GEOLOGICAL SURVEY OF ALABAMA

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GROUNDWATER ASSESMENT PROGRAM

ANNUAL REPORT

SURFACE WATER QUALITY UPDATE OF THE CHOCTAWHATCHEE, PEA AND YELLOW RIVERS IN SOUTHEAST ALABAMA

OPEN-FILE REPORT 1804

By

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Choctawhatchee, Pea and Yellow Rivers Watershed Management Authority

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Historical water quality data

EXECUTIVE SUMMARY

This investigation was commissioned by the Choctawhatchee, Pea and Yellow Rivers Watershed Management Authority. The study was funded by the Choctawhatchee, Pea, and Yellow Rivers Watershed Management Authority (CPYRWMA) and the Geological Survey of Alabama (GSA). Work on the project was initiated by the GSA on May 24, 2017.

The purpose of the project was to update water quality information in the Choctawhatchee, Pea and Yellow Rivers watersheds that may be used by the CPYRWMA, local, state, federal agencies and citizens to develop, manage, and protect the water resources of the region.

The water-quality and river discharge datasets are composed of six water samples (two per each site) collected by the GSA in 2017 and compared to samples collected from April to September 2002 for the Yellow River and August 2006 to February 2008 for the Choctawhatchee and Pea Rivers.

Most of the southern half of the study area is used for agriculture (for example, herbaceous planted/cultivated land uses). Nutrient enrichment is a cause of water-quality impairment in this region. Evaluations of normalized nitrate (NO_3^--N) and total phosphorus (total-P) loads indicate that site CR-1 in the Choctawhatchee River, had the greatest concentrations.

Metals are naturally present in surface waters in small concentrations. When metals exceed water-quality criteria it may be the result of man's activities. Lead concentrations exceeding the USEPA primary/secondary drinking water standard of 15 μg/L were historically measured at site CR-1 and PR-3 in the Pea River, but was not detected in any water samples collected in 2017. Lead concentrations in excess of the chronic aquatic life criterion for freshwater (0.48 μg/L) were recorded at all sites.

Analytical data linked with land-use/land-cover analyses helped identify potential contamination sources. When all primary constituents are considered, water quality was most impacted at sites PR-3 and CR-1. The sites that appear to be impacted by contamination correlated with pollutant sources and land uses in the respective watersheds, as predicted prior to monitoring.

INTRODUCTION

The Choctawhatchee, Pea and Yellow Rivers watersheds cover a significant portion of southeast Alabama. This report generated a recent set of hydrochemical and discharge data for the CPYRWMA to assist in protecting and managing water quality.

The primary constituents that affect water-quality of Alabama streams originate from nonpoint sources and consist mainly of suspended sediments, nutrients and metals. Evaluation of these constituents provides a good indication of overall water-quality and stream health. Land-use/land-cover analyses are important in evaluation and delineation of potential contaminant sources. Therefore, geochemical characterization of water-quality combined with evaluations of land use/land cover provides indications of pollutant sources, magnitudes of impact, and supports mitigation efforts.

Previous assessment in Yellow River watershed was performed by GSA in 2001- 2002 (Cook and Others, 2002) contained data used to determine the hydrogeochemical and biologic character of the selected streams and the viability of selected watersheds for development of surface-water sources. It also characterized cultural resources, threatened and endangered species, sedimentation, and water quality and quantity.

In 2010 an open file report was published (Murgulet and Cook 2010), which evaluated the cumulative effects of land use on water-quality from the Choctawhatchee and Pea Rivers, showing that the primary constituents that affected water-quality of streams in Alabama originated from nonpoint sources.

ACKNOWLEDGMENTS

The GSA acknowledges the CPYRWMA, including the CPYRWMA Board of Directors, Chairmen Mr. Randy Hale, and Executive Director Ms. Barbara Gibson, whose participation and cooperation made this study possible.

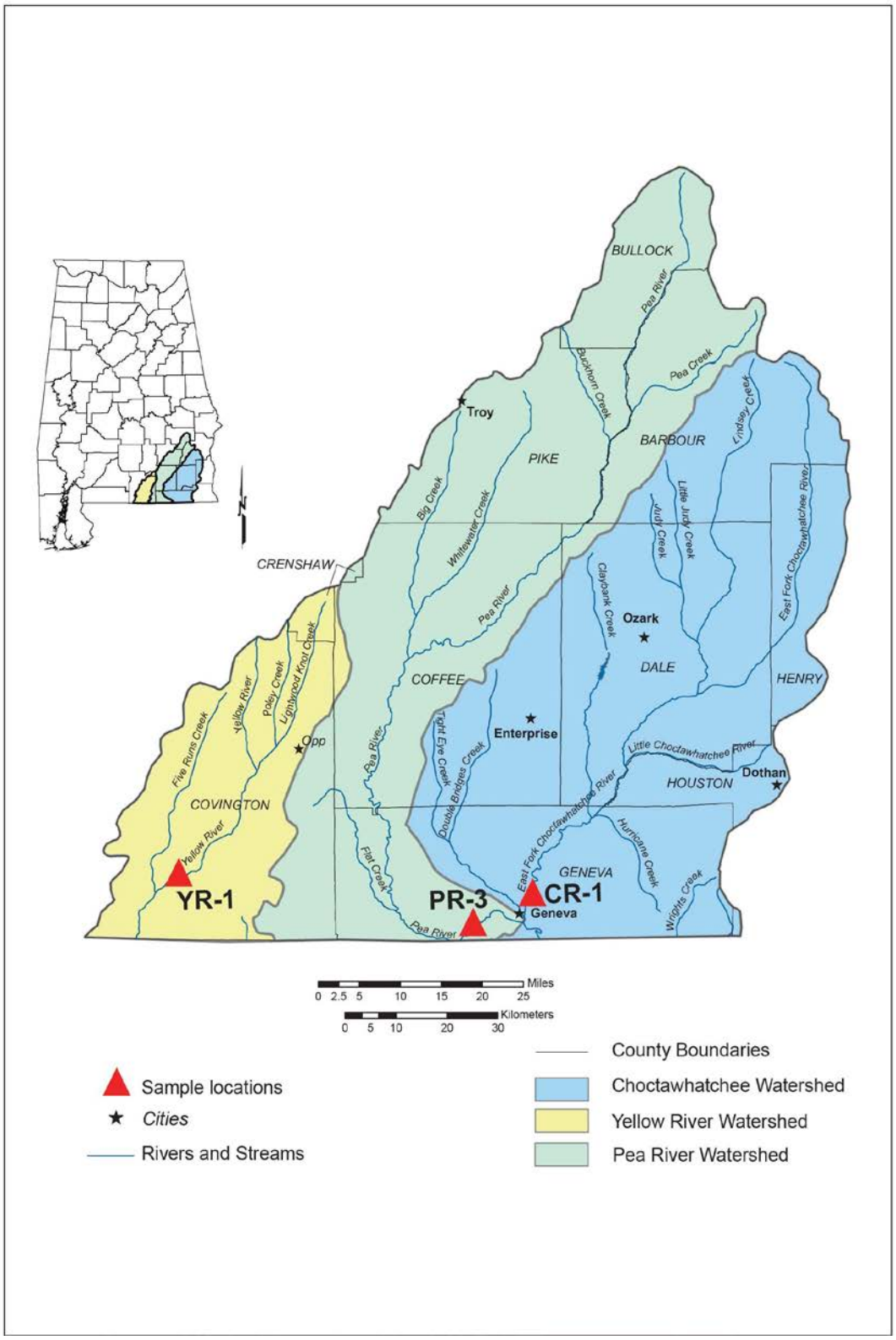

Figure 1. Choctawhatchee, Pea, and, Yellow Rivers watersheds and monitoring sites.

STUDY AREA

The CPYRWMA is an agency dedicated to ensuring water resources of the Choctawhatchee, Pea and Yellow Rivers are wisely developed, properly used, and enhanced for present and future generations. The Choctawhatchee River originates as two separate forks (East Fork and West Fork) in wetlands near Clayton in Barbour County. Near Ozark, the forks merge to form the Choctawhatchee River, which flows southwest to Geneva for about 48 miles. The Choctawhatchee River is one of the longest free-flowing rivers remaining in Alabama.

Its main tributary, the Pea River, joins the Choctawhatchee just below Geneva. The Pea River watershed drains an area west of the Choctawhatchee River and originates in Bullock County south of Union Springs. The Pea River then flows southwest toward Elba for approximately 68 miles, then south for 30 miles just west of Samson, gradually turning east and dipping slightly into Florida before joining the Choctawhatchee River south of Geneva.

The Yellow River originates just south of Bullock in Crenshaw County and flows south through Covington County, Alabama, across northwest Florida before entering Pensacola Bay.

Monitoring sites were located in downstream sections of the Choctawhatchee, Pea and Yellow Rivers (fig. 1). The location on the Choctawhatchee River (CR-1) is situated near the confluence of the Choctawhatchee River with Double Bridges Creek about one mile from the confluence with the Pea River. Site PR-3 on the Pea River is located in Geneva County near the confluence of the Pea and Choctawhatchee Rivers. The Yellow River site YR-1, is located in Covington County at Alabama Highway 55 crossing (Watkins Bridge) (table 1, fig. 1).

Table 1. Choctawhatchee, Pea, and Yellow Rivers monitoring sites, location and area.

Location	Site No.			Watershed area (mi^2)
		Latitude	Longitude	
Choctawhatchee River at Ala. Hwy. 52 crossing Geneva Co.	CR-1	31.0411171	85.8523428	3,097
Pea River at Ala. Hwy.27 crossing Geneva Co.	PR-3	31.0272540	85.8838628	1,552
Yellow River at Ala. Hwy. 55 crossing Covington Co.	YR-1	31.0950007	86.4358611	482

CLIMATE

The climate in Alabama, including the Choctawhatchee, Pea, and Yellow Rivers Watershed (CPYRW) area, is classified as humid sub-tropical with hot summers, mild winters, and moderate amounts of precipitation. Average daily temperatures range from a high of 91˚F to a low of 65˚F in the summer and a high of 60˚F to a low of 39˚F in the winter. Average precipitation ranges from 51 inches in the northeastern section of the basin to 61 inches in the southwest.

HYDROGEOLOGY AND GEOMORPHOLOGY

Rivers in this study area are underlain by Cretaceous and Tertiary age sediments. These sediments are chiefly composed of sand and clay, mixed clastic, residuum, and thin carbonate rocks. Several geologic units crop out in the CPYRW area (fig. 2). In the Double Bridges Creek, and Little Choctawhatchee River watersheds, erosion caused by water movement exposes the Hatchetigbee, Tallahatta, and Lisbon Formations and the Jackson Group along the sides of the incised stream valleys (Cook and Kopaska-Merkel, 1996). Further downstream, the watershed is underlain by sediments of Eocene-Oligocene age, primarily composed of clay and residuum. Sediment from erosion of incised valleys was deposited downstream along the floodplain. These relatively recent alluvial sediments are part of the Quaternary System and are composed of gravel, sand, and clay.

Groundwater moving through these unconsolidated sediments issues from seeps and springs in the stream valleys and is the major source of stream discharge during dry conditions. The topographic and geomorphologic characteristics of these streams cause flashy storm runoff, resulting in highly variable surface water levels, especially during winter and spring. The stream channels are characterized by steep banks and riverbeds composed of thick silt and sand. Tributaries are classified as youthful to mature with narrow floodplains, v-shaped valleys, and narrow meander belts. River gradients in the study area vary, dependent upon the uniformity of the erodible substrate and the proximity to the river source, with the lowest gradient at Little Choctawhatchee River (10 feet per mile) and the highest at Little Double Bridges Creek (22 feet per mile) (Cook and Kopaska-Merkel, 1996).

Recharge areas are the basis for groundwater/surface-water interaction and serve to provide base flow that supports stream discharge and reservoir levels, wetlands, and aquatic habitat throughout the study area. Major water-bearing geologic units underlying the CPYRW area vary in age from the Cretaceous system to the alluvial and terrace deposits of the Quaternary system (Moore, 1998).

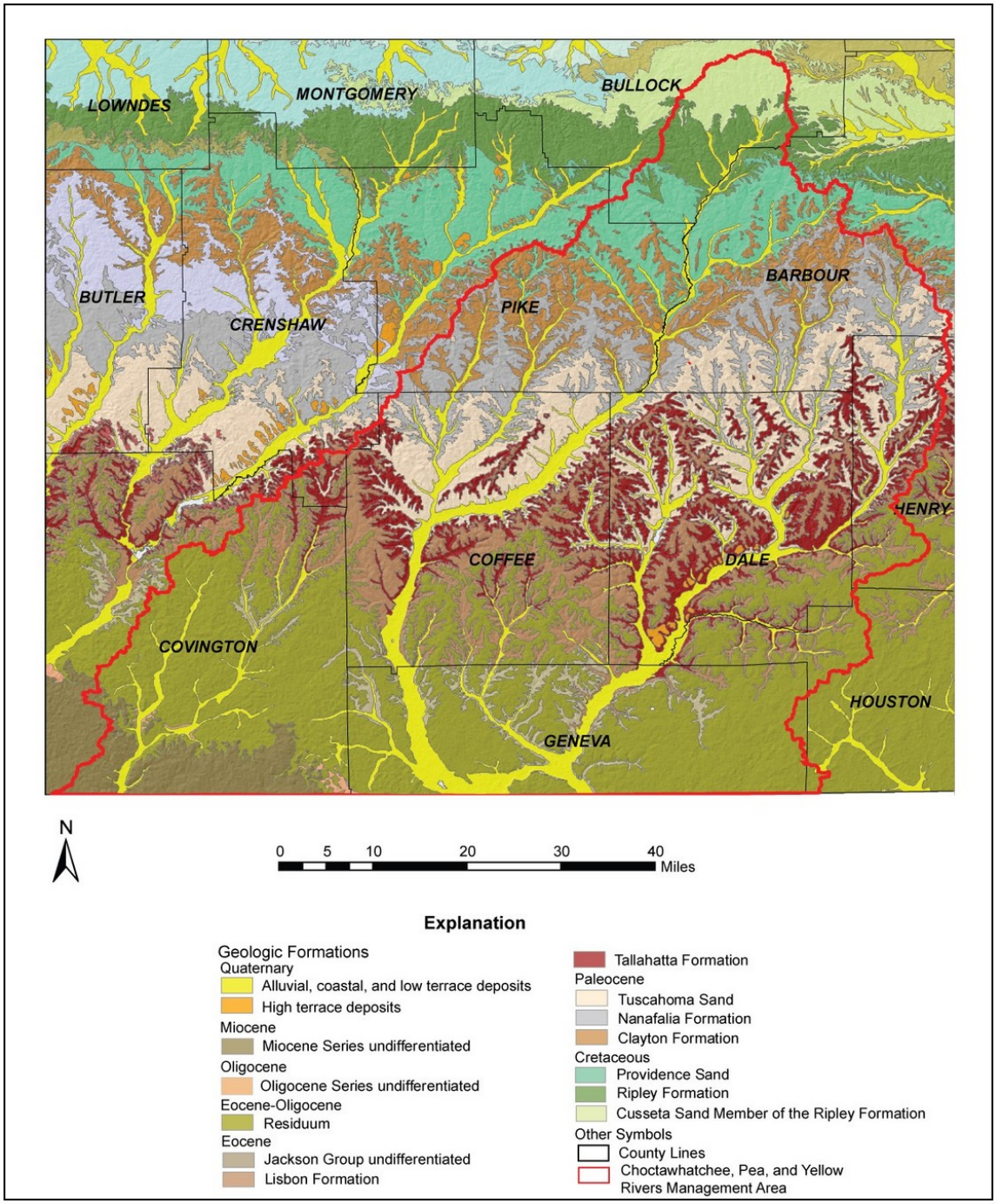

Figure 2. Geologic formations for the CPYRW study area (modified from Osborne and others, 1988).

PHYSIOGRAPHY AND GEOLOGY

The CPYRW study area lies within the East Gulf Coastal Plain physiographic section of Alabama, and is characterized by gently rolling hills, sharp

ridges, prairies, and alluvial flood plains. The highest point of elevation in the watershed is located in the upper northern portion where the crests reach approximately 640 feet above sea level.

Geologic units underlying the Coastal Plain are of sedimentary origin and consist of sand, gravel, porous limestone, chalk, marl, and clay. These strata dip underground to the south-southwest at approximately 35 to 40 feet per mile and strike generally in east-west belts (fig. 2). Some of the strata are more resistant to erosion and underlie broad saw-toothed ridges known as cuestas that slope gently to the south with steep north-facing slopes. Eight physiographic districts are delineated in the East Gulf Coastal Plain of Alabama including the Fall Line Hills, Black Belt, Chunnenuggee Hills, Southern Red Hills, Lime Hills, Dougherty Plain, Southern Pine Hills, and Coastal Lowlands (Sapp and Emplaincourt, 1975). Four of these districts including Chunnenuggee Hills, Southern Red Hills, Dougherty Plain, and Southern Pine Hills are present in the study area (fig. 3).

The Chunnenuggee Hills district consists of a series of pine-forested sand hills developed on hardened beds of clay, sandstone, siltstone, and chalk.

The Southern Red Hills district extends in a belt more than 60 miles wide across the study area. The Southern Red Hills is characterized by cuesta type ridges with steep, serrate north slopes and gentle back slopes. Topographic relief in the Southern Red Hills is some of the greatest in the Coastal Plain of Alabama. Streams in this area acquire upland characteristics with high gradient, hard-rock bottoms, and swifter flows. The headwaters of the Choctawhatchee River originate on the southern slope of the Ripley Cuesta in the Southern Red Hills.

The Dougherty Plain district or “wiregrass region” of the study area includes portions of Henry, Dale, Houston, Geneva, Coffee, Crenshaw, and Covington Counties. It is composed of limestone, sand, and clay. Active solution of the underlying limestone produces many shallow, flat-bottomed depressions that dot the landscape. Small headwater streams are noticeably absent from the Dougherty Plain because active solution transfers many of the drainages to underground channels. The name “wiregrass” originates from the common occurrence of needle rush in the wet, shallow depressions. The confluence of the Choctawhatchee and Pea Rivers occurs in the Dougherty Plain in southern Geneva County.

The Southern Pine Hills district in the study area includes extreme southern Covington County. Topography is low relief with broad, rounded ridges and V-shaped valleys with sand and clay sediments. The portion of the region in Covington County has thin sand and clay sediments overlying limestone. In this area, active solutions features similar to the Dougherty Plain are common. The most prominent of these features is Lake Jackson in Florala. Flat uplands with

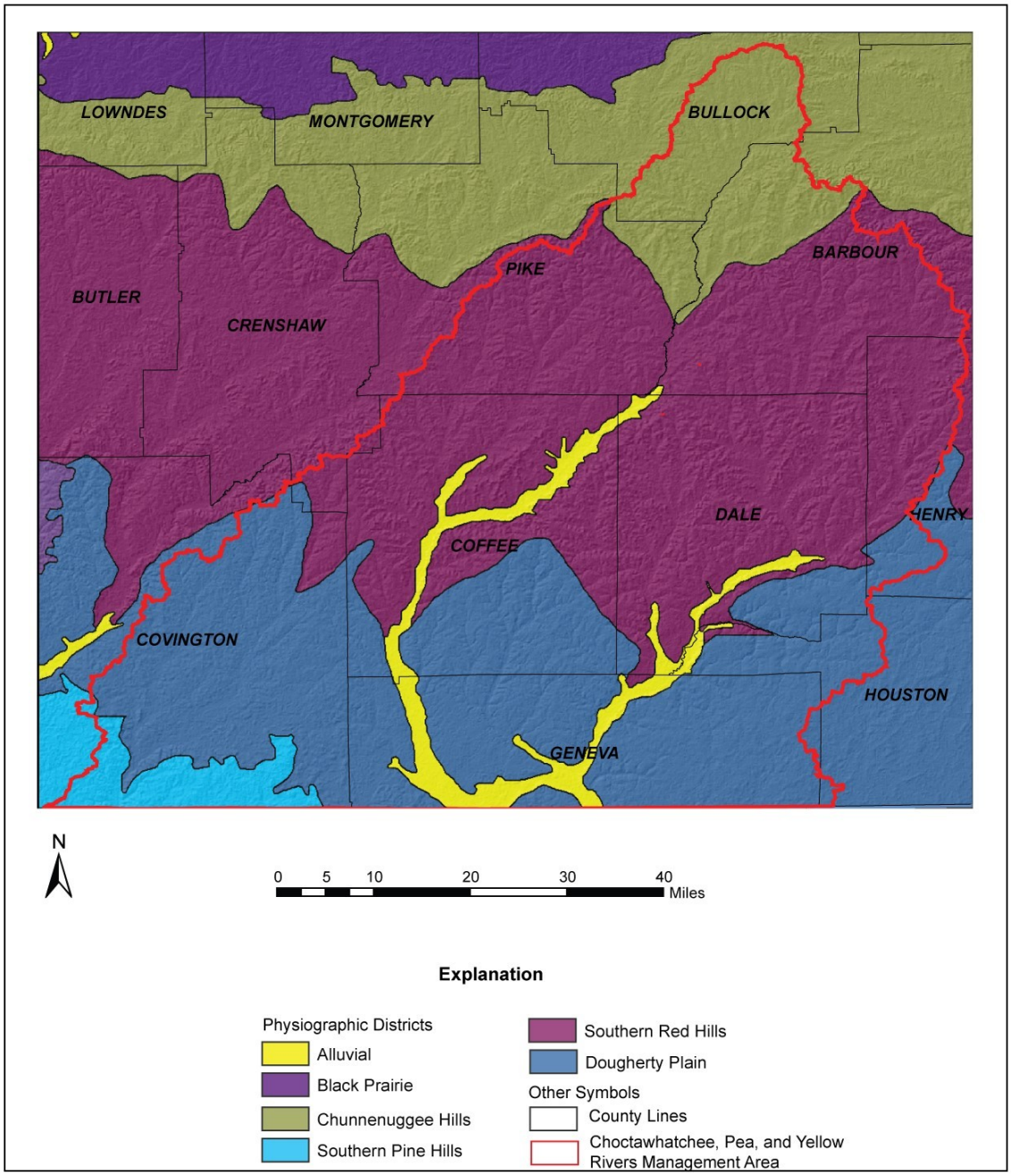

Figure 3. Physiographic regions and the Choctawhatchee, Pea and Yellow Rivers watershed.

shallow ponds, bogs, and marshes occur throughout the district and many of the valleys are saucer-like perpetually wetted by seepage from nearby hills.

The abundance of warm summer rains is a major factor in leaching fertility from the soil and favoring the growth of pines in this region. The Yellow River drains the Southern Pine Hills in the study area.

LAND USE/LAND COVER

Land-use practices are important factors that influence water-quality and water availability, but the impact of land use changes may be difficult to accurately determine on a regional scale. A landscape pattern is influenced by both natural processes and those related to human activity. However, in recent decades, human-generated processes have been the dominant force shaping landscape patterns in the United States. To see the change in land use over a 10 year time period, the 2001 and 2011 USGS Land Use/Land Cover data (Homer and others, 2004, 2015) were compared. These datasets were compiled from Landsat Thematic Mapper Plus (ETM+) satellite imagery (circa 2001 and 2011).

The LULC Level II classification maps includes an explanation with class description and corresponding color schemes, and the following subclasses: open water, developed-open space, developed-low intensity, developed-medium intensity, developed-high intensity, barren land (rock/sand/clay), deciduous forest, evergreen forest, mixed forest, shrub/scrub, grassland/herbaceous, pasture/hay, boundary cultivated crops, woody wetlands, and emergent herbaceous wetlands. These subclasses are grouped in five main categories: water bodies, urban, forest, agriculture, and wetlands (figs. 4 and 5; table 2).

The region is heavily forested with the dominant forest type being evergreen. The next common forest classes are deciduous, shrubland, mixed forest, and grassland herbaceous. The forest coverage increased from 57% - 66% in 2001 to 60 - 69 percent in 2011 in contrast to agricultural land, which declined.

Table 2. Area and proportion of agriculture and forest cover by watersheds in the study area with changes between 2001 and 2011.

			Upper Choctawhatchee River					Pea River					Yellow River				
			2001		2011		Change	2001		2011		Change	2001		2011		Change
		Land Cover	Acres	Percent	Acres	Percent	Acres	Acres	Percent	Acres	Percent	Acres	Acres	Percent	Acres	Percent	Acres
1	Water bodies	Open Water	7,253	1	7,944	1	692	7,671	1	7,670	1	-1	3,410	1	3,430	1	20
2	Urban	"Developed Open Space"	53,880		55,009		1,128	38,851		39,216		365	16,705		16,904		200
		"Developed Low Intensity"	14,335		16,430		2,095	4,421		4,914		492	2,374		2,456		82
		"Developed Medium Intensity"	4,918		6,200		1,282	1,219		1,848		630	451		654		203
		"Developed High Intensity"	2,174		2,519		345	457		628		170	179		206		27
			75,308	8	80,158	8	4,850	44,948	5	46,606	5	1,658	19,709	6	20,221	6	512
		Barren Land	1,432	0	1,319	0	-112	1,529	0	646	0	-883	64	0	97	0	33
3	Forest	Deciduous Forest	131,299		131,916		617	124,552		127,011		2,459	28,839		30,010		1,171
		Evergreen Forest	214,455		231,561		17,106	251,976		248,114		-3,862	108,533		108,605		71
		Mixed Forest	72,942		64,667		-8,275	103,547		89,734		-13,814	42,008		38,205		-3,803
		Shrub/Scrub	143,788		149,562		5,774	121,278		143,705		22,427	34,656		33,730		-926
		Herbaceuous	3,100		14,681		11,580	1,051		21,338		20,287	245		14,198		13,953
		Total forest	565,583	57	592,386	60	26,803	602,405	66	629,902	69	27,497	214,282	65	224,748	68	10,466
	Agriculture	Hay/Pasture	109,311		99,939		-9,372	98,185		85,250		-12,936	61,323		51,959		-9,365
		Cultivated Crops	174,171		153,174		-20,997	86,676		72,770		-13,906	14,427		12,864		-1,564
		Total agriculture	283,482	29	253,113	26	-30,369	184,861	20	158,020	17	-26,842	75,751	23	64,822	20	-10,928
4	Wetlands	Woody Wetlands	54,006		50,682		-3,324	68,242		65,513		-2,729	14,943		14,826		-117
		Emergent Herbaceuous Wetlands	984		2,447		1,462	3,310		4,616		1,306	823		830		7
		Total wetland	54,990	6	53,129	5	-1,861	71,552	8	70,129	8	-1,423	15,766	5	15,657	5	-110

color cells indicate a decline in LULC acreage

Table 2. Area and proportion of agriculture, forest, urban, wetland and open water cover in the study area, with changes between 2001 and 2011.

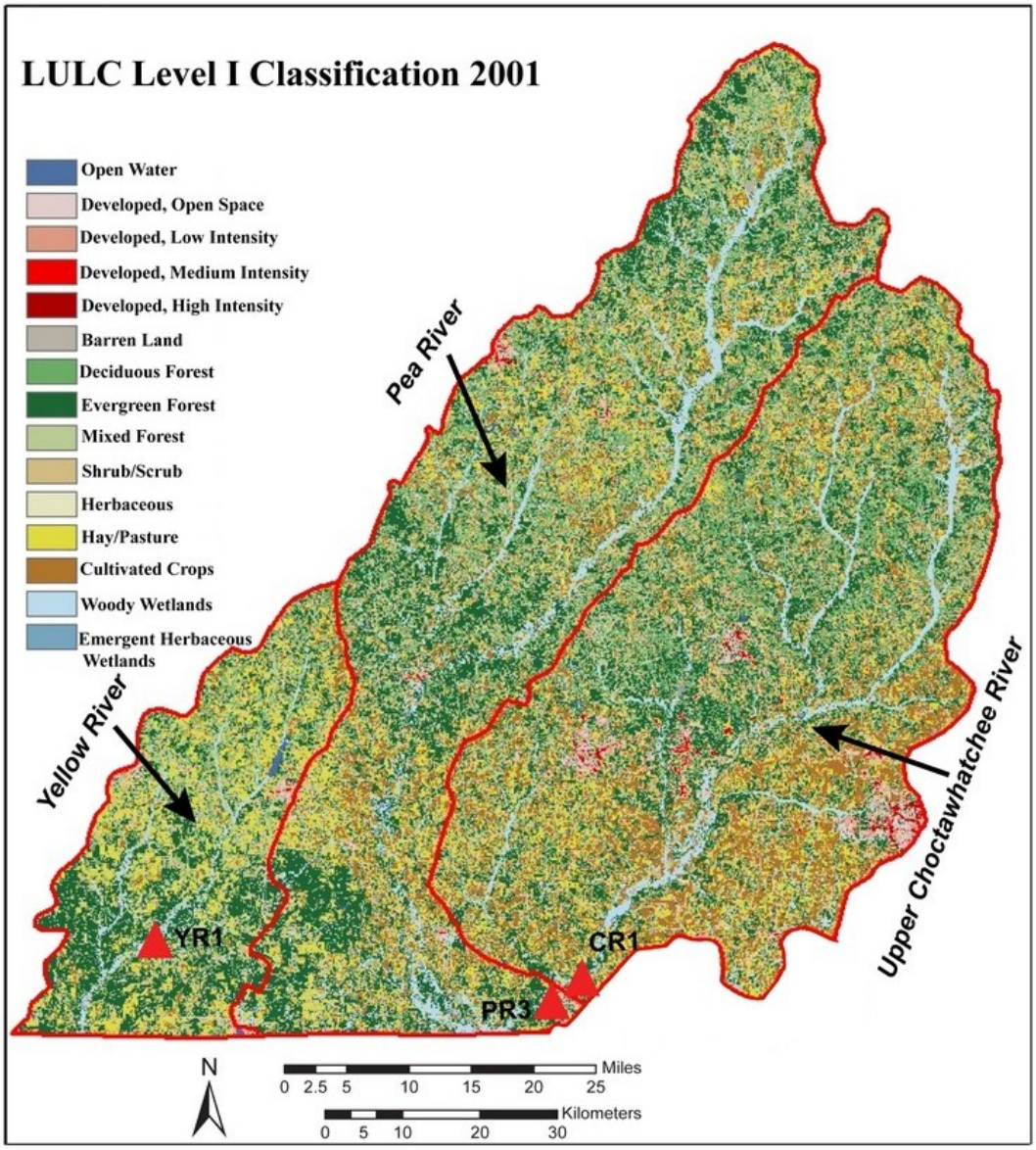

Figure 4. Land use/land cover, Level II classification of the Choctawhatchee, Pea, and Yellow Rivers watersheds (modified from USDA-Cropland Data Layer for Delta States, 2010).

Agriculture is the second largest land use category. The geology, soils, physiography, and topography collectively create an environment favorable for agriculture (figs.4 and 5), which, in large part is comprised of pasture, hay, and row crops. The variety of crops in the CPYRW area include corn, cotton, sorghum, soybeans, peanuts, millet, alfalfa, sweet corn, winter wheat, rye, oats, sweet potatoes, watermelons, peas, clover/wildflowers, cantaloupes, and squash. It has been recognized that these land-use activities are generally associated with

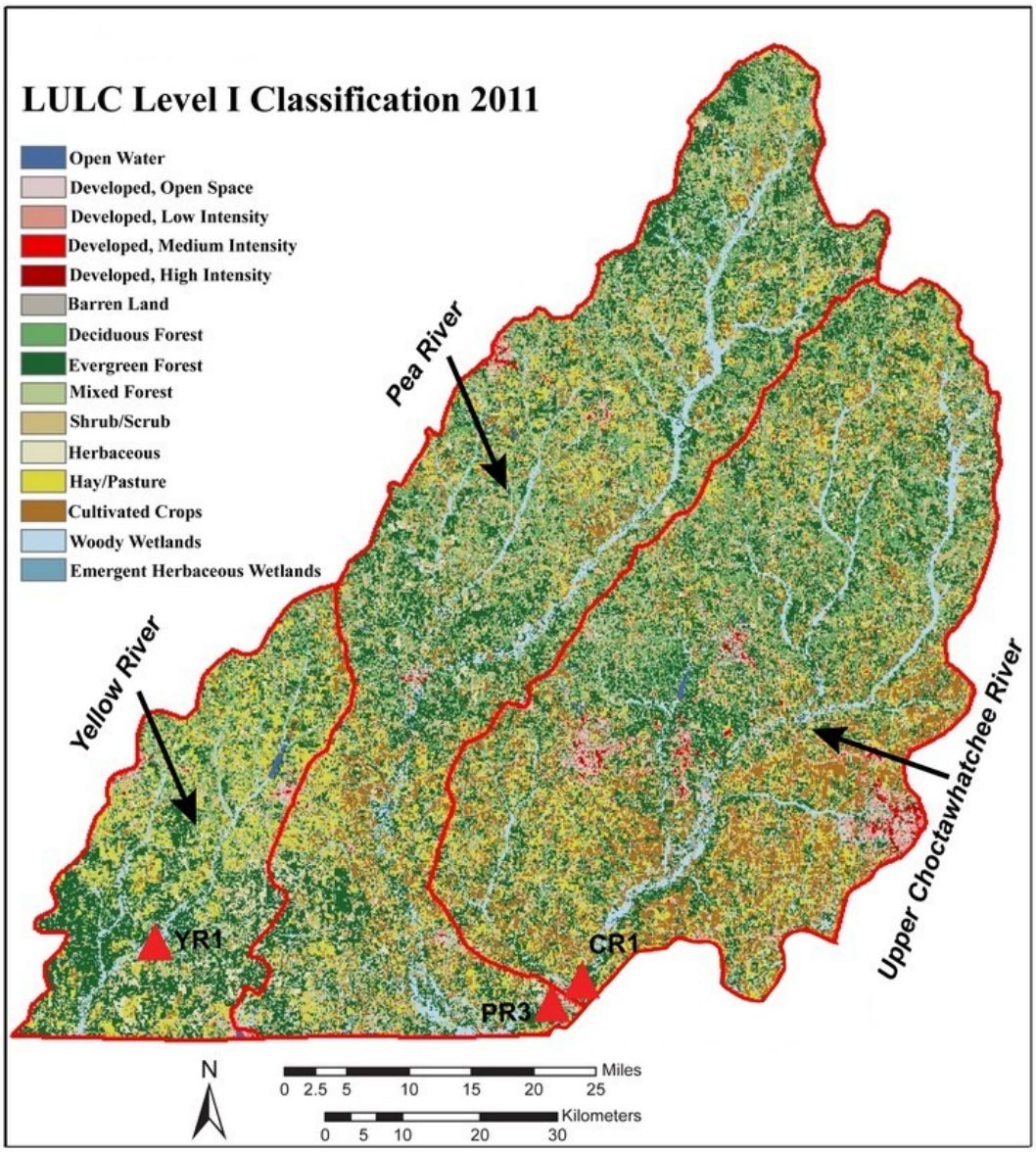

Figure 5. Land use/land cover, Level II classification of the Choctawhatchee, Pea, and Yellow Rivers watersheds (modified from USDA-Cropland Data Layer for Delta States, 2010).

increases in sedimentation, bacteria, and nutrients in many CPYR watersheds.

Runoff of fertilizers and animal waste transports excessive amounts of phosphorus and nitrate to streams and intensifies bacterial activity. Such factors are responsible for water-quality deterioration and reduced water availability and use.

Urban areas are classified into four categories: developed/open space, developed/low intensity, developed/medium intensity, and developed/high intensity. Urban area was unchanged between 2001 and 2011.

Wetland classes include woody wetlands and herbaceous wetlands. They were basically unchanged for the last 10 years except the Upper Choctawhatchee River watershed where wetlands declined from 6 to 5 percent. Land uses such as cropland, hayland, pastureland, nurseries, rangeland (grasslands, shrublands), disturbed forest land, construction sites, road surfaces, etc., are other major factors that influence the extent of sediment and contaminant loading to the Choctawhatchee, Pea, and Yellow Rivers watershed.

CLEAN WATER ACT SECTION 303(d) LISTED STREAMS

Section 303(d) of the Clean Water Act requires that states identify waters that do not support their designated uses, to determine the pollutants that cause degradation of water-quality, and to establish a total maximum daily load for the pollutants of concern (ADEM, 2008). In 1996, the Choctawhatchee River watershed was not on the 303(d) list. However, beginning in 1998, the Choctawhatchee River watershed appeared on the list of impaired waters with five stream segments: Hurricane, Beaver, Walnut, and Harrand Creeks and Dowling Branch. The number increased to seven in 2008 with the addition of Judy and Indian Camp Creeks and to 14 in 2014, including new segments in Choctawhatchee, Pea and Yellow Rivers.

- Judy and Beaver Creeks with headwaters in Barbour County, flowing into the West Fork Choctawhatchee River in Dale County, were listed for nutrient contaminants from an unknown source;

- Hurricane Creek, which discharges directly to the Choctawhatchee River in Geneva County, was listed for pathogens from agriculture and municipal and urban runoff/storm sewers;

- Beaver Creek, which receives effluent from the city of Dothan Waste Water Treatment Plant in Houston County, was listed as impaired by increased nutrients and organic enrichment (carbonaceous biochemical oxygen demand (CBOD) and from nitrogenous biochemical oxygen demand (NBOD)) from sources such as municipal and urban runoff/storm sewers;

- Dowling Branch, originating in Geneva County and discharging into Cox Mill Creek, is impaired due to pathogens and organic enrichment (Carbonaceous biochemical oxygen demand/CBOD, Nitrogenous biochemical oxygen demand/NBOD) derived from agriculture, urban runoff/storm sewers, and municipal sources;

- Harrand Creek, flowing from Coffee County and discharging to Claybank Creek in Dale County, was listed for siltation (habitat alteration) caused by urban runoff/storm sewers;

- Indian Camp Creek, originating in Coffee County and discharging into Harrand Creek (Coffee County, just east of Enterprise) is listed for siltation with sources such as urban runoff/storm sewers and land development;

- Walnut Creek, with headwaters in Pike County and discharging into Whitewater Creek, has unknown toxicity from municipal contamination sources;

- Cedar Creek, and sections of Choctawhatchee, Pea and Yellow Rivers are listed for metals.

METHODS

Water samples were collected from three surface water sites in the Choctawhatchee, Pea and Yellow River watersheds in May and October 2017 in accordance with the ADEM Alabama's Water Quality Assessment and Listing Methodology (ADEM, 2010) and analyzed form the parameters listed in table 3. Water-quality parameters measured in the field with an YSI Professional Plus instrument, included specific conductance, pH, dissolved oxygen, oxidation/reduction potential (ORP), and temperature.

Various instruments and methods are used in the analyses of water samples at the GSA Geochemical Laboratory. Equipment used for water sample analyses included a Leeman Labs Prodigy inductively coupled atomic-emission plasma spectrometer, a Perkin-Elmer Model AAnalyst600 Zeeman graphite furnace atomic absorption spectrometer, a Thermo Scientific Dionex Aquion ion chromatograph, a Seal AA3 Segmented Flow Analyzer, a Shimadzu UV-1800 ultraviolet-visible spectrophotometer, a Leeman Hydra cold-vapor atomic fluorescence spectrophotometer, total organic carbon is analyzed with a Shimadzu TOC-L, and a YSI Model 5000 meter for dissolved oxygen meter. Water analyses were conducted in accordance with established GSA procedures based on methods delineated in USEPA (1983, 1991), Fishman and Friedman (1989), and Greenburg and others (1992). Quality assurance/quality control procedures for the collection, preservation, and retention times of water samples were in accordance with O'Neil and Meintzer (1995).

Two methods were used to measure discharge: Acoustic Doppler Current Profiler (ADCP) and Bridge Board technique with Price AA meter. *The SonTek River Surveyor System* is a robust and highly accurate ADCP system specifically

Table 3. Analytical Methods of the Geological Survey of Alabama, Geochemical Laboratory

Analyte	GSA Method	Chemical/Physical Method	Parent Method
Aluminum	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Ammonia as Nitrogen	2350.4	Colorimetric, automated segmented-flow, salicylate-hypochlorite)	USGS I-2522-85
Arsenic	2200.9	Stabilized temperature platform graphite-furnace atomic absorption spectrometry	EPA 200.9 rev. 2.2
Barium	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Beryllium	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Biochemical Oxygen Demand, 5-day	2405	Electrometric, 5-day	SM 5210 B
Cadmium	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Calcium	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Carbon, Total Organic	2415.1	Catalytic combustion	EPA 415.1
Chloride	2300.1A	Ion chromatography	EPA 300.1 rev. 1.0
Chromium	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Conductance, Specific (Conductivity)	field		
Copper	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Iron	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Lead	2200.9	Stabilized temperature platform graphite-furnace atomic absorption spectrometry	EPA 200.9 rev. 2.2
Manganese	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Mercury	2245.7	Cold-vapor atomic fluorescence spectrometry	EPA 245.7
Nitrate as Nitrogen	2300.1A	Ion chromatography	EPA 300.1 rev. 1.0
Nitrite as Nitrogen	2300.1A	Ion chromatography	EPA 300.1 rev. 1.0
Oxygen, Dissolved	field		
pH	field		
Phosphorus, Total	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4
Selenium	2200.9	Stabilized temperature platform graphite-furnace atomic absorption spectrometry	EPA 200.9 rev. 2.2
Solids, Total Suspended	2160.3	Gravimetric, dried at 103-105°C	USGS I-3765-85
Solids, Total Dissolved	2160.2	Gravimetric, dried at 180°C	USGS I-1750-85
Temperature	field		
Thallium	2200.9	Stabilized temperature platform graphite-furnace atomic absorption spectrometry	EPA 200.9 rev. 2.2
Turbidity	2180	Nephelometric	EPA 180.1 rev. 2.0
Zinc	2200.7	Inductively coupled plasma-atomic emission spectrometry	EPA 200.7 rev. 4.4

designed to measure discharge in wide and deep channels, 3-dimensional water currents, depths, and bathymetry from a moving or stationary vessel.

The ADCP uses the Doppler Effect to determine water velocity by sending a sound pulse into the water and measuring the change in frequency of that sound pulse reflected back to the ADCP by sediment or other particulates being transported in the water. The change in frequency, or Doppler Shift, that is measured by the ADCP is translated into water velocity. The sound wave is transmitted by a transducer into the water the bottom of the river and receives return signals throughout the entire depth. The ADCP also uses acoustics to measure water depth by measuring the pulse travel time. To make a discharge measurement, the ADCP is mounted onto a boat or into a small watercraft with its acoustic beams directed into the water from the water surface. The ADCP is then guided across the surface of the river to obtain measurements of velocity and depth across the channel. Global Positioning System (GPS) is used to track the progress of the ADCP across the channel and provide channel-width measurements. Using the depth and width measurements for calculating the area and the velocity measurements, the discharge is computed by the ADCP, similar to the conventional current-meter method. The ADCP provides a detailed profile of water velocity and direction for the majority of a cross section instead of just at point locations with a mechanical current meter improving measurement accuracy.

To measure the flow in a non-wadable stream or river, a Price AA current meter can be suspended from a bridge board. In order to determine the velocity at a point with a current meter, it is necessary to count the revolutions of the rotor in a measured interval of time, usually 40-70 seconds. The velocity is then obtained from a meter-rating table. The current meter measures velocity at a point. The method of making discharge measurements at a cross section requires determination of the mean velocity in each of the selected verticals. The mean velocity in a vertical is obtained from velocity observations at selected points in that vertical.

RESULTS

CHEMICAL AND PHYSICAL PARAMETERS

DISCHARGE

Discharge is a fundamental hydrologic characteristic of watershed studies (Gore, 1996). Discharge integrates all components of the watershed ecosystem and influences surface water quality. Ionic concentrations, specific conductance, dissolved oxygen (DO), biochemical oxygen demand (BOD), total suspended solids (TSS), bed sediment, and bacterial concentrations are all influenced by the volume of discharge.

Rivers in the study area generally attain low flow status during August - October. Low flow discharge is of great importance in assessing groundwater contribution to surface water during drought or periods of low precipitation. Furthermore, low flow can be used to determine the volume of minimum discharge that can be expected during certain periods of the year. Except for occasional runoff from isolated storms, most of the discharge from the watersheds during August through October of each year can be attributed to groundwater discharge. Therefore, during these periods of the year, elevated contaminant levels in surface waters possibly may be attributed in part to contaminated groundwater that sustains surface water flow. Consequently, monitoring discharge and chemical parameter concentrations or contaminant loads at different times of the year provide information on the source and severity of contamination (runoff versus groundwater contaminant input). Field observations indicate that storm-water runoff is flashy and characterized by rapid rise and fall of river water levels.

Table 4. Discharge measured at monitoring sites in the Choctawhatchee, Pea and Yellow Rivers, 2017.

Site	Discharge (cfs)	
	5/24/2017	10/2/2017
CR-1	3,690*	805
PR-3	3,470*	828
YR-1	726	167

*Estimated flow from USGS stations 02362000 for site CR-1 and 02365200 for site PR-3

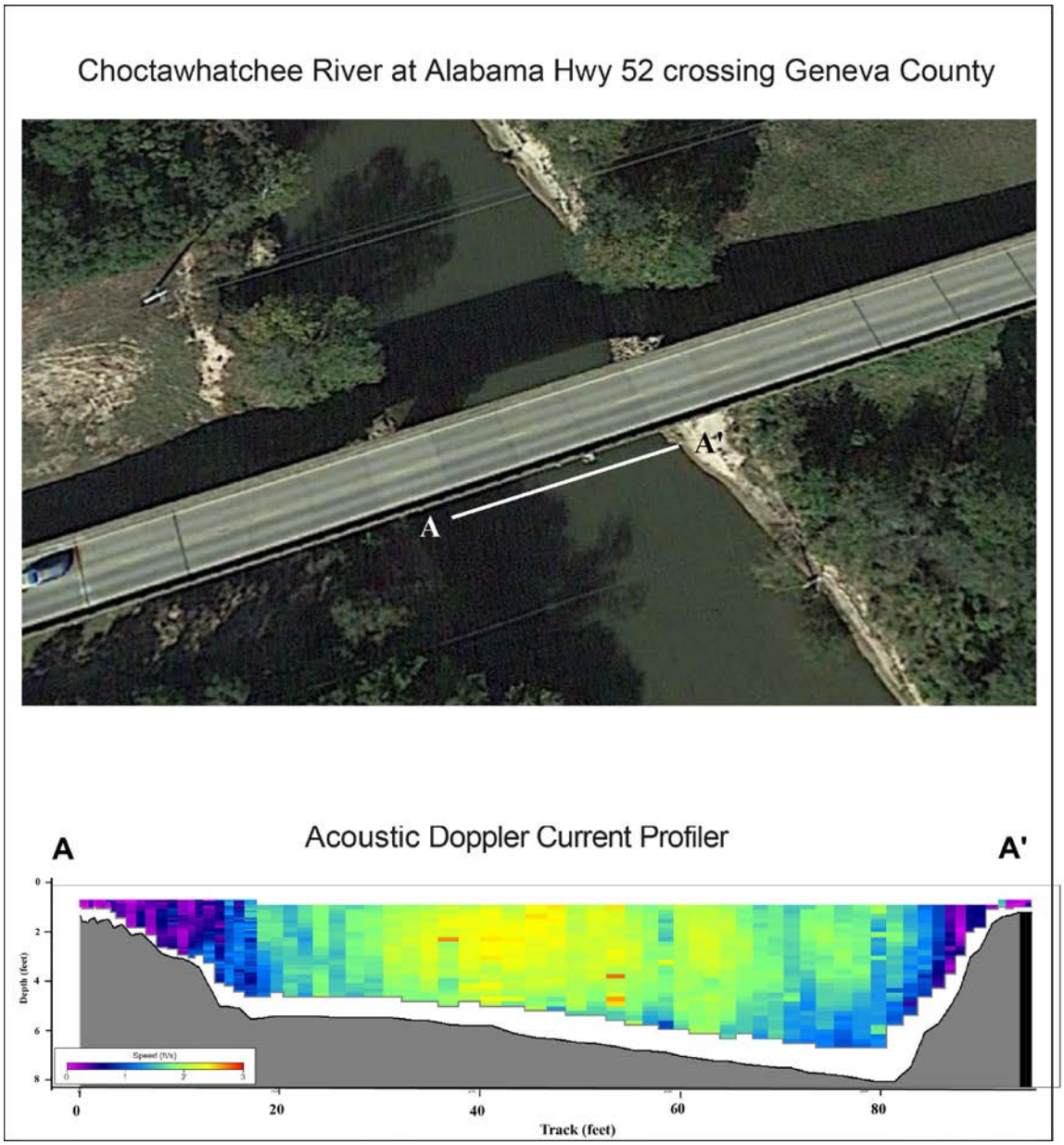

Figure 6. Location of discharge measurement with profile at Choctawhatchee River.

Flooding occurs periodically and is caused by cyclonic storms associated with spring weather fronts or by summer and fall tropical storms or hurricanes that move through southeast Alabama. Monitored discharge events were selected to establish a well-distributed data set from low to high flow.

The GSA data set is composed of two discharge measurements collected during 2017. The flow was measured using a Price AA flow meter attached to a

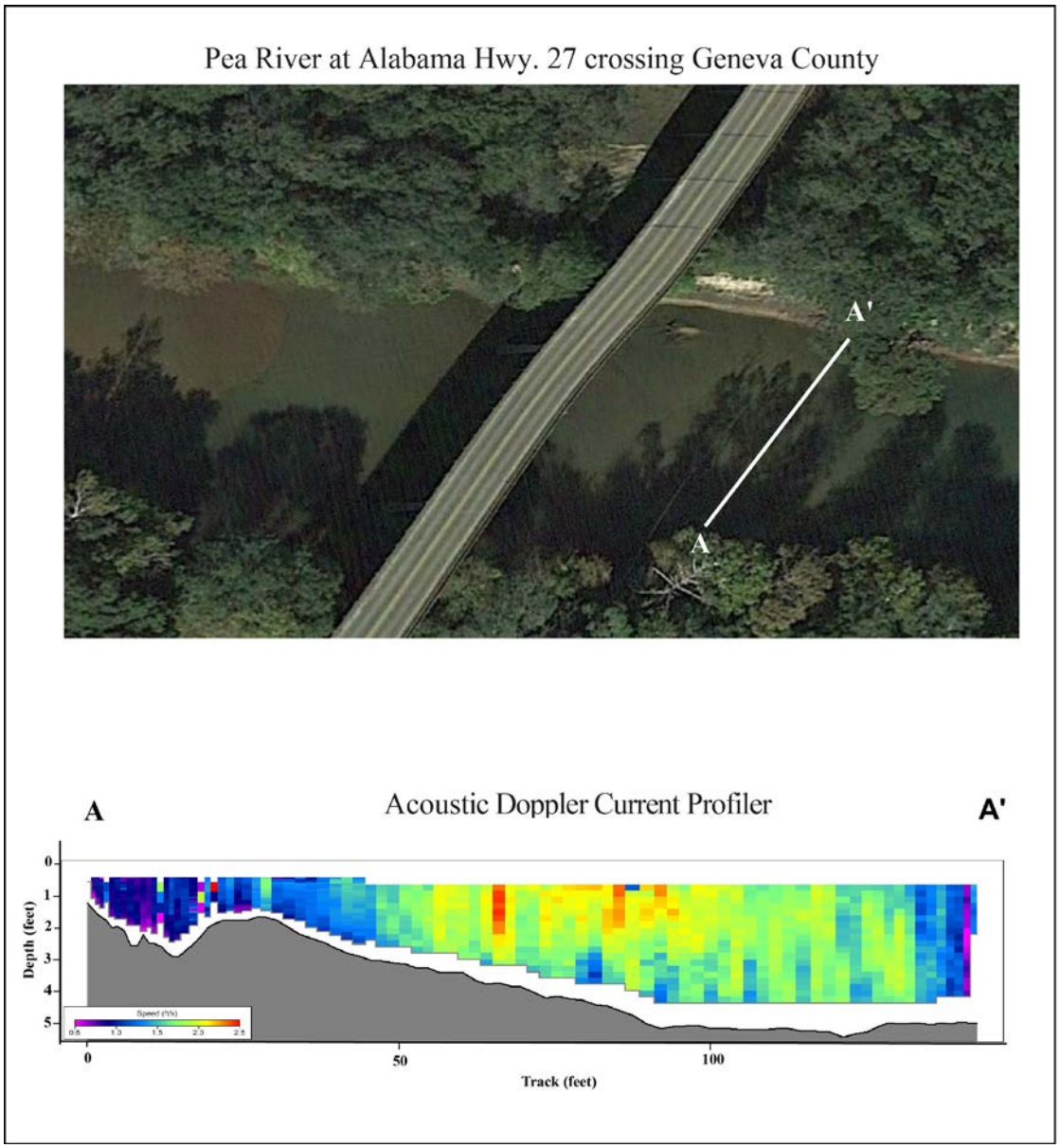

Figure 7. Location of discharge measurement with profile at Pea River.

Bridge Board in May (high flow) for Yellow River and an ADCP at all three sites in October 2017. The data were collected according to U. S. Geological Survey (USGS) flow measurement guidelines (Buchanan and Somers 1969). Discharge at sites CR-1 and PR-3 in May 2017 were estimated from USGS gauges (table 4). Discharge rates for previous studies are compared to the 2017 measurements in figs. 9-11.

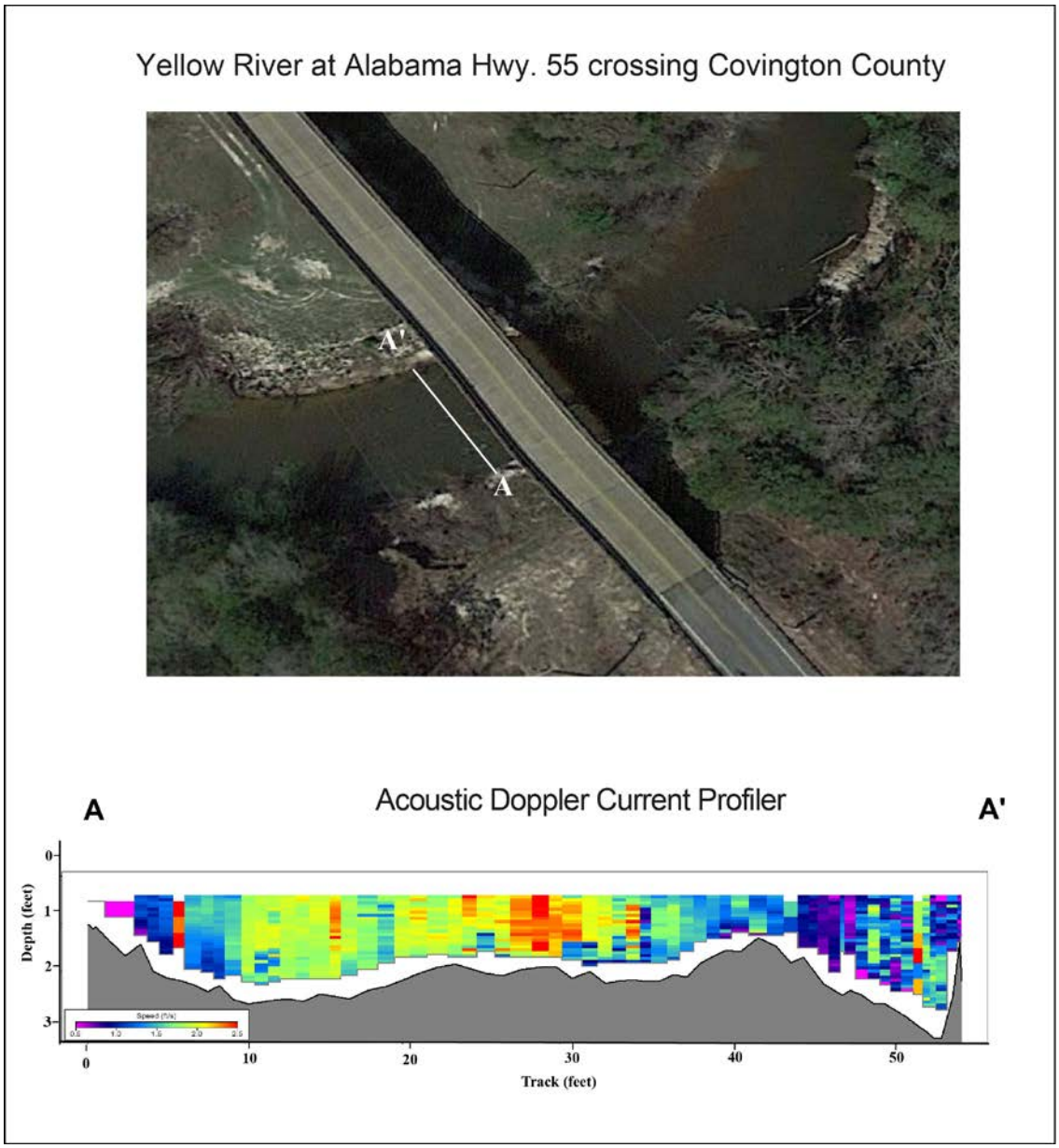

Figure 8. Location of discharge measurement with profile at Yellow River.

STREAM TEMPERATURE

Temperature affects the physical and chemical characteristics of water in a river. Dissolved oxygen, biological activity, and equilibrium reactions are significantly influenced by water temperature. Dependent on atmospheric conditions, surface water temperature can be highly variable. The criterion for maximum temperature established by the Alabama Department of Environmental Management (ADEM, 1992) for surface water classified as Fish and Wildlife is

32.2ºC. The highest and the lowest river temperatures, 29 ºC (August 2007), and 8ºC (winter months) respectively were measured in Pea River, at site PR-3. The measured temperature did not exceeded the criterion at any of the sites during the monitoring period (figures 10, 11, and 12). In table 6 are shown the temperatures measured in 2017.

Table 5. Water temperature values measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.

Site	Stream temperature (ºC)	
	5/24/2017	10/2/2017
CR-1	23.8	24.0
PR-3	25.0	24.0
YR-1	23.1	23.0

SPECIFIC CONDUCTANCE

Specific conductance (SC) or conductivity is a measure of the ionic content of water and offers information on how readily water can conduct an electrical current at 25^0C. The ability of water to conduct an electric current is dependent on ionic concentration and mobility in solution (their presence as dissolved ions in solution and their availability). Specific conductance is an indirect measure of dissolved solids such as potassium, nitrate, chloride, sulfate, phosphate, sodium, magnesium, calcium, bicarbonate, carbonate, and iron. Consequently, this parameter can be used as an indicator of water pollution. Typically, rainwater and surface water not influenced by groundwater has a SC value less than 50 μS/cm (microSiemens per centimeter), if not impacted by nonpoint pollution sources. Overall, SC variability is influenced by differences in temperature, discharge, local geology and soil conditions, and ionic influxes from nonpoint pollution sources.

Surface water from each project site is characterized by a unique specific conductance profile and there is generally an inverse relationship between discharge and conductivity in rivers (figs. 12-14).

Typically, the lowest conductivity values were measured during the largest discharge events (in April or May). Historically the highest conductivity values were measured in Yellow River at site YR-1 (fig. 14; table 6) and correspond to the lowest discharge events (in June 2007). Figure 12 show that overtime specific conductance compared with 2017 measurements is unchanged at CR-1. The 2017 samples are somewhat elevated at PR-3 (fig. 13) and even higher at YR-1 (fig. 14)

On average, temperature has a higher degree of influence on SC compared to total dissolved solids (TDS). Nevertheless, sites CR-1, and PR-3 exhibit slightly different behavior. At these sites, increasing discharge is occasionally associated

with higher TDS concentrations, lowest temperatures, and ambient conductivity values (figs. 9, 10). The highest conductivity values of 193 μS/cm were measured in Yellow River at site YR-1 in October 2017 (fig. 11).

Table 6. Specific conductance values measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.

Site	Specific conductance (μS/cm)	
	5/24/2017	10/2/2017
CR-1	56.6	84.7
PR-3	68.3	119.1
YR-1	72.2	211.0

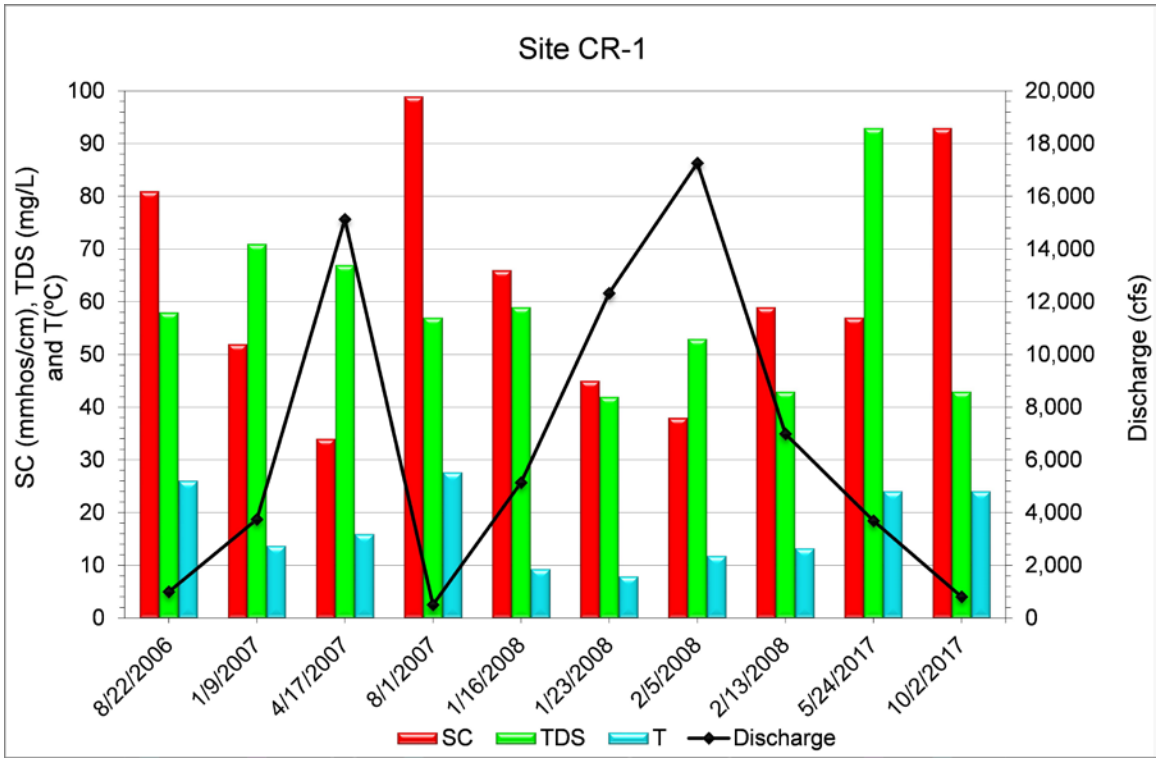

Figure 9. Specific conductance (SC), total dissolved solids (TDS), stream temperature (T), and discharge at monitoring site CR-1.

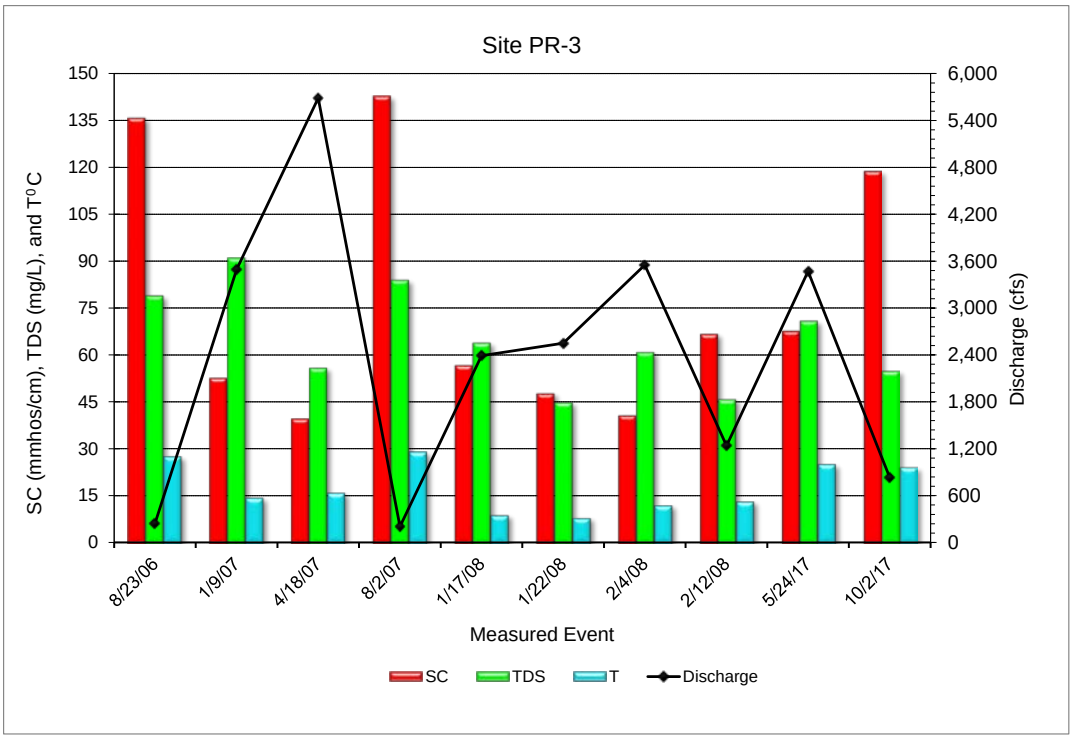

Figure 10. Specific conductance (SC), total dissolved solids (TDS), stream temperature (T), and discharge at monitoring site PR-3.

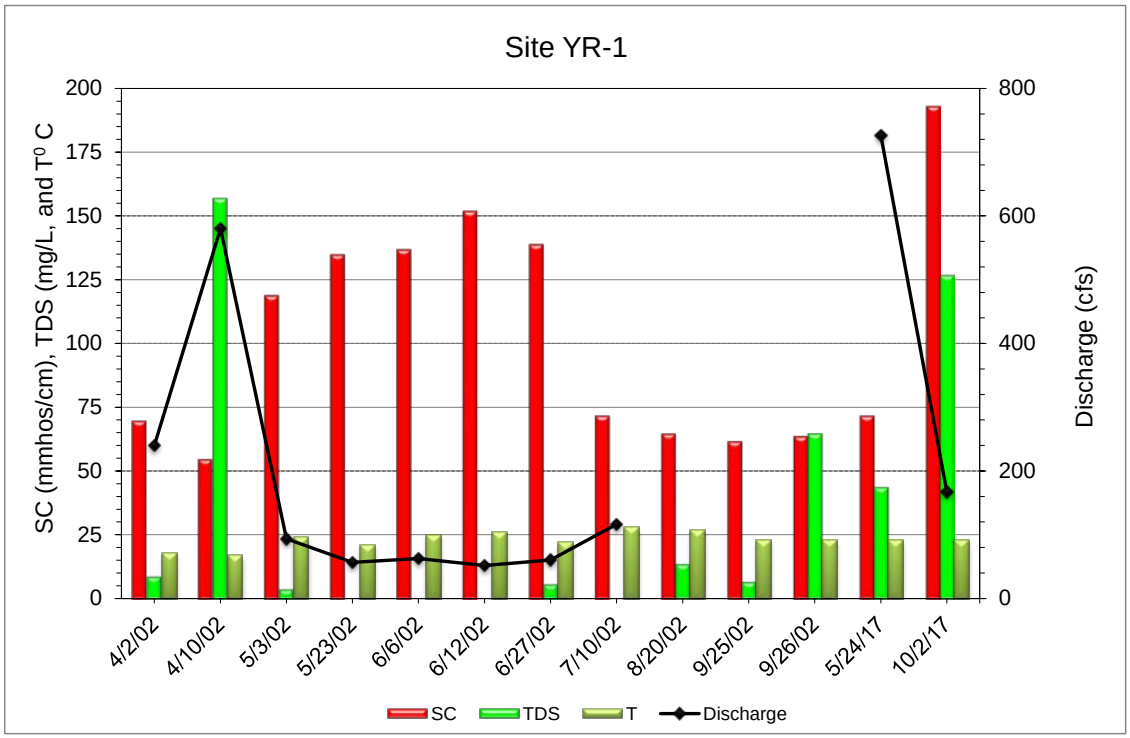

Figure 11. Specific conductance (SC), total dissolved solids (TDS), stream temperature (T), and discharge at monitoring site YR-1.

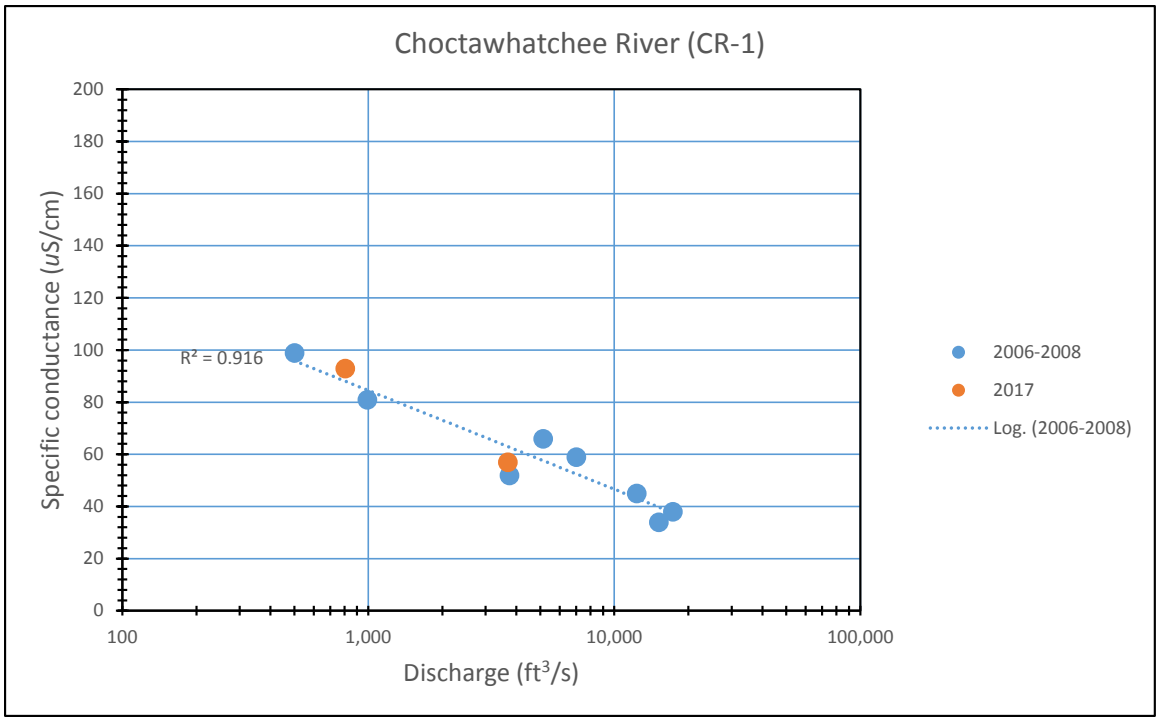

Figure 12. Specific conductance (SC), and discharge at monitoring site CR-1.

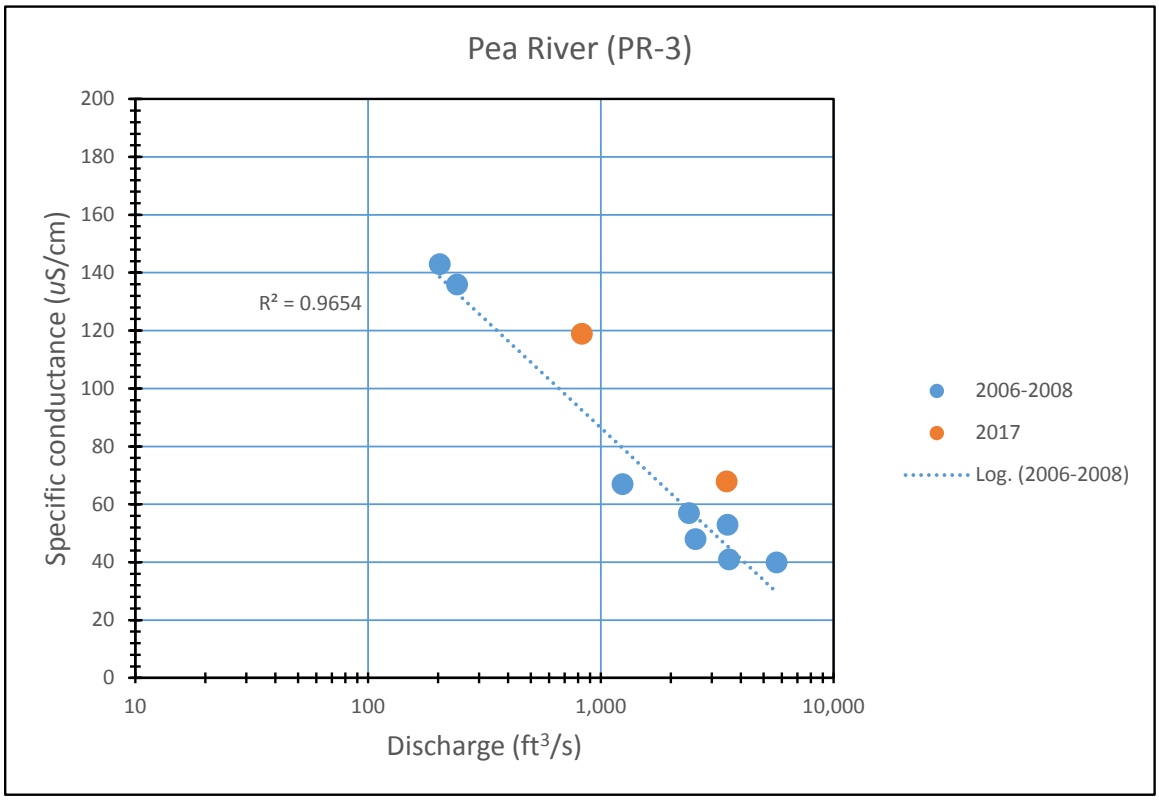

Figure 13. Specific conductance (SC), and discharge at monitoring site PR-3.

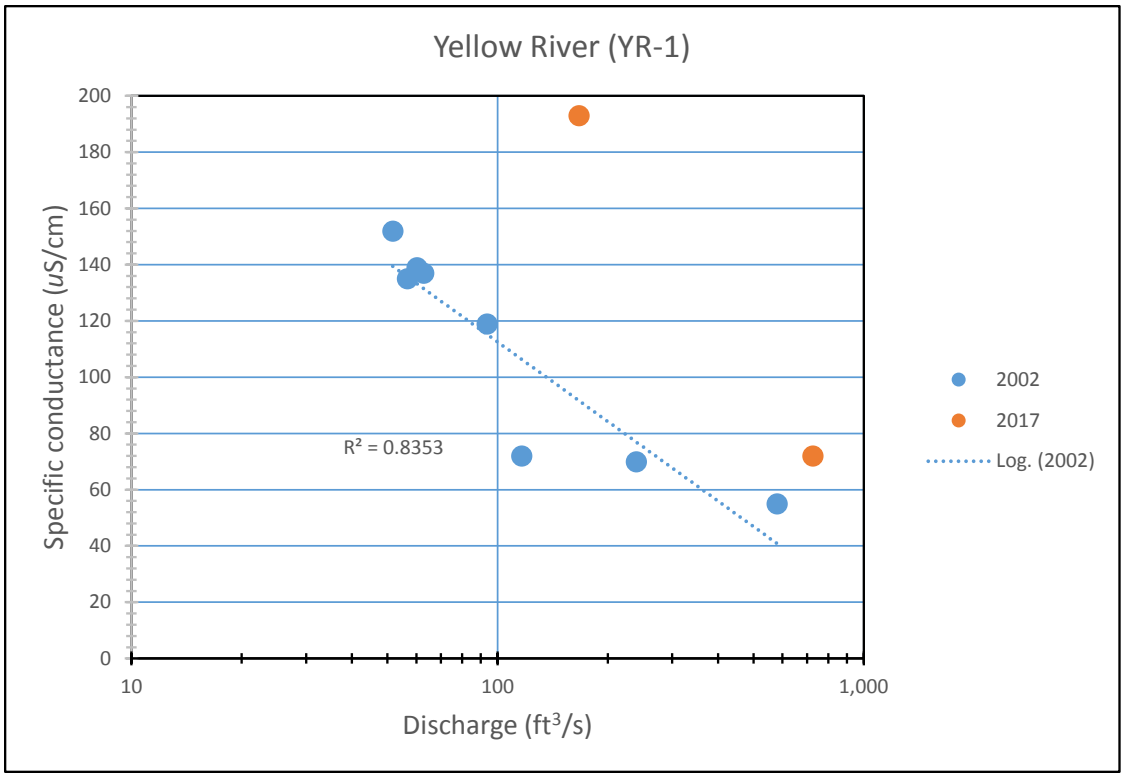

Figure 14. Specific conductance (SC), and discharge at monitoring site YR-1.

HYDROGEN ION CONCENTRATION (pH)

The concentration of hydrogen ions (H^+) is a critical water-quality parameter in natural and treated waters. Concentrations of hydrogen ions control speciation of other constituents, influence dissolution and precipitation of chemical elements, and determine whether the water will support aquatic life. Aquatic organisms are sensitive to pH changes and many species are adapted to a very narrow range of pH. The water-quality criterion for pH ranges from 6.0 to 9.0 (ADEM 1992).

Hydrogen ion activity is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1985). Therefore, pH is an important indicator of the equilibrium status of reactions that determine the ionic composition of water. The acid chemistry of surface waters is important because, among many negative effects on the environment, it adversely affects aquatic systems, contributes to corrosiveness, and can change the reaction rates in a system.

At all sites, historically maximum values of pH varied from 7.3 to 7.7 while minimum pH varied from 5.4 to 5.8 (App. A, fig. 16). In general, the lower pH values measured in each river during the monitoring period correspond to large discharge events (figs. 17-19). High flow episodes are usually linked to larger precipitation events that make up the majority of water in the rivers. Periods of low in-stream flow are accompanied by increased pH values (figs. 17-19). The lowest pH values

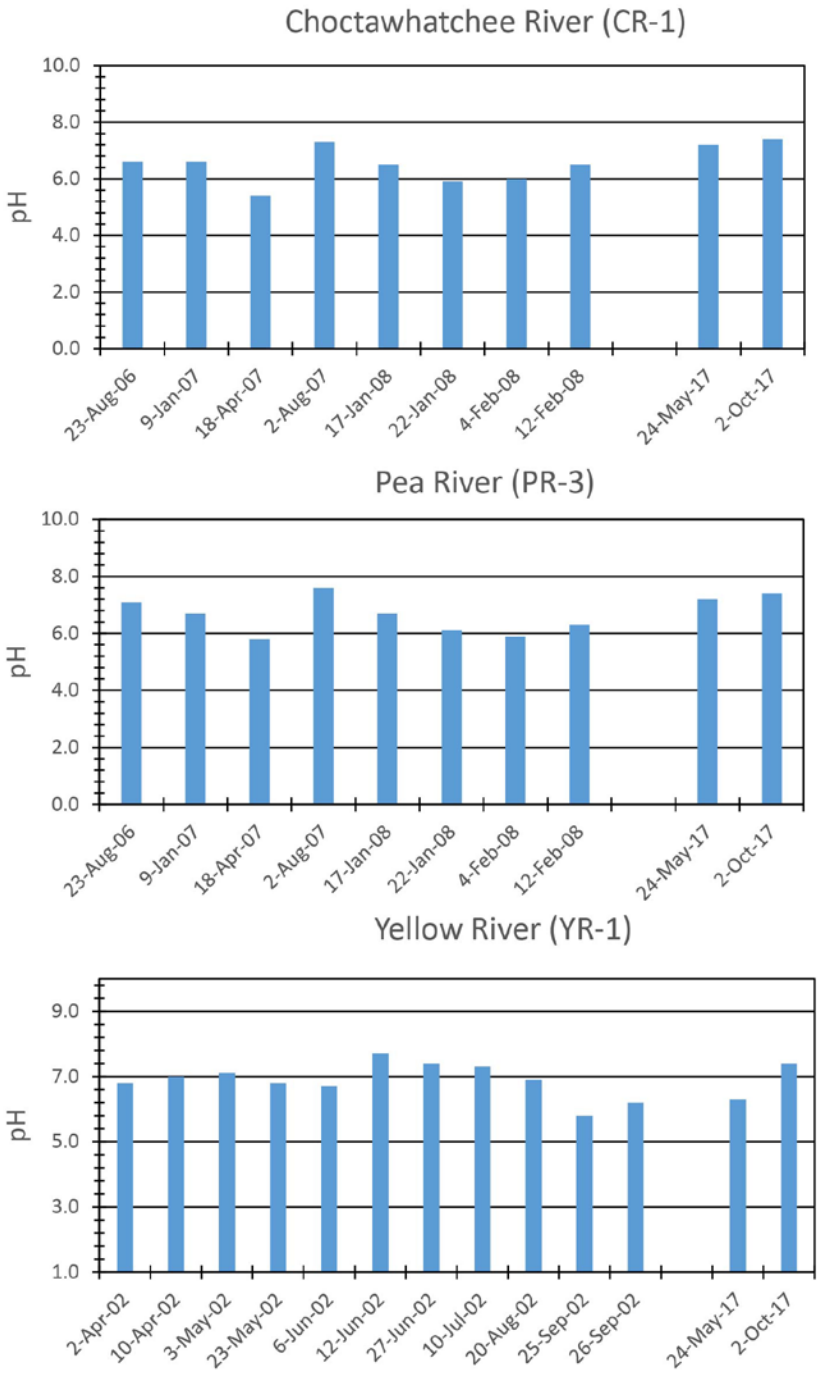

Figure 15. Measured pH at monitoring sites in the Choctawhatchee, Pea and Yellow Rivers watersheds

were measured in the Choctawhatchee River at site CR-1, other sites have constant pH values (App. A). The pH measurements in 2017 at all three sites were similar for both sampling events (table 7).

Table 7. Hydrogen ion concentration (pH) measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.

Site	pH	
	5/24/2017	10/2/2017
CR-1	7.2	7.4
PR-3	7.6	7.4
YR-1	7.2	7.4

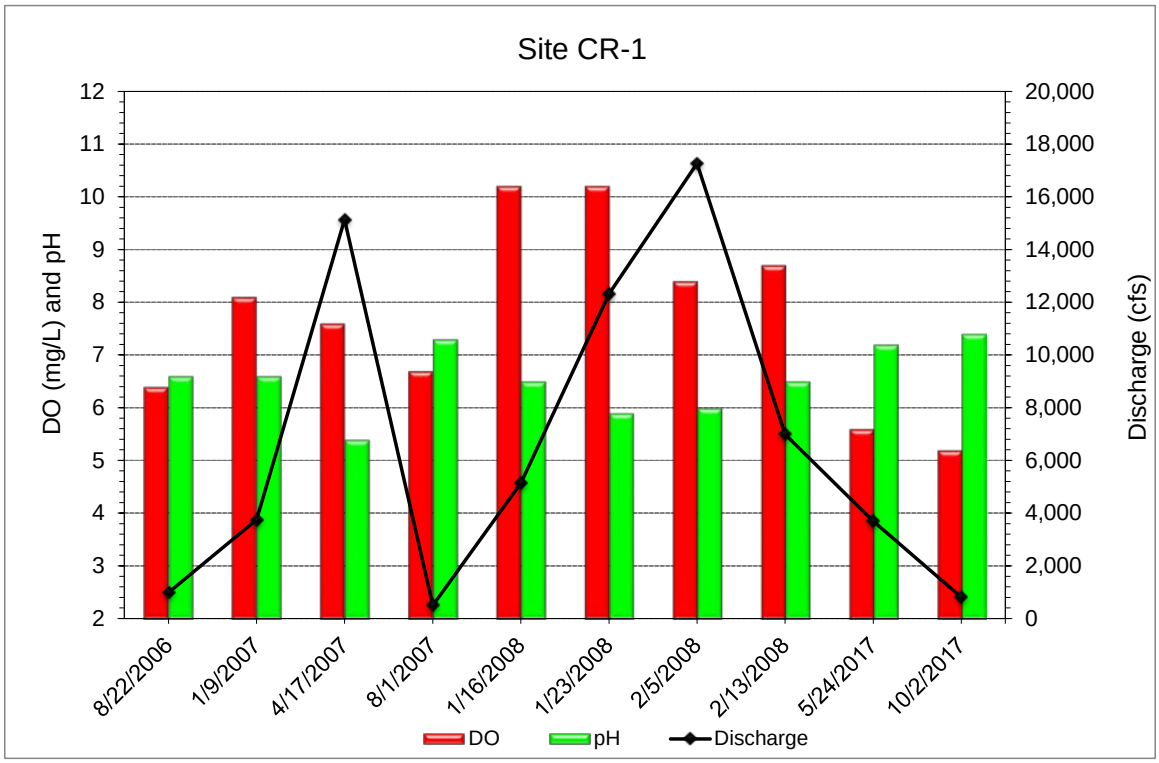

Figure 16. Discharge, dissolved oxygen (DO), and pH at monitoring site CR-1.

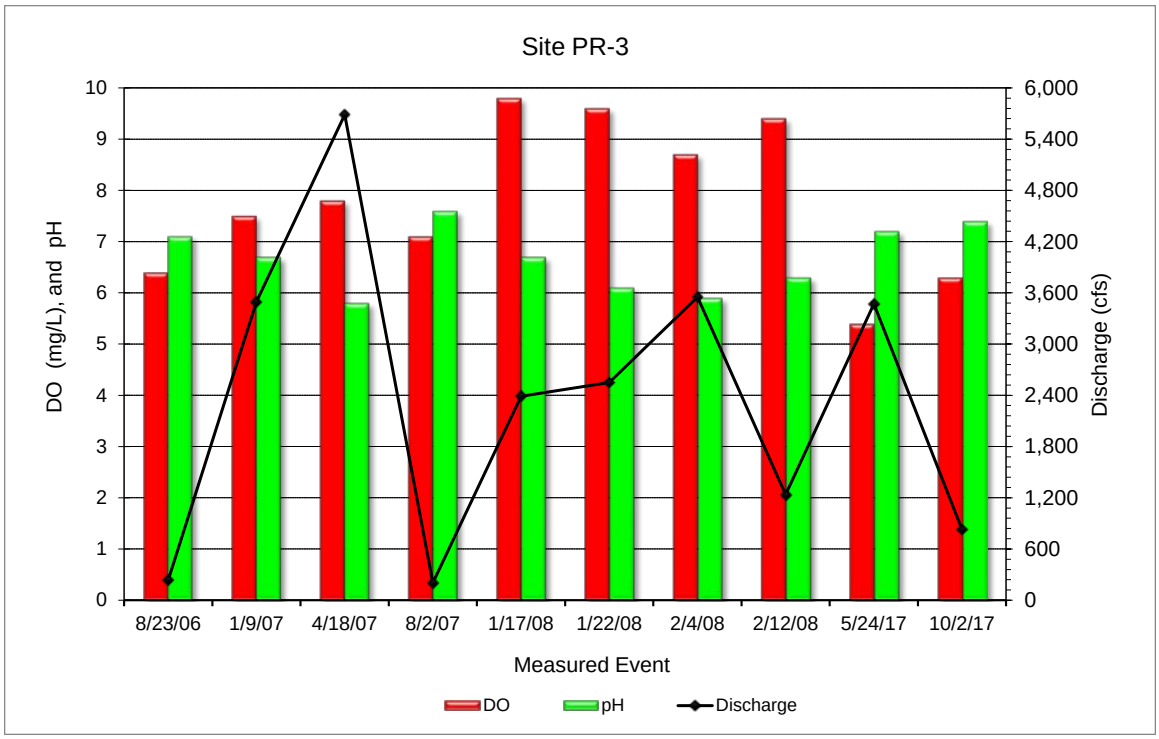

Figure 17. Discharge, dissolved oxygen (DO), and pH at monitoring site PR-3.

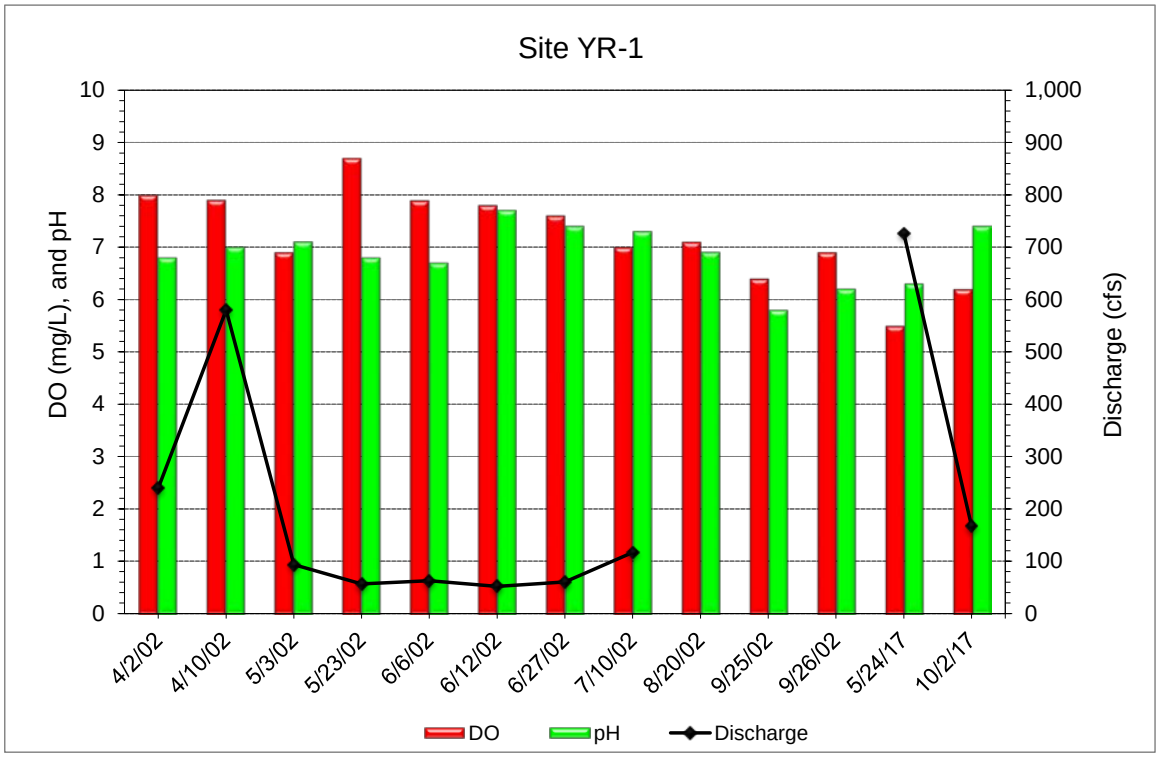

Figure 18. Discharge, dissolved oxygen (DO), and pH at monitoring site YR-1.

DISSOLVED OXYGEN

Dissolved oxygen (DO) concentration is an essential constituent that affects the biological health and the chemical composition of surface waters. Biological processes, oxidation, and sediment loads all contribute to depletion of DO in surface water. The ADEM (1992) criterion for DO in surface water classified as Fish and Wildlife is 5.0 milligrams per liter (mg/L) except under extreme conditions where it may be as low as 4.0 mg/L. The equilibrium concentration of DO in water that is in contact with air is primarily related to water temperature and barometric pressure and secondarily related to concentrations of other solutes (Hem, 1985). Equilibrium DO concentration in water at 10°C and 25°C is 11.27 mg/L and 8.24 mg/L, respectively.

Dissolved oxygen concentrations in the study rivers are significantly affected by water temperature, discharge, and concentrations of organic material in the water. The relationships between DO, pH, and temperature parameters are depicted in figs. 16 through 18. Table 8 includes the observed DO concentrations and temperature for 2017. The highest DO concentration for the monitoring period was 10.2 mg/L for site CR-1 and the lowest was 6.4 mg/L for all three rivers (App. A). The 2017 DO readings (fig. 19; table 8) are lower in 2017 versus the historical record at all three rivers. No values under 5 mg/L were recorded during any sampling event.

Table 8. Dissolved oxygen (DO) measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.

Site	DO (mg/L)	
	5/24/17	10/2/17
CR-1	5.6	5.2
PR-3	5.4	6.3
YR-1	5.5	6.2

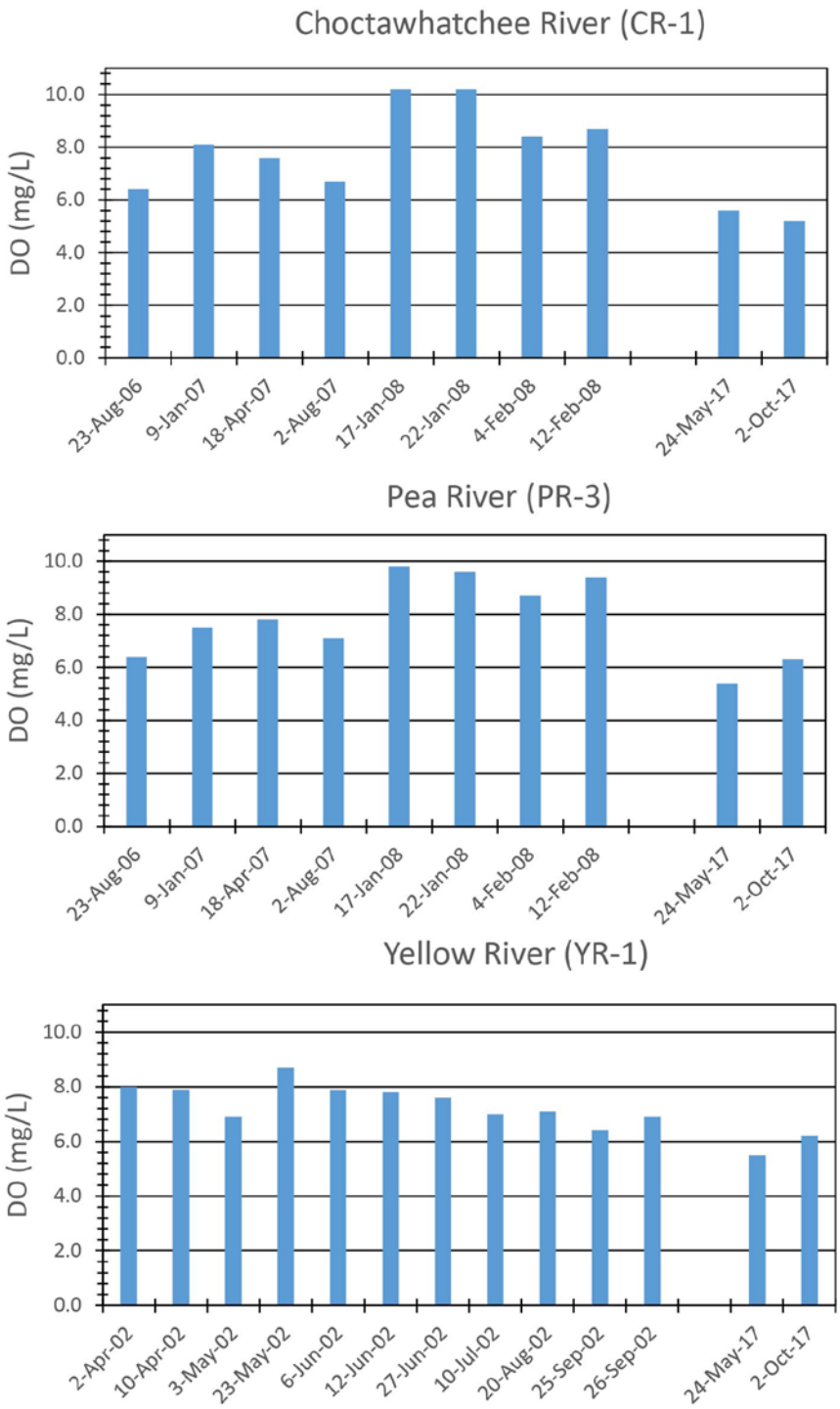

Figure 19. Measured dissolved oxigen (DO) at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

BIOCHEMICAL OXYGEN DEMAND

Biochemical oxygen demand (BOD) is an empirical measure of the amount of oxygen used for the biochemical oxidation of organic matter by the microbial population of a water body. This parameter can be used to indicate the presence and magnitude of organic pollutants. It is often used to determine the effect of waste discharges on the oxygen resources of receiving waters. Excessive BOD loads damage the quality of surface water by decreasing the DO concentration. This causes unsuitable life conditions for flora and fauna in streams and can lead to fish death. The relationship between BOD and DO concentrations is influenced by the degradation of organic material, exchange of constituents with the stream bed, and by the presence of nitrification and denitrification processes (Radwan and others, 2003). Dissolved oxygen levels, water temperature, discharge rates, chlorophyll *a*, and nutrient levels (ammonia, nitrite, and nitrate) are among the most critical factors influencing BOD concentrations in streams. The BOD limit established by the USEPA for biologically treated municipal wastewater effluent is 30 mg/L. Criteria established by some states for water-quality sensitive surface-water bodies may be as low as 5 mg/L (Mays, 1996).

The BOD concentrations for all three monitoring sites are presented in App. A. Figure 20 shows BOD concentrations at each site with respect to sampling date. The highest BOD value (1.8 mg/L) was recorded in Pea River at site PR-3 in January 2008 and in Yellow River at site YR-1 in May 2017 (App. A and table 9). Water samples collected from Choctawhatchee River at site CR-1 was below the detection limit during August 2006 (fig. 21 and App. A).

Table 9. Biochemical oxygen demand (BOD) measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.

Site	BOD (mg/L)	
	5/24/17	10/2/17
CR-1	1.3	0.7
PR-3	1.5	0.7
YR-1	1.8	0.9

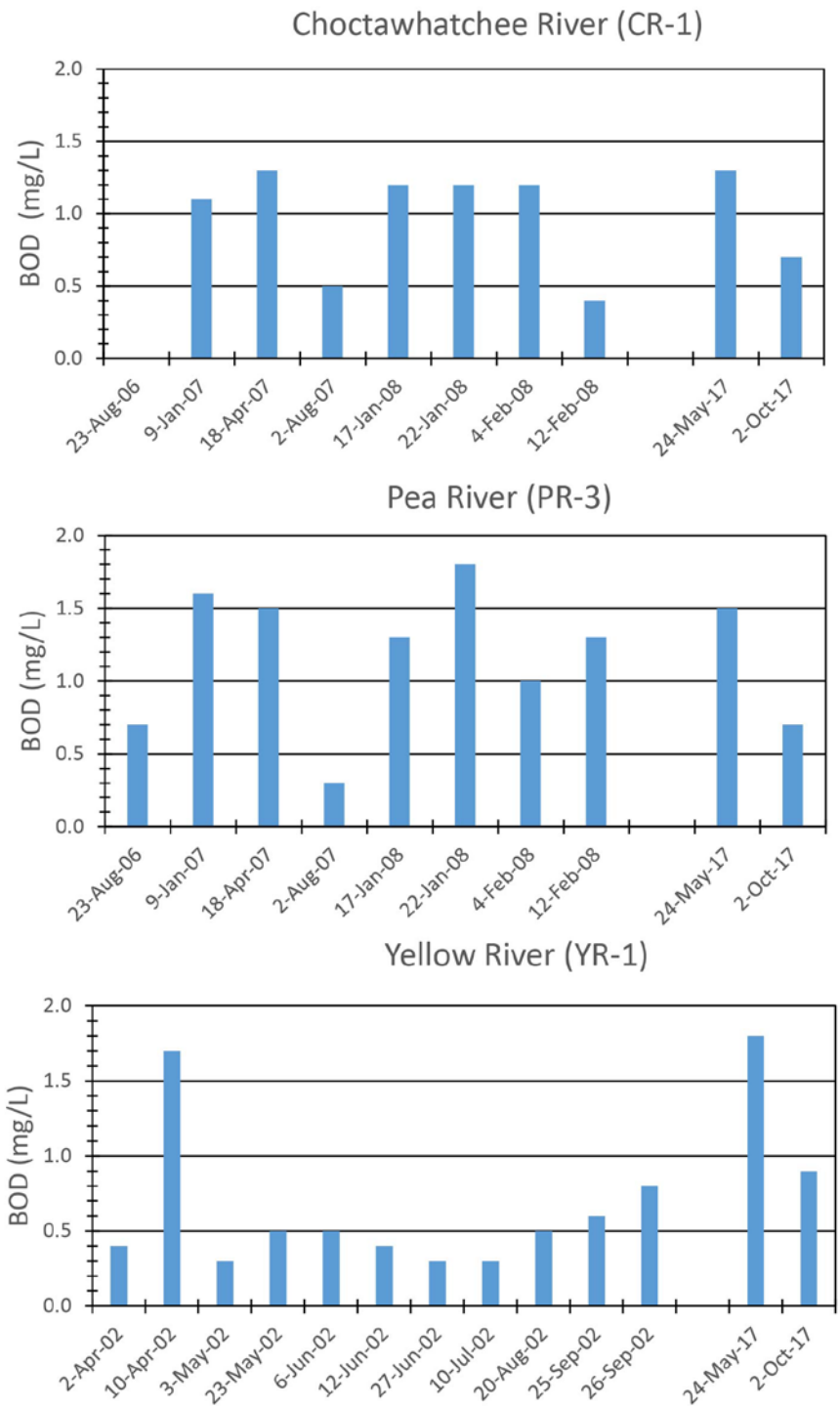

Figure 20. Measured biochemical oxigen demend (BOD) at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

TURBIDITY

Turbidity measurements can be used to estimate long-term trends of total suspended solids (TSS). It can also be used to evaluate the type of treatment necessary to remove sediment from water utilized for public water supply. Turbidity is reported in nephelometric turbidity units (NTU).

Turbidities measured at monitoring sites are shown in App. A and table 10 and are compared with TSS and discharge in figures 21-23. Analytical data revealed a good relationship between turbidity values and discharge for sites CR-1, PR-3 (figs. 21, 22 respectively). The highest turbidity values were recorded in April or May when discharge was the highest.

Table 10. Turbidity for water samples collected at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017

Site	Turbidity (NTU)	
	5/24/17	10/2/17
CR-1	47.4	11.0
PR-3	78.9	11.0
YR-1	28.5	6.0

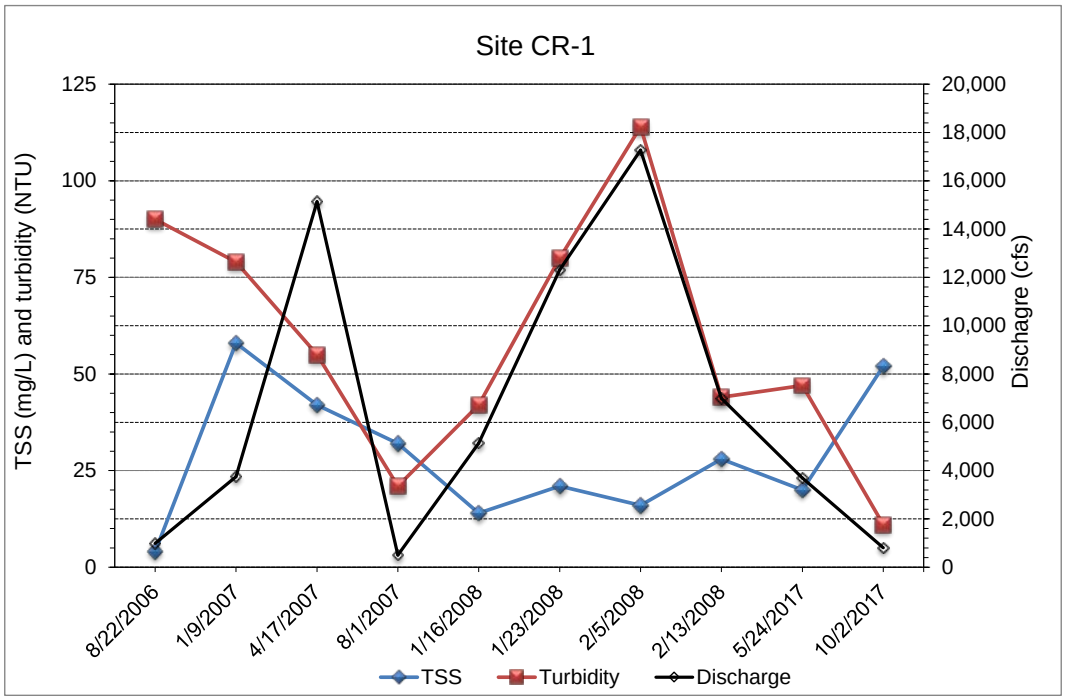

Figure 21. Discharge, turbidity, and total suspended solids (TSS) at monitoring site CR-1.

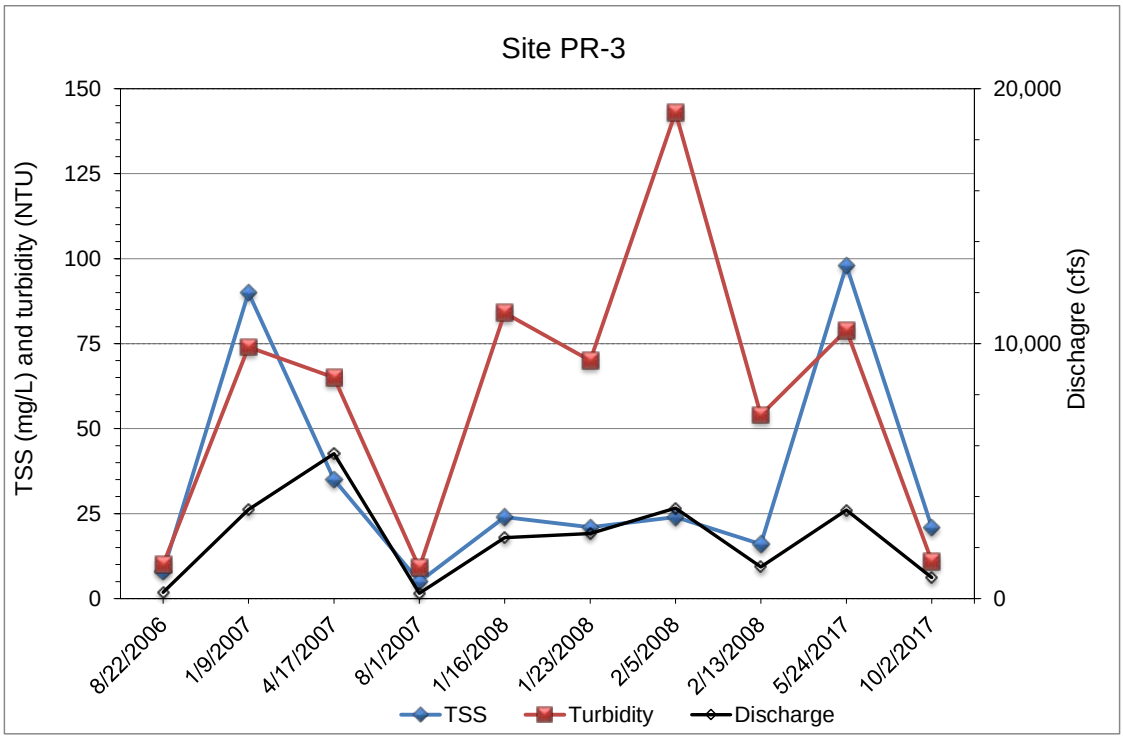

Figure 22. Discharge, turbidity, and total suspended solids (TSS) at monitoring site PR-3.

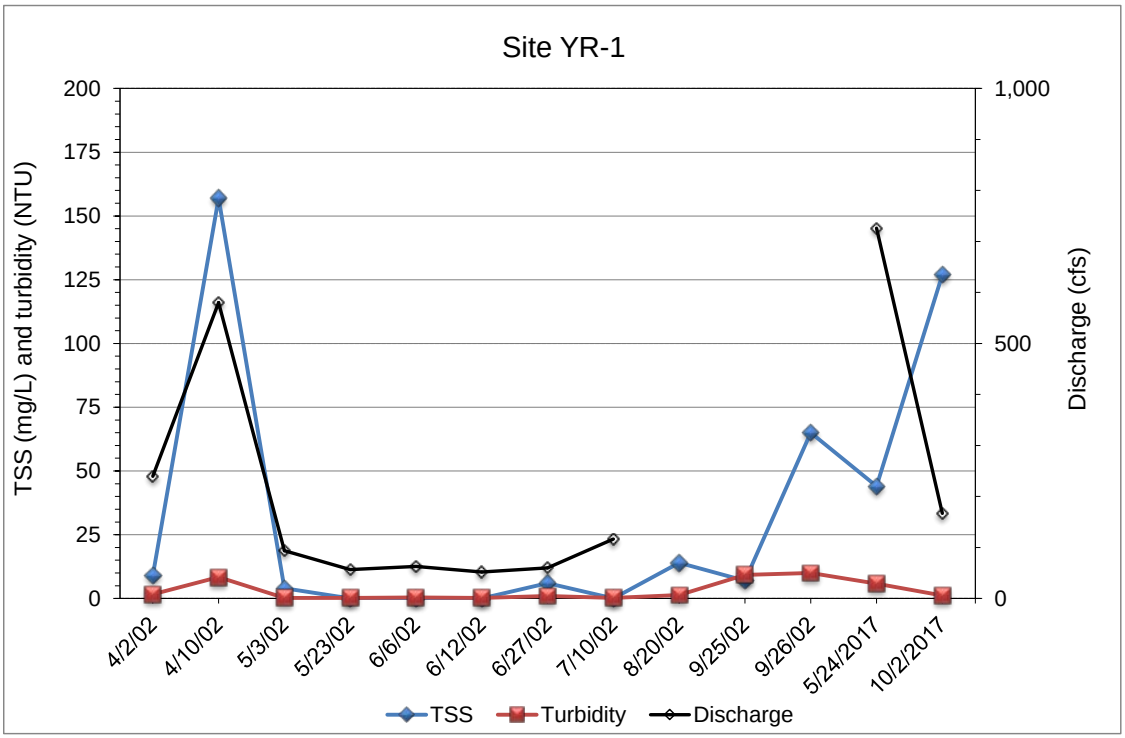

Figure 23. Discharge, turbidity, and total suspended solids (TSS) at monitoring site YR-1.

NUTRIENTS

Excessive nutrient enrichment is a major cause of water-quality impairment. Excessive concentrations of nutrients, primarily nitrogen and phosphorus, in the aquatic environment may lead to increased biological activity, increased algal growth, decreased dissolved oxygen concentrations at times, and decreased numbers of species (Mays, 1996). This process is called eutrophication.

Nutrient-impaired waters are characterized by numerous problems related to the growth of algae, other aquatic vegetation, and associated bacterial strains. Blooms of algae and associated bacteria can cause taste and odor problems in drinking water. Toxins also can be produced during blooms of particular algal species. Nutrient-impaired water can dramatically increase treatment costs required to meet drinking water standards.

AMMONIA

An essential nutrient for all plants and animals used in the formation of amino acids is nitrogen (N). Most aquatic plants cannot use nitrogen in its molecular form, thus it must be converted to an available form such as un-ionized ammonia (NH_3). Ammonia is also the principal form of toxic ammonia. Elevated ammonia levels may adversely impact aquatic life. Concentrations of ammonia in uncontaminated streams may be as low as 0.01 mg/L (NH_3 as N) (Maidment, 1993). Concentrations of ammonia in contaminated streams and in streams downstream from wastewater discharges range generally from 0.5 to 3.0 mg/L (Maidment, 1993). Laboratory experiments demonstrated that exposure to un-ionized ammonia concentration as low as 0.002 mg/L for long periods of time (up to six weeks) may be harmful to aquatic organisms causing, for example, hyperplasia of gill linings in salmon fingerlings, which may lead to bacterial gill disease (USEPA, 2004). Furthermore, at levels higher than 0.1 mg/L ammonia as N, even relatively short exposures can lead to skin, eye, and gills damage (USEPA, 2004).

Analytical results for the investigated rivers indicated, on average, low NH_3 concentrations with just a few exceptions (App. A and 12). Sites PR-3, and CR-1 exhibited elevated NH_3 levels at times (0.08 and 0.095 mg/L, respectively) (fig. 24). Ammonia concentrations exceeded the background concentration level of 0.01 mg/L for uncontaminated streams (Maidment, 1993) at all monitoring sites, except water samples collected in Yellow River at site YR-1 between April and September 2002 when NH_3 concentrations were below detection limit. However, the toxicity limit (0.5 mg/L) was not exceeded in any of the samples in 2017 (table 11).

Table 11. Ammonia concentrations measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.		
Site	Ammonia (mg/L as NH_3-N)	
	5/24/17	10/2/17
CR-1	0.095	BDL
PR-3	0.064	0.025
YR-1	0.048	0.021

*BDL = below detection limit 0.02 mg/L

NITRATE

Nitrate in surface water may be derived from anthropogenic as well as natural sources. Significant nitrate concentrations have been attributed to common contamination sources such as septic tanks, animal feedlots, and fertilizer applications. Agricultural practices generally have the highest nitrate input to surface waters (Maidment, 1993). Hem (1985) stated that water from small- and medium-sized rivers, which drain agricultural areas, could have nitrate concentrations exceeding 10 mg/L NO_3^-. The USEPA Maximum Contaminant Level (MCL) for nitrate as nitrogen (NO_3^--N) in drinking water is 10 mg/L. Furthermore, streams fed by shallow ground water underlying agricultural areas may also have concentrations of NO_3^- as high as 10 mg/L or greater (Maidment, 1993). Concentrations of NO_3^- in streams without significant nonpoint sources of pollution vary from 0.1 to 0.5 mg/L. For the purpose of this study NO_3^--N is referred to as nitrate.

The critical nitrate concentration of surface water for excessive algae growth is 0.5 mg/L (Maidment, 1993). The 0.5 mg/L nitrate criterion was exceeded at two locations (fig. 26). Nitrate values ranged from below the detection limit to 0.78 mg/L (App. A and table 12). The highest nitrate concentrations were exhibited at sites CR-1 (0.78 mg/L) and PR-3 (0.61 mg/L) in the Choctawhatchee and Pea Rivers, respectively (fig. 25, App. A and table 12). The lowest nitrate concentrations for all monitoring sites were measured in April 2002. Generally, an inverse correlation between nitrate concentrations and discharge was observed at CR-1 and PR-3 (figs. 26 and 27). All samples collected in 2017 have an elevated or high concentration compared with the historical data.

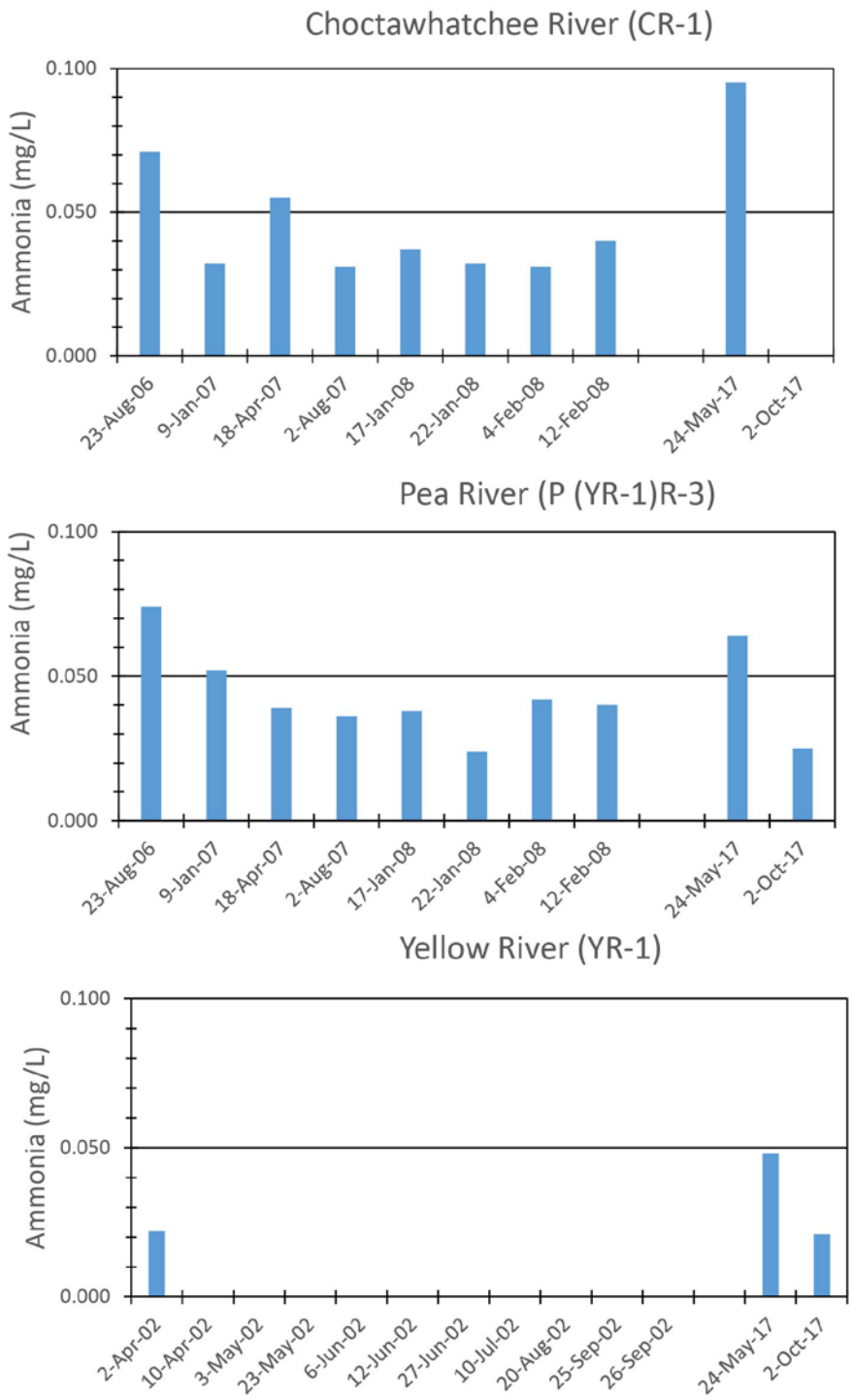

Figure 24. Measured ammonia (NH_3 as N) at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

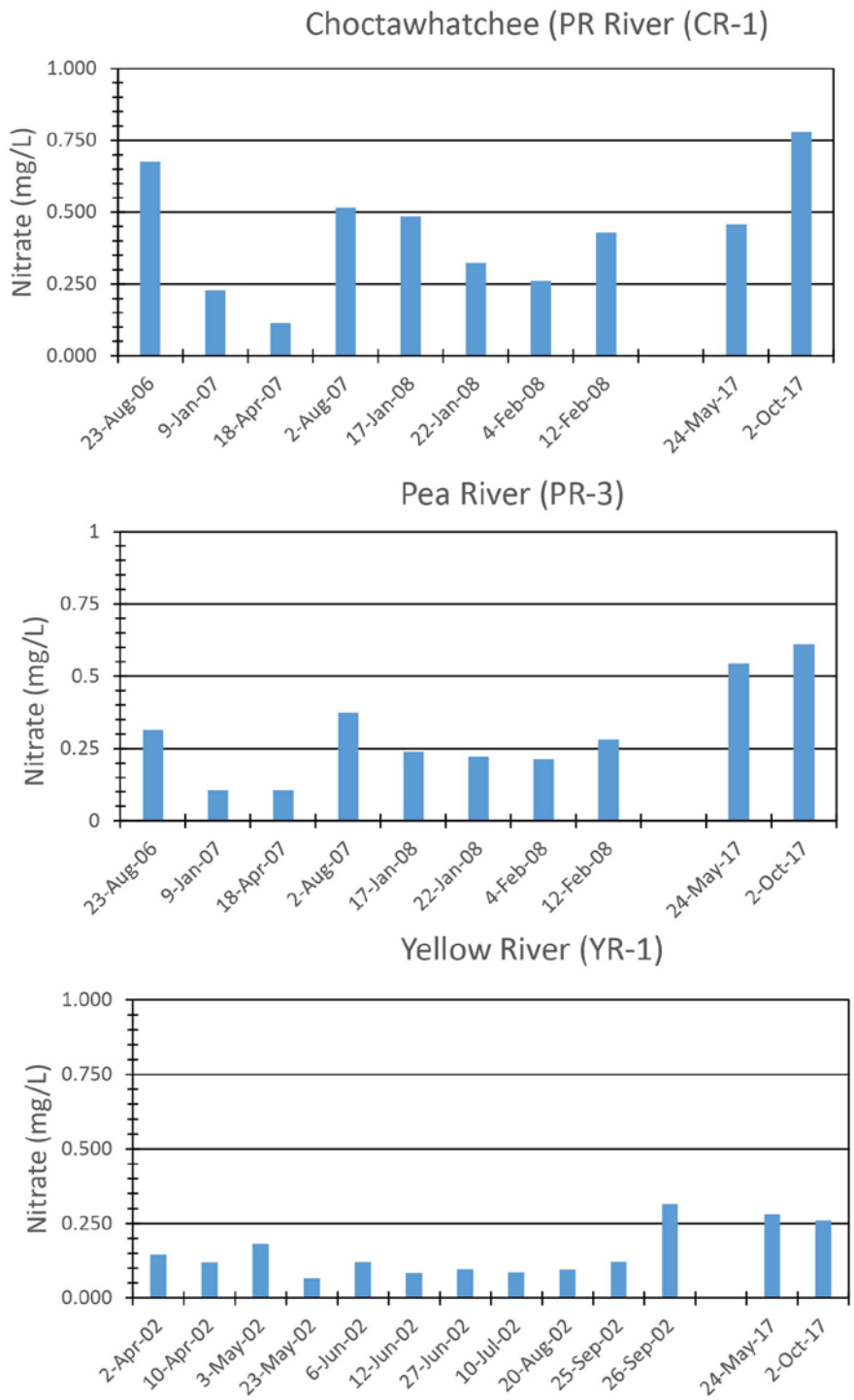

Figure 25. Measured nitrate (NO_3 as N) at monitoring sites in the Choctawhatchee, Pea and Yellow Rivers watersheds

Table 12. Nitrate as N and Chloride concentrations measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017				
Site	Nitrate concentrations: mg/L		Chloride concentrations: mg/L	
	5/24/17	10/2/17	5/24/17	10/2/17
CR-1	0.46	**0.78**	3.88	5.42
PR-3	**0.54***	**0.61**	3.90	4.4
YR-1	0.28	0.26	3.75	3.4

*In bold above 0.5 mg/L nitrate criterion

PHOSPHORUS

Phosphorus in streams originates from the mineralization of phosphates from soil and rocks or runoff and effluent containing fertilizer or other industrial products. The principal components of the phosphorus cycle involve organic phosphorus and inorganic phosphorus in the form of orthophosphate (PO_4) (Maidment, 1993). Orthophosphate is soluble and is considered to be the only biologically available form of phosphorus. The natural background concentration of total dissolved phosphorus is approximately 0.025 mg/L. Phosphorus concentrations as low as 0.005 to 0.01 mg/L may cause excessive algae growth, but the critical level of phosphorus necessary for excessive algae is around 0.05 mg/L. Although no official water-quality criterion for phosphorus has been established in the United States, total phosphorus should not exceed 0.05 mg/L in any stream or 0.025 mg/L within a lake or reservoir to prevent the development of biological nuisances (Maidment, 1993). In many streams phosphorus is the primary nutrient that influences excessive biological activity. These streams are termed “phosphorus limited.”

Total phosphorus (total-P) concentrations in the watersheds exceeded the algal productivity limit (0.05 mg/L total-P) at two sites (CR-1 and PR-3) in January and April 2007 (fig.26, App. A). High concentrations (0.19 and 0.18 mg/L) were measured at each of the two sites and were related to the highest flow event in April (2007). However, total-P concentrations measured in January and February 2008 were lower or below detection limit and were not related to discharge. All six samples collected in 2017 were at or below detection limit (figs. 26-29; table 13).

Table 13. Total phosphorus (total-P) concentrations measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017.		
Site	Total-P concentrations: mg/L	
	5/24/17	10/2/17
CR-1	BDL*	BDL*
PR-3	0.01 at detection limit	BDL*
YR-1	BDL*	BDL*

* BDL = below detection limit 0.01 mg/L

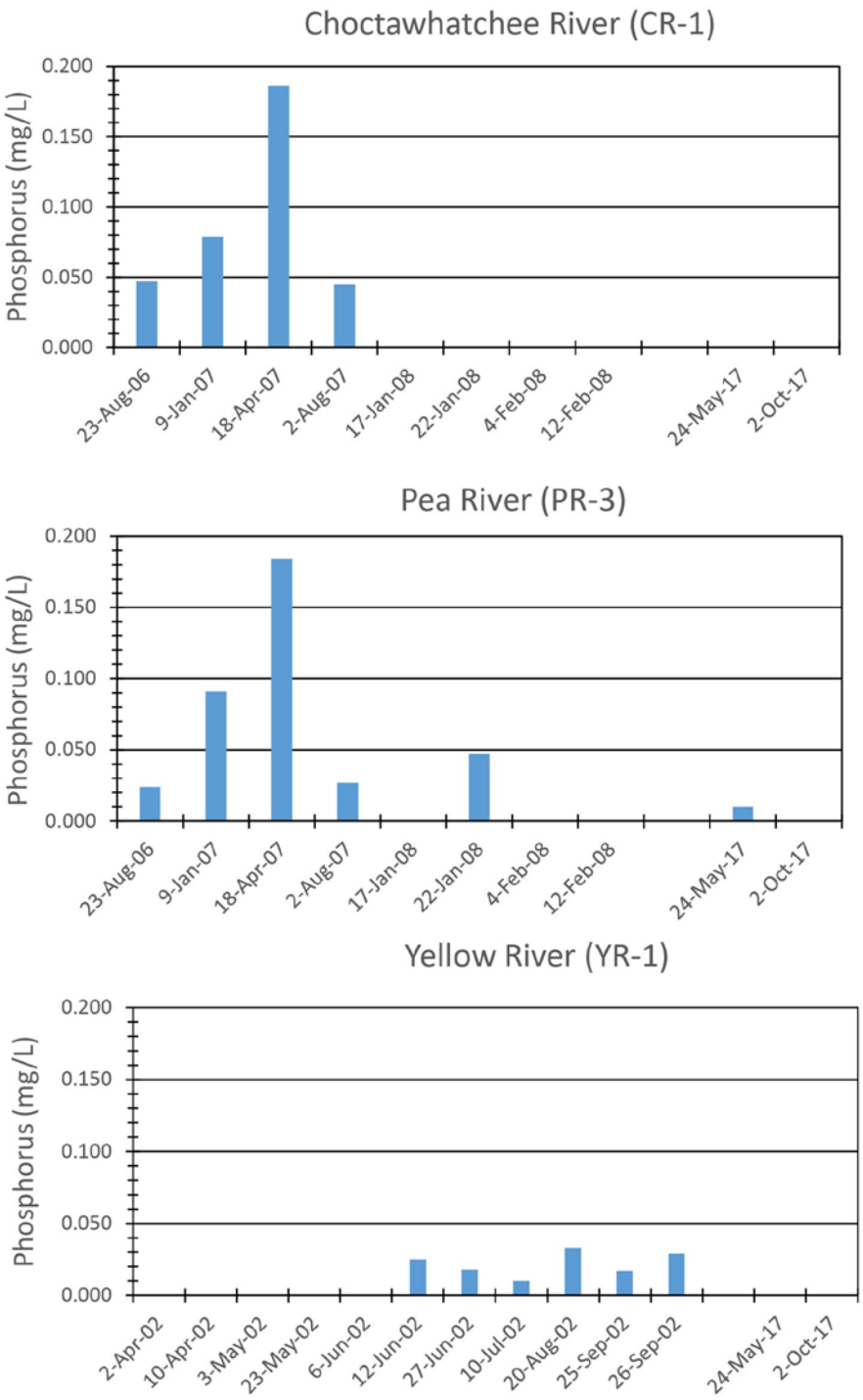

Figure 26. Measured phophorus at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

METAL CONSTITUENTS

Numerous metals in small concentrations are naturally present in rivers. For example, toxic metals in rivers are usually a result of man's activities. Detectable concentrations of lead are commonly found in rivers and may originate from local sources or through atmospheric transport from sources that may be located long distances from the site of deposition. Other toxic metals are found in relatively large concentrations and may be correlated with point sources.

Water samples collected from the rivers were analyzed for selected metallic constituents. Table 14 shows average, minimum, and maximum concentrations and percent detections for the sample period. Naturally occurring metals such as aluminum, barium, iron, manganese, and zinc are commonly found in small concentrations in coastal plain rivers. Lead (Pb) is pervasive in the Choctawhatchee and Pea Rivers watersheds. At PR-3 and CR-1 lead concentration exceeded the USEPA primary/secondary drinking water standard of 15 μg/L (USEPA, 1996) (fig. 30, table 14). The highest concentration was measured at site PR-3 (120 μg/l) (fig. 27). The elevated concentrations were related with higher flow events (April 2007) and low pH values. This relationship is explained by the fact that Pb availability in water increases as pH values decrease (the higher the solubility, the higher the availability). Iron (Fe) concentrations exceeded the USEPA (1996) primary/secondary drinking water standard of 300 μg/L at (table 14), at all sites. Aluminum (Al) concentrations exceed the USEPA (1996) primary/secondary drinking water standards of 50 – 200 μg/L (table 14), at all sites. Barium (Ba) concentrations exceed the USEPA (1996) primary/secondary drinking water standards of 60 μg/L (table 14), at CR-1 and PR-3. Manganese (Mn) concentrations exceed the USEPA (1996) primary/secondary drinking water standards of 50 μg/L (table 14), at PR-3, and YR-1.

ORGANIC CONSTITUENTS

Organic compounds are commonly used in our society today. Frequently, these compounds appear in streams and groundwater aquifers. Many of these compounds are harmful to human health and the health of the aquatic environment. A limited group of organic constituents were analyzed in collected water samples. They include total organic carbon (TOC), phenol, and oil and grease. Total organic carbon (TOC) analysis is a well-defined and commonly used methodology that measures the carbon content of dissolved and particulate organic matter present in water. Many water utilities monitor TOC to determine raw water-quality or to evaluate the effectiveness of processes designed to remove organic carbon. Some wastewater utilities also employ TOC analysis to monitor the efficiency of the treatment process. In addition to these uses for TOC monitoring, measuring changes in TOC concentrations can be an effective "surrogate" for detecting contamination from organic compounds such as petrochemicals, solvents, and pesticides. Thus, while TOC analysis does not give specific information about the nature of the threat, identifying changes in TOC can

Table 14.—Concentrations of metallic constituents detected in water samples collected at monitoring sites in the Choctawhatchee, Pea, and Rivers watersheds.

Metallic Constituent	USEPA primary/ secondary drinking water standards (µg/L)	Freshwater aquatic life criterion (µg/L)		CR1 (µg/L)						PR-3 (µg/L)						YR-1 (µg/L)					
				Historical Data			2017		Average	Historical Data			2017		Average	Historical Data			2017		Average
		Acute	Chronic	% detected	Max	Min	May-17	Oct-17		% detected	Max	Min	May-17	Oct-17		% detected	Max	Min	May-17	Oct-17	
Aluminum	50-200	-	-	90	339	*BDL	204	BDL	189.4	63.6	353	BDL	257	BDL	202.2	61.5	347	BDL	138	BDL	101
Arsenic	10	340	150	BDL	BDL	BDL	0.83	0.64	0.2	BDL	BDL	BDL	0.55	0.61	0.11	BDL	BDL	BDL	BDL	BDL	BDL
Barium	60	-	-	100	63	30.1	16.6	129	50.1	100	89.8	28	16.8	73.5	55.2	100	50.8	11.9	13.8	14.6	23.7
Beryllium	4	-	-	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium**	5	0.47	0.09	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	8	3.6	BDL	BDL	BDL	0.28
Calcium				100	10.5	3.33	3.78	8.78	5.81	100	16.8	4.13	6.22	12.5	9.12	100	25.4	5.29	5.38	13.1	13.76
Chromium	100	16	11	BDL	BDL	BDL	BDL	BDL	BDL*	BDL	BDL	BDL	2.2	BDL	BDL*	BDL	BDL	BDL	2	BDL	0.15
Copper**	1,300/1,000	3.27	2.48	BDL	BDL	BDL	BDL	BDL	BDL*	BDL	BDL	BDL	BDL	BDL	BDL*	BDL	BDL	BDL	2.1	BDL	BDL
Iron	300	-	-	100	770	314	327	700	570.4	100	829	230	253	694	471.4	100	1010	165	435	750	502.76
Lead**	15	12.2	0.48	90	28.4	BDL	7.6	1.2	10.12	91	120	BDL	5.1	0.6	23.1	BDL	BDL	BDL	13.6	1	1.12
Manganese	50	-	-	100	20.8	3.8	4.6	14.4	14.56	100	41.6	19.1	1.7	58.2	27.35	100	99.3	18.9	6.7	52	48.95
Mercury	2	2.4	0.12	BDL	BDL	BDL	0.0043	BDL	0.0004	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0069	BDL	0.0005
Selenium	50	-	-	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Thallium	2	-	-	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zinc**	5,000	32.9	33.1	100	36.4	10.2	35.2	63.7	27.73	100	43.2	8.8	22.1	28.7	28.21	100	26.3	4.5	13.9	8.2	11.25

*BDL = below detection limit

** The aquatic life criteria for cadmium, copper, lead, and zinc was determined as a function of the average hardness (in mg/L as $CaCO_3$) measured at each monitoring site.

Numbers in red represent constituent concentrations exceeding the USEPA primary/secondary drinking water standards.

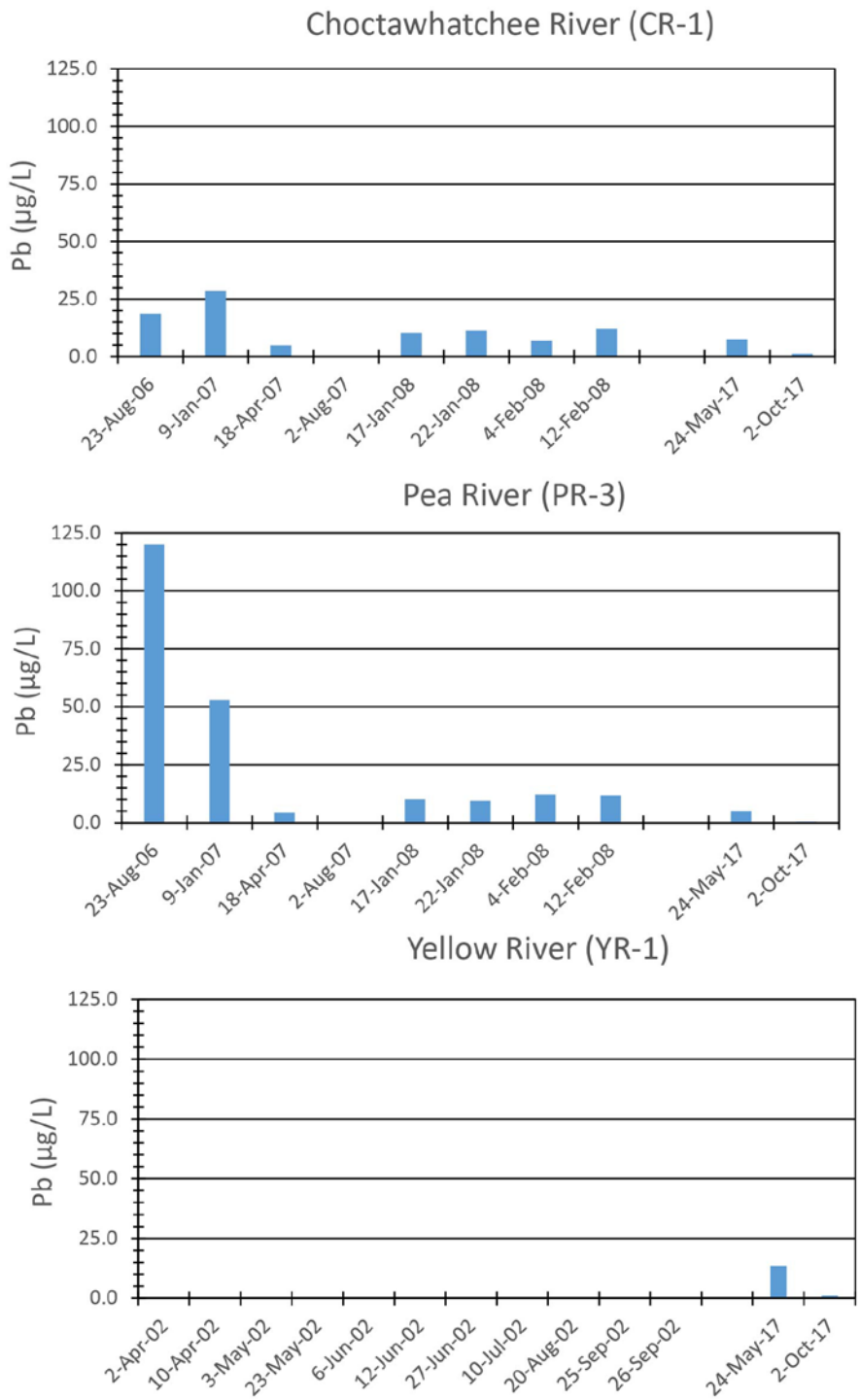

Figure 27. Measured lead at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

be a good indicator of potential threats to a system (USEPA, 2005). Typical TOC values for natural waters vary from 1 to 10 mg/L (Mays, 1996). The TOC values for monitoring sites are shown in App. A and table 15 (sampled in 2017).

The highest TOC concentration (11.2 mg/L) was measured in Yellow River at site YR-1 (App. A and table 15; fig. 28) and was associated with a high flow event in May 2017.

Phenols are used in the production of phenolic resins, germicides, herbicides, fungicides, pharmaceuticals, dyes, plastics, and explosives (Fenelon, 1998). They may occur in domestic and industrial wastewaters, natural waters, and potable water supplies, and they are generally traceable to industrial effluents or landfills (Eaton and others, 1995). The USEPA (1996) states that in order to protect human health from the possible harmful effects of exposure to phenol contaminated water, phenol concentrations in lakes and rivers should not exceed 0.3 mg/L. Phenols cause acute and chronic toxicity to freshwater aquatic life. Historically neither phenols nor oil and grease were detected in any samples collected during the project period. Traces of phenols were identified in YR-1 (0.0051 mg/L – October 2017) and at PR-3 (0.0035 mg/L – May 2017).

Table 15. Total organic carbon (TOC) concentrations measured at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers, 2017

Site	TOC concentrations: mg/L	
	5/24/17	10/2/17
CR-1	5.33	2.94
PR-3	6.37	3.57
YR-1	11.2	4.36

SUMMARY OF FINDINGS

The Choctawhatchee, Pea, and Yellow Rivers watersheds cover much of south-southeast Alabama, but relatively little water-quality data are available to determine the current status of water conditions, effects of land use, and a course of action to protect these waters. The primary objective of this study was to generate data that can be used by the CPYRWMA in cooperation with local, state, and federal agencies, and citizens to develop, manage, and protect the surface-water resources of the region. Land-use/land-cover analysis was combined with geochemical investigations of surface water samples collected from the study area to provide an understanding potential contamination sources and their relation to the land-use practices in the watershed.

Land use is one factor that has a great impact on surface-water and groundwater-quality. Previous studies conducted by the GSA indicated that water-quality is directly related to the intensity and type of land-use practices in the

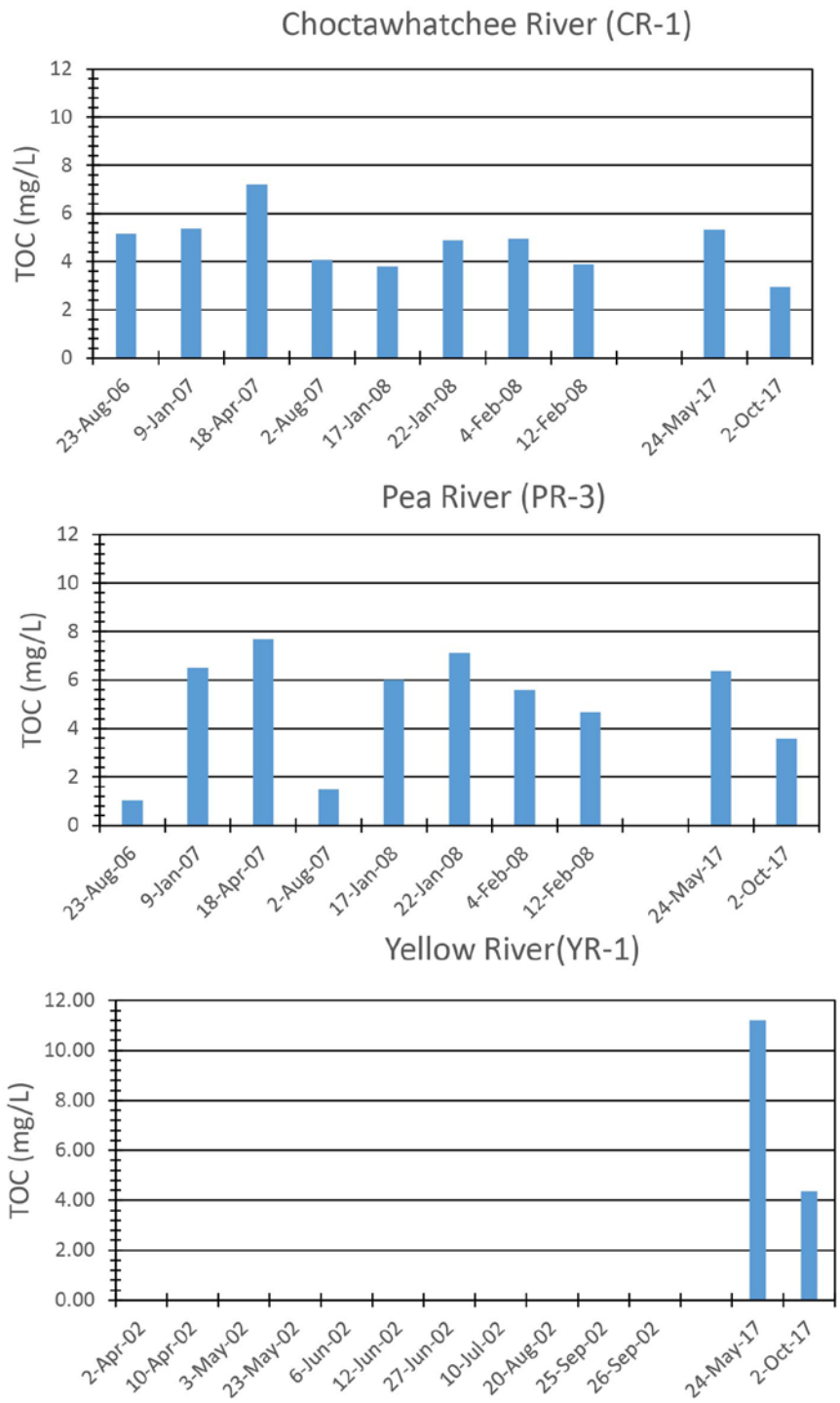

Figure 28. Measured Total Organic carbon (TOC) at monitoring sites in the Choctawhatchee, Pea, and Yellow Rivers watersheds

Choctawhatchee, Pea, and Yellow Rivers watersheds. Agriculture, wastewater discharge, sewer breakthrough, animal waste, and construction activities pose contamination threats to waters in the study area.

The two prevalent land-use categories in the study area are agriculture and forests (figs. 4 and 5).

The southeastern most corner of the study area (Houston County and parts of Henry, Dale, and Geneva Counties) is dominated by agriculture. Therefore, a greater input of fertilizers and herbicides in these areas may cause an increase in the concentration of contaminants such as NO_3^--N, total-P, TDS, and TSS and may adversely impact the quality and availability of water in the watersheds.

Monitoring site selections were based on the location of confluence points of the investigated rivers with major tributaries (fig. 1) and land uses associated with particular river reaches. Site YR-1 was considered low-impact site because it is located downstream of primarily forested lands and less developed urban and agricultural areas. Sites CR-1 and PR-3 were expected to have the highest water quality impacts as they are the most downstream sites and drain large agricultural and urban areas.

Several impaired streams that discharge into the Choctawhatchee River are on the ADEM 303(d) list. The number of impaired streams in the Choctawhatchee River watershed increased over the years from 1996 to 2014. This may be caused by several factors such as contaminant spreading, greater contaminant input, increased number of contaminant sources, and/or an increase of data availability. Parameters investigated in this study exhibit seasonal as well as spatial variability. Although the specific causes of these variations are not simply and immediately explained, their spatial consistency is sufficient to suggest some systematic causes.

In the investigated watersheds, specific conductance values vary with discharge and contaminant concentration. Generally, the highest conductivity values correspond to the lowest discharge events (in August) when river levels decrease and ionic concentrations increase. Given the association of higher conductivity values with low flow events, it is possible that waters with higher contaminant levels during low flow are diluted during higher discharge episodes (figs. 9 - 11).

Occasionally at sites CR-1 and YR-1 increasing discharge is associated with higher TDS concentrations, lower stream temperatures, and medium conductivity values (figs. 9, 11). Therefore, this may indicate an input of contaminants from runoff during colder times of the monitoring period. These three sites are located in close proximity to agricultural areas, road surfaces, and rural/urban areas; therefore, contamination to the streams may be chronic (for example, sewer breakthrough or leaching from livestock waste)

Waters in the investigated rivers are slightly acidic. The range of pH values and the higher frequency of acidic pH values (App. A and fig. 16) indicate that the water is not very well buffered and has a higher potential for contamination through changes in pH. The general inverse relationship between pH and discharge for both rivers may reflect relatively acidic rainfall and/or dilution.

A positive relationship between DO and pH, as well as DO and stream temperature, was observed and this may be the result of natural biological processes that take place in surface waters and (or) in the presence of contaminants. The relatively low DO concentrations observed at three sites sampled in 2017 (table 9, fig. 20) are possibly the result of contamination from surrounding urban and residential land uses (fig. 6). Moreover, the relationship between DO and BOD may be explained by runoff that not only brings oxygenated waters, but more contaminated waters with higher BOD concentrations. During the monitoring period, an inverse relationship between BOD concentrations and stream temperature was observed at all sites which is suggestive of increased biological activity during the warmer seasons. The lowest BOD values were recorded in August (2006 and 2007) and October 2017 at CR-1 and PR-3 and almost for the entire period of monitoring at YR-1. Furthermore, higher BOD levels were accompanied by lower pH values and increased chlorophyll and DO levels.

Historically a positive relationship between total-P and flow and an inverse relationship between nitrate concentrations and flow were observed for all three monitoring sites. The increases observed in the total-P concentrations with increasing flow for both rivers at all sampling sites could be associated with soil erosion linked with high flow events (Hem, 1985). In both rivers, nitrate is the major form of nitrogen present. The low levels of ammonia suggest that nitrate in the river waters may originate from the nitrification of ammonia in the unsaturated zone. Nevertheless, higher ammonia concentrations may be indicative of contamination from releases associated with sources such as livestock waste and (or) sewage breakthrough. The decrease in nitrate, associated with increased flow, may reflect dilution of stream waters with low nitrate input waters. However, it should be mentioned that there are limitations related to the analyzed population size (for example, concentrations below the detection limit were not included in the correlation matrix).

Furthermore, high nitrate concentrations are associated with elevated chloride concentrations (App. A). Consequently, the presence of nitrate in monitoring rivers may be associated with leaching of residual nitrate from soil during the times when the photosynthesis process is dormant and/or from sewer breakthrough.

Metals, with the exception of lead, which is pervasive in the investigated watersheds, do not pose a contamination problem in the Choctawhatchee, Pea, and Yellow Rivers watersheds. At two of the monitoring sites (CR-1 and PR-3), average lead concentrations were above the USEPA primary/secondary drinking

water standard of 15 μg/L (USEPA, 1996) and the acute freshwater aquatic life criterion (fig. 47, App. A) (ADEM, 2008). The chronic freshwater aquatic life criterion was exceeded at all sites (table 14). The highest concentrations measured related to the higher flow events and lower pH values. Lead contamination may be attributed to sources such as atmospheric transport, industrial wastewater discharge, urban runoff, leaching batteries, and lead paint.

Aluminum (Al), barium (Ba), iron (Fe), and manganese (MN) concentrations exceeding the USEPA primary/secondary drinking water standards may presumably be the result of surface weathering and erosion of clay minerals.

Overall, the analytical data indicate that the investigated watersheds are impacted by agricultural practices and developed land from surrounding drained areas. The presence of highly conductive soils in the study area and relatively low topographic relief results in an environment favorable to rapid water infiltration and reduced runoff rates. Therefore, contaminants such as nitrate will migrate through the soil to the saturated zone. Additionally, analytical data suggest that shallow groundwater may have a greater input of nutrients to surface water than runoff.

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Appendix A.