Appendix III Evaluation of Water Quality, Flow Data & Spring Flow Reversals

## 1.0 INTRODUCTION AND OBJECTIVE

The Suwannee River Water Management District (SRWMD or District) is tasked with developing minimum flows and levels (MFL) on both lentic and lotic water bodies within its boundary. Each year, the District produces the MFL Priority List which lists water bodies for which an MFL will be determined within a specified time frame. The purpose of an MFL is to protect a specified water body from what is known as "significant harm." In order to address this, the District has adopted a threshold of no more than a 15% reduction for in-channel habitat before "significant harm" is reached.

The Suwannee River is approximately 246 miles long and represents the second largest river system in Florida. Its headwaters originate in the Okefenokee Swamp in southeastern Georgia and flows south and southwest toward the Gulf of Mexico. Decaying vegetation in the Okefenokee Swamp is responsible for the river's tannic color, which is maintained as the river flows south. The middle portion of the Suwannee River stretches 92 miles from the town of Ellaville south to Wilcox, near Fanning Springs, and is the focus of MFL efforts (**Figure 1**).



Figure 1 - Map of the Suwannee River outlining the MSR project area

This technical memo describes the water quality analysis sub-task that Amec Foster Wheeler Environment and Infrastructure Inc. (Amec Foster Wheeler) conducted for the Middle Suwannee River (MSR) as part of the larger ongoing effort to support minimum flows and levels determinations for the MSR. The primary purpose of this assessment is to compile and analyze water quality and flow distributions and conduct correlations of certain water quality parameter concentrations with flow within the study reach. This effort focuses on water quality and flow data for select Middle Suwannee River and springs stations within the study area. Relationships between flow and key water quality parameters such as specific conductance (SpC) and nitrate-nitrite nitrogen (NOx) are provided below. The relationships between flow and parameter concentrations were considered in the establishment of the MFL.

Specific tasks included summarizing data for water quality parameters, conducting cumulative concentration frequency distribution curves, and concentration-flow associations to determine if water quality could be considered a relevant water resource value (WRV). Water quality and flow data were analyzed for five river stations, which included Ellaville, Luraville, Branford, Bell, and Wilcox. Data were analyzed for relationships between flow and water quality parameters for three springs stations including Troy, Lafayette Blue and Ruth (Little Sulphur). The potential for spring flow reversals was evaluated for Troy Springs using continuous *in-situ* and ambient grab water chemistry sample data. Selection of stations for each type of analysis was limited to available data for key water chemistry parameters. The following sections describe the methods utilized and the results of the analyses.

## 2.0 <u>METHODS</u>

#### 2.1 Water Quality and Flow Data Analysis

#### 2.1.1 Data Acquisition and Summary

The data used for water quality analyses represents the full body of data available on the District's websites that were available to the public during the time that this technical memorandum was being developed. Some of the data downloaded from the District's website was obtained from the U. S. Geological Survey's (USGS) automated database through the District's web portal. Water quality data for the river stations and spring stations were queried for the study area and were obtained from the SRWMD Water Portal websites, respectively:

- River Stations: <u>http://www.mysuwanneeriver.org/portal/rivers.htm</u>
- Spring Stations: <u>http://www.mysuwanneeriver.org/portal/springs.htm</u>

Available continuous (daily mean specific conductance, stage and flow) and ambient grab (water quality parameters) data were downloaded from the above websites for river and springs sites on September 30, 2015. The POR used for the five river site water quality and flow parameters was from February 1989 to September 2014. The springs sites had more variable PORs. For the extensive descriptive statistical analyses, the full PORs that were available for each spring was used to create summary tables. For the three selected springs correlations analyses, the POR was restricted from 1997 to 2007 for Troy Spring and from 1997 to 2013 for Lafayette Blue and Ruth (Little Sulfur) Spring.

Data were processed to provide paired data points for flow and the key water quality parameter associations. Data used for statistical correlations only included dates that had coincident data for key water quality parameters and flow. So that sufficient statistical power could be employed, a minimum number of 30 paired sampling points within the study period of record (POR, WY1933-2014) was used as a target to select springs stations. The three springs stations mentioned above met that criteria. Data were summarized with descriptive statistics for all river and springs stations.

## 2.1.2 Annual Medians Analysis

Lognormal empirical cumulative frequency distributions (CDF) were prepared for all river stations for annual median NOx, SpC and flow. Empirical cumulative frequency distribution is an analysis tool in the Minitab Statistical Software program that is summarized as the following:

- An empirical CDF plot is a graph that can be used to evaluate the fit of a distribution to the data, estimate percentiles, and compare different sample distributions. An empirical CDF plot does the following:
  - Plots each unique value versus the percentage of values in the sample that are less than or equal to it, and connects the points with a stepped line
  - Fits a cumulative distribution function (CDF) for the selected distribution so that the data can be examined to see how well the distribution fits the data
  - Displays a table with the distribution parameter estimates and the number of observations (N)

The CDF statistical program in Minitab was used to create the CDF plots. Different distributions, such as the normal and lognormal distributions, were used to create CDF plots and to determine which distribution was most appropriate for the available data. The lognormal distribution was the most reasonable distribution for the variables analyzed, and was selected to create the CDF plots. The lognormal distribution was also selected because the majority of water quality data do not follow a normal distribution. Instead, the dataset comprising the logarithm of a selected variable will exhibit a normal distribution. As mentioned, the empirical CDF plots were prepared for annual medians calculated from the long-term POR for NOx, SpC, and flow at the Suwannee River stations to evaluate the fit of a distribution of data, estimate percentiles, and compare different station distributions. The 90<sup>th</sup> percentile values from the CDFs were used to assess unusual events (i.e. extreme events that have a large impact, but occur less frequently) and to compare across sites.

#### 2.1.3 Correlations between Flow and Key Water Quality Parameters in River Stations

Locally weighted scatterplot smoothing (LOWESS) graphs and nonparametric correlations (Spearman's Rho) were constructed for NOx, SpC, and flow for the five river stations.

#### 2.1.4 Correlations between Flow and Key Water Quality Parameters in Springs Stations

Similar to the river stations, LOWESS graphs and nonparametric correlations were constructed for NOx, SpC, and flow for the three springs stations.

#### 2.2 Spring Flow Reversal Evaluation

Under typical baseflow conditions, water discharging from springs from the Upper Floridan Aquifer (UFA) is generally higher in SpC and calcium (Ca) concentrations than surface water or stormwater runoff and low in dissolved organic carbon (DOC) and dissolved oxygen (DO) concentrations due to characteristics and processes in the karst aquifer matrix. However, during flood events, the Suwannee River water elevation rises, which leads to a change in the hydraulic gradients in springs and can cause springs to reverse flow (i.e. recharge) and bring river flood waters into the spring vents and conduits. Flooding events can temporarily change the characteristics of water chemistry discharging from the springs by reducing SpC and Ca concentrations, and increasing DO and DOC.

Due to the pronounced changes in water chemistry characteristics that occur in spring discharge during floods, and given available data, it was possible to identify potential spring flow reversals by evaluating the chemical composition in the data POR.

Data were downloaded for Troy Springs on January 26, 2016 to include available data up to that date. Data available from the SRWMD and USGS for Troy Springs that were used for data analyses included the following parameters:

- Ambient Grab (SRWMD Station ID TRY010C1; POR: 11/13/1992 to 1/11/2016)
  SpC, DO, color (as a proxy for DOC), and Ca concentrations
- Continuous (USGS Station ID 2320250; POR: 7/30/2014 to 1/10/2016)
  - Daily SpC, DO, and gage height data

These data were used to evaluate potential spring flow reversals in Troy Springs. Median values for each constituent calculated from the entire POR dataset were compared against the corresponding individual measured values to assess deviation of a single measured value from long-term median estimate. Nonparametric correlation analyses were conducted to evaluate potential thresholds based on identifying inflection points in the scatterplots that allow an inference into suspected cases of flooding and associated spring flow reversals. Substantial departures from the long-term median and exceedance of thresholds for multiple constituents at a time indicated periods or events where potential spring flow reversals may have occurred. Due to the large gaps (i.e. 2-6 months) between ambient grab samples, it was not possible to identify durations of spring reversal events for the long-term POR, rather the potential of oncoming or receding events were identified. Results for all analyses are provided below.

#### 3.0 RESULTS

#### 3.1 Water Quality and Flow Data Analysis

#### 3.1.1 Descriptive Statistics of Water Quality for Suwannee River and Springs Stations

A map of river and springs station locations is shown in **Figure 2**. Summary data for long-term mean, median, minimum, maximum, and standard deviation for water quality parameters are shown in **Table 1** for Suwannee River stations and **Table 2** for associated springs stations. Graphical representations for long-term median flow, and NOx are provided in Figures 3 and 4, respectively. As mentioned previously, the POR used to produce data for **Table 1** was February 1989 to September 2014. The PORs used to produce **Table 2** and **Figures 3** and **4** are as follows:

Spring	Available Flow POR	Available SpC POR	Available NOx POR
Allen Mill Pond*	11/26/1973 - 7/8/2015	12/20/2013 - 9/23/2015	NA
Charles	5/13/1927 - 3/31/2015	8/18/1995 - 3/24/2015	8/18/1995 - 3/24/2015
Lafayette Blue*	11/23/1973 - 6/24/2015	8/11/1995 - 3/23/2015	8/11/1995 - 3/23/2015
Telford	5/14/1927 - 8/6/2014	11/12/1992 - 3/17/2015	11/12/1992 - 3/17/2015
Peacock*	11/20/1973 - 9/3/2015	12/10/2013 - 9/23/2015	NA
Convict	11/26/1973 - 4/22/2015	11/12/1992 - 4/22/2015	11/12/1992 - 4/22/2015
Royal	5/19/1977 - 6/2/2015	11/13/1992 - 3/17/2015	11/13/1992 - 3/17/2015
Suwannee Blue	6/23/1997 - 6/2/2015	6/23/1997 - 3/17/2015	6/23/1997 - 3/17/2015
Ravine	7/18/1997 - 12/19/2013	7/18/1997 - 3/17/2015	7/18/1997 - 3/17/2015
Troy*	5/15/1927 - 12/3/2014	11/13/1992 - 4/8/2015	11/13/1992 - 4/8/2015
Ruth	11/14/1973 - 11/18/2014	6/19/1996 - 3/16/2015	6/19/1996 - 3/16/2015
Little River	11/27/1973 - 8/26/2015	6/10/1994 - 3/18/2015	6/10/1994 - 3/18/2015
Branford	5/15/1927 - 12/9/2014	6/19/1996 - 3/18/2015	6/22/1999 - 3/18/2015
Rock Bluff	12/8/1942 - 7/17/2014	11/5/1992 - 12/4/2014	11/5/1992 - 12/4/2014
Hart*	3/14/1932 - 12/9/2014	6/12/1996 - 9/23/2015	6/12/1996 - 12/2/2014
Otter	3/14/1932 - 11/19/2014	9/19/1997 - 3/19/2015	9/19/1997 - 3/19/2015
Note: * indicates that	continuous and ambient specific of	conductance data were compiled	1

f indicates that continuous and ambient specific conductance data were compiled inole:







Note: Number of samples (N) are provided in Table 2





Figure 4 - Springs Stations Long-term Median SpC and Median Nitrate-Nitrite N

Site	Station ID	Parameter	Ν	Mean	Median	Minimum	Maximum	Standard Deviation
		Alkalinity (mg/L)	264	73.07	75.75	1.00	148.00	42.51
		Calcium (mg/L)	112	22.33	23.45	2.20	45.00	12.43
		Chloride (mg/L)	250	7.57	7.20	1.00	17.00	2.03
		Color (PCU)	258	162.02	125.00	13.00	750.00	134.06
		Dissolved Oxygen (mg/L)	282	5.76	5.40	2.70	10.80	1.42
		Fluoride (mg/L)	250	0.16	0.15	0.04	0.63	0.07
		Flow (cfs)	9364	5474.47	2890.00	100.00	56400.00	6309.71
		Potassium (mg/L)	250	1.47	1.30	0.00	5.90	0.72
		Magnesium (mg/L)	250	5.33	5.30	0.10	11.30	2.64
Ellaville	02319500	Sodium (mg/L)	250	7.61	7.00	0.00	17.50	3.21
		Ammonia (mg/L)	276	0.04	0.03	0.00	0.20	0.03
		Nitrate-Nitrite N (mg/L)	282	0.43	0.41	0.00	1.30	0.24
		Orthophosphate (mg/L)	276	0.14	0.12	0.00	0.51	0.09
		Total Phosphorus (mg/L)	282	0.19	0.16	0.01	0.76	0.10
		Sulfate (mg/L)	250	17.31	16.35	0.20	38.50	9.84
		SpC (us/cm)	282	198.35	203.00	29.00	380.00	92.25
		Total Dissolved Solids (mg/L)	251	156.11	158.00	64.00	328.00	46.14
		Total Organic Carbon (mg/L)	264	17.02	15.40	1.90	61.50	10.69
		Turbidity (NTU)	264	3.89	2.15	0.20	30.00	4.48
		Alkalinity (mg/L)	264	82.16	85.85	1.90	160.00	45.06
		Calcium (mg/L)	256	29.17	30.45	3.00	55.50	14.49
		Chloride (mg/L)	256	7.28	7.00	0.00	12.00	1.91
		Color (PCU)	261	167.77	150.00	20.00	880.00	129.31
		Dissolved Oxygen (mg/L)	277	6.54	6.50	2.20	11.10	1.40
		Fluoride (mg/L)	256	0.15	0.15	0.02	0.34	0.06
		Flow (cfs)	9364	5705.55	3222.87	930.00	47500.00	6158.02
		Potassium (mg/L)	256	1.29	1.20	0.20	3.40	0.56
		Magnesium (mg/L)	256	6.09	6.15	0.80	12.40	2.95
Luraville	02320000	Sodium (mg/L)	256	6.67	6.35	0.70	14.60	2.38
		Ammonia (mg/L)	272	0.04	0.03	0.00	0.25	0.03
		Nitrate-Nitrite N (mg/L)	277	0.47	0.47	0.00	1.20	0.24
		Orthophosphate (mg/L)	272	0.15	0.12	0.01	1.29	0.10
		Total Phosphorus (mg/L)	277	0.20	0.17	0.05	1.32	0.11
		Sulfate (mg/L)	256	17.46	17.35	0.90	37.50	9.41
		SpC (us/cm)	277	215.26	220.00	30.00	404.00	99.31
		Total Dissolved Solids (mg/L)	252	166.87	170.00	50.00	358.00	50.41
		Total Organic Carbon (mg/L)	264	17.39	16.10	1.20	50.25	10.44
		Turbidity (NTU)	264	3.28	2.08	0.20	22.00	3.38

## Table 1 - Summary Statistics of River Sites Designated by USGS Station ID

Site	Station ID	Parameter	Ν	Mean	Median	Minimum	Maximum	Standard Deviation
		Alkalinity (mg/L)	266	91.79	100.50	1.50	167.00	47.41
		Calcium (mg/L)	258	32.89	34.40	3.40	68.00	15.90
		Chloride (mg/L)	258	7.10	7.00	0.00	12.00	1.87
		Color (PCU)	260	153.61	135.00	10.00	750.00	127.83
		Dissolved Oxygen (mg/L)	283	6.45	6.50	2.40	9.80	1.31
		Fluoride (mg/L)	NA	NA	NA	NA	NA	NA
		Flow (cfs)	9364	6258.44	3840.00	1230.00	46500.00	6062.06
		Potassium (mg/L)	258	1.28	1.20	0.25	3.00	0.52
		Magnesium (mg/L)	258	6.64	6.95	0.80	21.20	3.18
Branford	02320500	Sodium (mg/L)	258	6.03	5.80	2.60	13.65	1.90
		Ammonia (mg/L)	278	0.04	0.03	0.00	0.18	0.03
		Nitrate-Nitrite N (mg/L)	283	0.74	0.74	0.00	2.00	0.40
		Orthophosphate (mg/L)	278	91.79	100.50	1.50	167.00	47.41
		Total Phosphorus (mg/L)	283	0.16	0.15	0.05	0.66	0.06
		Sulfate (mg/L)	258	16.56	17.50	1.00	35.05	8.23
		SpC (us/cm)	283	232.30	244.00	29.00	447.00	102.09
		Total Dissolved Solids (mg/L)	253	168.90	178.00	30.00	283.00	47.48
		Total Organic Carbon (mg/L)	266	15.60	13.83	1.20	53.20	10.29
		Turbidity (NTU)	266	3.05	1.75	0.26	20.00	3.40
		Alkalinity (mg/L)	262	101.18	112.00	1.90	171.00	45.36
		Calcium (mg/L)	254	37.82	41.10	2.30	67.80	15.78
		Chloride (mg/L)	254	7.64	7.50	0.00	17.50	1.99
		Color (PCU)	260	139.75	100.00	7.00	700.00	125.89
		Dissolved Oxygen (mg/L)	275	6.67	6.70	2.30	10.60	1.28
		Fluoride (mg/L)	NA	NA	NA	NA	NA	NA
		Flow (cfs)	9364	7858.73	5490.00	1820.00	49363.31	6188.12
		Potassium (mg/L)	254	1.15	1.00	0.20	4.60	0.50
		Magnesium (mg/L)	254	6.29	6.70	1.10	11.40	2.45
Bell	02323000	Sodium (mg/L)	254	5.63	5.50	2.70	10.30	1.40
		Ammonia (mg/L)	273	0.04	0.03	0.00	0.35	0.03
		Nitrate-Nitrite N (mg/L)	275	0.68	0.70	0.01	1.90	0.33
		Orthophosphate (mg/L)	273	0.10	0.09	0.03	0.27	0.04
		Total Phosphorus (mg/L)	275	0.14	0.13	0.05	1.10	0.08
		Sulfate (mg/L)	254	17.95	19.15	1.00	35.00	7.55
		SpC (us/cm)	275	254.27	282.00	30.00	476.00	98.47
		Total Dissolved Solids (mg/L)	250	179.44	189.50	59.00	390.00	47.85
		Total Organic Carbon (mg/L)	262	13.95	11.75	1.30	49.20	9.67
		Turbidity (NTU)	262	2.68	1.60	0.20	21.10	2.90
Wilcox	02323500	Alkalinity (mg/L)	263	103.85	118.00	1.90	173.00	44.37

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Calcium (mg/L)	254	39.11	42.68	5.90	66.30	15.64
		Chloride (mg/L)	255	7.64	7.75	0.00	13.30	1.80
		Color (PCU)	260	129.53	100.00	5.00	750.00	115.81
		Dissolved Oxygen (mg/L)	276	6.67	6.70	1.60	10.80	1.29
		Fluoride (mg/L)	NA	NA	NA	NA	NA	NA
		Flow (cfs)	9364	8182.35	5955.00	1070.00	47600.00	6140.27
		Potassium (mg/L)	255	1.18	1.05	0.20	10.00	0.77
		Magnesium (mg/L)	255	6.17	6.70	0.90	10.70	2.32
		Sodium (mg/L)	255	5.76	5.50	2.60	41.50	2.67
		Ammonia (mg/L)	273	0.04	0.03	0.00	0.30	0.04
		Nitrate-Nitrite N (mg/L)	275	0.66	0.69	0.00	2.30	0.33
		Orthophosphate (mg/L)	273	0.09	0.09	0.01	0.27	0.04
		Total Phosphorus (mg/L)	276	0.14	0.12	0.04	1.30	0.08
		Sulfate (mg/L)	255	17.56	19.00	0.80	31.20	7.07
		SpC (us/cm)	276	260.30	282.50	48.00	492.00	99.30
		Total Dissolved Solids (mg/L)	250	183.79	190.00	68.00	394.00	51.97
		Total Organic Carbon (mg/L)	263	13.44	11.40	1.10	47.80	9.29
		Turbidity (NTU)	263	2.91	1.95	0.40	25.00	2.87
* Water qu	uality samplin	g frequency varied over the perio	od of rec	ord, but wa	s, for the m	ost part, condi	ucted on a monthly	basis.
** Flow m	easurements	were collected on a daily basis, a Foster Wheeler 2016 MSR Hydro	ind any n	nissing data	were gap f			

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Alkalinity (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Calcium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Chloride (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Color (PCU)	0	N/A	N/A	N/A	N/A	N/A
		Dissolved Oxygen (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Fluoride (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Flow (cfs)	21	21.78	22.07	-32.50	51.27	18.60
		Potassium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Magnesium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
Allen Mill	02240045	Sodium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
Pond	02319915	Ammonia (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Nitrate-Nitrite N (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Orthophosphate (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Total Phosphorus (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Sulfate (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		SpC (us/cm)	285	391.68	423.20	58.10	561.80	97.10
		Total Dissolved Solids (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Total Organic Carbon (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Turbidity (NTU)	0	N/A	N/A	N/A	N/A	N/A
		Stage (ft NGVD29)	285	26.68	24.06	23.82	41.51	4.73
		Alkalinity (mg/L)	18	150.42	163.00	7.68	194.00	41.92
		Calcium (mg/L)	18	50.05	50.15	5.33	70.28	14.14
		Chloride (mg/L)	18	5.36	5.00	1.00	10.40	2.22
		Color (PCU)	15	4.87	5.00	1.00	10.00	2.80
		Dissolved Oxygen (mg/L)	18	1.70	1.35	0.29	7.64	1.61
		Fluoride (mg/L)	18	0.13	0.14	0.02	0.32	0.06
		Flow (cfs)	32	20.31	19.21	-25.90	48.90	17.01
		Potassium (mg/L)	18	0.71	0.65	0.00	1.80	0.48
	00040000	Magnesium (mg/L)	18	8.97	9.49	1.81	12.70	2.59
Charles	02319900	Sodium (mg/L)	18	3.14	2.84	2.30	6.30	1.01
		Ammonia (mg/L)	15	0.02	0.02	0.00	0.05	0.01
		Nitrate-Nitrite N (mg/L)	19	1.88	2.00	0.12	3.45	0.72
		Orthophosphate (mg/L)	15	0.05	0.05	0.04		0.01
		Total Phosphorus (mg/L)	18	0.07	0.06	0.04	0.18	0.03
		Sulfate (mg/L)	18	15.26	15.75	5.34		3.45
		SpC (us/cm)	18	319.61	329.50	58.00	381.00	67.55
		Total Dissolved Solids (mg/L)	18	221.22	213.00	94.00		76.80
		Total Organic Carbon (mg/L)	18	5.57	2.44	0.00	32.83	8.58

## Table 2 - Summary Statistics of Springs Sites Designated by USGS Station ID

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Turbidity (NTU)	18	1.01	0.35	0.17	11.60	2.65
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	122	197.05	198.25	7.45	227.00	20.11
		Calcium (mg/L)	122	68.22	68.50	5.49	11.60        N/A        227.00        81.70        16.80        25.00        7.81        0.24        257.00        5.10        16.80        28.70        0.10        3.35        0.07        0.20        18.40        498.00	8.10
		Chloride (mg/L)	125	9.64	9.50	1.50	16.80	1.75
		Color (PCU)	119	7.11	5.00	1.00	25.00	3.97
		Dissolved Oxygen (mg/L)	131	0.84	0.60	0.10	7.81	0.91
		Fluoride (mg/L)	122	0.12	0.12	0.04	0.24	0.04
		Flow (cfs)	115	78.14	61.10	-4.76	257.00	49.70
		Potassium (mg/L)	122	1.09	1.10	0.00	5.10	0.50
		Magnesium (mg/L)	122	11.77	12.10	1.86	16.80	1.72
Lafayette	02210050	Sodium (mg/L)	122	5.62	5.40	3.20	28.70	2.29
Blue	02319950	Ammonia (mg/L)	128	0.03	0.02	0.00	0.10	0.03
		Nitrate-Nitrite N (mg/L)	132	1.88	1.88	0.11	3.35	0.61
		Orthophosphate (mg/L)	128	0.04	0.04	0.00	0.07	0.01
		Total Phosphorus (mg/L)	131	0.05	0.05	0.01	0.20	0.02
		Sulfate (mg/L)	122	13.86	13.95	5.23	18.40	2.05
		SpC (us/cm)	442	387.55	435.50	49.40	498.00	115.25
		Total Dissolved Solids (mg/L)	122	255.57	254.25	101.00	356.00	24.45
		Total Organic Carbon (mg/L)	121	4.58	1.70	0.40	55.50	7.75
		Turbidity (NTU)	122	0.52	0.31	0.07	11.30	1.06
		Stage (ft NGVD29)	315	27.41	25.17	21.52	44.41	5.96
		Alkalinity (mg/L)	141	177.45	180.00	6.99	210.14	19.52
		Calcium (mg/L)	141	62.38	61.90	5.58	119.00	9.40
		Chloride (mg/L)	141	5.90	6.00	1.00	9.00	1.19
		Color (PCU)	137	6.33	5.00	1.00	100.00	8.51
		Dissolved Oxygen (mg/L)	148	1.44	1.40	0.10	7.67	0.76
		Fluoride (mg/L)	134	0.20	0.20	0.04	0.30	0.04
		Flow (cfs)	100	35.25	31.84	15.84	107.00	15.86
		Potassium (mg/L)	141	0.55	0.50	0.00	1.48	0.22
Telford	02320003	Magnesium (mg/L)	141	17.68	18.00	1.84	28.70	2.64
		Sodium (mg/L)	141	3.50	3.50	2.40	6.30	0.50
		Ammonia (mg/L)	144	0.03	0.02	0.00	0.10	0.03
		Nitrate-Nitrite N (mg/L)	149	2.45	2.50	0.12	5.40	0.68
		Orthophosphate (mg/L)	144	0.04	0.04	0.02	0.13	0.01
		Total Phosphate (mg/L)	147	0.06	0.05	0.01	0.20	0.02
		Sulfate (mg/L)	141	43.21	45.00	5.45	60.80	8.22
		SpC (us/cm)	147	419.97	425.00	59.00	485.00	36.53
		Total Dissolved Solids (mg/L)	141	271.39	273.00	68.00	339.00	32.88

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Total Organic Carbon (mg/L)	133	2.73	0.90	0.00	32.91	4.15
		Turbidity (NTU)	141	0.38	0.22	0.03	9.80	0.84
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Calcium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Chloride (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Color (PCU)	0	N/A	N/A	N/A	N/A	N/A
		Dissolved Oxygen (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Fluoride (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Flow (cfs)	16	75.75	68.46	5.78	201.00	59.66
		Potassium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Magnesium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Sodium (mg/L)	0	N/A	N/A	N/A	N/A	N/A
Peacock	02320048	Ammonia (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Nitrate-Nitrite N (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Orthophosphate (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Total Phosphorus (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Sulfate (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		SpC (us/cm)	295	348.21	391.10	53.10	425.20	104.54
		Total Dissolved Solids (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Total Organic Carbon (mg/L)	0	N/A	N/A	N/A	N/A	N/A
		Turbidity (NTU)	0	N/A	N/A	N/A	N/A	N/A
		Stage (ft NGVD29)	295	4.09	2.61	1.35	16.40	3.70
		Alkalinity (mg/L)	40	152.50	168.00	0.30	223.00	58.78
		Calcium (mg/L)	40	53.67	53.75	5.78	77.00	17.59
		Chloride (mg/L)	40	10.08	10.20	3.00	14.00	2.33
		Color (PCU)	33	15.64	5.00	1.00	320.00	55.05
		Dissolved Oxygen (mg/L)	46	3.82	3.49	0.10	8.25	1.47
		Fluoride (mg/L)	32	0.13	0.13	0.07	0.20	0.03
		Flow (cfs)	31	6.76	6.25	-21.70	41.20	10.92
		Potassium (mg/L)	40	3.92	3.50	0.70	8.62	1.95
Convict	02320100	Magnesium (mg/L)	40	12.93	12.85	1.86	19.58	4.29
		Sodium (mg/L)	40	6.05	5.90	3.80	9.17	1.48
		Ammonia (mg/L)	38	0.03	0.02	0.00	0.10	0.02
		Nitrate-Nitrite N (mg/L)	47	8.29	8.36	0.09	16.67	4.31
		Orthophosphate (mg/L)	38	0.04	0.04	0.02	0.10	0.02
		Total Phosphorus (mg/L)	45	0.07	0.04	0.03	0.28	0.06
		Sulfate (mg/L)	40	10.37	9.58	3.80	15.90	3.33
		SpC (us/cm)	45	400.20	411.00	60.00	567.00	120.21

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Total Dissolved Solids (mg/L)	40	253.95	261.00	98.00	372.00	59.71
		Total Organic Carbon (mg/L)	33	4.48	1.20	0.00	32.34	7.97
		Turbidity (NTU)	40	1.22	0.40	0.10	10.90	2.35
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	34	168.33	170.00	144.00	189.00	9.39
		Calcium (mg/L)	34	50.18	50.70	0.00	61.60	10.47
		Chloride (mg/L)	34	5.27	5.20	0.40	8.00	1.64
		Color (PCU)	31	4.23	5.00	1.00	5.00	1.61
		Dissolved Oxygen (mg/L)	38	1.57	1.25	0.60	5.80	0.99
		Fluoride (mg/L)	27	0.14	0.14	0.09	0.22	0.03
		Flow (cfs)	31	11.95	12.00	0.00	29.20	10.22
		Potassium (mg/L)	34	0.69	0.50	0.10	1.90	0.42
		Magnesium (mg/L)	34	11.44	11.10	8.60	15.50	1.71
Davial	02220120	Sodium (mg/L)	34	2.92	2.70	2.00	5.20	0.73
Royal	02320130	Ammonia (mg/L)	35	0.02	0.02	0.00	0.10	0.02
		Nitrate-Nitrite N (mg/L)	38	1.73	1.62	0.20	4.00	0.81
		Orthophosphate (mg/L)	35	0.02	0.02	0.00	0.04	0.01
		Total Phosphorus (mg/L)	38	0.03	0.03	0.00	0.09	0.02
		Sulfate (mg/L)	34	9.63	9.50	6.60	14.00	1.59
		SpC (us/cm)	38	354.21	347.00	322.00	458.00	25.57
		Total Dissolved Solids (mg/L)	34	214.32	210.00	163.00	465.00	48.68
		Total Organic Carbon (mg/L)	26	2.71	1.46	0.00	13.50	3.62
		Turbidity (NTU)	34	0.41	0.30	0.10	2.58	0.47
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	128	158.68	160.00	2.00	199.00	17.60
		Calcium (mg/L)	128	56.71	56.85	44.00	72.60	5.54
		Chloride (mg/L)	128	6.92	6.60	4.50	13.00	1.77
		Color (PCU)	124	5.95	5.00	5.00	80.00	7.61
		Dissolved Oxygen (mg/L)	135	3.61	3.50	1.60	6.60	0.73
		Fluoride (mg/L)	128	0.14	0.14	0.02	0.22	0.04
		Flow (cfs)	86	15.45	13.45	4.50	39.25	8.44
Suwannee Blue	02320132	Potassium (mg/L)	128	1.14	0.90	0.00	4.80	0.77
		Magnesium (mg/L)	128	11.16	11.20	7.10	14.34	1.33
		Sodium (mg/L)	128	3.26	3.10	1.80	5.90	0.64
		Ammonia (mg/L)	130	0.03	0.02	0.01	0.10	0.03
		Nitrate-Nitrite N (mg/L)	138	4.44	4.06	0.11	10.70	2.04
		Orthophosphate (mg/L)	130	0.02	0.02	0.00	0.05	0.01
		Total Phosphorus (mg/L)	133	0.03	0.03	0.01	0.43	0.04
		Sulfate (mg/L)	128	12.18	11.35	7.00	25.40	3.53

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		SpC (us/cm)	134	356.46	355.00	289.00	422.00	19.83
		Total Dissolved Solids (mg/L)	128	221.50	218.00	173.00	518.00	31.42
		Total Organic Carbon (mg/L)	127	2.05	0.70	0.00	14.90	2.79
		Turbidity (NTU)	128	0.25	0.20	0.03	2.44	0.31
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	100	140.30	142.00	7.64	182.00	21.81
		Calcium (mg/L)	100	60.37	61.60	5.40	72.00	8.52
		Chloride (mg/L)	100	13.67	14.15	6.00	20.60	3.20
		Color (PCU)	98	10.93	5.00	5.00	240.00	30.18
		Dissolved Oxygen (mg/L)	106	3.16	3.00	1.00	8.40	1.14
		Fluoride (mg/L)	100	0.16	0.16	0.04	0.25	0.04
		Flow (cfs)	68	4.57	4.19	0.12	11.40	2.30
		Potassium (mg/L)	100	4.01	4.10	0.20	6.70	1.56
		Magnesium (mg/L)	100	15.77	16.30	1.96	20.40	2.87
Davina	02320140	Sodium (mg/L)	100	5.27	5.30	1.70	7.50	0.96
Ravine	02320140	Ammonia (mg/L)	102	0.04	0.02	0.01	0.10	0.03
		Nitrate-Nitrite N (mg/L)	110	12.10	12.55	0.09	21.40	4.37
		Orthophosphate (mg/L)	103	0.02	0.02	0.00	0.28	0.03
		Total Phosphorus (mg/L)	105	0.04	0.03	0.01	0.33	0.03
		Sulfate (mg/L)	100	28.98	30.05	4.59	43.40	6.91
		SpC (us/cm)	105	433.32	445.00	57.00	533.00	58.76
		Total Dissolved Solids (mg/L)	100	281.07	284.00	108.00	392.00	41.68
		Total Organic Carbon (mg/L)	99	2.61	0.70	0.00	46.50	6.98
		Turbidity (NTU)	100	0.49	0.26	0.05	7.17	0.83
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	138	160.11	161.00	58.80	207.00	14.72
		Calcium (mg/L)	137	59.17	59.90	0.10	75.10	8.23
		Chloride (mg/L)	138	7.88	5.80	2.00	297.00	24.81
		Color (PCU)	132	8.43	5.00	1.00	125.00	16.03
		Dissolved Oxygen (mg/L)	145	0.86	0.70	0.10	5.10	0.77
		Fluoride (mg/L)	131	0.10	0.11	0.00	0.25	0.04
Trov	02220250	Flow (cfs)	113	107.48	99.70	-87.10	379.00	54.55
Troy	02320250	Potassium (mg/L)	138	1.03	1.00	0.10	2.11	0.44
		Magnesium (mg/L)	138	6.98	7.10	0.00	11.90	1.00
		Sodium (mg/L)	138	3.03	3.10	1.70	4.39	0.47
		Ammonia (mg/L)	139	0.03	0.02	0.00	0.20	0.03
		Nitrate-Nitrite N (mg/L)	147	1.92	1.80	0.57	3.20	0.51
		Orthophosphate (mg/L)	139	0.03	0.03	0.00	0.10	0.01
		Total Phosphorus (mg/L)	144	0.04	0.04	0.02	0.14	0.02

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Sulfate (mg/L)	138	12.62	12.20	8.50	69.50	5.09
		SpC (us/cm)	139	334.00	337.00	180.00	375.00	23.14
		Total Dissolved Solids (mg/L)	138	211.44	208.00	154.00	700.00	44.98
		Total Organic Carbon (mg/L)	130	2.70	1.25	0.00	14.90	3.31
		Turbidity (NTU)	138	0.32	0.20	0.01	3.30	0.49
		Stage (ft NGVD29)	4458	18.60	17.72	9.12	42.62	6.43
		Alkalinity (mg/L)	120	169.70	172.00	0.30	211.00	25.90
		Calcium (mg/L)	119	69.84	70.80	15.20	112.00	10.29
		Chloride (mg/L)	124	8.93	8.80	3.00	27.60	2.35
		Color (PCU)	119	14.47	10.00	5.00	400.00	40.04
		Dissolved Oxygen (mg/L)	130	1.06	0.85	0.10	7.70	1.15
		Fluoride (mg/L)	120	0.08	0.08	0.02	0.16	0.03
		Flow (cfs)	81	8.01	6.30	0.00	27.50	6.26
		Potassium (mg/L)	120	3.78	3.90	0.40	9.00	1.67
		Magnesium (mg/L)	120	7.06	7.20	3.10	9.80	1.18
		Sodium (mg/L)	120	5.25	5.30	2.10	8.60	1.22
Ruth	02320260	Ammonia (mg/L)	129	0.04	0.02	0.00	0.16	0.03
		Nitrate-Nitrite N (mg/L)	133	5.07	5.05	0.52	13.00	2.46
		Orthophosphate (mg/L)	129	0.03	0.03	0.01	0.13	0.01
		Total Phosphorus (mg/L)	130	0.05	0.04	0.03	0.18	0.02
		Sulfate (mg/L)	120	15.56	16.18	7.60	24.40	3.29
		SpC (us/cm)	130	397.39	400.00	89.00	490.00	46.63
		Total Dissolved Solids (mg/L)	121	254.76	253.00	105.00	345.00	30.12
		Total Organic Carbon (mg/L)	119	4.11	2.30	0.40	24.90	4.43
		Turbidity (NTU)	120	0.48	0.24	0.03	6.86	0.83
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	132	161.74	164.00	14.00	184.00	17.25
		Calcium (mg/L)	132	62.32	62.60	37.05	96.60	7.06
		Chloride (mg/L)	132	5.73	5.80	0.00	15.50	1.32
		Color (PCU)	130	10.08	5.00	1.00	300.00	29.68
		Dissolved Oxygen (mg/L)	138	1.52	1.40	0.10	4.70	0.62
		Fluoride (mg/L)	131	0.11	0.11	0.02	0.25	0.04
Little River	02320400	Flow (cfs)	103	66.65	58.80	12.20	217.00	36.44
		Potassium (mg/L)	132	0.68	0.70	0.10	1.35	0.23
		Magnesium (mg/L)	132	7.56	7.60	5.00	12.20	0.87
		Sodium (mg/L)	132	2.75	2.70	1.30	4.60	0.45
		Ammonia (mg/L)	136	0.04	0.02	0.00	0.20	0.03
		Nitrate-Nitrite N (mg/L)	139	1.17	1.15	0.11	1.80	0.24
		Orthophosphate (mg/L)	136	0.02	0.02	0.00	0.09	0.01

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Total Phosphorus (mg/L)	137	0.03	0.02	0.01	0.16	0.02
		Sulfate (mg/L)	132	20.20	20.20	13.35	27.35	3.06
		SpC (us/cm)	137	351.36	351.00	250.00	440.00	17.71
		Total Dissolved Solids (mg/L)	132	219.31	218.25	161.50	324.00	19.07
		Total Organic Carbon (mg/L)	130	2.59	0.88	0.00	19.90	3.65
		Turbidity (NTU)	132	0.29	0.20	0.01	3.66	0.38
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	7	214.35	217.00	197.00	233.00	12.87
		Calcium (mg/L)	5	67.28	76.00	0.10	95.31	38.82
		Chloride (mg/L)	9	5.03	6.00	1.60	6.90	1.94
		Color (PCU)	3	6.67	5.00	5.00	10.00	2.89
		Dissolved Oxygen (mg/L)	9	1.06	1.00	0.29	2.10	0.50
		Fluoride (mg/L)	5	0.08	0.11	0.03	0.12	0.05
		Flow (cfs)	16	31.36	31.73	6.63	82.50	18.84
		Potassium (mg/L)	5	0.74	0.80	0.20	1.39	0.47
		Magnesium (mg/L)	5	5.81	6.70	0.00	8.43	3.37
Dranford	02220502	Sodium (mg/L)	5	2.47	2.90	0.10	3.53	1.37
Branford	02320502	Ammonia (mg/L)	7	0.01	0.02	0.00	0.02	0.01
		Nitrate-Nitrite N (mg/L)	3	0.58	0.79	0.02	0.95	0.49
		Orthophosphate (mg/L)	9	0.03	0.03	0.02	0.05	0.01
		Total Phosphorus (mg/L)	9	0.04	0.04	0.03	0.07	0.01
		Sulfate (mg/L)	5	23.14	22.30	18.40	27.50	3.50
		SpC (us/cm)	9	449.11	445.00	411.00	506.00	26.12
		Total Dissolved Solids (mg/L)	6	280.33	278.00	246.00	318.00	23.68
		Total Organic Carbon (mg/L)	5	1.82	2.10	0.54	2.30	0.73
		Turbidity (NTU)	5	0.60	0.69	0.30	0.80	0.21
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	132	136.62	137.00	49.80	170.00	14.15
		Calcium (mg/L)	132	55.74	55.35	22.10	74.90	7.77
		Chloride (mg/L)	132	5.32	5.00	0.10	39.00	3.23
		Color (PCU)	128	9.65	5.00	1.00	250.00	26.42
		Dissolved Oxygen (mg/L)	140	1.56	1.40	0.10	7.80	1.06
Rock Bluff	02322997	Fluoride (mg/L)	124	0.08	0.07	0.02	0.32	0.04
NOCK DIUII	02322331	Flow (cfs)	96	27.90	25.97	-21.40	114.00	16.07
		Potassium (mg/L)	132	0.51	0.50	0.00	1.40	0.25
		Magnesium (mg/L)	132	3.50	3.60	2.20	5.53	0.52
		Sodium (mg/L)	132	2.40	2.30	1.40	4.36	0.53
		Ammonia (mg/L)	137	0.04	0.02	0.00	0.20	0.03
		Nitrate-Nitrite N (mg/L)	139	1.24	1.05	0.27	3.16	0.60

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Orthophosphate (mg/L)	137	0.06	0.06	0.01	0.24	0.02
		Total Phosphorus (mg/L)	139	0.07	0.06	0.04	0.35	0.04
		Sulfate (mg/L)	132	12.98	12.80	0.20	25.50	2.54
		SpC (us/cm)	140	293.30	291.00	123.00	388.00	28.99
		Total Dissolved Solids (mg/L)	132	179.23	178.00	65.00	450.00	33.19
		Total Organic Carbon (mg/L)	123	2.82	1.40	0.00	32.90	4.27
		Turbidity (NTU)	132	0.38	0.20	0.03	5.25	0.63
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A
		Alkalinity (mg/L)	47	197.60	199.00	170.00	229.50	12.26
		Calcium (mg/L)	47	82.91	82.70	60.60	102.00	8.97
		Chloride (mg/L)	51	7.89	8.00	0.00	16.00	2.25
		Color (PCU)	45	5.33	5.00	5.00	10.00	1.26
		Dissolved Oxygen (mg/L)	56	1.63	1.50	0.20	7.80	1.30
		Fluoride (mg/L)	47	0.11	0.11	0.04	0.25	0.04
		Flow (cfs)	67	60.09	55.50	-18.20	152.00	24.46
		Potassium (mg/L)	47	0.75	0.70	0.10	1.50	0.33
		Magnesium (mg/L)	47	5.54	5.70	4.20	7.40	0.73
Hart	02323150	Sodium (mg/L)	47	3.36	3.30	2.50	4.30	0.54
Hdit	02323150	Ammonia (mg/L)	54	0.03	0.02	0.00	0.10	0.02
		Nitrate-Nitrite N (mg/L)	57	1.30	1.25	0.36	2.40	0.37
		Orthophosphate (mg/L)	55	0.06	0.07	0.03	0.13	0.01
		Total Phosphorus (mg/L)	57	0.08	0.07	0.06	0.17	0.02
		Sulfate (mg/L)	47	23.88	24.00	18.20	30.20	3.32
		SpC (us/cm)	270	378.61	446.45	60.70	642.30	141.00
		Total Dissolved Solids (mg/L)	48	262.32	260.50	205.00	333.00	23.85
		Total Organic Carbon (mg/L)	46	3.70	1.25	0.20	34.80	6.38
		Turbidity (NTU)	47	0.25	0.20	0.03	0.85	0.16
		Stage (ft NGVD29)	215	9.14	8.42	4.62	16.48	3.57
		Alkalinity (mg/L)	16	195.61	194.75	168.00	218.00	12.23
		Calcium (mg/L)	16	88.16	87.21	77.50	103.00	7.16
		Chloride (mg/L)	17	8.76	8.70	7.55	10.06	0.66
		Color (PCU)	14	6.43	5.00	5.00	20.00	4.13
		Dissolved Oxygen (mg/L)	23	2.13	2.00	0.50	5.30	1.18
Otter	02323200	Fluoride (mg/L)	16	0.14	0.14	0.11	0.17	0.02
		Flow (cfs)	30	11.35	9.21	-0.25	26.00	7.47
		Potassium (mg/L)	16	0.90	0.90	0.70	1.10	0.15
		Magnesium (mg/L)	16	7.17	7.05	6.30	9.10	0.67
		Sodium (mg/L)	16	3.78	3.75	2.90	4.70	0.38
		Ammonia (mg/L)	21	0.03	0.02	0.02	0.08	0.02

Site	Station ID	Parameter	N	Mean	Median	Minimum	Maximum	Standard Deviation
		Nitrate-Nitrite N (mg/L)	24	1.24	1.26	0.07	2.00	0.47
		Orthophosphate (mg/L)	21	0.06	0.05	0.04	0.08	0.01
		Total Phosphorus (mg/L)	23	0.06	0.06	0.04	0.13	0.02
		Sulfate (mg/L)	16	30.65	31.00	13.50	37.60	5.44
		SpC (us/cm)	24	431.75	449.00	174.00	485.00	65.21
		Total Dissolved Solids (mg/L)	17	271.79	272.00	239.00	289.00	12.06
		Total Organic Carbon (mg/L)	16	4.05	1.09	0.50	48.40	11.84
		Turbidity (NTU)	16	0.42	0.42	0.20	1.30	0.27
		Stage (ft NGVD29)	0	N/A	N/A	N/A	N/A	N/A

#### 3.1.2 <u>Annual Medians Analysis Using 90th Percentiles Obtained from Empirical Lognormal</u> <u>CDFs</u>

**Nitrate-Nitrite N**: As shown in **Table 3** and **Figure 5**, the two most upstream sites had relatively low concentrations, with a significant increase between Luraville and Branford. A significant decrease in concentration occurred between Branford and Bell, which may be caused by dilution from the Santa Fe River joining the Suwannee River below Branford. Ellaville and Luraville grouped together as one group, and Bell and Wilcox was the second group. Branford stood alone likely due to the influence from elevated NOx concentrations in spring discharge between Luraville and Branford.

**SpC**: As shown in **Table 3** and **Figure 6**, there were apparent small but gradual increases along the longitudinal gradient from Ellaville to Branford, again likely due to influence from spring contributions, but no change was seen between Bell and Wilcox.

**Flow**: As shown in **Table 3** and **Figure 7**, an apparent small but gradual increase occurred along the longitudinal gradient from Ellaville to Branford, with a significant increase between Branford and Bell, and an incremental increase between Bell and Wilcox. There appears to be a possible grouping for Ellaville to Branford, and Bell to Wilcox, which is likely due to the Santa Fe River joining the Suwannee River below Branford.

Station	Nitrate-Nitrite N (mg/L)	SpC (us/cm)	Flow (cfs)
Ellaville	Ellaville 0.582		7653
Luraville	0.668	319.3	8062
Branford	1.051	334	8637
Bell	1.023	360.1	10612
Wilcox	0.919	360.6	11476

# Table 3 - Comparison of 90<sup>th</sup> Percentile Values of Annual Medians of Nitrate-Nitrite N, SpC, and Flow at Suwannee River stations near Ellaville, Luraville, Branford, Bell, and Wilcox (POR: 1989-2014)



Figure 5 – Empirical Lognormal CDF for Annual Median Nitrate-Nitrite N at Suwannee River stations near Ellaville, Luraville, Branford, Bell, and Wilcox (POR: 1989-2014)



Figure 6 - Empirical Lognormal CDF for Annual Median SpC at Suwannee River stations near Ellaville, Luraville, Branford, Bell, and Wilcox (POR: 1989-2014)



Figure 7 - Empirical Lognormal CDF for Annual Median Flow at Suwannee River stations near Ellaville, Luraville, Branford, Bell, and Wilcox (POR: 1989-2014)

#### 3.1.3 Correlations between Flow and Key Water Quality Parameters in River Stations

LOWESS graphs along with nonparametric correlation results (Spearman's Rho with associated p-values) are provided below for key water quality parameters for the Suwannee River stations. All five river stations exhibited statistically significant inverse relationships between flow and NOx (**Figures 8-12**), and flow and SpC as shown in **Figures 13** through **17**.



Figure 8 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration vs. Flow Data at Suwannee River station near Ellaville (POR 1989-2014)



Figure 9 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration vs. Flow Data at Suwannee River station near Luraville (POR 1989-2014)



Figure 10 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration vs. Flow Data at Suwannee River station near Branford (POR 1989-2014)



Figure 11 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration vs. Flow Data at Suwannee River station near Bell (POR 1989-2014)



Figure 12 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration vs. Flow Data at Suwannee River station near Wilcox (POR 1989-2014)



Figure 13 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration vs. Flow Data at Suwannee River station near Ellaville (POR 1989-2014)



Figure 14 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration vs. Flow Data at Suwannee River station near Luraville (POR 1989-2014)



Figure 15 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration vs. Flow Data at Suwannee River station near Branford (POR 1989-2014)



Figure 16 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration vs. Flow Data at Suwannee River station near Bell (POR 1989-2014)



Figure 17 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration vs. Flow Data at Suwannee River station near Wilcox (POR 1989-2014)

#### 3.1.4 <u>Correlations between Flow and Key Water Quality Parameters in Springs Stations</u>

LOWESS graphs along with nonparametric correlation results (with associated p-values) are provided below for key water quality parameters for the springs stations. Troy Springs flow and NOx, flow and SpC and SpC and NOx had statistically significant positive relationships, as shown in **Figures 18** to **20**. **Figure 21** shows a statistically significant positive relationship between flow and NOx in Lafayette Blue Springs. Flow and SpC had a statistically significant inverse relationship (**Figure 22**), and SpC and NOx did not have a statistically significantly relationship (**Figure 23**). Ruth (Little Sulphur) Springs flow and NOx, and SpC and NOx both had statistically significant positive relationships (**Figure 24** and **26**). Flow and SpC did not have a statistically significantly relationship significantly relationship (**Figure 25**). Based on the correlation results, these three springs likely receive water from different water sources, which could include a combination of diffuse flow derived from the springshed and direct conduit flow originating from swallets or the river reversing into the spring vent.



Figure 18 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration and Flow Data at Troy Springs (POR 1997-2007)



Figure 19 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and Flow Data at Troy Springs (POR 1997-2007)



Figure 20 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and NOx Data at Troy Springs (POR 1997-2007)



Figure 21 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration and Flow Data at Lafayette Blue Springs (POR 1997-2013)



Figure 22 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and Flow Data at Lafayette Blue Springs (POR 1997-2013)



Figure 23 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and NOx Data at Lafayette Blue Springs (POR 1997-2013)



Figure 24 - LOWESS Curve with Correlation Coefficients and P-values for NOx Concentration and Flow Data at Ruth (Little Sulphur) Springs (POR 1997-2013)



Figure 25 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and Flow Data at Ruth (Little Sulphur) Springs (POR 1997-2013)



Figure 26 - LOWESS Curve with Correlation Coefficients and P-values for SpC Concentration and NOx Data at Ruth (Little Sulphur) Springs (POR 1997-2013)

#### 3.2 Troy Springs Flow Reversal Evaluation

To evaluate spring flow reversals in Troy Spring, the long term ambient water chemistry (DO, NOx, Ca, color, and SpC) and hydrologic (flow and gage height) data time series were constructed, which are shown in **Figure 27**. The POR for this dataset was from 11/1992-1/2016 for most parameters except for stage and flow. Stage collection began in 7/1998 and had several data gaps throughout the POR. Flow had a much shorter and spottier POR, thus it was not included in subsequent data analyses. Data were collected on a variable frequency, generally every 2 to 12 months from 11/1992 through 1/2016. At first glance, it appears that spring flow reversals may have occurred in the winter, fall and spring months on the following seventeen dates due to substantial changes in either one or several parameters, specifically SpC, DO, gage height, color, NOx, and calcium (Ca) concentrations:

- 1. 12/11/1992 (change in SpC, DO, color, NOx, and Ca)
- 2. 8/3/1993 (change in DO, and Ca)
- 3. 8/19/1996 (change in DO)
- 4. 10/24/2000 (change in DO)
- 5. 3/14/2001 (change in DO)
- 6. 12/17/2003 (change in DO)
- 7. 3/8/2005 (change in SpC, DO, and color)
- 8. 1/19/2006 (change in SpC, DO, and color)
- 9. 11/28/2007 (change in DO)
- 10. 11/4/2009 (change in DO)
- 11. 9/11/2013 (change in SpC, DO, NOx, and stage)
- 12. 3/11/2014 (change in SpC, DO, color, and Ca)
- 13. 9/23/2014 (change in color)
- 14. 1/26/2015 (change in stage, SpC, DO, color, NOx, and Ca)
- 15. 2/18/2015 (change in stage, SpC, DO, color, NOx, and Ca)
- 16. 3/3/2015 (change in stage, SpC, DO, color, NOx, and Ca)
- 17. 1/11/2016 (change in stage, DO, and color)

It is generally understood that spring water that is derived from the Floridan Aquifer typically has lower DO, lower color, higher NOx, and higher Ca than river water. In addition, spring flow SpC concentrations in groundwater derived from the Floridan Aquifer are typically an order of magnitude higher than surface runoff or river water. This is true during normal conditions due to dissolution processes that occur in the diffuse karst matrix during prolonged contact time of the water with limestone rock. Based on this understanding, it can be inferred that during high flow and flooding events, substantial decreases in SpC in the spring vent may be suggestive of possible spring flow reversals that are siphoning Suwannee River water into the spring vent. Therefore, SpC was classified as an indicator and correlated with other water quality parameters to determine if there were obvious inflections in the slope of the curves defining the relationships between SpC and DO, color, NOx, and Ca.



Figure 27 - Ambient Water Chemistry and Hydrologic Data Time Series (stage, DO, NOx, Ca, color, flow, SpC (CONDF)) at Troy Springs (POR 11/1992-1/2016, SRWMD Station TRY010C1)

The goal of evaluating inflection points was to identify a threshold or breakpoint within each relationship where it is evident that spring flow has changed in chemical signature (i.e changing from groundwater source to surface water source) due to spring flow reversals on a weight of evidence approach. Figure 28 illustrates scatterplots of the relationships between SpC and the other four water quality parameters, DO, color, NOx, and Ca. Inflections were visually identified using the LOWESS line (degree of smoothing, f = 0.4) to identify the point (threshold) where the relationships between SpC and the other parameters had an abrupt and obvious change in slope and shape. It can be seen from Figures 28 through 31 that data clustered tightly in one region of the graph for most of the relationships, which likely indicates a groundwater source. The data points that were not within the tight clusters below the inflection points are assumed to be reflecting points in the record that indicate surface water influence on the spring flow (i.e. spring reversal events). The identified inflection point for SpC based on each of the parameters are provided in Table 4. In addition, thresholds for each of the parameters were identified based on the inflection points described (**Table 4**). The threshold for SpC was calculated as the mean value of the SpC concentration ranges based on each of the four explanatory variables (DO, color, NOx, and Ca).

If multiple (at least three) constituent concentrations exceeded their respective thresholds identified in **Table 4**, then a potential spring flow reversal was likely identified. Based on the threshold evaluation, eight of the seventeen dates mentioned above appear to have sufficient corroborating evidence to suspect a spring flow reversal, which include the following dates:

- 1. 12/11/1992
- 2. 3/8/2005
- 3. 1/19/2006
- 4. 9/11/2013
- 5. 3/11/2014
- 6. 1/26/2015
- 7. 2/18/2015
- 8. 3/3/2015

The other potential nine dates mentioned earlier did not have concentrations that exceeded enough of the specified thresholds to support describing those as reversal events. **Table 5** shows the POR divided into five-year increments and the percentage of the year based on the number of sampling events for that five-year span that spring reversals likely occurred. **Table 5** shows that the first five-year period (1992-1996) had spring reversals during 7% of the sampling events for that periods did not have any expected reversals. The last period (2012 -2016) had the most reversals during any of the five-year periods, with 17% of that five-year period having expected spring flow reversals.



Figure 28 - Scatterplots of the Relationship between SpC and DO at Troy Springs (POR 11/1992-1/2016, SRWMD Station TRY010C1)



Figure 29 - Scatterplots of the Relationship between SpC and Color at Troy Springs (POR 11/1992-1/2016, SRWMD Station TRY010C1)



Figure 30 - Scatterplots of the Relationship between SpC and NOx at Troy Springs (POR 11/1992-1/2016, SRWMD Station TRY010C1)



Figure 31 - Scatterplots of the Relationship between SpC and Ca at Troy Springs (POR 11/1992-1/2016, SRWMD Station TRY010C1)

	SpC (uS/cm)	DO (mg/L)	Color (PCU)	NOx (mg/L)	Ca (mg/L)
Threshold	<294*	>2	>30	<1.0	<48
SpC Concentration at Inflection Point	NA	338	329	314	330

Note: \*Departure threshold for SpC was calculated as the mean value of the SpC concentration ranges for each of the four explanatory variables (DO, color, NOx, and Ca).

# Table 5 – Number of and Percentage of Expected Spring Flow Reversals per Five-yearSpan in Troy Spring

Five-year Span	Number of Spring Reversals	Number of Sampling Events per Five-year Span	Percentage of Five- year Span Spring Reversals Occurred
1992-1996	1	15	7%
1997-2001	0	38	0%
2002-2006	2	41	5%
2007-2011	0	38	0%
2012-2016	5	29	17%

Departures from the long term median were calculated and used to further evaluate the potential for spring flow reversals occurring on the dates above as another line of evidence. SpC concentration time series, long term median, and departure from the median are provided in **Figure 32** for a closer look at potential spring flow reversals using SpC as a tracer.



Figure 32 - Long Term Specific Conductance Time Series, Median and Departure from the Median for Troy Springs (SRWMD Station TRY010C1)

It must be noted that significant data gaps were evident in the entire POR, which makes it difficult to assess how long a spring flow reversal may be occurring. The current long-term POR does not provide sufficient data frequency to identify any durations for suspected events since samples were collected every two to six months. Especially when most reversals may endure less than a month. Furthermore, the evident characteristic changes seen in the available spring discharge dataset do not likely encompass all of the reversals that may have occurred during the POR. Data availability is highly variable for the entire POR as shown in **Figure 33**. Based on the large gaps between samples for some years (2-6 months), it is not possible to estimate the duration of the potential spring reversal events.



Note: 2016 only included January data due to data retrieval occurring in January 2016.

# Figure 33 - Variability of Ambient Data Collection Frequency for Troy Springs (SRWMD Station TRY010C1)

In addition to the ambient grab sample data discussed above, continuous USGS (Station 2320250, POR 7/3/2014-1/10/2016) daily gage height, temperature, DO, pH, NOx, and SpC (both continuous: SpCond\_min and ambient: SpCond\_F) data were reviewed to further investigate the potential for spring flow reversals on a different time scale at Troy Springs and is presented in **Figure 34**. Specific conductance was measured the same way for both the continuously collected SpCond\_min and the less frequently collected SpCond\_F that's collected as part of the ambient monitoring program using a multiparameter probe in the field. The only difference is the frequency of observations, which is either continuous or monthly/ bimonthly/ quarterly, respectively. **Figure 35** provides a pared down version of **Figure 34** that only includes daily continuous NOx, DO, and gage height at Troy Springs for the same POR.



Figure 34 - Continuous Daily Water Chemistry and Hydrologic Data Time Series (stage, Temperature, DO, pH, NOx, SpC (continuous), and Ambient SpC (SpCond\_F) at Troy Springs (POR 7/3/2014-1/10/2016, USGS Station 2320250)



Figure 35 - Continuous Daily Water Chemistry and Hydrologic Data Time Series (stage, DO, and NOx) at Troy Springs (POR 7/3/2014-1/10/2016, USGS Station 2320250)

As seen in both **Figures 34** and **35**, the USGS does not report water chemistry data collected during flood or backwater events. This is evident from the gap in the water chemistry dataset during the elevated stage height during a flood that began on 12/26/2014 and appeared to last for 78 days until 3/16/2015. During the flooding event, gage height increased by 11.3 ft, from 12.61 ft to 23.91 ft. This flooding event appears to have associated reductions in SpC, as is shown with the ambient data that were plotted along with the continuous data in **Figure 34**. The continuous dataset corroborates the suspected flooding event(s) that were identified with the ambient grab sample data on 1/26/15, 2/18/2015, and 3/3/2015. It is more likely that the three discrete events previously identified with the ambient dataset were part of a single longer sustained flooding event. However, without the continuous water chemistry data, it is not possible to fully confirm whether or not this was one potential prolonged or several discrete spring flow reversal events. Reporting data during backwater or flooding events will allow for better documentation of potential spring flow reversals.

## 4.0 SUMMARY AND CONCLUSIONS

Five Middle Suwannee River stations and three springs were evaluated to characterize the water quality parameter concentration distributions and associations made between parameter concentrations and flow to determine if water quality is an appropriate water resource value that could be used for the development of the MFL for the river and/or the springs. Best available data were used to conduct all of the data analyses.

All five river stations exhibited statistically significant inverse relationships between flow and NOx and flow and SpC. The consistency of relationships between flow and NOx and flow and SpC was not maintained for the three springs sites. Based on the correlation results between flow, specific conductance, and nitrate, the three assessed springs likely receive water from different water sources, with the dominant source being dependent on discharge levels and flooding conditions. These differences can likely be extrapolated to the other many springs that occur within the MSR basin.

Although the results are variable, during high flows and flooding events, it's possible that water is mostly being sourced from direct conduit flow originating from swallets or the river reversing into the spring vents. During low flows, diffuse groundwater flow derived from storage within the springshed may be the dominant source of water to the springs. These temporally-specific and site-specific differences likely preclude the ability to use water quality concentrations as an acceptable water resource value (WRV) and assign a collective MFL for the spring based on the variable relationships between water quality concentrations and flow. The spring discharge is clearly derived from various sources and not only groundwater from the Floridan Aquifer, with the contribution from the dominant sources being highly dependent on the water level and climatic conditions.

To evaluate the different water sources being discharged from the springs, spring reversals caused by flooding events were evaluated based on a number of water quality and hydrological parameters. Spring flow reversals in the Middle Suwannee River are not simply based on river stage above a weir outlet. The occurrence and magnitude of spring-flow reversals is a function of the difference between the water-surface elevation of the spring pool (which is often the same as the river) and the head(s) in the aquifer, as well as the nature and degree of connection(s) between the spring and the aquifer. Due to the pronounced changes in water chemistry characteristics that occur in spring discharge during floods, and given available data, it was possible to identify potential spring flow reversals by evaluating the chemical composition in the data POR for Troy Spring. Based on the results, it is suspected that at least eight spring flow

reversals have occurred at Troy Spring between 1992 and 2015. The durations of these reversals are unknown, but may have lasted from one month to several months.

These relationships need to be explored in site-specific detail before springs MFLs aimed at preventing any conceivable significant harm from excessive reversals can be determined. Further, the existing hydrologic and water quality data is not available at a sufficient frequency over a long enough POR to make defensible calculations of baseline reversal frequency for any of the springs along the MSR to use the relationships between water quality and flow as an applicable WRV. Although the difference in water sources to the springs and the insufficiency in best available data precludes the ability to establish a flow reversal component as a WRV for the MFL for priority springs, the information gathered from this task is highly instructive in elucidating the potential for utilizing water quality in determining MFLs for individual springs in the MSR. This technical memorandum also serves as a foundation for planning future data collection efforts focused upon water quality-flow relationships in these springs.