American Datum of 1927, in SW. 1/4 sec.23, T.43 S., R.26 E., Lee County, FLA, Hydrologic Unit 03090205, in control house at southeast end of lock at salinity-control structure 79, 1 mile (mi) upstream from Telegraph Creek, and 1.2 mi northeast of Olga.

Equipment: The water-quality station is on the right bank on the South Florida Water Management District platform approximately 600 feet (ft) upstream from the lock structure. A YSI EXO2 water-quality monitor equipped with sensors for water temperature, specific conductance (SC), turbidity, and a fDOM sensor. The monitor is housed in an 8-inch-diameter polyvinyl chloride pipe on a diagonal off the end of the structure into the stream. Readings from the YSI EXO were recorded every 15 minutes and transmitted by way of satellite, hourly. The model applies only to this site (02292900) and specified time period (July 31, 2014, to October 4, 2017).

Model number: 1.0

Date model was created: April 20, 2018

Model calibration data period: July 31, 2014, to October 4, 2017

Model application date: July 31, 2014, to October 4, 2017

Computed by: Amanda Booth, U.S. Geological Survey (USGS), Caribbean-Florida Water Science Center

Reviewed by: M. Stone and T. Rasmussen, USGS Kansas Water Science Center, Lawrence, Kansas

Approved by: D. Sumner, USGS, Caribbean-Florida Water Science Center

Model Data

All data were collected using USGS protocols and are stored in the National Water Information System (NWIS) database (U.S. Geological Survey, 2019). fDOM data were corrected for temperature, turbidity, and inner filter effects (Downing and others, 2012). The regression model is based on 36 concurrent DOC samples, fDOM measurements and SC measurements collected during July 31, 2014 through October 4, 2017. DOC samples were collected throughout the range of observed hydrologic and water-quality conditions. Summary statistics and the complete model-calibration data are provided in the dataset. Studentized residuals from the final model were inspected for values greater than 3 or less than negative 3 to identify potential outliers. Using the Studentized residuals criterion, no outliers were found within the dataset. One observation was flagged on the basis of Leverage, Cook’s distance (Cook’s D) and difference in fits (DFFITS) criteria, but all samples were retained in the dataset.

Dissolved Organic Carbon Data

Discrete samples were collected near the sensors, filtered through a 0.45-micron capsule filter into amber glass 2-liter bottles within 15 minutes of being collected and stored immediately on ice as described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S.

Geological Survey, variously dated). Samples used in model development were analyzed for DOC by the USGS NWQL. Laboratory replicates were collected on July 23, 2015, February 25, 2016, May 3, 2017, and October 4, 2017. Blank samples were collected on February 25, 2016 and June 12, 2017.

Replicate pairs compared within 0.2 milligrams per liter (mg/L). Relative percent differences from the replicate samples ranged from -1 to 1 percent and averaged -0.1 percent. Blank samples were run for station 02292900 twice during the study period. On February 25, 2016, the blank concentration of DOC was less than the detection level of 0.23 mg/L, and on June 12, 2017, the blank DOC concentration was 0.59 mg/L.

Surrogate Data

The fDOM data used in this analysis were measured using a YSI EXO V2, serial numbers 12h101755, 13f100955, 14c100465, 14c100466, 14c100474, 15G100778, 15G100779 and 15C104523. fDOM data were corrected for temperature, turbidity, and inner filter effects (Downing and others, 2012). Equations for turbidity corrections were provided by B. Pellerin (USGS, written commun., 2017) and determined using YSI EXO V2, temperature, turbidity and fDOM sensors. The equation is provided below.

Elliot Silt Loam turbidity correction – exponential fit (table curve) (RFU Turb CorrE):

$$fDOM_{turbcorr} = \frac{fDOM_{tempcorr}}{e^{(-0.027567-0.006259 \bullet FNU)}}$$

where

$fDOM_{tempcorr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature corrected, in parts per billion quinine sulfate equivalent (QSE).

$fDOM_{turbcorr}$ = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature and turbidity corrected, in parts per billion quinine sulfate equivalent (QSE).

FNU = Turbidity, YSI EXO V2, formazin nepholemtric units.

Serial dilutions were performed to determine the inner filter effect using Caloosahatchee River at S-79 (station 02292900) native water, filtered through a 0.45-micron filter, and collected on August 16, 2017. Water-quality sensors were inspected for fouling approximately every 4 weeks, and calibration verifications were performed every 8 weeks. Drift and fouling corrections were determined and applied on the basis of formulas provided in Wagner and others (2006). Drift and fouling corrections were applied when the instrument was more than 5 percent from the standard value for fDOM and more than 3 percent for SC.

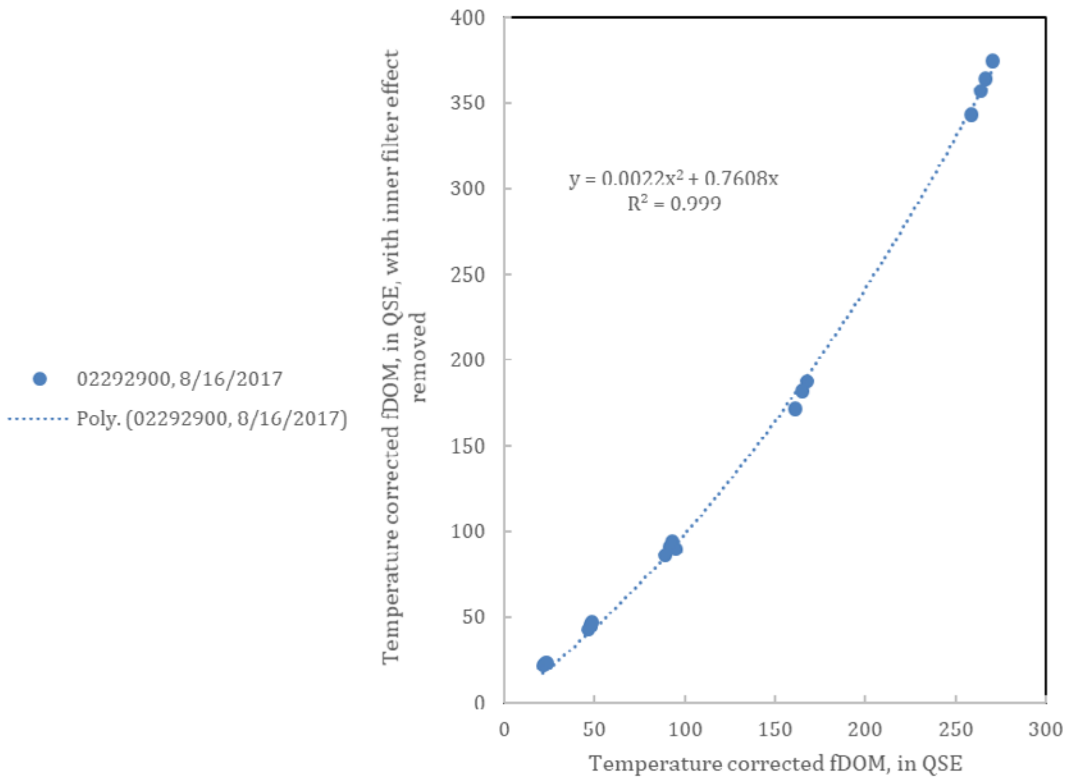


Figure 1-1. Relationship between temperature corrected fDOM, with the inner filter effect removed and temperature corrected fDOM, QSE without the inner filter effect removed. The dashed blue line is the fit of all data using a second-order polynomial function. (fDOM, fluorescence of chromophoric dissolved organic matter; QSE, quinine sulfate equivalent; Poly, polynomial regression)

fDOM values at S-79 ranged from 132.1 parts per billion quinine sulfate equivalent (QSE) on April 5, 2017, to 470.1 QSE on November 3, 2014. SC at S-79 ranged from 181 microsiemens per centimeter at 25 degrees Celsius (µS/cm) on September 13, 2017, to 745 µS/cm on May 6, 2017.

Vertical profiles of water-quality sensor data at six locations were recorded across the sampling cross section to describe vertical and horizontal stratification within the channel. A depth-integrated profile was recorded at the station, 500 feet upstream from the lock chamber, and 500 feet upstream from the mid-section of each gate. To ensure data comparability between cross-sectional profiles and site monitor readings, the same calibration verifications for the profile meter were used as for the site monitor sensors. A total of 12 cross-sectional profiles were made between July 23, 2014, and June 12, 2017. Raw fDOM values were used for comparison (meaning no corrections were applied for temperature, turbidity or inner filter effect). The purpose of these raw data comparisons was to verify whether the single location represented by the time-series data was representative of the channel as a whole. The data collected during the six vertical profiles were averaged to represent the mean channel conditions on that date. In-situ measurements were representative of the stream cross section: fDOM and SC profile averages compared within 10 percent and 5 percent, respectively, of site monitor readings. The assumption was made that the station data were representative of the mean channel under most conditions; therefore, no corrections for cross-sectional representativeness were applied.

Model Development

Regression analysis was done using Microsoft Excel XLstat add-in package, by examining fDOM and other continuously measured data as explanatory variables for estimating DOC concentration. A variety of models that predict DOC were evaluated. The distribution of residuals was examined for normality. Residuals (the difference between the observed and calculated values) were compared to calculated DOC and examined for homoscedasticity. fDOM and SC were selected as the best predictors of DOC on the basis of residual plots, relatively high adjusted coefficient of determination (adjusted R^2), and relatively low model standard percentage error (MSPE).

Model Summary

Summary of final regression analysis for DOC concentration at station 02292900.

Dissolved organ carbon concentration-based model:

$$\text{DOC} = -0.0132(SC) + 0.0285(fDOM) + 16.2,$$

where

DOC = dissolved organic carbon concentration, in milligrams per liter;

SC= specific conductance in μS/cm at 25 degrees Celsius; and

fDOM = fluorescence of chromophoric dissolved organic matter, YSI EXO V2, temperature, turbidity and inner filter effect corrected, in parts per billion quinine sulfate equivalent (QSE).

The use of fDOM as an explanatory variable is appropriate physically and statistically because fDOM represents the fraction of chromophoric dissolved organic matter that fluoresces and is often used as a surrogate for DOC (Spencer and others, 2007; Pellerin and others, 2012; Bergamaschi and others, 2012). The use of specific conductance as a variable is also supported statistically and within the literature (Curtis and Adams, 1995; Monteiro and others, 2014).

Model Statistics, Data, and Plots

Model

DOC = - 0.0132 * SC + 0.0285 * fDOM + 16.2

Variable Summary Statistics

	DOC	SC	fDOM
Minimum	13.9	297	143
1st Quartile	15.6	399	202
Median	18.5	422	279
Mean	18.3	433	276
3rd Quartile	20.4	478	337
Maximum	23.5	599	417

Exploratory Plots

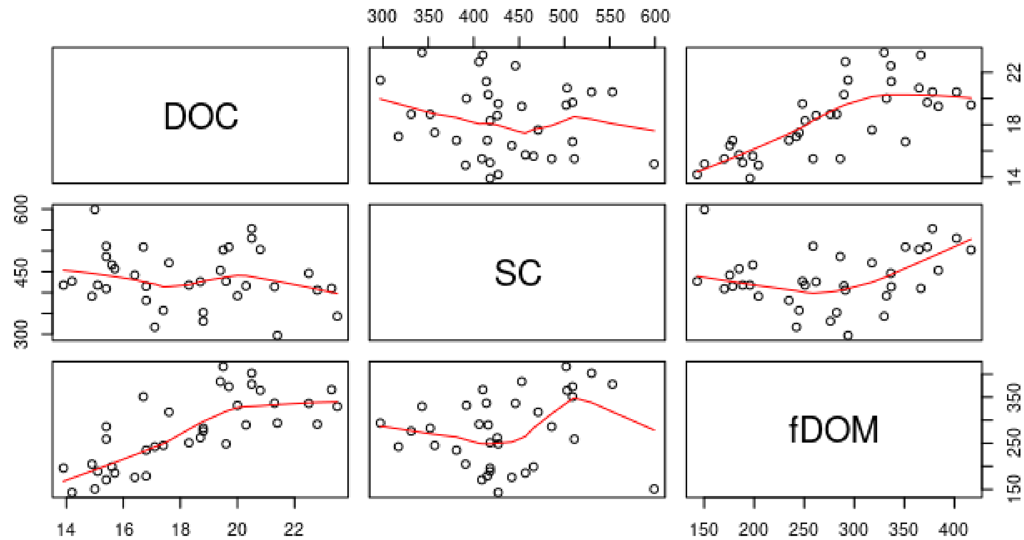


Figure 1-2. Comparison of dissolved organic carbon concentrations, in milligrams per liter; specific conductance, in microsiemens per centimeter at 25 degrees Celsius; and fluorescence of chromophoric dissolved organic matter, in parts per billion quinine sulfate equivalent.

(DOC, dissolved organic carbon; fDOM, fluorescence of chromophoric dissolved organic matter; SC, specific conductance)

Basic Model Statistics

```
Number of Observations                                36
Standard error                                      1.66
Average Model standard percentage error (MSPE)      9.05
Coefficient of determination (R²)              0.651
Adjusted Coefficient of Determination (Adj. R²)  0.63
```

```
Variance Inflation Factors (VIF)
 SC fDOM
1.04 1.04
```

Explanatory Variables

	Coefficients	Standard Error	t value	Pr(>|t|)
(Intercept)	16.2000	1.94000	8.33	1.28e-09
SC	-0.0132	0.00426	-3.11	3.87e-03
fDOM	0.0285	0.00371	7.68	7.59e-09

Correlation Matrix

	Intercept	SC	fDOM
Intercept	1.000	-0.844	-0.336
SC	-0.844	1.000	-0.201
fDOM	-0.336	-0.201	1.000

Outlier Test Criteria

Leverage	Cook's D	DFFITS
0.250	0.262	0.577

Flagged Observations

	DOC	Estimate	Residual	Standard Residual	Studentized Residual	Leverage	Cook's D	DFFITS
05/03/2017 10:30	15	12.5	2.46	1.82	1.89	0.336	0.562	1.35

The DOC concentration on May 3, 2017, was flagged as a potential outlier, owing to elevated leverage, Cook's D, and DFFITS. All flagged observations were included in model development.

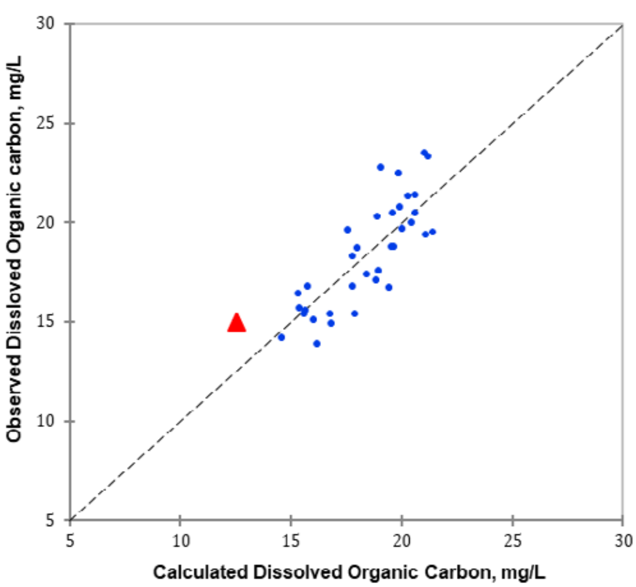


Figure 1-3. Relation between observed dissolved organic carbon and calculated dissolved organic carbon. Flagged observations are highlighted in red.

Statistical Plots

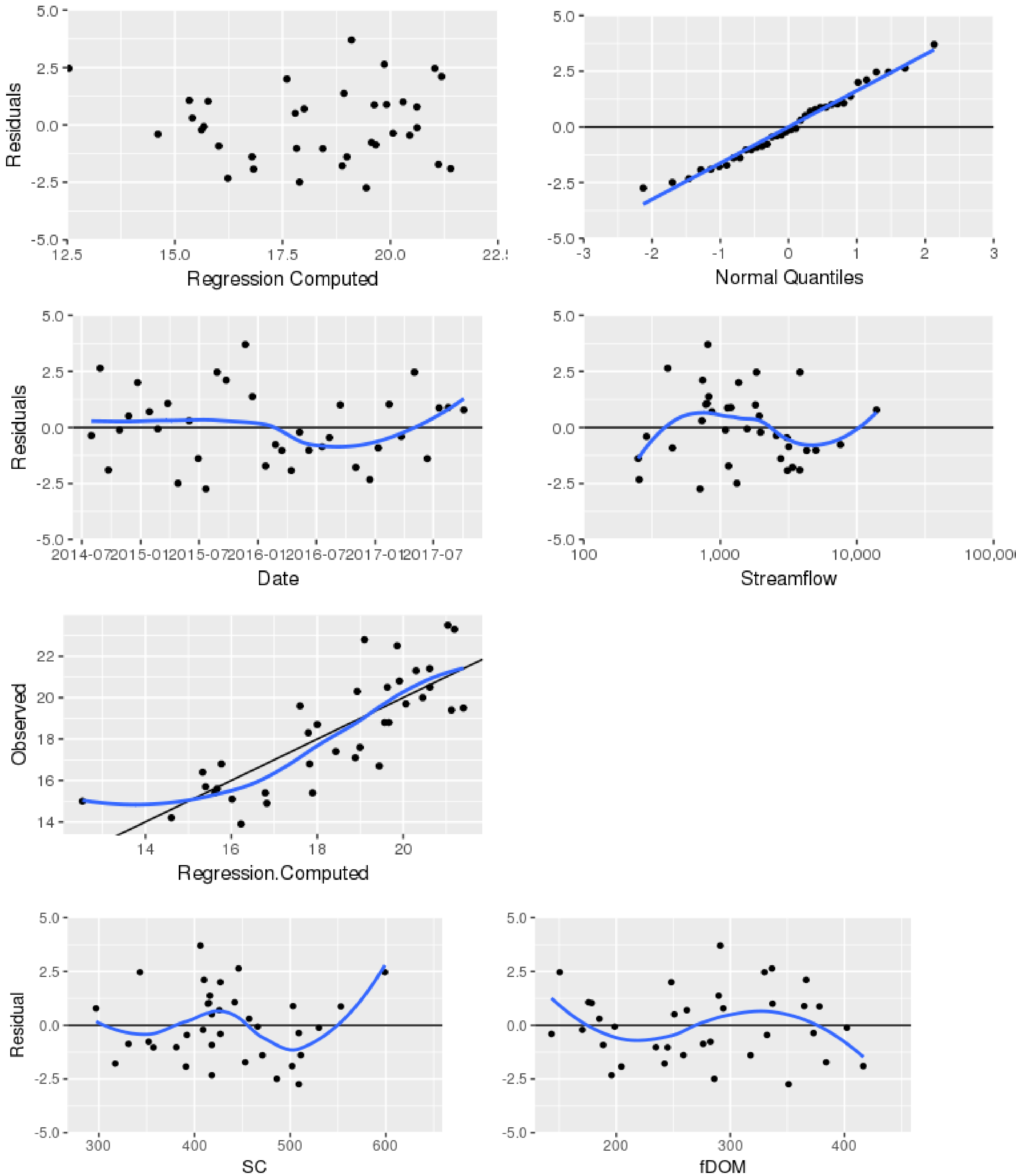


Figure 1-4. Residual and observed values versus calculated values. (SC, specific conductance; fDOM, fluorescence of chromophoric dissolved organic matter)

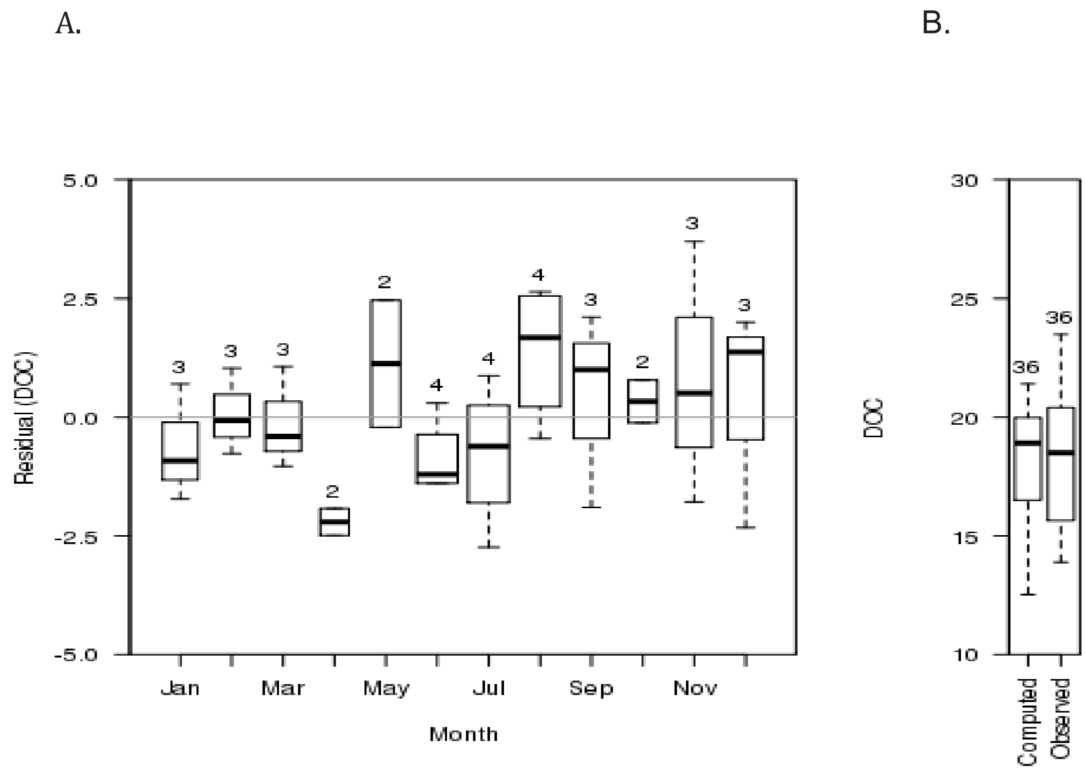


Figure 1-5. A, Seasonal variation in residuals, and B, computed and observed DOC, in milligrams per liter. (DOC, dissolved organic carbon)

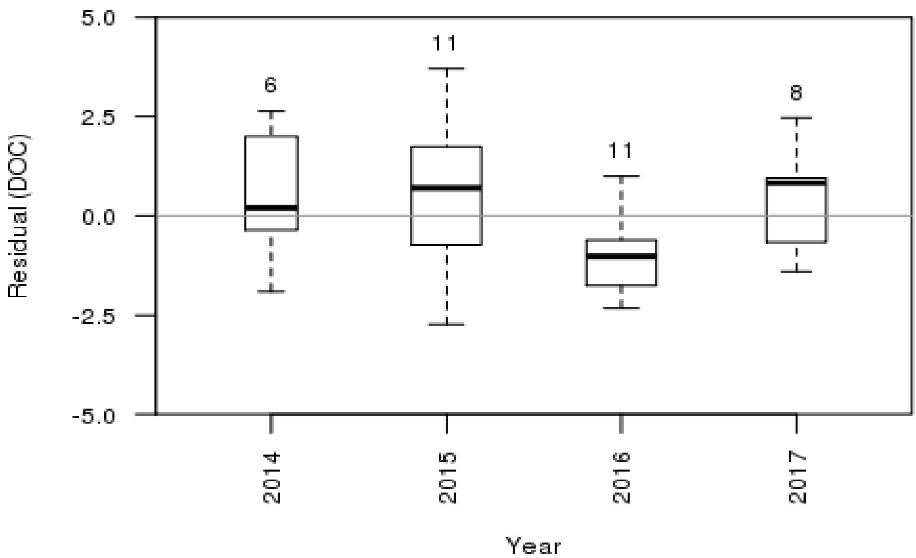
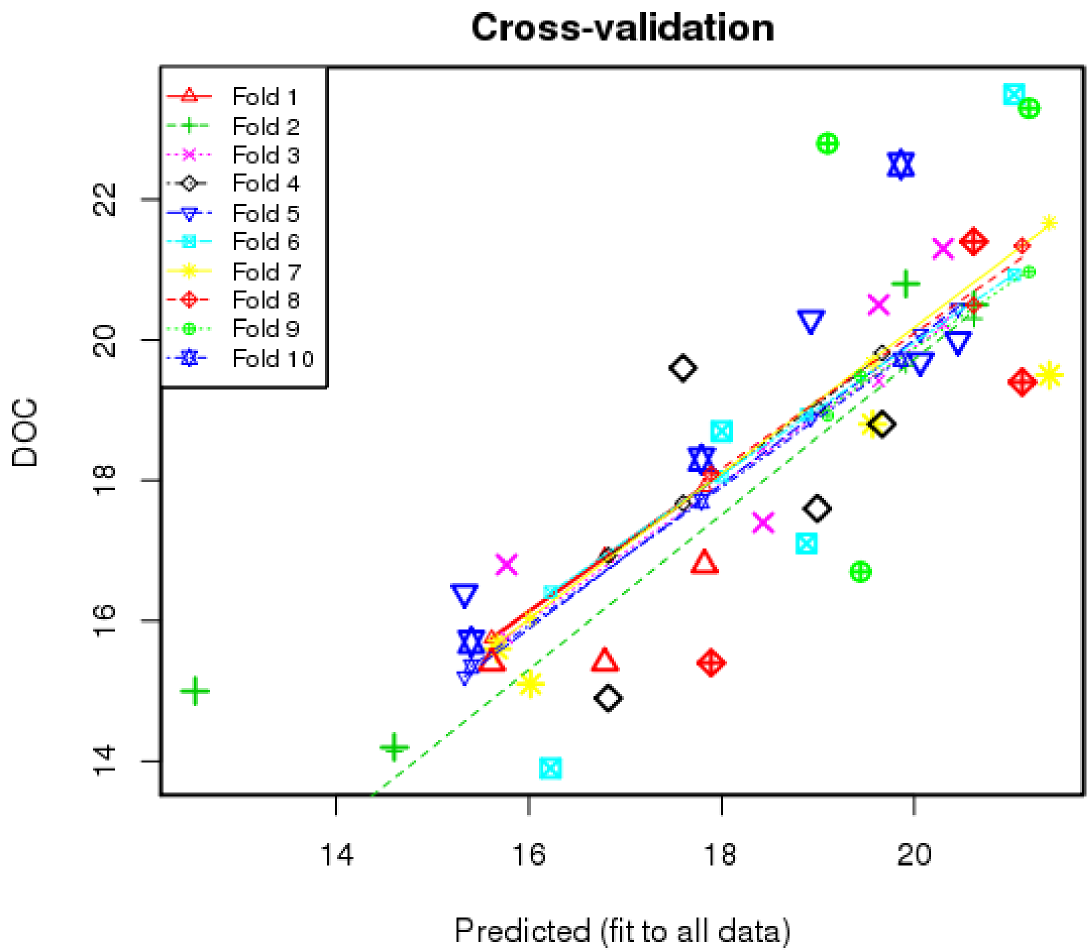


Figure 1-6. Annual variation in residuals of DOC.

(DOC, dissolved organic carbon)

Cross Validation

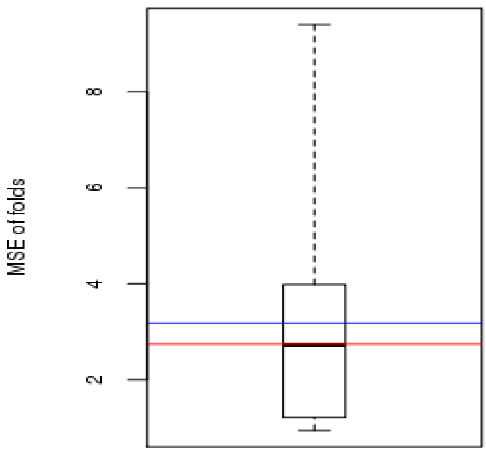
K-fold cross-validation was used to validate the model. The advantage of K-fold cross validation is that all the examples in the dataset are eventually used for training and testing. The data were split randomly into 10 experiments or folds.




```
               Minimum MSE of folds:  0.944
                  Mean MSE of folds:  3.180
                Median MSE of folds:  2.730
               Maximum MSE of folds:  9.400
(Mean MSE of folds) / (Model MSE):  1.160
```

Figure 1-7. Cross validation of dissolved organic carbon.

(DOC, dissolved organic carbon; MSE, mean standard error)



Red line - Model MSE

Blue line - Mean MSE of folds

Figure 1-8. Boxplot showing mean standard error of folds.

(MSE, mean standard error)

Model-Calibration Data Set

	Date	DOC	SC	fDOM	Calculated DOC	Residual	Normal Quantiles	Censored Values
0								
1	2014-07-31	19.7	509	373	20.1	-0.364	-0.104	--
2	2014-08-27	22.5	446	336	19.9	2.64	1.7	--
3	2014-09-22	19.5	502	417	21.4	-1.9	-1.14	--
4	2014-10-27	20.5	530	402	20.6	-0.12	0.0346	--
5	2014-11-24	18.3	418	251	17.8	0.508	0.245	--
6	2014-12-22	19.6	427	248	17.6	2	1.02	--
7	2015-01-28	18.7	426	262	18	0.7	0.317	--
8	2015-02-23	15.6	466	199	15.7	-0.0695	0.104	--
9	2015-03-26	16.4	442	176	15.3	1.07	0.807	--
10	2015-04-27	15.4	486	286	17.9	-2.49	-1.7	--

11	2015-06-01	15.7	457	185	15.4	0.299	0.174	--
12	2015-06-29	15.4	511	259	16.8	-1.39	-0.714	--
13	2015-07-23	16.7	509	351	19.4	-2.74	-2.13	--
14	2015-08-27	23.5	343	330	21	2.46	1.28	--
15	2015-09-24	23.3	410	366	21.2	2.11	1.14	--
16	2015-11-23	22.8	406	291	19.1	3.7	2.13	--
17	2015-12-15	20.3	416	290	18.9	1.37	0.907	--
18	2016-01-25	19.4	453	384	21.1	-1.72	-0.907	--
19	2016-02-25	18.8	352	282	19.6	-0.766	-0.317	--
20	2016-03-16	17.4	357	245	18.4	-1.03	-0.627	--
21	2016-04-14	14.9	391	204	16.8	-1.92	-1.28	--
22	2016-05-10	15.4	409	170	15.6	-0.215	-0.0346	--
23	2016-06-08	16.8	381	235	17.8	-1.02	-0.545	--
24	2016-07-19	18.8	331	276	19.7	-0.865	-0.391	--
25	2016-08-11	20	392	332	20.5	-0.453	-0.245	--
26	2016-09-14	21.3	414	337	20.3	1	0.627	--
27	2016-11-01	17.1	317	242	18.9	-1.78	-1.02	--
28	2016-12-15	13.9	418	196	16.2	-2.33	-1.46	--
29	2017-01-10	15.1	418	189	16	-0.917	-0.466	--
30	2017-02-13	16.8	415	178	15.8	1.03	0.714	--
31	2017-03-23	14.2	427	143	14.6	-0.404	-0.174	--
32	2017-05-03	15	599	150	12.5	2.46	1.46	--
33	2017-06-12	17.6	471	318	19	-1.39	-0.807	--
34	2017-07-19	20.5	553	378	19.6	0.871	0.466	--
35	2017-08-16	20.8	503	365	19.9	0.888	0.545	--
36	2017-10-04	21.4	297	294	20.6	0.784	0.391	--

Model Limitations

Errors in the DOC surrogate model can be attributed to several factors, including those related to fDOM and specific conductance data. There is error associated in the calibration of the standards, and corrections were applied only when the instrument value was more than 5 percent from the standard value for fDOM and 3 percent for specific conductance. Additionally, corrections for turbidity and inner filter effects may change over time on the basis of the size and makeup of the sediment and organic matter. Although the influence of turbidity on fDOM at this location is small, the change in the inner filter effect on fDOM is potentially substantial. After Hurricane Irma in September 2017, the inner filter effect changed substantially at the Caloosahatchee River at S-79 (02292900), figure 1-9, indicating that variations are possible at this location as well. Unfortunately, changes in the inner filter effect were not monitored throughout this study.

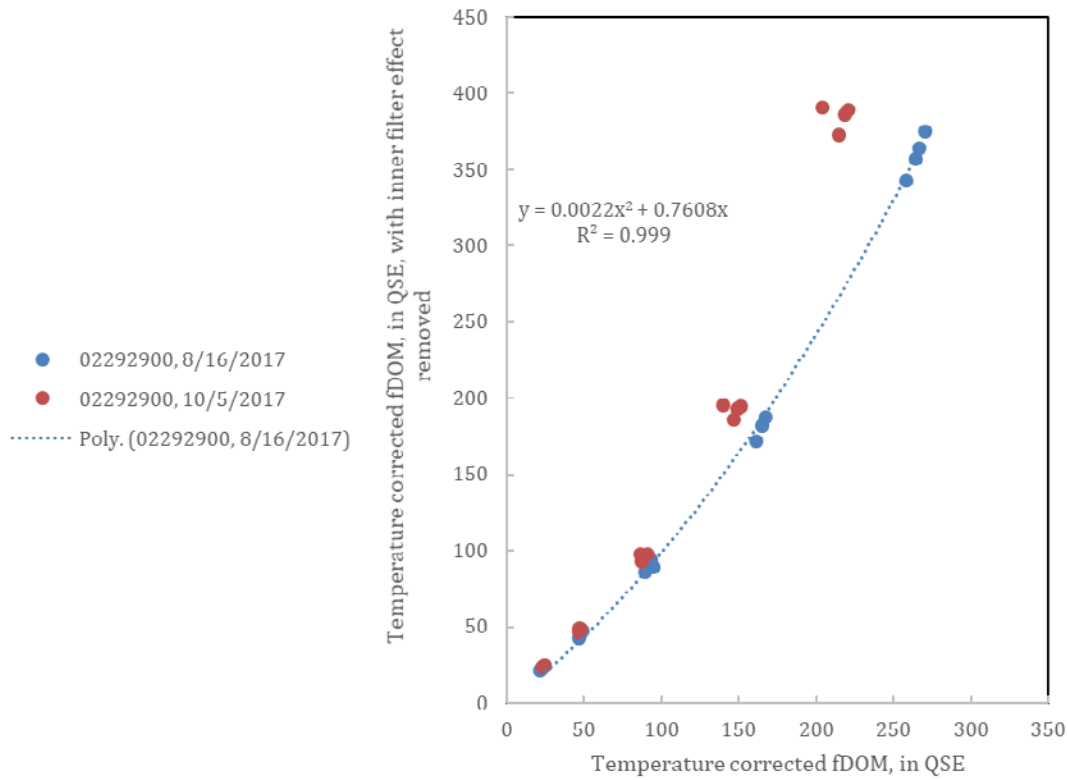


Figure 1-9. Relation between temperature corrected fDOM, with the inner filter effect removed and temperature corrected fDOM, QSE without the inner filter effect removed. The dashed blue line is the fit of all data using a second-order polynomial function. (fDOM, QSE, fluorescence of dissolved organic matter, in quinine sulfate equivalent; poly., Poly, polynomial regression)

The model was developed using only 36 samples and included 2 variables; therefore, one of the limitations is the possibility that the model is overfitted. Another limitation to this model is in the assumption that the discrete data collected at the station are representative of the mean channel. In-situ measurements were representative of the stream cross-section: fDOM and specific conductance profile averages compared within 10 percent and 5 percent, respectively, to site monitor readings; however, width- and depth-integrated DOC samples were not collected for this study.

An additional source of model error is from discrete data analysis. Although all replicates were within 0.2 mg/L or 1 percent, one blank had detectable DOC. The highest detectable concentrations of DOC in a blank for station 02292900 was 0.6 mg/L, which is 4 percent of the lowest concentration in a sample collected during the study (13.9 mg/L DOC on December 15, 2016).

Definitions

```
DOC: Dissolved organic carbon in mg/L (00681)
SC: Specific conductance in µS/cm at 25 degrees Celsius (00095)
fDOM: Colored dissolved organic matter in µg/L quinine sulfate equivalent (32295)
```

App Version 1.0

References Cited

Aiken, G.R., Gilmour, C.C., Krabbenhoft, D.P., and Orem, W., 2011, Dissolved organic matter in the Florida Everglades—Implications for ecosystem restoration: Critical Reviews in Environmental Science and Technology, v. 41, p. 217–248, accessed December 1, 2018, at https://www.tandfonline.com/doi/full/10.1080/10643389.2010.530934.

Booth, A.C., Soderqvist, L.E., and Knight, T.M., 2016, Effects of variations in flow characteristics through W.P. Franklin Lock and Dam on downstream water quality in the Caloosahatchee River Estuary and in McIntyre Creek in the J.N. “Ding” Darling National Wildlife Refuge, southern Florida, 2010–13: U.S. Geological Survey Scientific Investigations Report 2016–5033, 33 p., accessed December 1, 2017, at http://dx.doi.org/10.3133/sir20165033.

Booth, A. 2020, Calculated carbon concentrations, Franklin Lock and Dam (S-79), southern Florida, 2014-2017: U.S. Geological Survey data release, https://doi.org/10.5066/P9V4ZGWU.

Bergamaschi, B.A., Krabbenhoft, D.P., Aiken, G.R., Patino, E., Rumbold, D.G., and Orem, W.H., 2012, Tidally driven export of dissolved organic carbon, total mercury, and methylmercury from a mangrove-dominated estuary: Environmental Science and Technology, v. 46, no. 3, p. 1371–1378, accessed October 1, 2017, at https://doi.org/10.1021/es2029137.

Curtis, P.J., and Adams, H.E., 1995, Dissolved organic matter quantity and quality from freshwater and saltwater lakes in east-central Alberta: Biogeochemistry, v. 30, p. 59–76, accessed April 24, 2019, at https://link.springer.com/article/10.1007/BF02181040.

Downing, B.D., Pellerin, B.A., Bergamaschi, B. A., Saraceno, J.F., and Kraus, T. E., 2012, Seeing the light—The effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers and streams: Limnology and Oceanography—Methods, v. 10, no. 10, p. 767–775, accessed January 12, 2019 at https://aslopubs.onlinelibrary.wiley.com/doi/10.4319/lom.2012.10.767.

Monteiro, M.T., Oliveira, S.M., Luizao, F.J., Candido, L.A., Ishida, F.Y., and Tomasella, J., 2014, Dissolved organic carbon concentration and its relationship to electrical conductivity in the waters of a stream in forested Amazonian blackwater catchment: Plant Ecology and Diversity, v. 4, p. 205–2013, accessed December 1, 2018, at https://doi.org/10.1080/17550874.2013.820223.

Pellerin, B.A., Saraceno, J.F., Shanley, J.B., Sebestyen, S.D., Aiken, G.R., Wollheim, G.R., and Bergamaschi, B.A., 2012, Taking the pulse of snowmelt—in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream: Biogeochemistry, v. 108, p. 183–198, accessed January 8, 2019, at https://doi.org/10.1007/s10533-011-9589-8.

South Florida Water Management District, 2018, Lake Okeechobee Operations, accessed January 29, 2018, at https://www.sfwmd.gov/sites/default/files/documents/fyi_lakeo_responsiblities.pdf.

Spencer, R.G.M., Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Kraus, T.E.C., Smart, D.R., Dahlgren, R.A., and Hernes, P.J., 2007, Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA): Hydrological Processes, v. 21, no. 23, p. 3181–3189, accessed October 1, 2018, at https://doi.org/10.1002/hyp.6887.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data, Collection of Samples, vers. 2.0: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed May 2, 2017, at http://water.usgs.gov/owq/FieldManual/chapter4/html/Ch4_contents.html.

U.S. Geological Survey, 2019, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed May 8, 2019, at https://doi.org/10.5066/F7P55KJN.

Wagner, R.J., Boulger, Jr., R.W., Oblinger, C.J., and Smith, B.A. 2006, Guidelines and standard procedures for continuous water-quality monitors—Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods 1-D3, 51 p., accessed May 2, 2017, at http://pubs.usgs.gov/tm/2006/tm1D3/.

Yang, Y.G., He, Z.L., Wang, Y.B., Liu, Y.L., Liang, Z.B., Fan, J.H., and Stoffella, J.P., 2012, Dissolved organic carbon in association with water soluble nutrients and metals in soils from Lake Okeechobee watershed, south Florida: Water, Air, & Soil Pollution, v. 223, p. 4075–4088, accessed May 2, 2017, at https://link.springer.com/article/10.1007/s11270-012-1174-9.

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