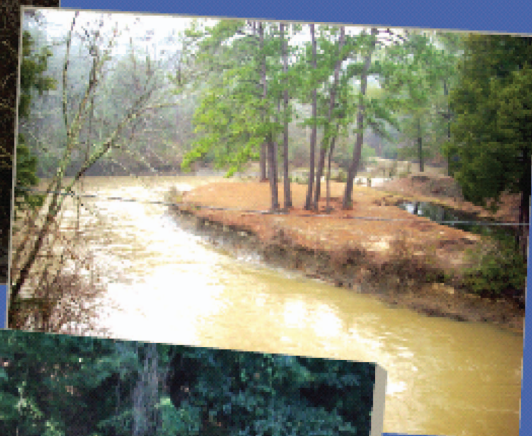
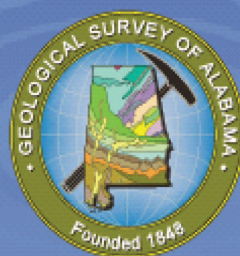


*Water-Quality Evaluation of the
Choctawhatchee and Pea
Rivers in Southeast Alabama*



*Geological Survey of Alabama
Bulletin 182*



GEOLOGICAL SURVEY OF ALABAMA

Berry H. (Nick) Tew, Jr.
State Geologist

GROUNDWATER ASSESSMENT PROGRAM

**WATER-QUALITY EVALUATION OF THE CHOCTAWHATCHEE
AND PEA RIVERS IN SOUTHEAST ALABAMA**

Bulletin 182

by

Dorina Murgulet and Marlon R. Cook

Tuscaloosa, Alabama
2010

GEOLOGICAL SURVEY OF ALABAMA

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August 12, 2010

The Honorable Bob Riley
Governor of Alabama
Montgomery, Alabama

Dear Governor Riley:

It is with pleasure that I make available to you this report entitled *Water-Quality Evaluation of the Choctawhatchee and Pea Rivers in Southeast Alabama*, by Dorina Murgulet and Marlon R. Cook, which has been published as Bulletin 182 by the Geological Survey of Alabama.

Bulletin 182 provides seasonal information about water quality, stream discharge, nutrient and sediment loads, land use/land cover, and overall stream health for the Choctawhatchee and Pea Rivers watersheds. The data provided by this study can be used by the Choctawhatchee, Pea, and Yellow Rivers Watershed Management Authority (CPYRWMA) in cooperation with local, state, and federal agencies and citizens to identify potential sources of contamination and to develop, manage, and protect the surface water resources in this watershed.

Publication of this report fulfills a need for water quality data for the southeastern part of the state.

Respectfully,

Berry H. (Nick) Tew, Jr.
State Geologist

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WATER-QUALITY EVALUATION OF THE CHOCTAWHATCHEE AND PEA RIVERS IN SOUTHEAST ALABAMA

by

Dorina Murgulet and Marlon R. Cook

ABSTRACT

The Choctawhatchee and Pea Rivers watersheds cover much of southeast Alabama, but relatively little comprehensive water-quality data are available to determine the current status of water-quality conditions, land-use impacts, and a course of action to protect these waters. The purpose of this project has been to generate data that can be used by the Choctawhatchee, Pea, and Yellow Rivers Watershed Management Authority (CPYRWMA) in cooperation with local, state, and federal agencies and citizens to develop, manage, and protect the surface-water resources of the Choctawhatchee and Pea Rivers watersheds.

The monitoring sites for this assessment were selected to evaluate the cumulative effects of land use on water-quality from the upstream part of the watershed in Bullock and Barbour Counties to the downstream part of the watershed in Geneva County where the Choctawhatchee and Pea Rivers join and flow into Florida. The primary constituents that affect water quality of streams in Alabama originate from nonpoint sources and consist of sediment, nutrients, bacteria, 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 as well as magnitudes of impact.

Excessive nutrient enrichment is a major cause of water-quality impairment in this region. Evaluations of normalized nitrate

(NO₃⁻-N) and total phosphorus (total-P) loads indicate that sites CR1 and PR2 had the greatest concentrations. The smallest loads were estimated for sites ECR and WCR on the Choctawhatchee River. Excess nutrients originate from agricultural activities and developed residential and urban areas. Land-use/land-cover classification of the Choctawhatchee and Pea Rivers watersheds indicates that most of the southern half of the area is used for agriculture (for example, herbaceous planted/cultivated land uses). Sedimentation is an additional factor that contributes to the water-quality degradation in this area. The largest and smallest suspended sediment loads were estimated for the Pea River at sites PR2 and PR1, respectively. Nutrients in the investigated area are potential nonpoint contaminant sources, and metals are naturally present in streams in small concentrations. Metals that exceed water-quality criteria may be the result of human activity. Lead concentration exceeding the USEPA primary/secondary drinking water standard of 15 µg/L and the acute aquatic life criterion for freshwater (12.2 µg/L) were measured at sites PR1 and PR3. Lead concentrations above 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 help identify potential contamination sources. When all primary constituents were considered, water quality was most impacted at sites PR2 and PR3 (Pea River) and CR1 (Choctawhatchee River), and least impacted at sites PR1 (Pea River) and ECR and WCR (Choctawhatchee River). However, it should be noted that element concentrations change with sampling dates as a function of discharge and erosion

rates, biological processes, and source contaminant input at the time of sampling. The sites that appear to be impacted by contamination generally correlate well with pollutant sources and land uses in the respective watersheds, as predicted prior to monitoring. An exception was data from Pea River site PR2, which was less impacted by nutrient contamination than expected considering its location in a forested area further away from agricultural lands. High nitrate and chloride concentrations at this site during August (2006 and 2007) and during the colder season (2007 and 2008) suggest sewer breakthrough and/or industrial discharge as plausible sources of this contamination.

INTRODUCTION

The Choctawhatchee and Pea Rivers watershed covers much of southeast Alabama (fig. 1), but relatively little water-quality data were previously available to determine the current status of water-quality conditions, effects of land use, and a course of action to protect these waters. The purpose of the project has been 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 these essential surface-water resources.

Monitoring sites were selected upstream, midreach, and downstream at major confluences of creeks with Choctawhatchee and Pea Rivers (fig. 2). Water-quality data were collected at three sites for each of the two rivers. Monitoring sites on the Pea River include PR1, the northernmost site, located in Pike County between the confluence of Pea River with two unnamed creeks; PR2, located in Coffee County at midreach on the Pea River at its confluence with Big and Whitewater Creeks; and PR3, the southernmost site, located in Geneva County near the confluence of the Pea and Choctawhatchee Rivers. Sites on the Choctawhatchee River include WCR, the upstream site on the West Fork of Choctawhatchee River at its confluence with the East Fork in Dale County;

ECR, located on the East Fork of Choctawhatchee River; and CR1, the southernmost downstream site, located near the confluence of the Choctawhatchee River with Double Bridges Creek about 1 mile from the confluence with the Pea River. Monitoring site locations appear in table 1 and are depicted in figures 2, 3, 4A, B, 5.

The data presented in this report characterize water quality, stream discharge, nutrients and sediment loads, and land use/land cover. The water-quality and stream discharge datasets are composed of samples collected by the Geological Survey of Alabama (GSA) from October 2006 to April 2008. The data are sorted by sampling sites and monitoring event. The results of the chemical analyses are incorporated in tables accompanying each section and depicted in several graphs. Dates on the graphs represent one day of a two-day sampling event. Land-use/land-cover (LULC) data used for this study are the U.S. Geological Survey (USGS) *National Land Cover Data (NLCD)* 2001 Level I data (Homer and others, 2004). These analyses provide valuable information for the qualification and quantification of water quality and resources in the rivers and the evaluation of the effects of land-use practices in the assessed watershed.

ACKNOWLEDGMENTS

The Geological Survey of Alabama acknowledges the CPYRWMA, including the CPYRWMA Board of Directors, Chairmen Mr. Steve Stevens and Mr. Don Halford, and Executive Director Ms. Barbara Gibson, whose participation and cooperation made this study possible. Neil Moss (GSA) also provided valuable field assistance.

GEOGRAPHIC CHARACTERIZATION OF ASSESSED WATERSHEDS

In Alabama, the Choctawhatchee River consists of the east and west forks in the northern part of the watershed in Dale, Henry, and Barbour Counties and a single channel in the southern part of the watershed flowing through Dale, Houston, and Geneva

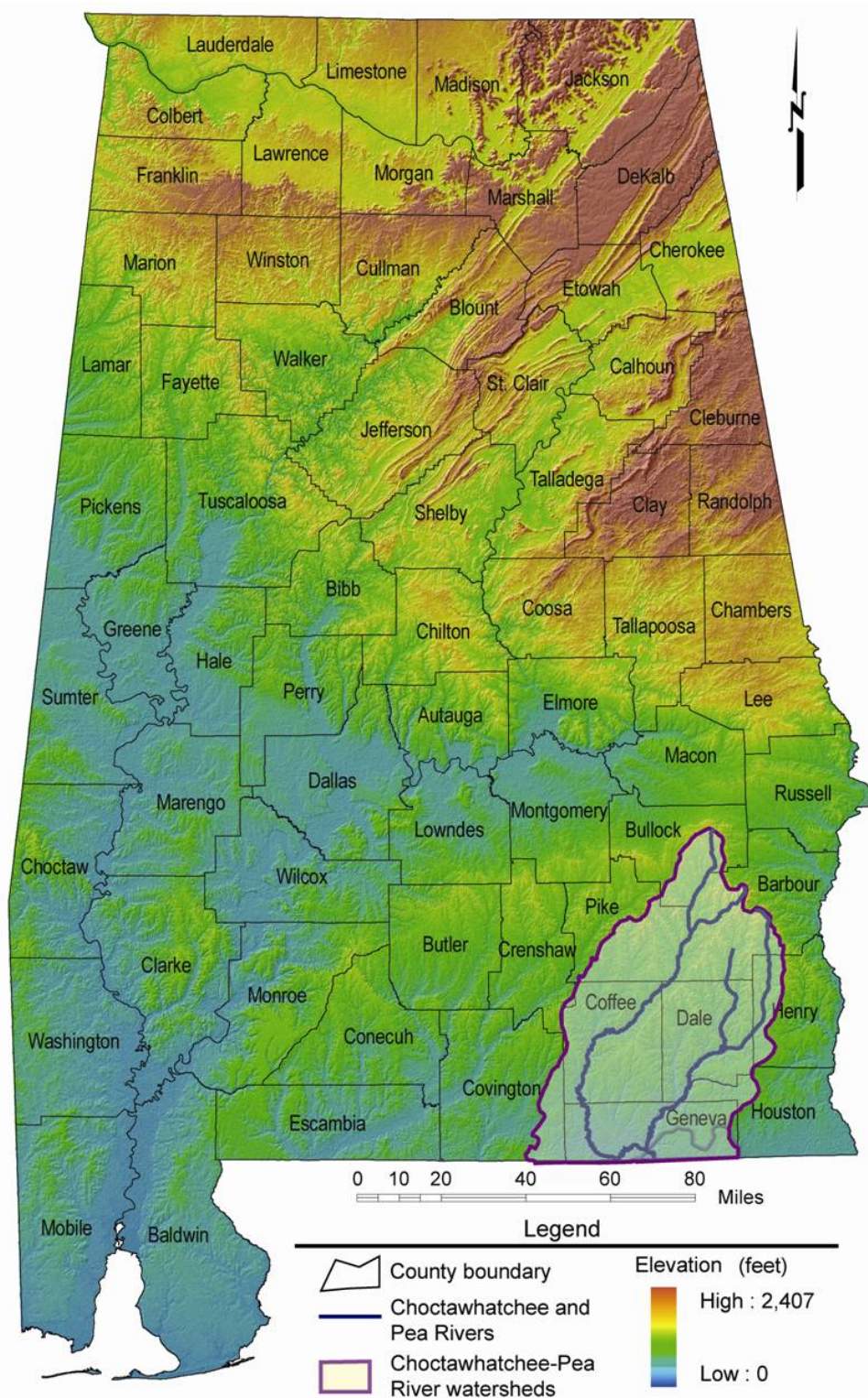


Figure 1.—Index map showing the location of the Choctawhatchee and Pea Rivers project area.

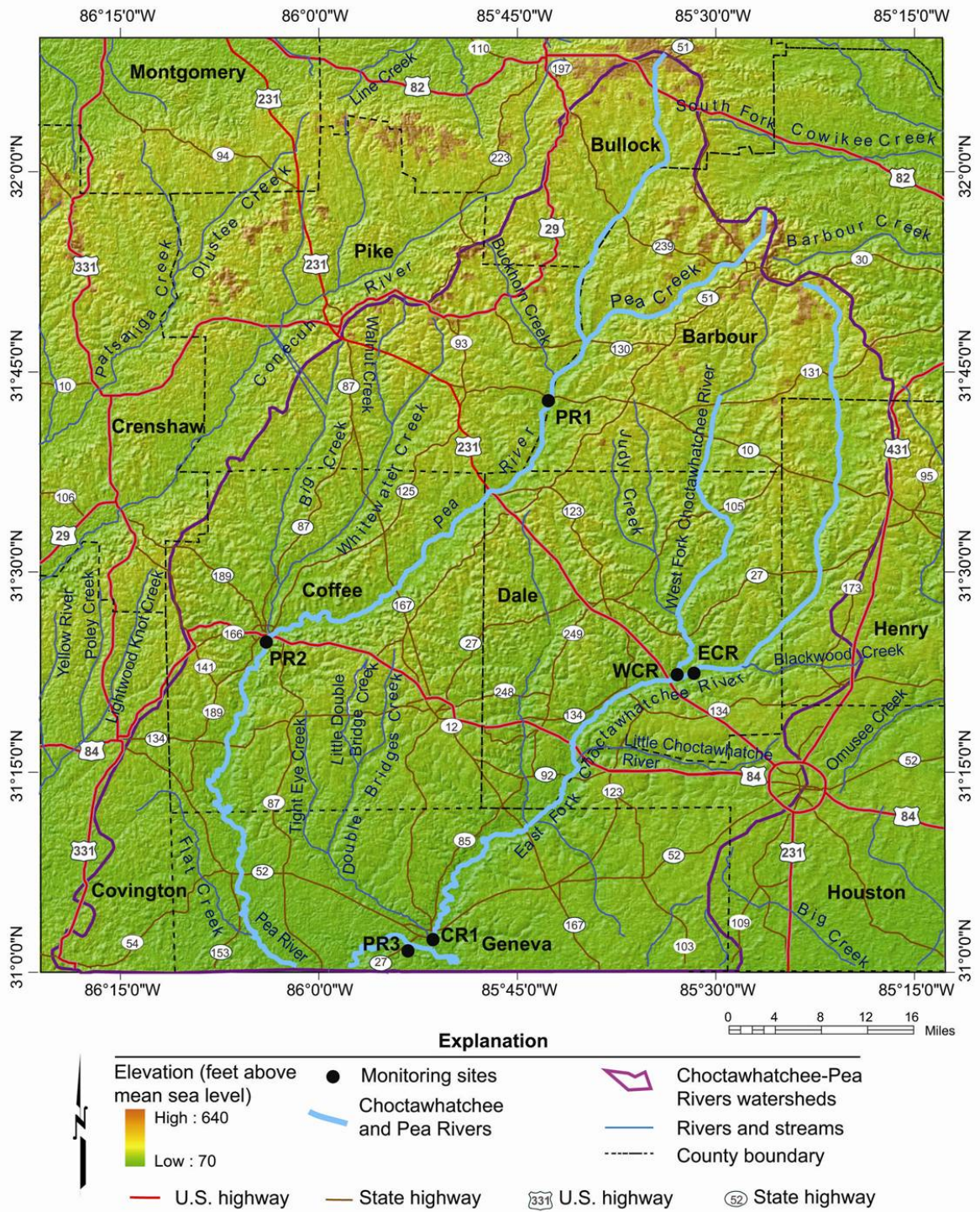


Figure 2.—Choctawhatchee and Pea Rivers watersheds and monitoring sites.

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

Stream and monitoring site location	Site	Location		Watershed area (mi ²)
		Latitude	Longitude	
Pea River @ Alabama Hwy. 10 crossing Pike County	PR1	31°42'51.8" N	85°42'24.3" W	361
Pea River @ U.S. Hwy. 84 crossing Coffee County	PR2	31°22'19.1" N	85°32'38.9" W	959
Pea River @ Alabama Hwy. 27 crossing Geneva County	PR3	31°22'25.5" N	85°31'22.6" W	1,552
East Fork Choctawhatchee River @ County Rd. 59 crossing Dale County	ECR	31°02'27.5"N	85°51'08.3" W	225
West Fork Choctawhatchee River @ County Rd. 20 crossing Dale County	WCR	31°01'36.8" N	85°53'01.5" W	355
Choctawhatchee River @ Alabama Hwy. 52 crossing Geneva County	CR1	31°24'46.0" N	86°03'46.2" W	3,097

Counties. It is the longest unregulated river in Alabama with a total length of approximately 170 miles. The Pea River, which serves as a border between Barbour and Pike Counties (figs. 1, 2), originates from beaver swamps in Bullock County and serves as the major western tributary of the Choctawhatchee River watershed. The Choctawhatchee and Pea Rivers flow southward across southeastern Alabama and join at the city of Geneva, near the Florida state line. The water from these streams eventually leaves Alabama and flows across northwest Florida to the Gulf of Mexico through Choctawhatchee Bay. Monitoring sites and watershed areas are shown in table 1 and figures 2, 3, 4A, and 5.

The Choctawhatchee River watershed includes portions of 10 counties in southeast Alabama and covers approximately 3,400 square miles (mi²) of the Alabama Coastal Plain and 1,348 mi² of Florida's northwestern Coastal Plain (U.S. Army Corps of Engineers, 1992). The evaluated watershed is contained by Bullock, Pike, Barbour, Coffee, Dale, Henry, Houston, Covington and Geneva Counties, Alabama. This area lies for the most part on the Dougherty Plain and Southern Red Hills physiographic regions and partially within the Chunnenugee Hills physiographic region (for example, Pea River) (Sapp and Emplainscourt, 1975) (figs. 1, 3). The Dougherty Plain, located in the

southern part of the study area, consists of undifferentiated limestone residuum, bedded sand and clay, and surficial terrace material with a low cuesta-like topography (Sapp and Emplainscourt, 1975). The confluence of the Choctawhatchee and Pea Rivers occurs in the Dougherty Plain in southern Geneva County. North of this physiographic region is the Southern Red Hills district with southward-sloping upland and moderate relief. Topographic relief in the Southern Red Hills is some of the greatest in the Coastal Plain of Alabama where streams are characterized by high gradient, hard-rock bottoms, and swifter flows. The headwaters of the Choctawhatchee River originate in this physiographic region. The Chunnenugee Hills district (fig. 3) consists of a series of pine-forested sand hills and cuestas developed on chalk (west Alabama) and more resistant beds of clay, siltstone, and sandstone. The Pea River headwaters originate in this district (Sapp and Emplainscourt, 1975) (fig. 3).

As the rivers flow southwestward, they collect waters from streams that dissect the area and form relatively narrow floodplains. Streams receive waters draining natural and cultivated herbaceous areas as well as developed and undeveloped eroding areas. Elevation in the study area is generally lower than 350 feet above mean sea level and the topographic relief does not exceed 100 feet.

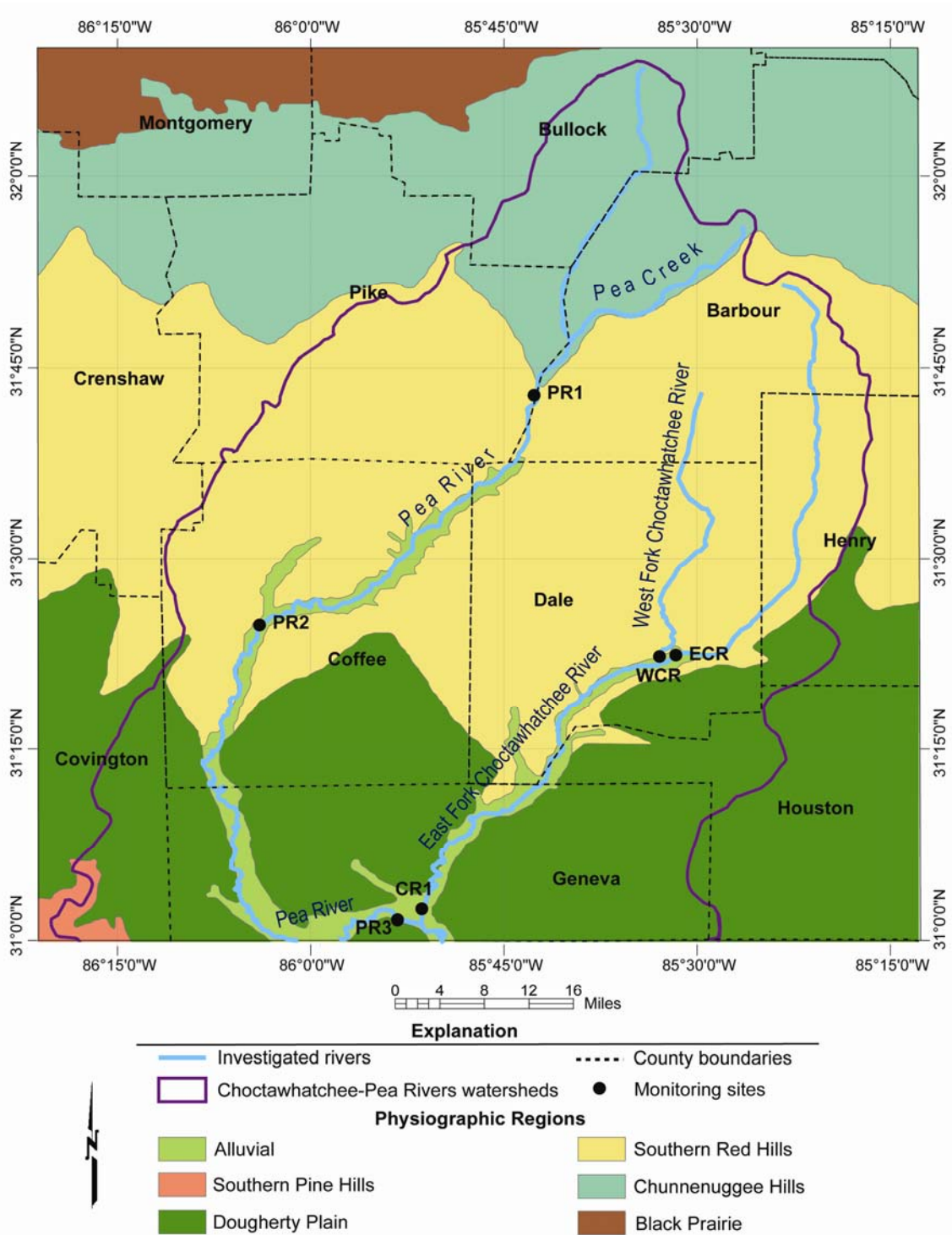


Figure 3.—Physiographic regions and Choctawhatchee and Pea Rivers watersheds extent (physiography from Sapp and Emplaincourt, 1975).

Nevertheless, the Southern Red Hills are noticeable in the northern and western portions of the study area where ridges are

relatively steep and narrow with noticeable increases in elevation and topographic relief.

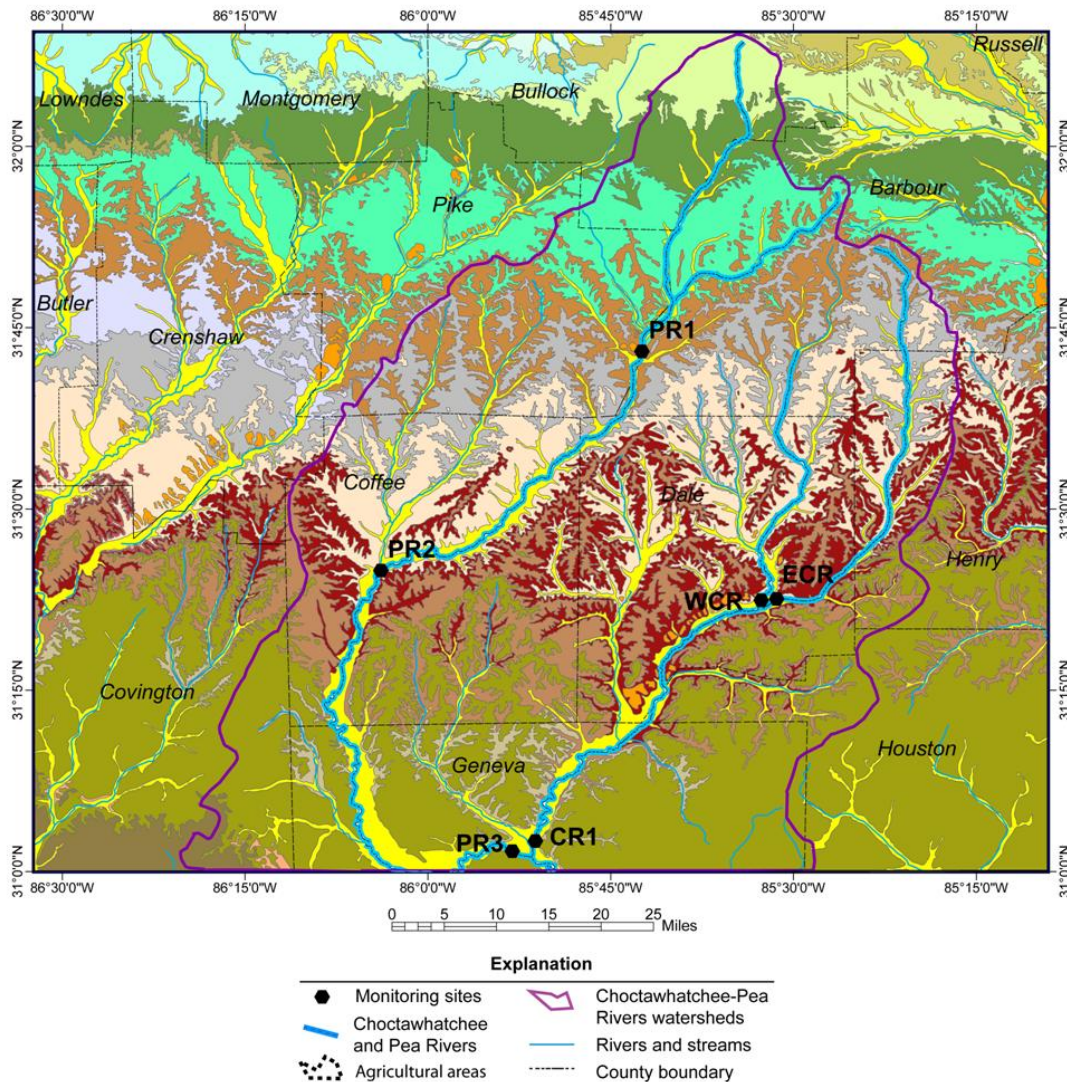
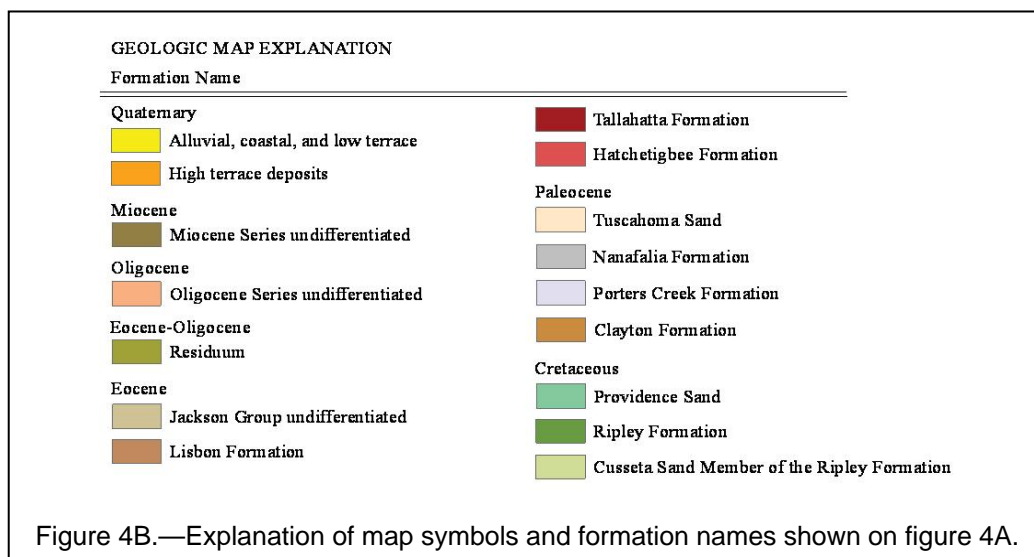


Figure 4A.—Geology of the Choctawhatchee and Pea Rivers watersheds.



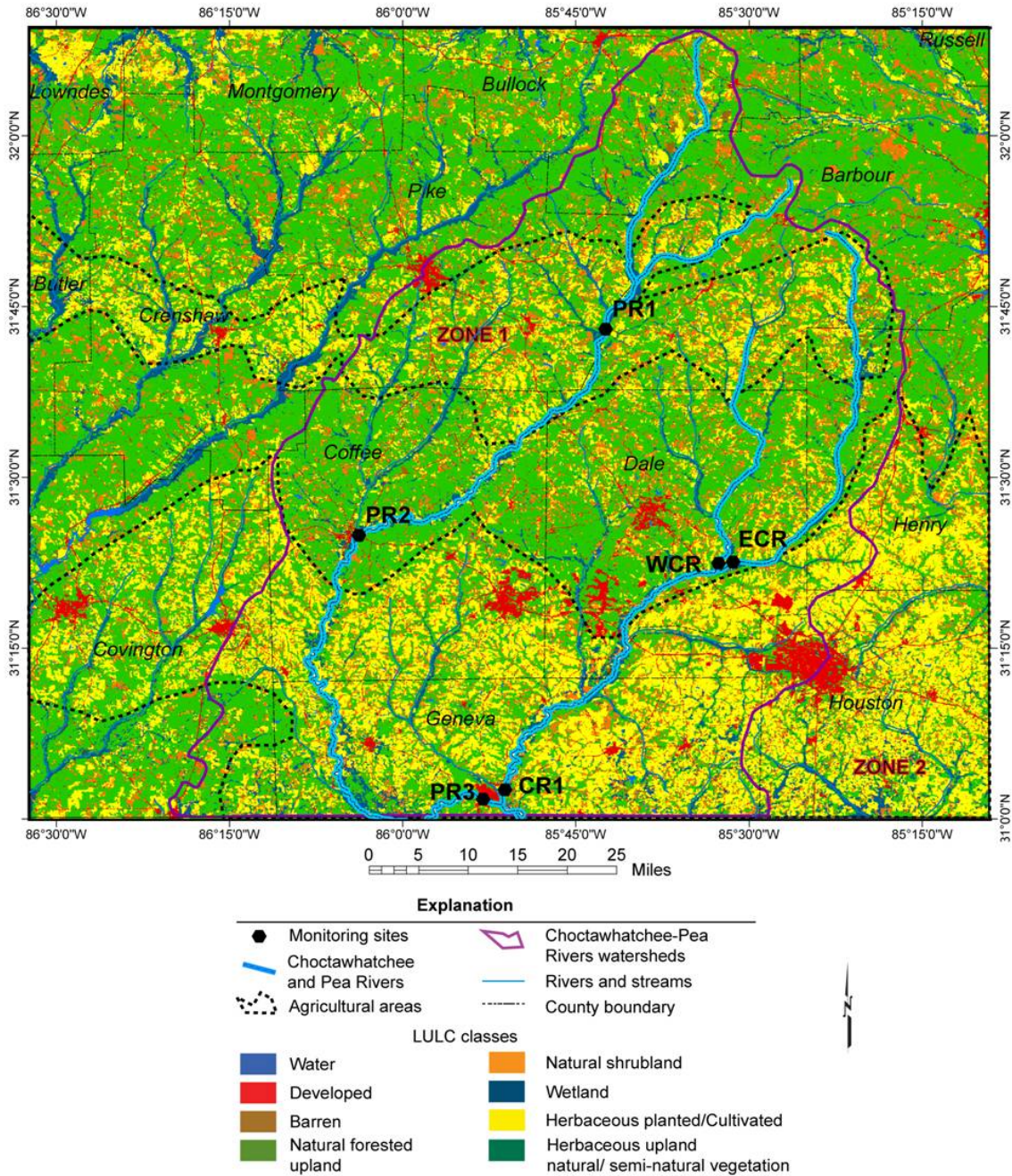


Figure 5.—LULC Level I classification of the Choctawhatchee and Pea Rivers watersheds.

HYDROGEOLOGY AND GEOMORPHOLOGY

Streams under investigation in this study are underlain by Cretaceous and Tertiary sediments. These sediments are chiefly composed of sand and clay, mixed clastic, residuum, and thin carbonate rocks. Several

geologic units crop out in the Choctawhatchee River watershed (figs. 2, 4A, B). In the Blackwood Creek, Double Bridges Creek, Little 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). Erosion in the Walnut Creek watershed has exposed the Providence and Clayton Formations (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 drought conditions. The topographic and geomorphologic characteristics of these streams cause flashy storm runoff, resulting in highly variable stream water levels, especially during winter and spring. The stream channels are characterized by steep banks and stream beds composed of thick silt and sand. Tributaries in the watershed are classified as youthful to mature with narrow floodplains, v-shaped valleys, and narrow meander belts. Stream gradients for the study area vary, dependent upon the uniformity of the erodible substrate and the proximity to the stream source, with the lowest gradient at Walnut Creek and Little Choctawhatchee River (10 feet per mile) and the highest at Little Double Bridges Creek (22 feet per mile) (Cook and Kopaska-Merkel, 1996).

LAND-USE IMPACTS ON WATER QUALITY

Land-use practices are important factors that influence water quality and availability, but their impact 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 in shaping landscape patterns in the United States. The 2001 USGS LU/LC data (Homer and others, 2004) were used in delineating LULC classes and contaminant

sources, and in predicting future impacts. This dataset was compiled from Landsat Thematic Mapper Plus (ETM+) satellite imagery (circa 2001) and it was supplemented by various ancillary data such as the National Land Cover Database 2001 for mapping zone 46, produced by the Multi-Resolution Land Characteristics (MRLC) Consortium. Landsat 7, the Landsat Thematic Mapper Plus (ETM+), is a multispectral scanning radiometer that scans bands 1 through 5 and 7 (3 visible, 2 middle infrared, and 1 near infrared,) with 30-meter (m) pixel resolution, and the thermal infrared, band 6, with a 60-m resolution. Applications of Landsat ETM+ include mapping of large areas, natural resource mapping, pipeline routing, historical use analyses, and historical impact assessment. From this dataset, eight Level I LULC classes were identified for the area under investigation and are presented in figure 5. Fifteen Level II classes were identified for the study area (map not included in the report). The LULC classification map includes an explanation with class description and corresponding color schemes. The Level I classification includes the following classes: water, developed, barren, natural forested upland, natural shrubland, herbaceous upland natural/semi-natural vegetation, herbaceous planted/cultivated, and wetland (fig. 5). The Level II classification is a more detailed description of the LULC and consists of several subclasses for most of the Level I classes. The following subclasses were identified: 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, cultivated crops, woody wetlands, and emergent herbaceous wetlands (not included in the report). Most of the area is dominated by herbaceous planted/cultivated and natural forested upland classes (table 2).

Table 2 presents results of the LULC analysis for counties that include the Choctawhatchee and Pea Rivers watersheds. Based on these analyses, the LULC data for the study area are depicted in three major

Table 2.—Area and proportion of agriculture and forest cover by county in the study area

County name	County area (mi ²)	LULC class area (mi ²)			Percent of LULC class		
		Agriculture	Forest	Other	Agriculture	Forest	Other
Barbour	904.5	134.9	511.8	257.8	15.0	56.6	28.4
Coffee	680.5	168.1	349.0	163.4	24.7	51.3	24.0
Covington	1,043.9	201.8	612.7	229.4	19.3	58.7	22.0
Crenshaw	610.9	99.6	307.1	204.2	16.3	50.3	33.4
Dale	562.7	117.4	398.5	46.8	20.9	70.8	8.3
Geneva	578.9	224.5	184.9	169.5	38.8	32.0	29.2
Henry	568.3	165.7	254.1	148.5	30.0	44.7	25.3
Houston	581.6	247.5	148.0	186.1	42.6	25.4	32.0
Pike	672.1	123.3	357.8	191.0	18.3	53.2	28.5

classes: agriculture, forest, and other land uses. Furthermore, counties in the southern half of the watershed (for example, Houston and Geneva Counties) have the highest percentage of agricultural land use (fig. 5). The county with the highest percentage of agriculture is Houston. Additionally, Geneva and Henry Counties exhibit a high percentage of agricultural land use. The remaining analyzed counties have a higher percentage of forest and may pose a smaller contamination risk to the Choctawhatchee and Pea Rivers watersheds. However, even within forested areas, scattered agricultural areas and residential homes are present. Therefore, the potential of contamination derived from the forested areas should not be underestimated.

Intensive agriculture was observed in the Choctawhatchee River watershed in most of Houston and Geneva Counties, the southern half of Coffee County, and the southeastern corner of Dale County. The remainder of the Choctawhatchee River watershed includes upland forest with sparse planted/cultivated areas. Boundaries for cultivated/agricultural areas can be derived by assessing the geology, soils, physiography, topography, and land-use patterns. There is an obvious relationship between certain geologic formations (figs. 4A, B), soil types, and the distribution of cultivated/planted areas (fig. 5). These analyses indicate that agricultural areas are associated primarily with the

Tertiary Residuum, Nanafalia Formation, and Clayton Formation (figs. 4A, B, 5), which are largely composed of clay and residuum (sand, clay, claystone, chert, and limestone). Additionally, these areas lie within two zones that correspond to the outcrop patterns of the underlying geologic formations (figs. 4A, B, 5). Zone 1 (northern zone) overlies mainly the Nanafalia Formation and Clayton Formation and to a smaller extent the Tuscahoma Sand, Porters Creek Formation, and the Providence Sand. However, most of the agricultural land uses in zone 1 are concentrated in the area overlying the Nanafalia Formation (figs. 4A, B, 5). Zone 2 (the southern zone) is underlain primarily by Residuum (figs. 4A, B, 5).

In most cases, weathered geologic materials as well as freshly exposed geologic materials provide a good foundation for soils. Soils in the two designated areas are described as the Ultisols and Entisols. Ultisols occur in humid areas and have clay-enriched subsoil that is low in nutrients. With soil amendments, they are productive for row crops. The Entisols are characterized by the properties of their parent material. They include soils on steep slopes, flood plains, and sand dunes. Both Ultisols and Entisols have a strong reliance on the base material or geology. These soils are particularly valuable for agricultural production.

The geology, soils, physiography, and topography collectively create an

environment favorable for the land uses observed in the two agricultural areas (fig. 5), which, in large part, are pasture, hay, and row crops. It has been recognized that these land-use activities are generally associated with excessive sedimentation, bacteria, and nutrients in many watersheds in the U.S. as well as in the Choctawhatchee watershed (Clean Water Act, 2008 Alabama 303(d) List, Alabama Department of Environmental Management (ADEM, 2008). Runoff of fertilizers and animal waste transports excessive amounts of phosphorus and nitrate to streams in the watersheds and intensifies bacterial activity. Such factors are responsible for water-quality deterioration and reduced water availability and use.

Land uses such as cropland, hayland, pastureland, nurseries, rangeland (grasslands, shrublands), disturbed forest land, construction sites, and road surfaces, for example, are major factors influencing sediment and contaminant loading in the Choctawhatchee and Pea Rivers watersheds.

CLEAN WATER ACT SECTION 303(D) LISTED STREAMS

Section 303(d) of the Clean Water Act requires states to 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 listed on the 303(d) List. However, beginning in 1998, the Choctawhatchee River watershed appeared on the list of impaired Alabama waters with five stream segments: Hurricane, Beaver, Walnut, and Harrant Creeks and Dowling Branch. The number increased to seven in 2008 with the addition of Judy and Indian Camp Creeks.

Judy Creek, with headwaters in Barbour County, flowing into the West Fork Choctawhatchee River in Dale County, was listed for nutrient contaminants and an unknown source. Beaver Creek, which receives effluent from the city of Dothan Waste Water Treatment Plant in Houston

County, was listed as impaired as a result of increased nutrients and organic enrichment (carbonaceous biochemical oxygen demand (CBOD) and nitrogenous biochemical oxygen demand (NBOD)) from sources such as municipal and urban runoff/storm sewers. Hurricane Creek, which discharges directly to the Choctawhatchee River in Geneva County, was listed for pathogens from sources such as agriculture and 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 (CBOD, NBOD) derived from agriculture, urban runoff/storm sewers, and municipal sources. Harrant 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 Harrant Creek (Coffee County, just east of Enterprise) is listed as contaminated with nutrients, pathogens, and siltation (habitat alteration) 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 (Clean Water Act, 2008 Alabama 303 (d) List, ADEM; 2008). Pea River watershed currently has no streams listed as impaired.

CHEMICAL AND PHYSICAL PARAMETERS

STREAM DISCHARGE

Stream discharge is a fundamental hydrologic characteristic of watershed studies (Gore, 1996). Discharge interacts with 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 stream discharge. Discharge is an essential component of constituent loading

calculations and interwatershed comparisons of ionic concentrations and normalization of water-quality data.

Streams in the study area generally attain low flow status during August. 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 cyclonic storms, most of the discharge from the watersheds during August, September, and October of each year can be attributed to groundwater discharge. Therefore, during these periods of the year, elevated contaminant levels in streams may be attributed 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 stream water levels. 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. Discharge events to be monitored were selected to establish a well-distributed dataset from low to high flow. Discharge data were estimated for each site from the nearest USGS flow measurement station.

Mean daily discharge values from the USGS sites were used to normalize discharge values at the six monitoring sites (USGS, 2008). This was accomplished by establishing ratios of watershed drainage area between each site and the nearest USGS monitoring site. Mean daily discharge was used in regression models to estimate selected constituent loads. The highest average discharge rates in Choctawhatchee and Pea Rivers were recorded at the downstream sites CR1 (7,759 cubic feet per

second (cfs)) and PR3 (2,419 cfs), respectively (table 3, fig. 6).

Table 3.—Discharge measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Discharge (cfs)		
	Maximum	Minimum	Average
PR1	1,990	15.8	678
PR2	3,515	149	1,687
PR3	5,685	203	2,419
ECR	4,150	42.6	1,001
WCR	4,150	67.1	1,118
CR1	17,260	500	7,759

STREAM TEMPERATURE

Water temperature is an important catalyst that affects the physical and geochemical characteristics of a stream. 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 32.2°C. The highest stream temperature, 30.4°C was measured during August in West Choctawhatchee River, site WCR, and the lowest value of 6.7°C was recorded in Pea River, sites PR1 and PR2, during the winter months. The maximum stream temperature criterion was not exceeded at any of the sites during the monitoring period (table 4).

SPECIFIC CONDUCTANCE

Specific conductance (SC) is a measure of the ion content of water and is an indicator of how well water can conduct an electrical current. The ability of water to conduct electric current is dependent on ionic concentration and mobility in solution (the presence and availability of dissolved ions in solution). Specific conductance is an indirect

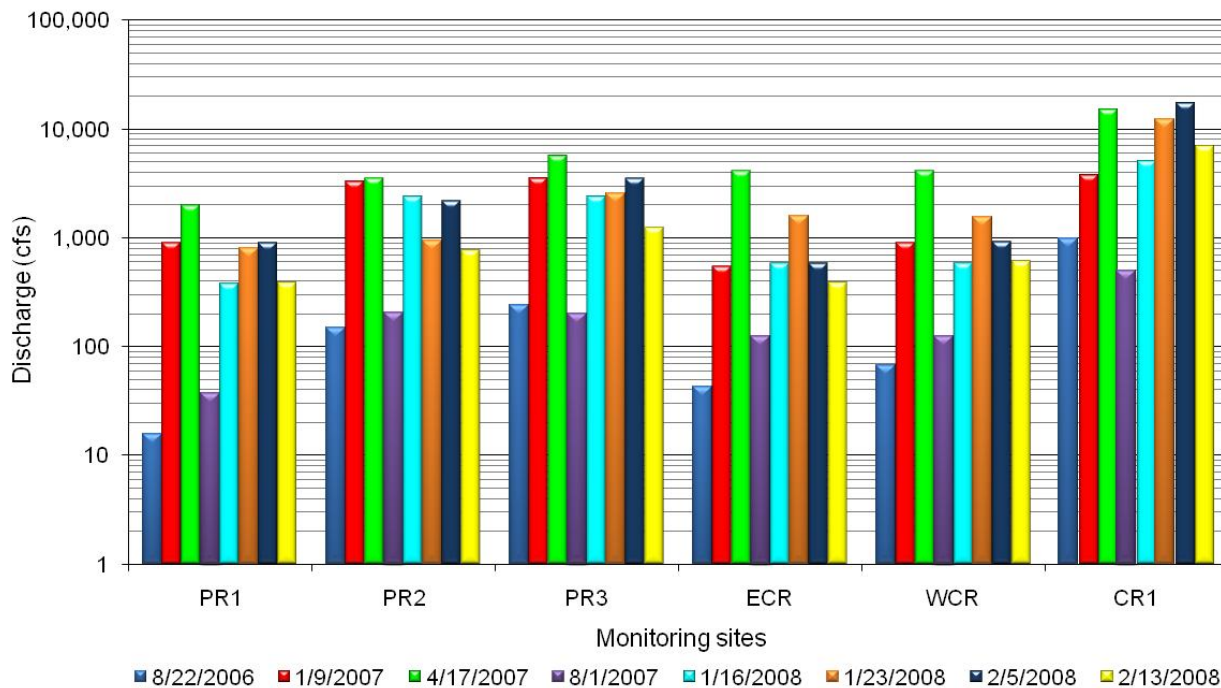


Figure 6.—Measured discharge at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

measure of dissolved solids such as potassium, nitrate, chloride, sulfate, phosphate, sodium, magnesium, calcium, and iron. Consequently, this parameter can be used as an indicator of water pollution. Typically, rain water and surface water not influenced by groundwater has a SC value less than 50 $\mu\text{S}/\text{cm}$ (micro Siemens per centimeter), if not impacted by nonpoint pollution sources. Overall, SC variability is

influenced by differences in stream 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 ($\mu\text{S}/\text{cm}$) profile (figs. 7-12). There is an inverse relationship between discharge and conductivity in streams with no significant source of contamination (figs. 7-12).

Table 4.—Water temperature values measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Stream temperature ($^{\circ}\text{C}$)		
	Maximum	Minimum	Average
PR1	29.6	6.7	15.6
PR2	28.3	6.7	15.5
PR3	28.9	8.1	16.2
ECR	28.4	7.7	15.8
WCR	30.4	7.6	16.6
CR1	27.6	7.9	16.7

Typically, the lowest conductance values were measured during the largest discharge events (in April), indicating that rainfall made up the majority of stream discharge during these measurement periods. The highest conductivity values were measured in Pea River at sites PR2 and PR3 and in Choctawhatchee River at sites ECR and WCR (table 5, figs. 7-12) and correspond to the lowest discharge events (in August). However, the negative relationship between the two parameters declines for the early

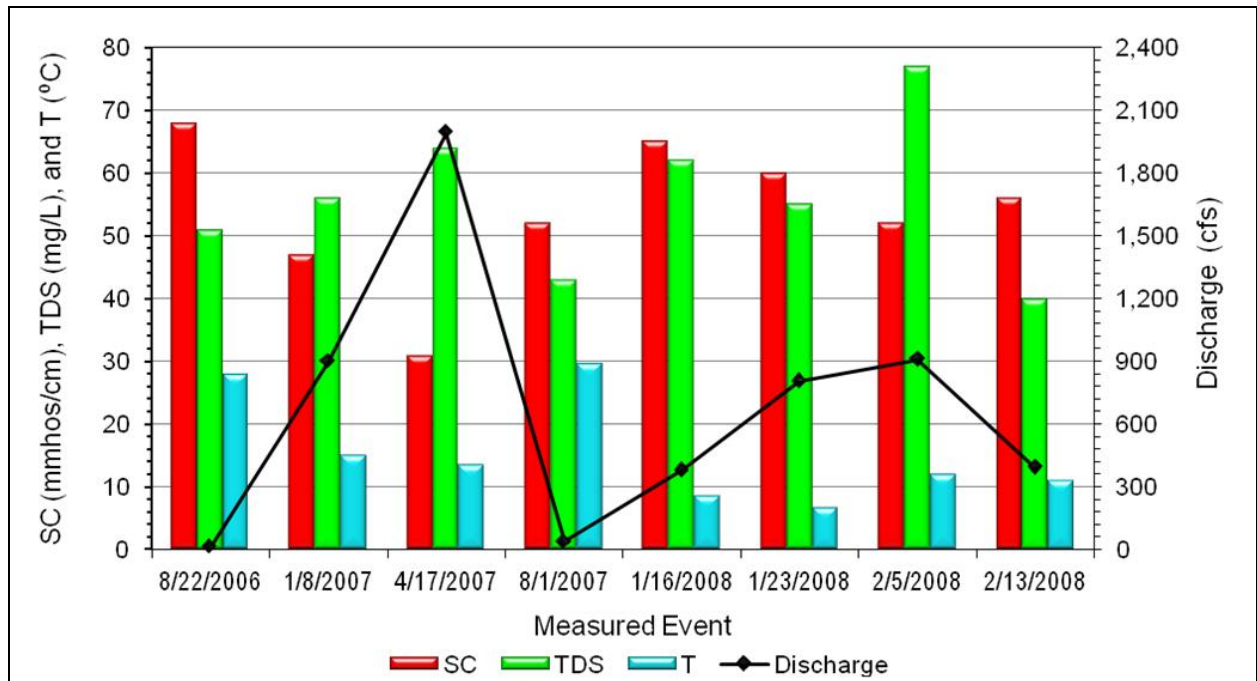


Figure 7.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site PR1.

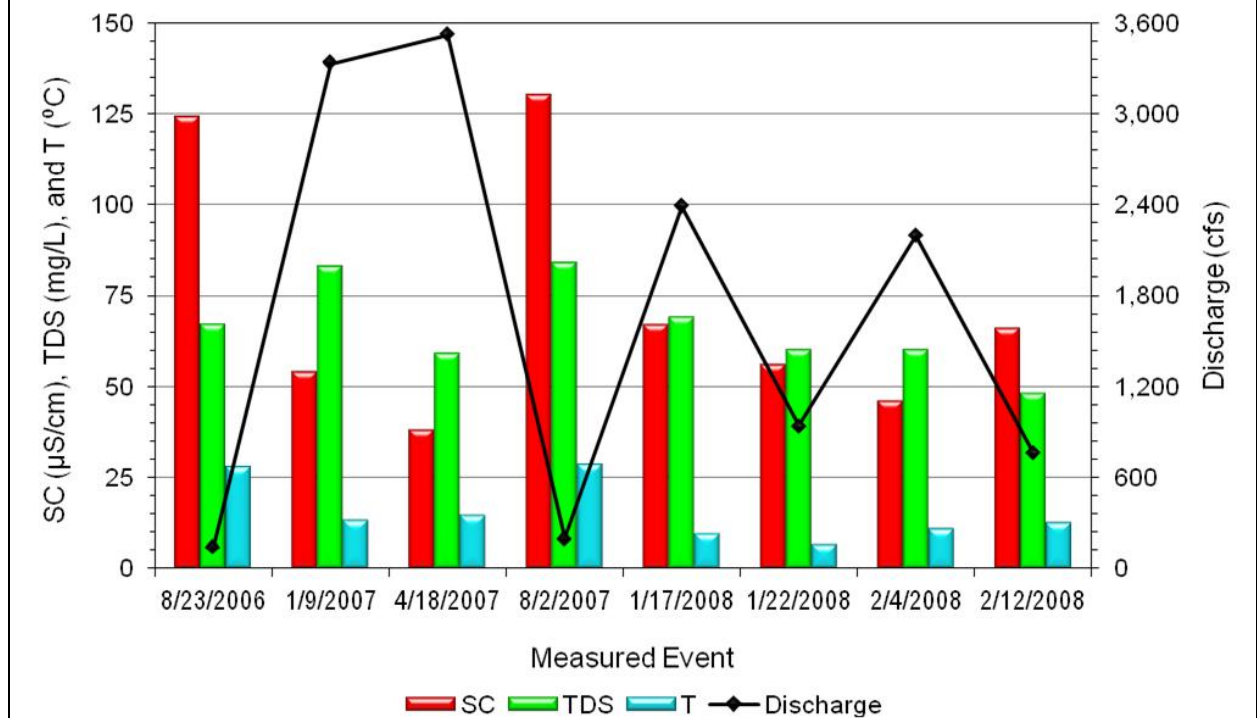


Figure 8.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site PR2.

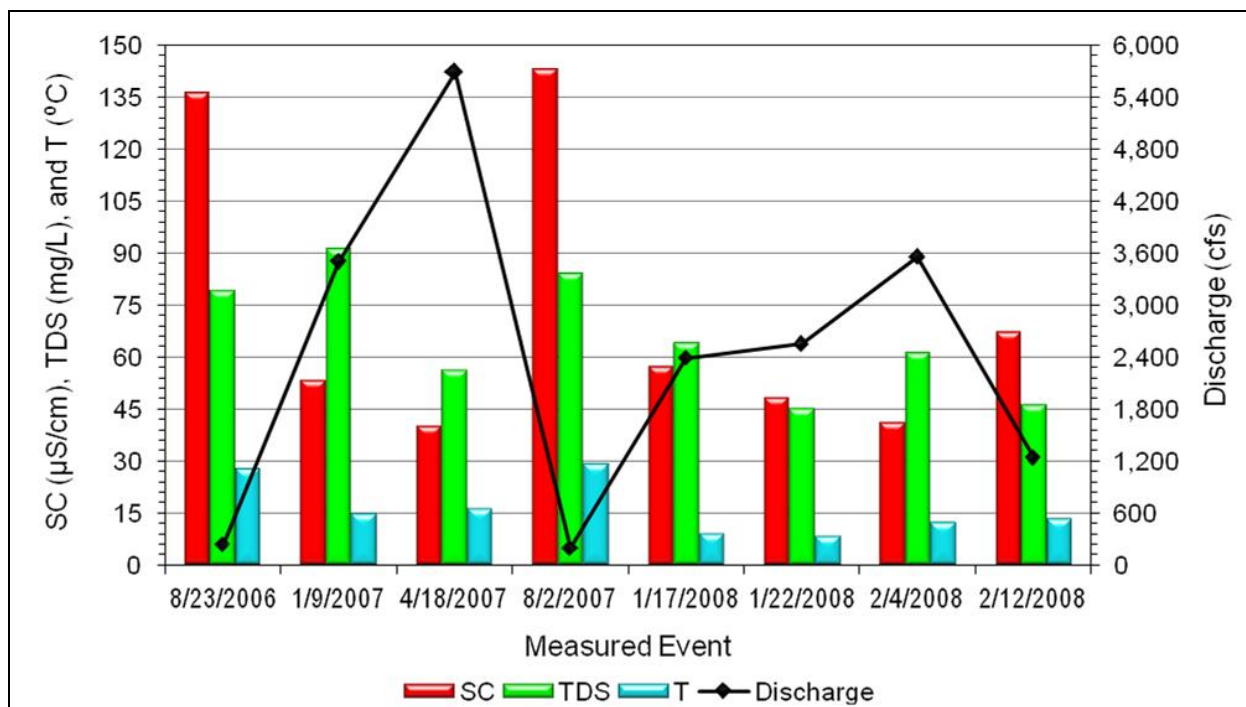


Figure 9.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site PR3.

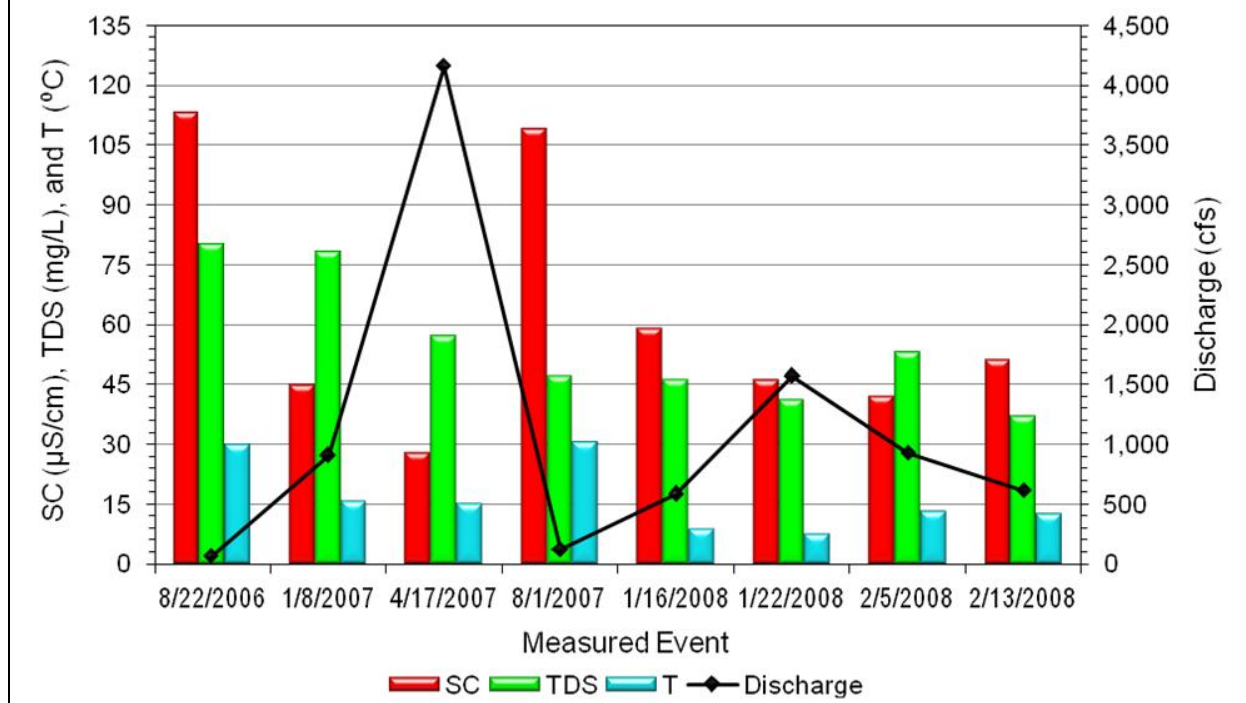


Figure 10.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site ECR.

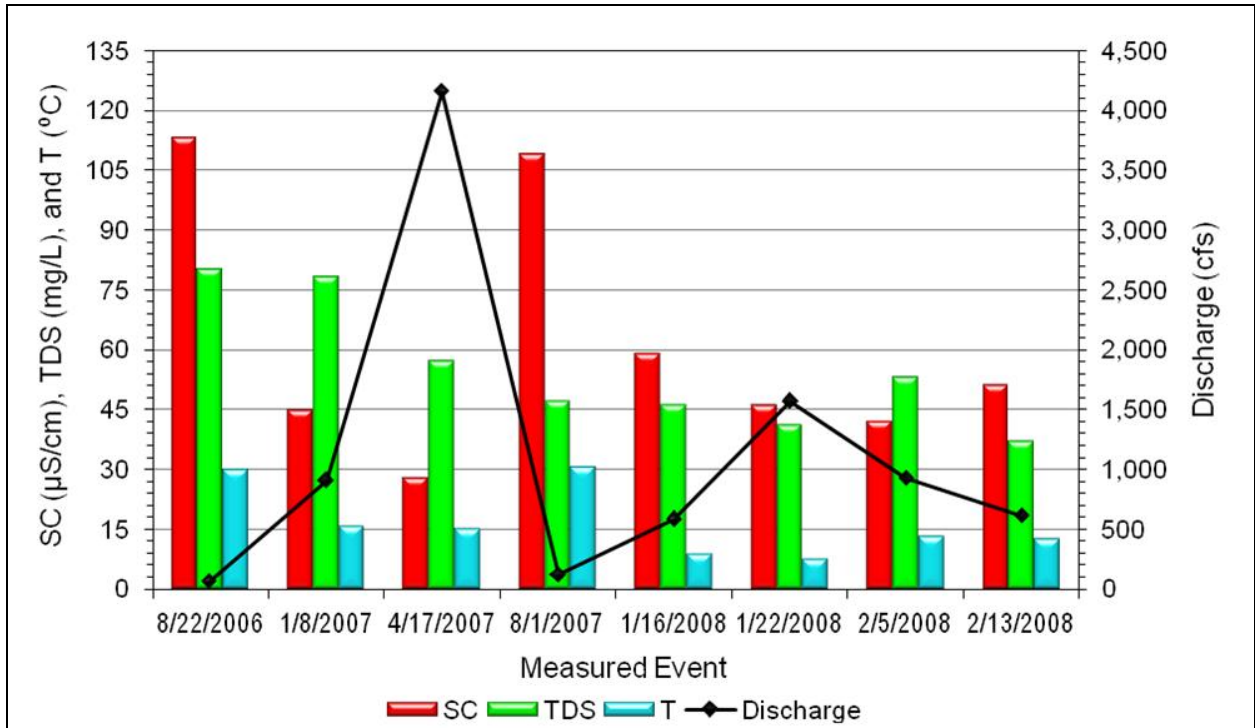


Figure 11.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site WCR

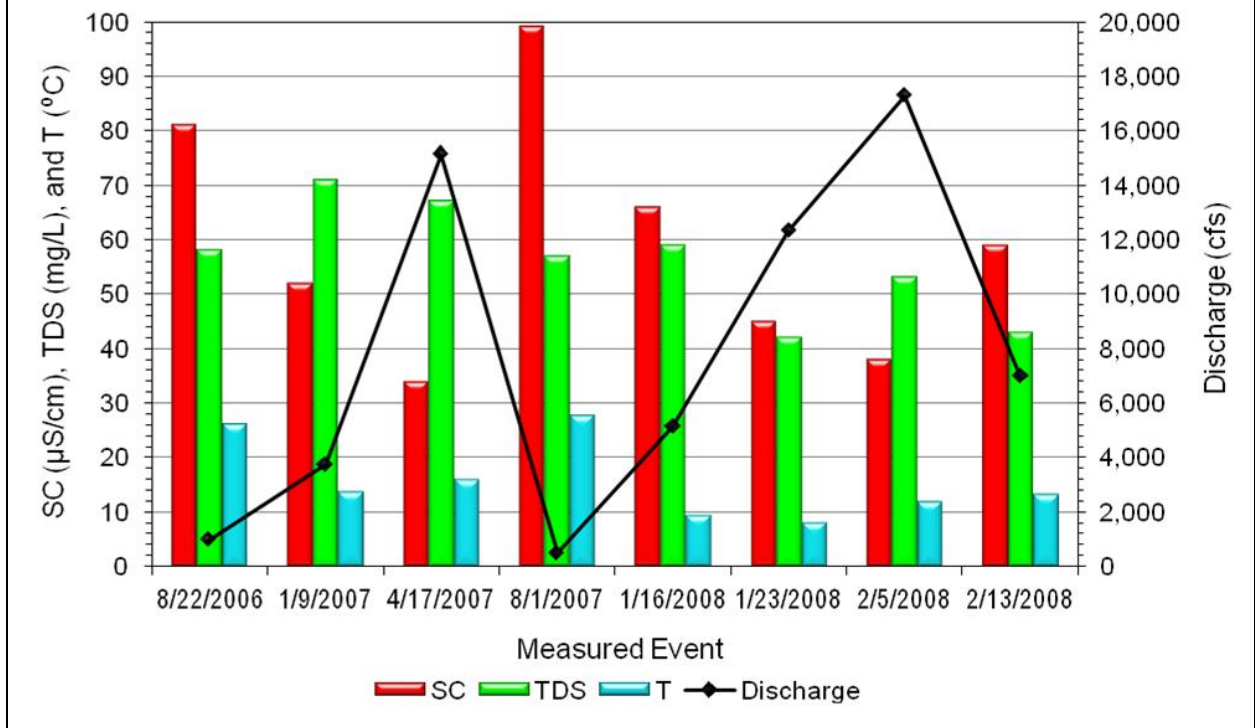


Figure 12.—Specific conductance, total dissolved solids, stream temperature, and discharge at monitoring site CR1.

Table 5.—Specific conductance values measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Specific conductance ($\mu\text{S}/\text{cm}$)		
	Maximum	Minimum	Average
PR1	68	31	53.0
PR2	130	38	72.6
PR3	136	40	73.1
ECR	125	30	67.0
WCR	113	28	61.6
CR1	99	34	59.3

monitoring events during January and February. During these monitoring events, increasing discharge rates do not correspond to decreasing SC values. In contrast, there is a positive relationship between the total dissolved solids (TDS) and SC as well as between TDS and stream temperature (T). On average, stream temperature has a higher degree of influence on SC compared to TDS. Nevertheless, sites PR1, PR3, and CR1 exhibit slightly different behavior (figs. 7, 9, 12). At these sites, increasing discharge is associated with higher TDS concentrations, lowest stream temperatures, and medium conductivity values (figs. 7, 9, 12).

HYDROGEN ION CONCENTRATION

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 they are adapted to a narrow range of pH. Thus, the water-quality criterion for pH ranges from 6 to 9 (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 status of equilibrium 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.

Maximum values of pH varied from 6.5 to 7.9 while minimum pH varied from 5.3 to 5.8 (table 6, fig. 13). Average values ranged from 5.9 to 6.6 (table 6). There is a general inverse relationship between pH and discharge for both rivers. The lowest pH values measured in each river during the monitoring period correspond to large discharge events (figs. 14-19). High flow episodes are usually linked to larger precipitation events that account for most of the increase in stream flow. Periods of low stream flow are accompanied by increased pH values (figs. 14-19). The lowest pH values were measured in the Pea River at site PR1. The other five sites have similar pH values (table 6). There is a positive correlation between stream temperature and pH in both rivers. However, site PR1 exhibits a poor relationship between the two parameters (fig. 20).

Table 6.—Hydrogen ion concentration measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	pH		
	Maximum	Minimum	Average
PR1	6.5	5.3	5.9
PR2	7.6	5.8	6.5
PR3	7.6	5.8	6.5
ECR	7.9	5.8	6.6
WCR	7.7	5.8	6.6
CR1	7.3	5.4	6.4

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

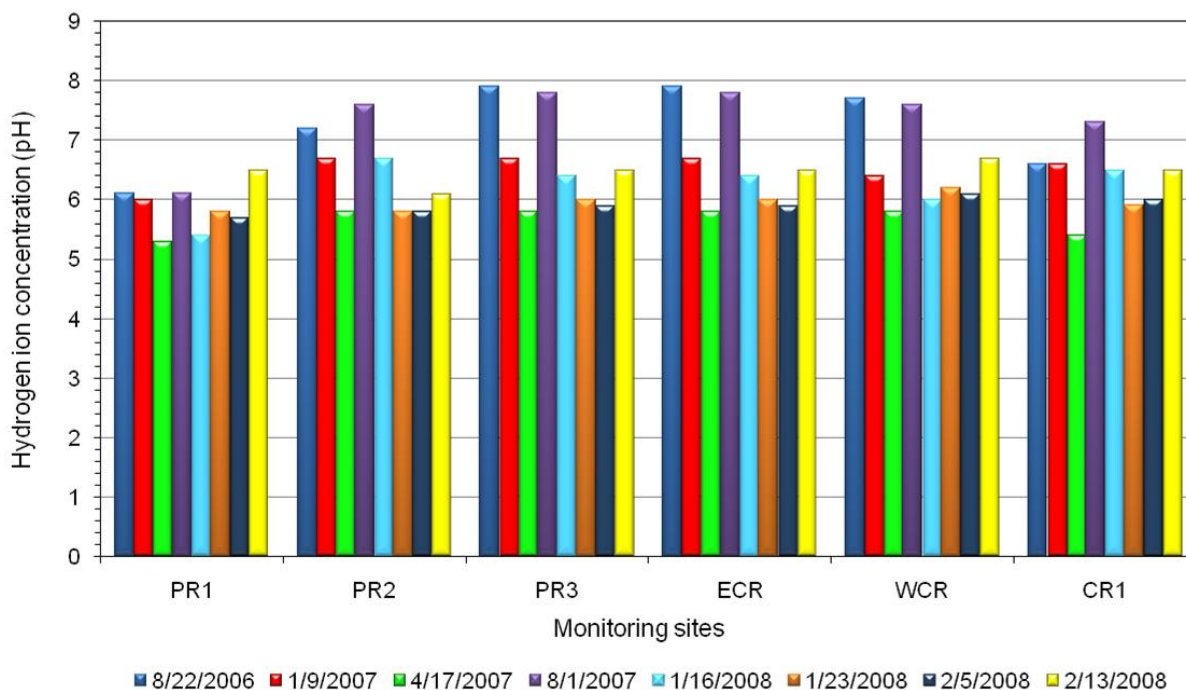


Figure 13.—Measured pH at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

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 streams are significantly affected by water temperature, stream discharge, and concentrations of organic material in the water. The relationships between DO, oxygen saturation (DO Sat %), pH, and stream temperature parameters are depicted in figures 20, 21, 22, 23, 24 and 25. Table 7 includes the observed DO concentrations and the average DO saturation (percentage of atmospheric saturation) for the observed stream temperature for each of the monitoring periods. A positive correlation exists between DO and pH as well as between DO and stream temperature (figs. 20-25). The highest value of DO saturation for the monitoring period was 117 mg/L for the West Choctawhatchee River at site WCR

and the lowest was 68 mg/L for Pea River at site PR2 (table 7). Dissolved oxygen concentrations were lowest in Pea River waters at site PR2 (5.8 mg/L) in August 2006 and highest (12.6 mg/L) at the same location in January 2008 (table 7). No values under 5 mg/L were recorded during the sampling events (fig. 26).

BIOCHEMICAL OXYGEN DEMAND

Biochemical oxygen demand 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

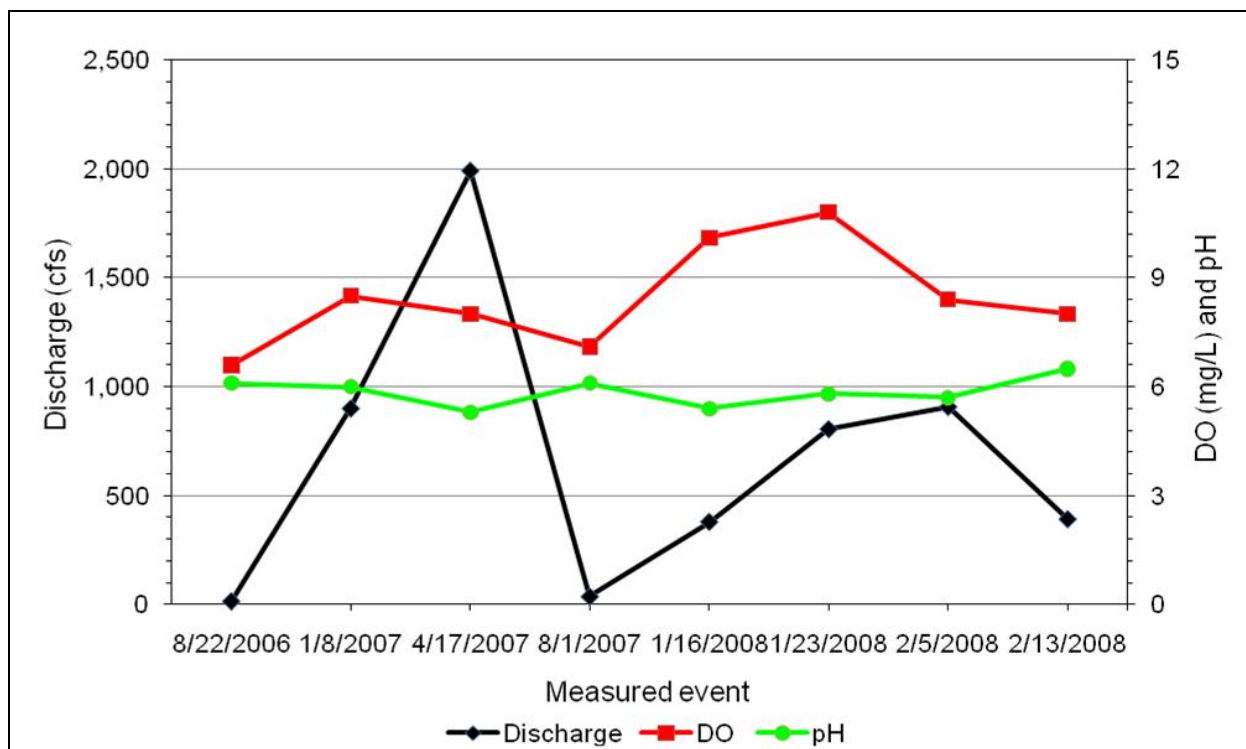


Figure 14.—Discharge, dissolved oxygen, and pH at monitoring site PR1.

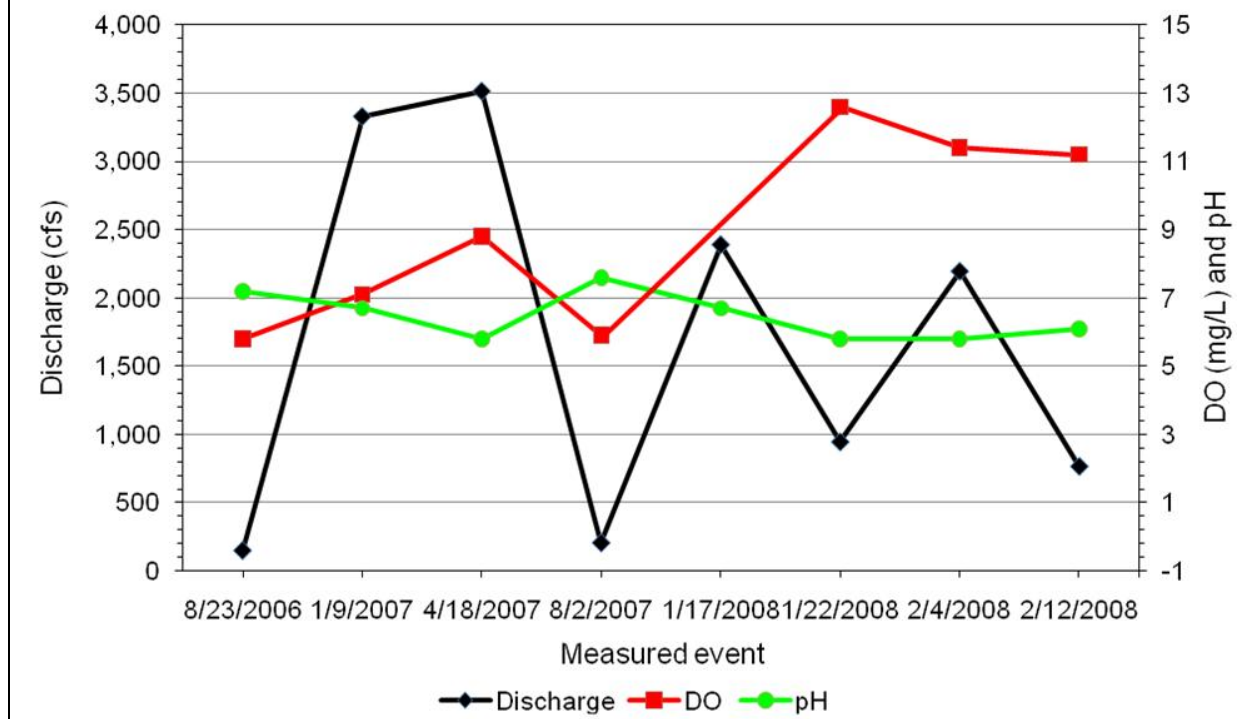


Figure 15.—Discharge, dissolved oxygen, and pH at monitoring site PR2.

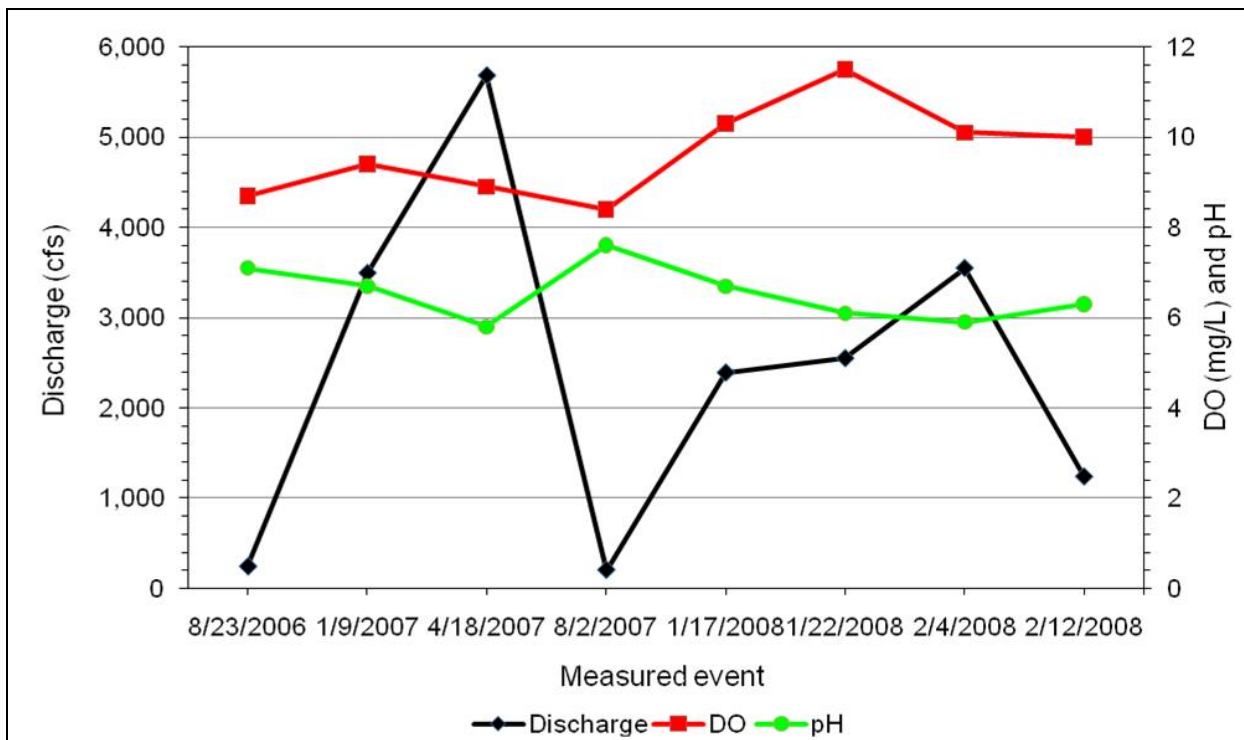


Figure 16.—Discharge, dissolved oxygen, and pH at monitoring site PR3.

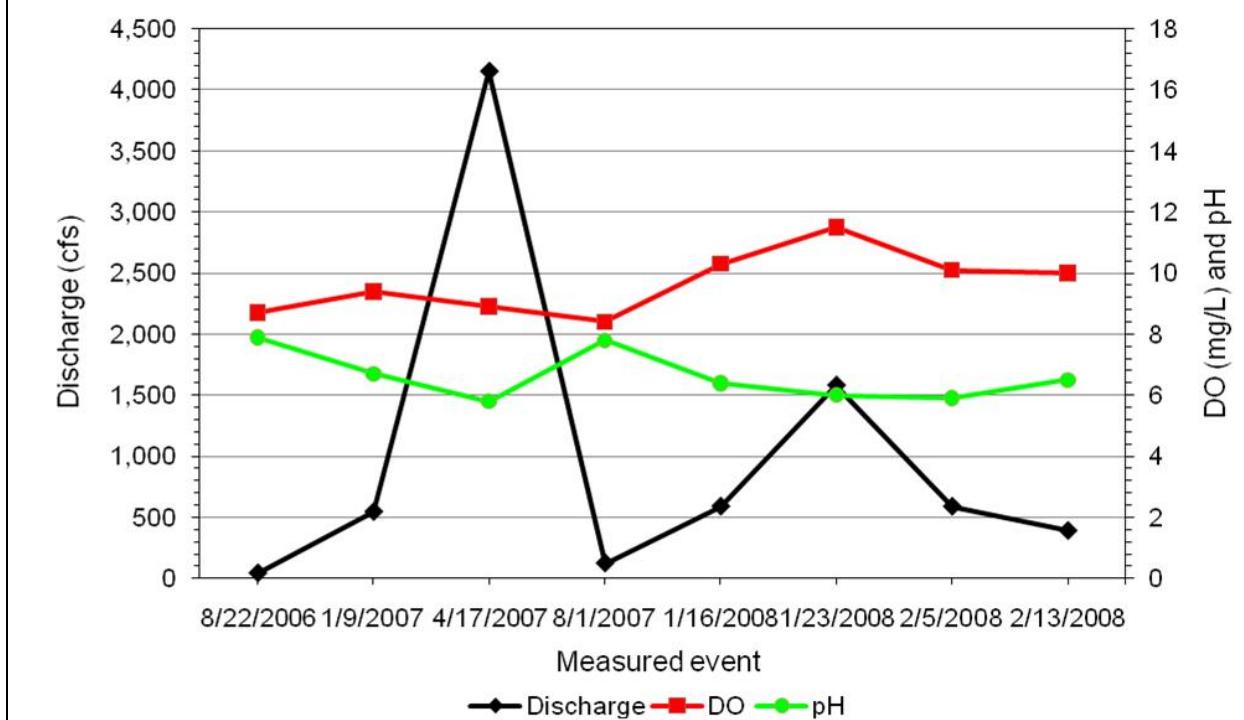


Figure 17.—Discharge, dissolved oxygen, and pH at monitoring site ECR.

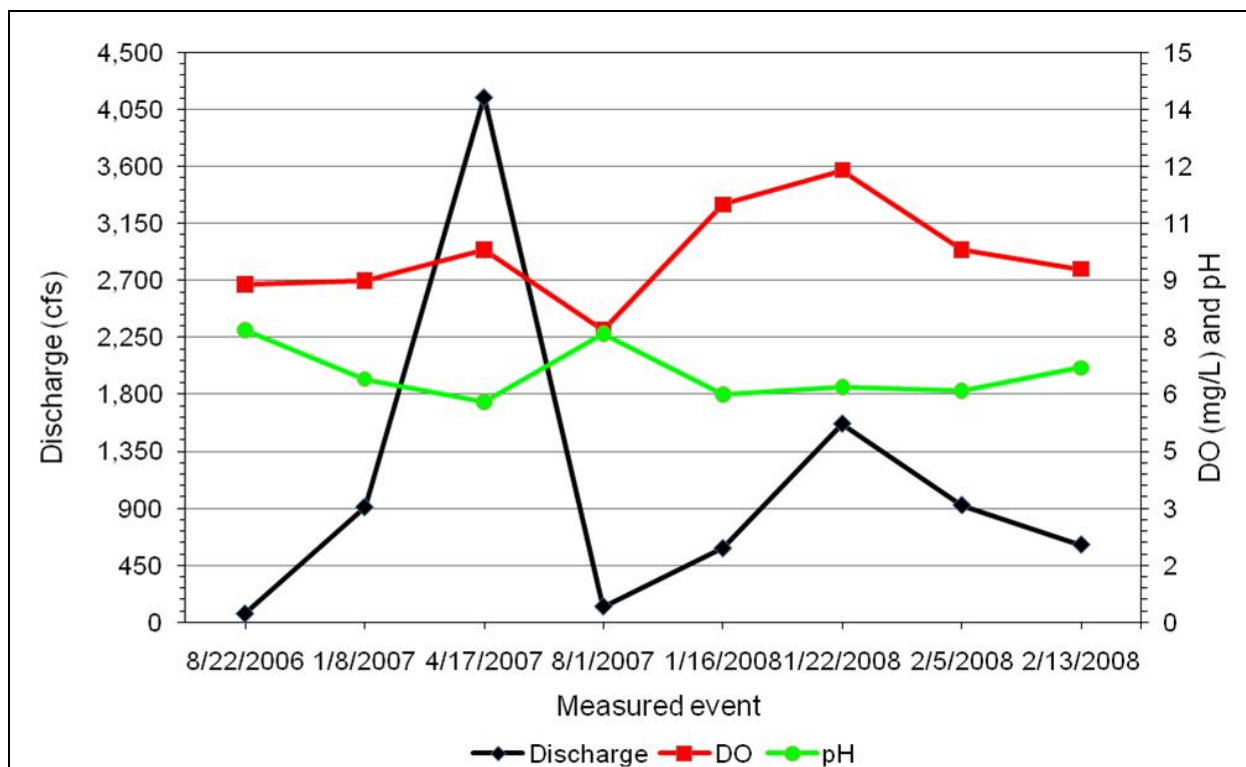


Figure 18.—Discharge, dissolved oxygen, and pH at monitoring site WCR.

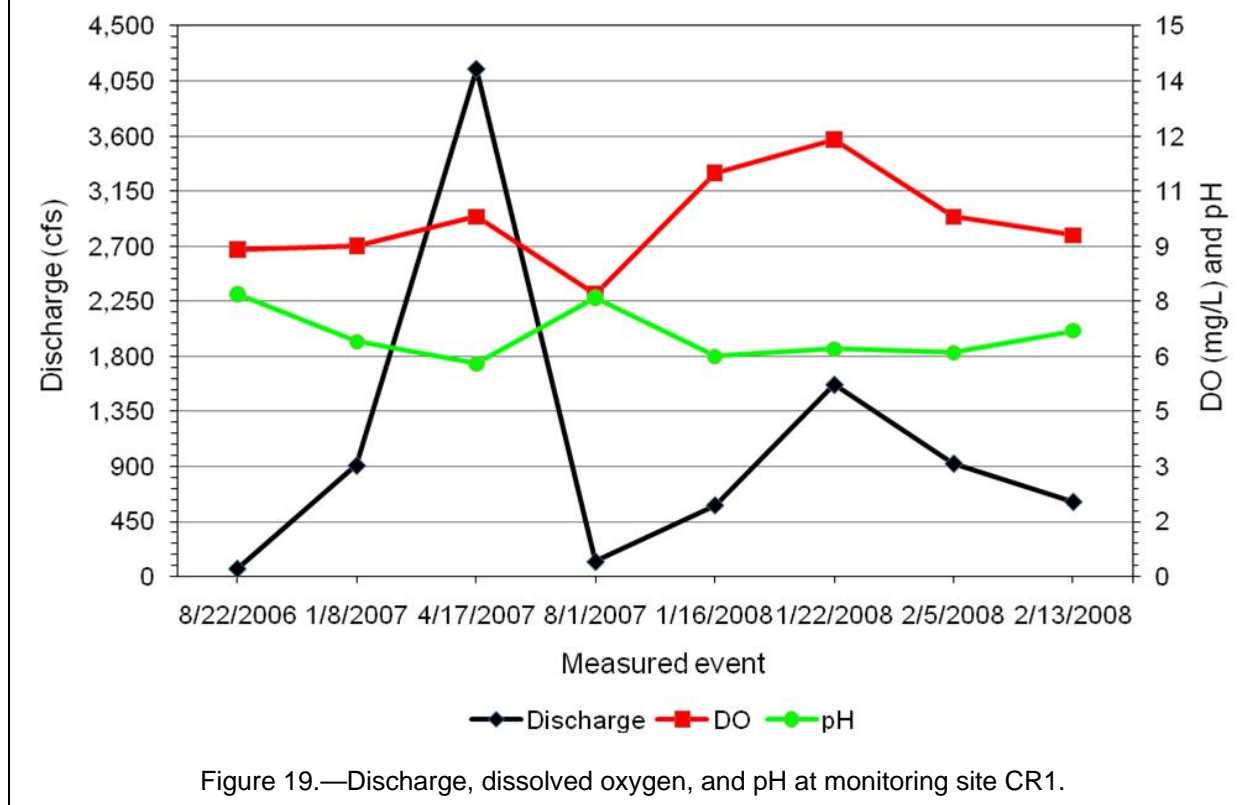


Figure 19.—Discharge, dissolved oxygen, and pH at monitoring site CR1.

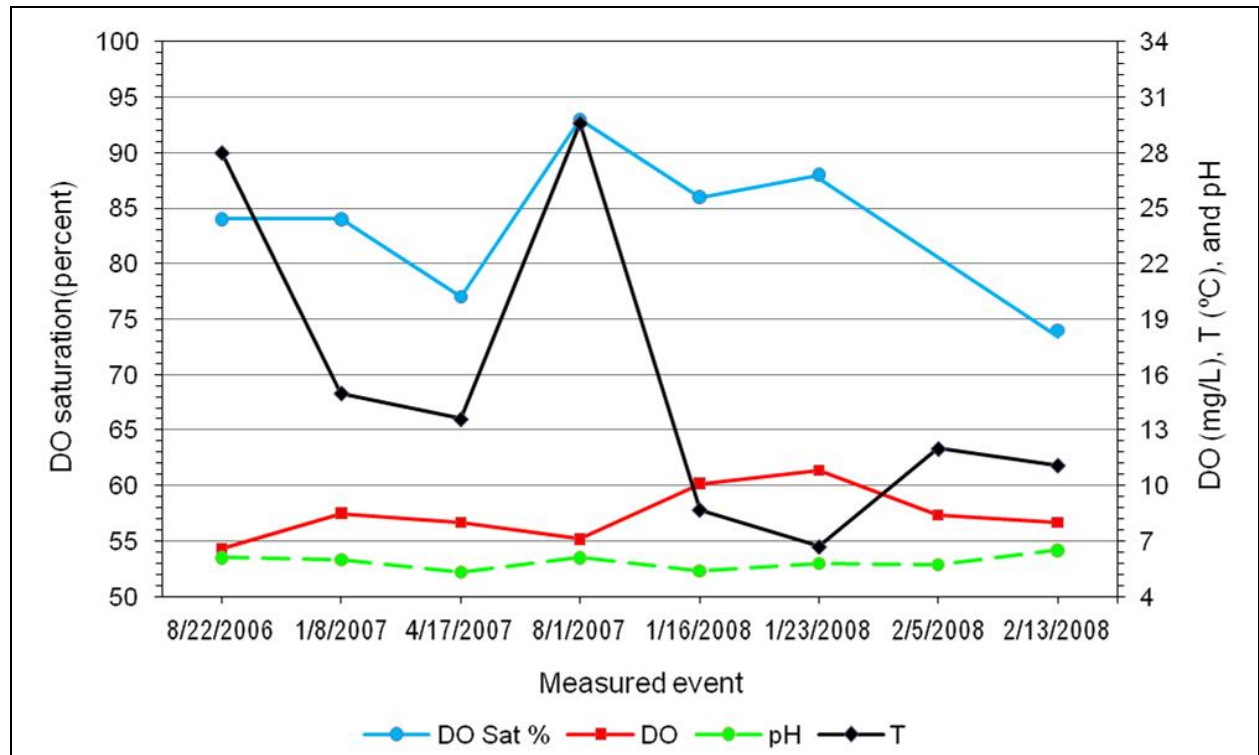


Figure 20.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site PR1.

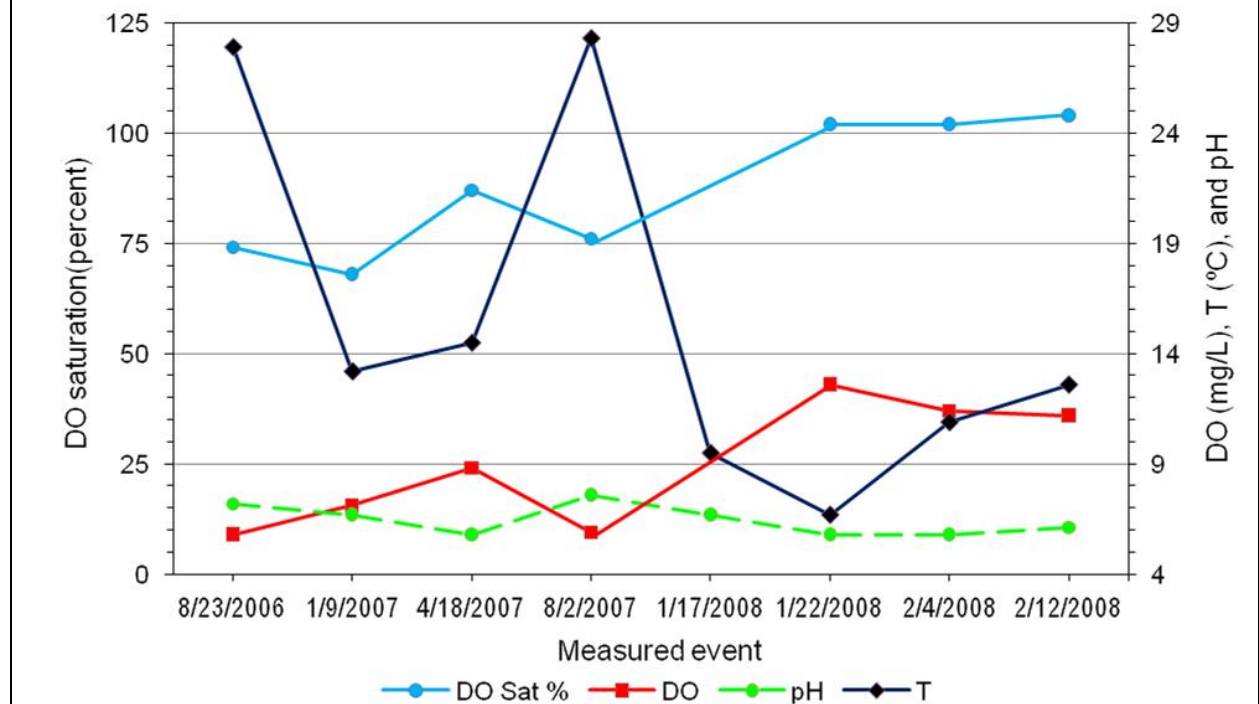


Figure 21.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site PR2.

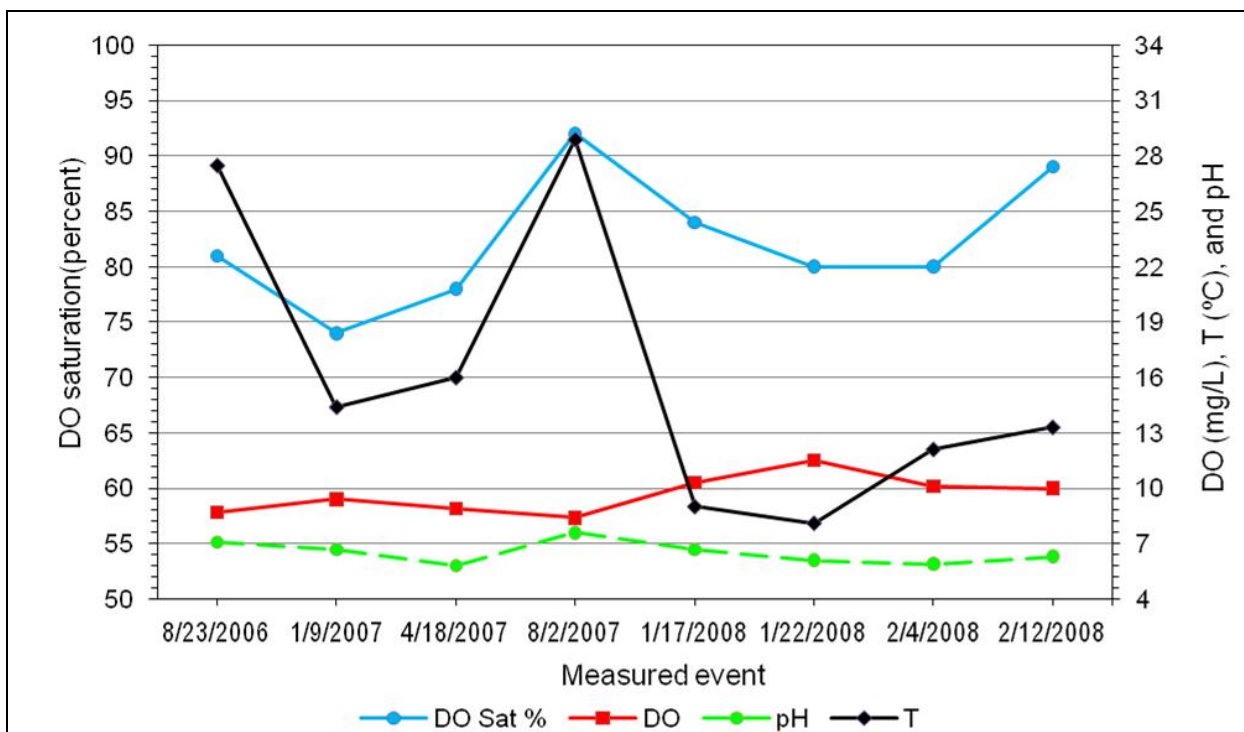


Figure 22.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site PR3.

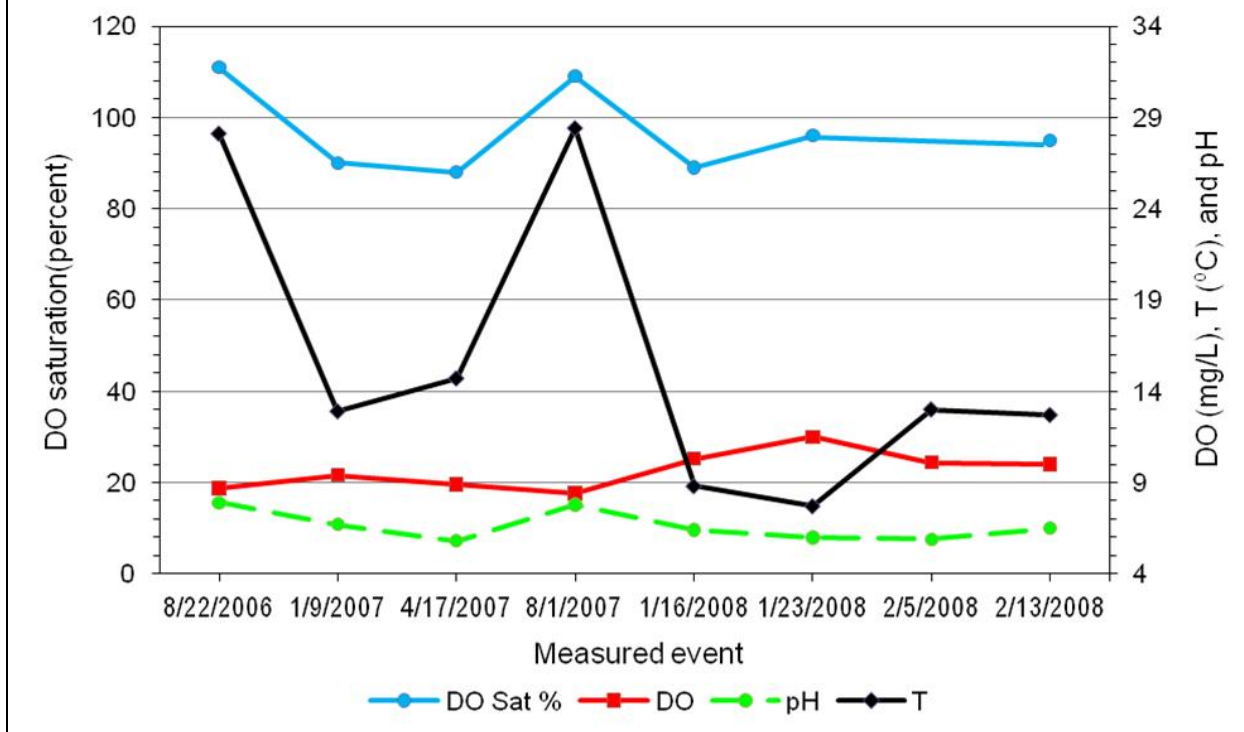


Figure 23.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site ECR.

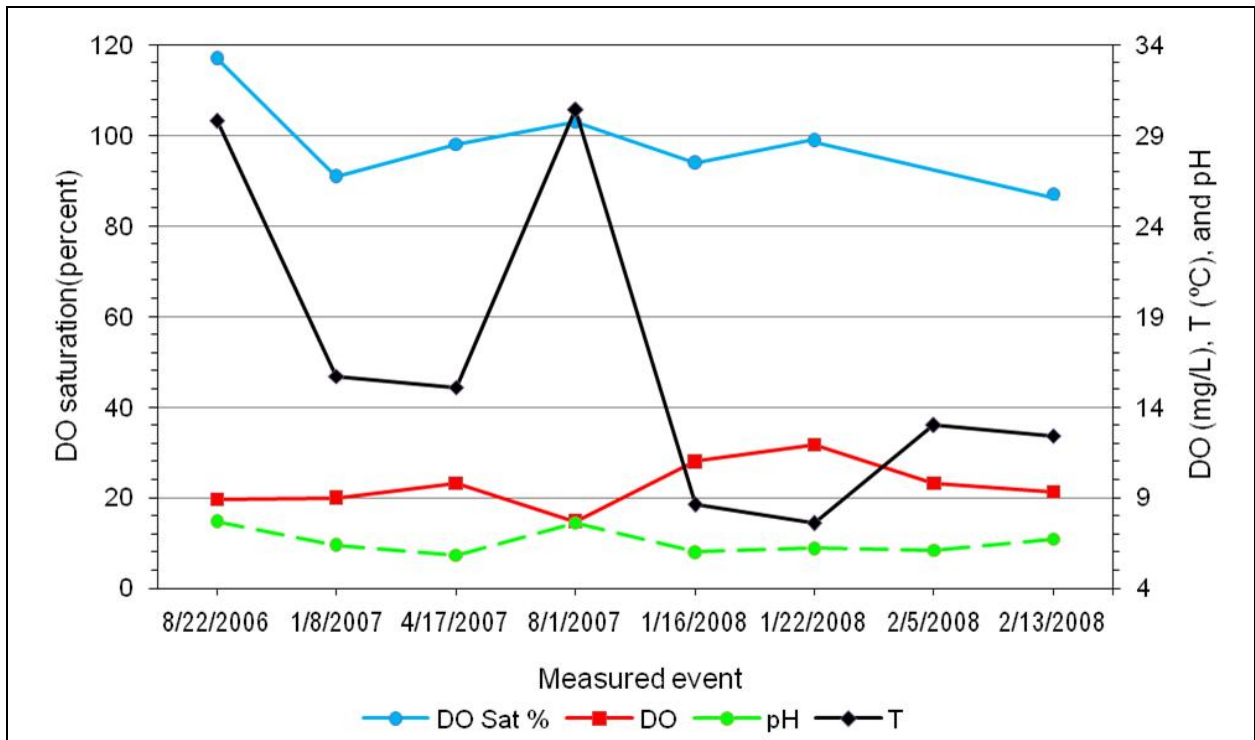


Figure 24.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site WCR.

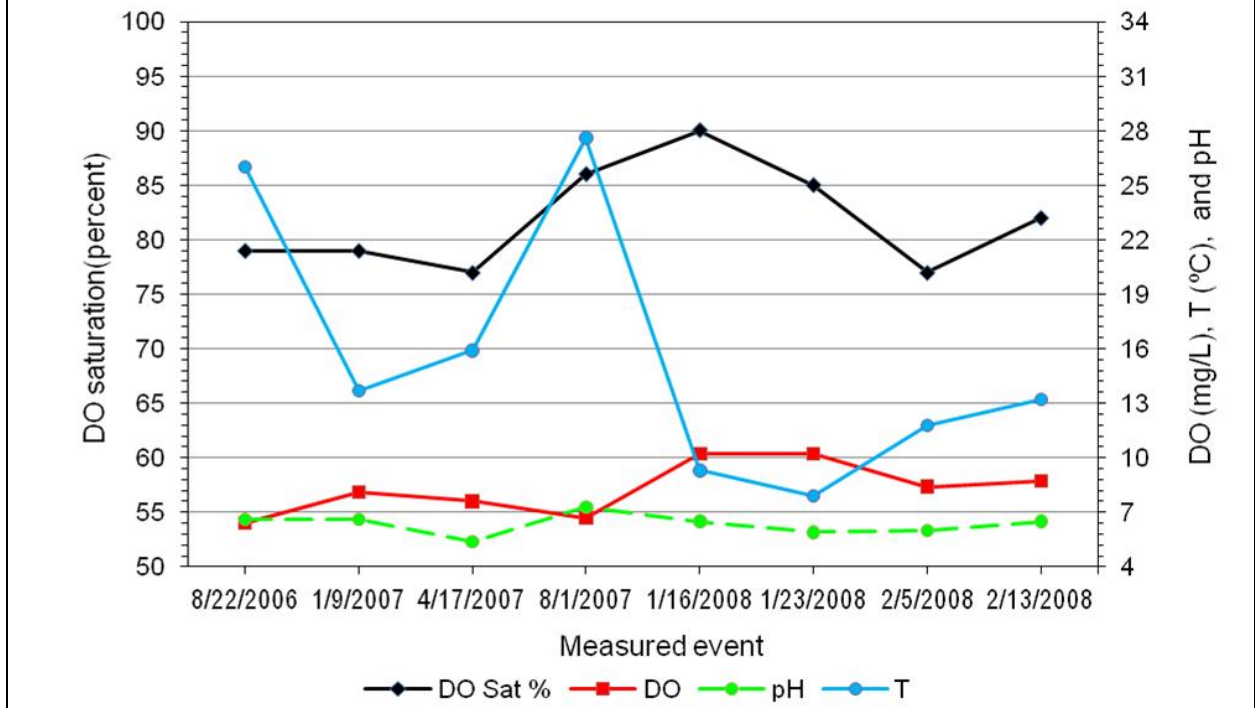


Figure 25.—Dissolved oxygen saturation, dissolved oxygen, pH, and stream temperature at monitoring site CR1.

Table 7.—Dissolved oxygen, dissolved oxygen saturation, and stream temperature measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	DO (mg/L)			DO saturation (percentage of atmospheric saturation)			Stream temperature (°C)		
	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
PR1	10.8	6.6	8.4	93	74	84	29.6	6.7	15.6
PR2	12.6	5.8	9.0	104	68	88	28.3	6.7	15.5
PR3	9.8	6.4	8.3	92	74	82	28.9	8.1	16.2
ECR	11.5	8.4	9.7	111	88	97	28.4	7.7	15.8
WCR	11.9	7.7	9.7	117	87	98	30.4	7.6	16.6
CR1	10.2	6.4	8.3	90	77	82	27.6	7.9	16.7

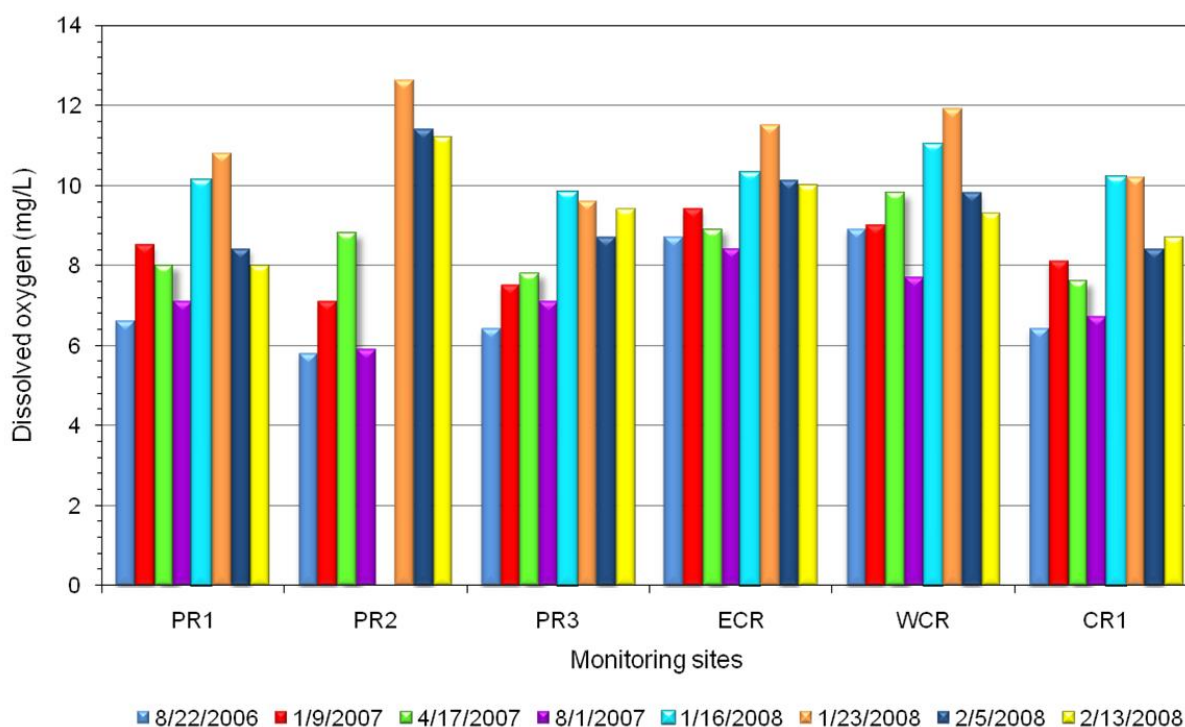


Figure 26.—Measured dissolved oxygen at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

degradation of organic material, exchange of constituents with the stream bed, and 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 is as low as 5 mg/L (Mays, 1996).

Maximum, minimum, and average BOD concentrations for all six monitoring sites are presented in table 8. Figure 27 shows BOD concentrations at each site with respect to sampling date. The highest BOD value (2.7 mg/L) was recorded in Pea River at site PR1 (table 8). The next highest BOD value (2.6 mg/L) was measured in the East Fork Choctawhatchee River at site ECR (table 8).

Table 8.—Biochemical oxygen demand measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	BOD (mg/L)		
	Maximum	Minimum	Average
PR1	2.7	0.4	1.2
PR2	2.2	0.9	1.5
PR3	1.8	0.3	1.2
ECR	2.6	0.4	1.2
WCR	1.3	0.2	0.8
CR1	1.3	0.0	0.9

Water samples collected from Choctawhatchee River at site CR1 exhibited the lowest minimum BOD concentration (below the detection limit) during the monitoring period (fig. 27, table 8). The highest and lowest average BOD concentrations were recorded in Pea River at site PR2 and in the West Fork Choctawhatchee River at site WCR, respectively (table 8).

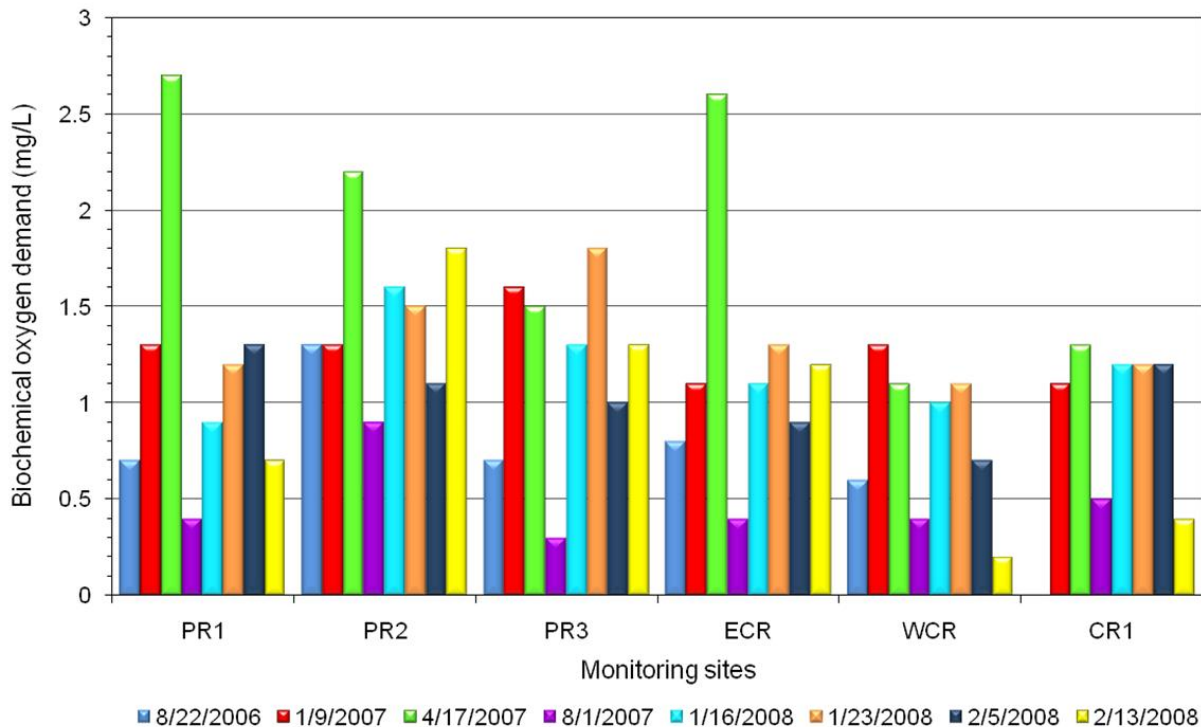


Figure 27.—Measured biochemical oxygen demand at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

Relationships between BOD concentrations and chlorophyll *a*, DO, pH, and T are presented in figures 28, 29, 30, 31, 32, and 33. During the monitoring period, an inverse correlation between BOD concentrations and stream temperature was observed at all sites. Generally, the lowest BOD values were recorded in August (2006 and 2007), when water samples exhibited the highest stream temperatures. Furthermore, higher BOD levels were accompanied by lower pH values and increased chlorophyll *a* and DO levels (figs. 28-33). However, there are some exceptions to this relationship given that some high BOD levels are associated with higher chlorophyll *a* concentrations. In April, when discharge was highest, BOD concentrations were also highest. A decrease in pH was also observed during this period. BOD in both Pea and Choctawhatchee Rivers exhibited a positive correlation with total-P concentrations and an inverse correlation with NO₃⁻-N concentrations (figs. 28-33). Nevertheless, none of the BOD measurements exceeded the 5 mg/L standard established for water-quality-sensitive surface-water bodies (fig. 27).

TURBIDITY

Turbidity measured in water samples 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 project monitoring sites are shown in table 9 and are compared with total suspended solids (TSS) and discharge in figures 34-39. Analytical data revealed a good correlation between turbidity values and discharge for sites PR1, PR2, ECR, and WCR (figs. 34, 35, 37, 38, respectively). Thus, the highest turbidity values were recorded in April when discharge was the highest. However, exceptions from this general trend were observed at sites PR3 and CR1 (figs. 36, 39, respectively). At these sites the highest turbidity values were recorded in January and February 2008 and

were not necessarily associated with the highest discharge.

Table 9.—Turbidity measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Turbidity (NTU)		
	Maximum	Minimum	Average
PR1	60	1	22
PR2	86	6	48
PR3	143	9	64
ECR	106	4	38
WCR	60	1	24
CR1	114	21	66

CONSTITUENT LOADING

The constituent load is the mass or weight of a constituent that passes a cross-section of a stream in a specific amount of time. Loads are expressed in mass units (such as tons, kilograms) and are considered for time intervals that are relative to the type of pollutant and the watershed area for which the loads are calculated. Loads are calculated from concentrations of constituents obtained from analysis of water samples and stream discharge, which is the volume of water that passes a cross-section of the river in a specific amount of time.

The computer model Regr_Cntr.xls (*Regression with Centering*) was selected to calculate constituent loads for this project. The program is an EXCEL implementation of the USGS seven-parameter regression model for load estimation (Cohn and others, 1992). It estimates loads in a manner very similar to that used most often by the Estimatr.exe (*USGS Estimator*) program. The Regr_Cntr.xls program was adapted by R. Peter Richards at the Water Quality Laboratory at Heidelberg College (Richards, 1999).

The program establishes a regression model using a calibration dataset composed of concentrations of the constituent of interest and discharge values measured at the time of water sampling. Constituent loads can be estimated for any year for which mean daily discharge data are provided.

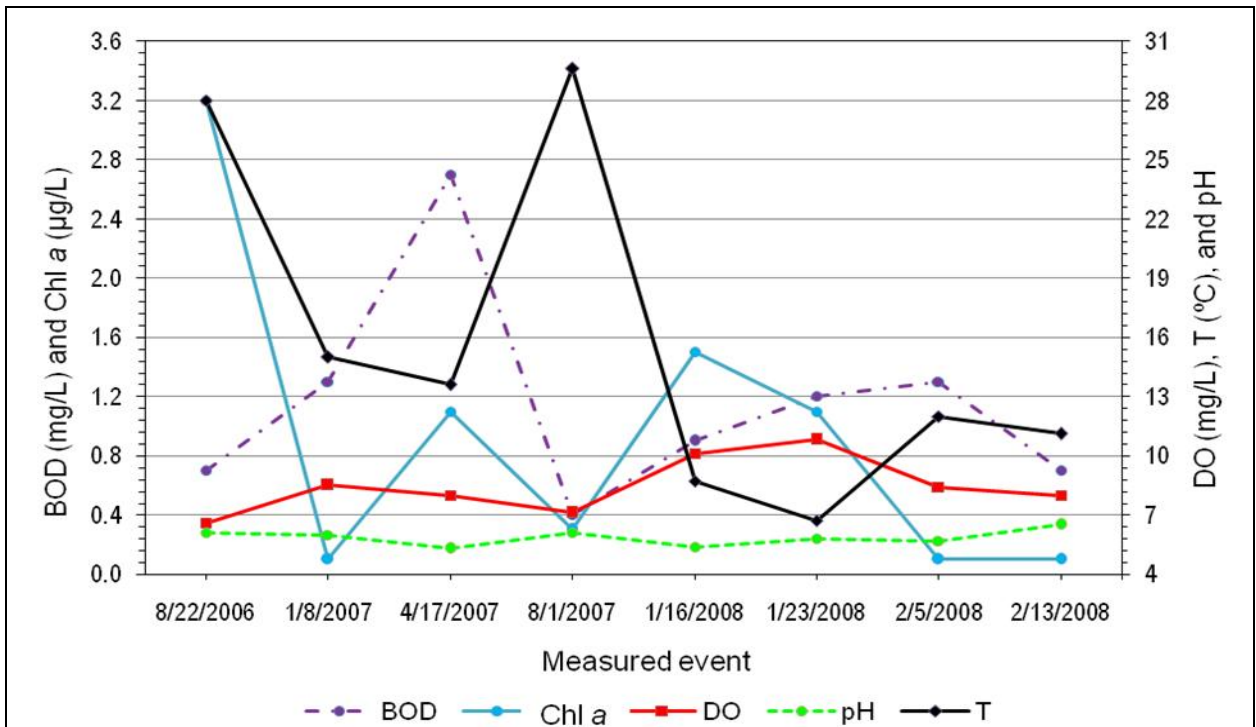


Figure 28.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site PR1.

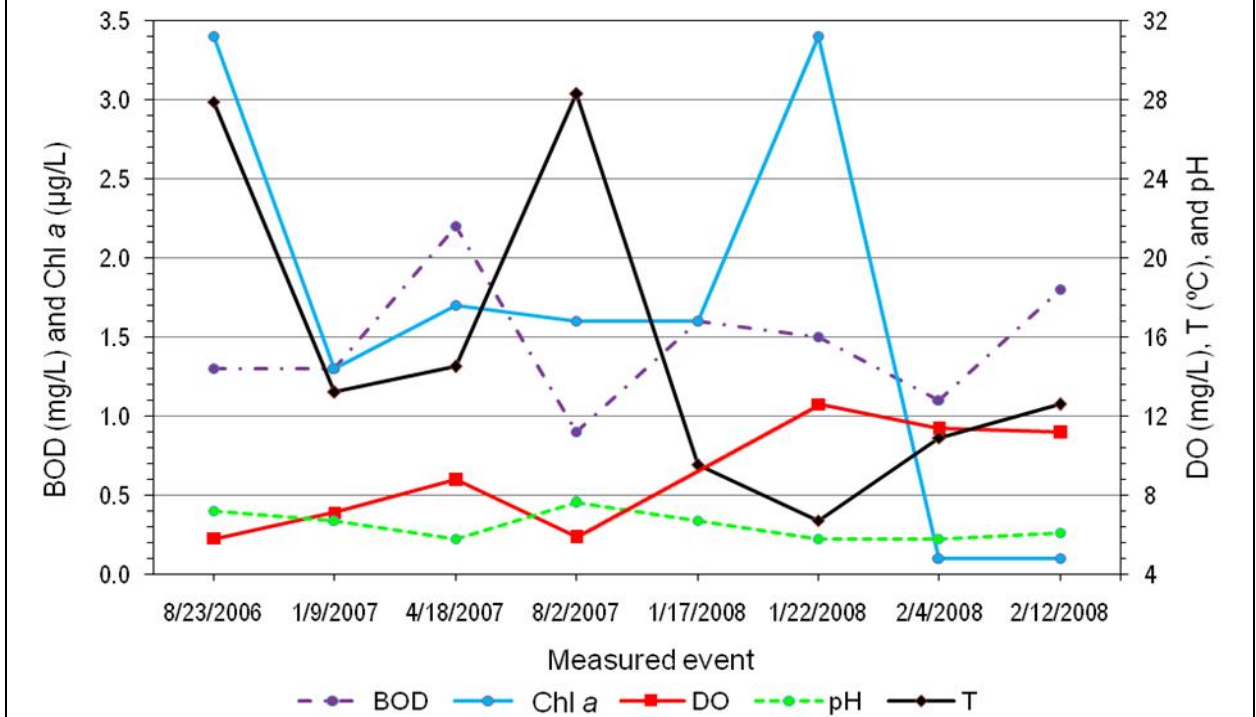


Figure 29.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site PR2.

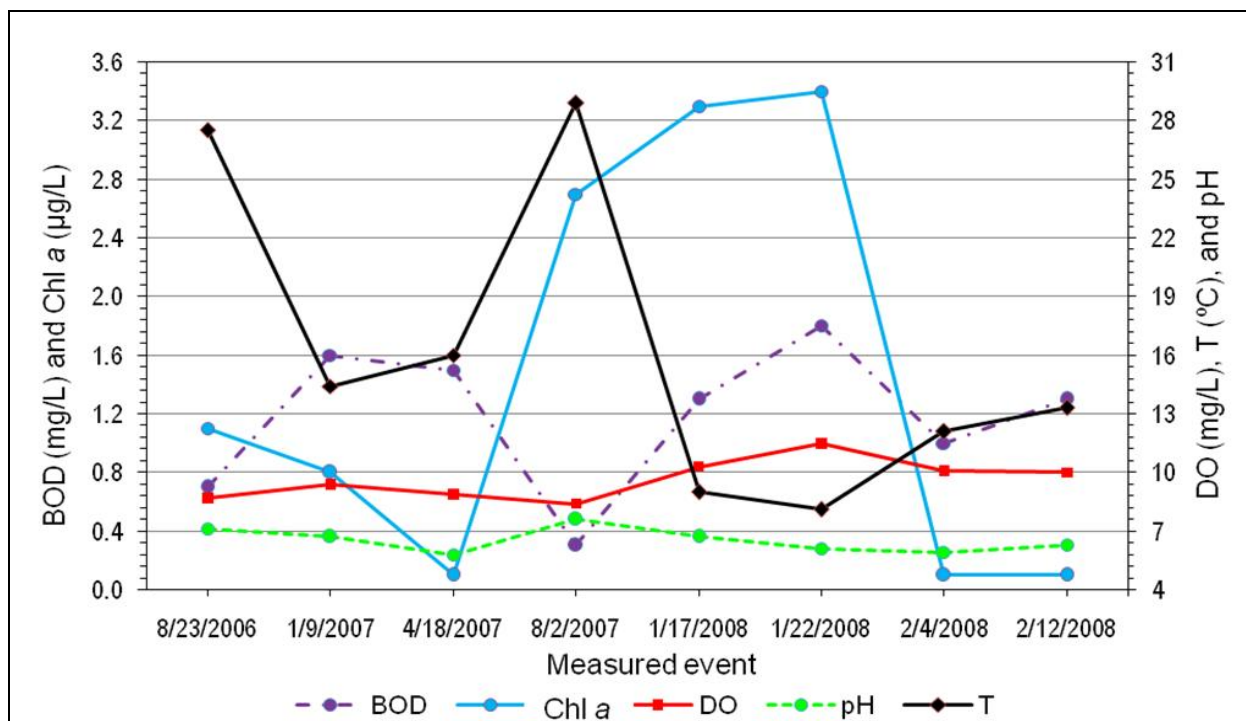


Figure 30.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site PR3.

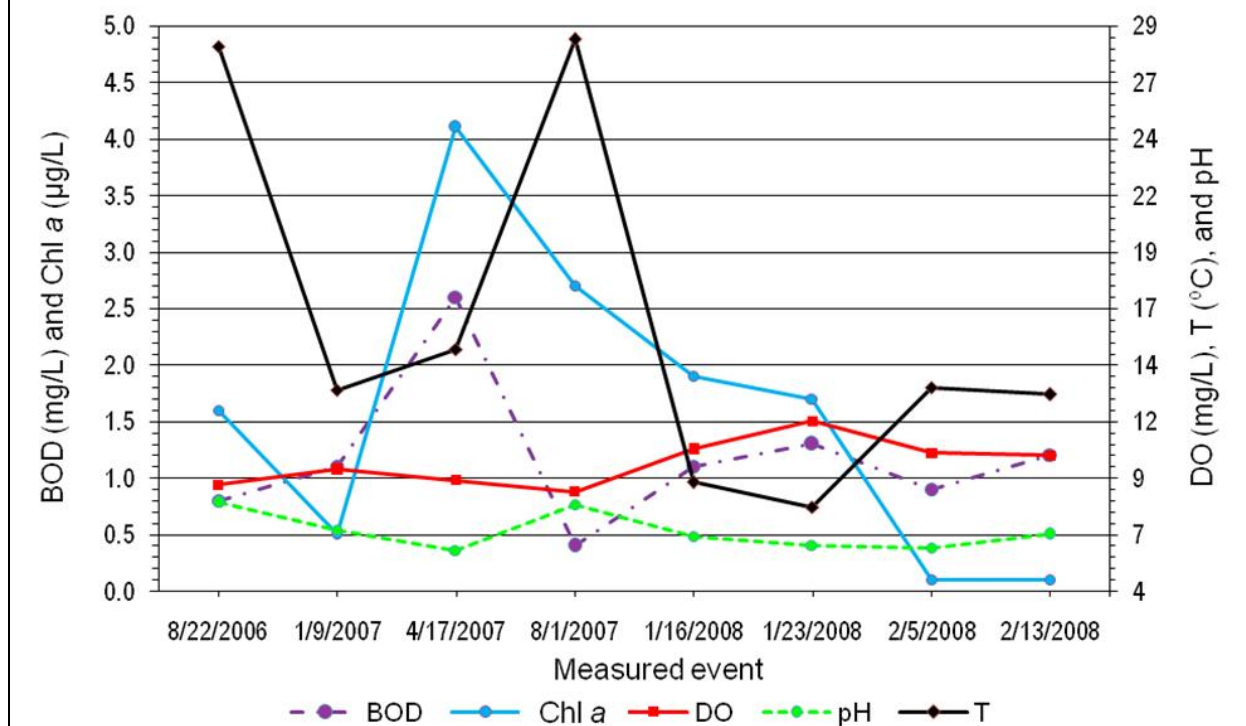


Figure 31.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site ECR.

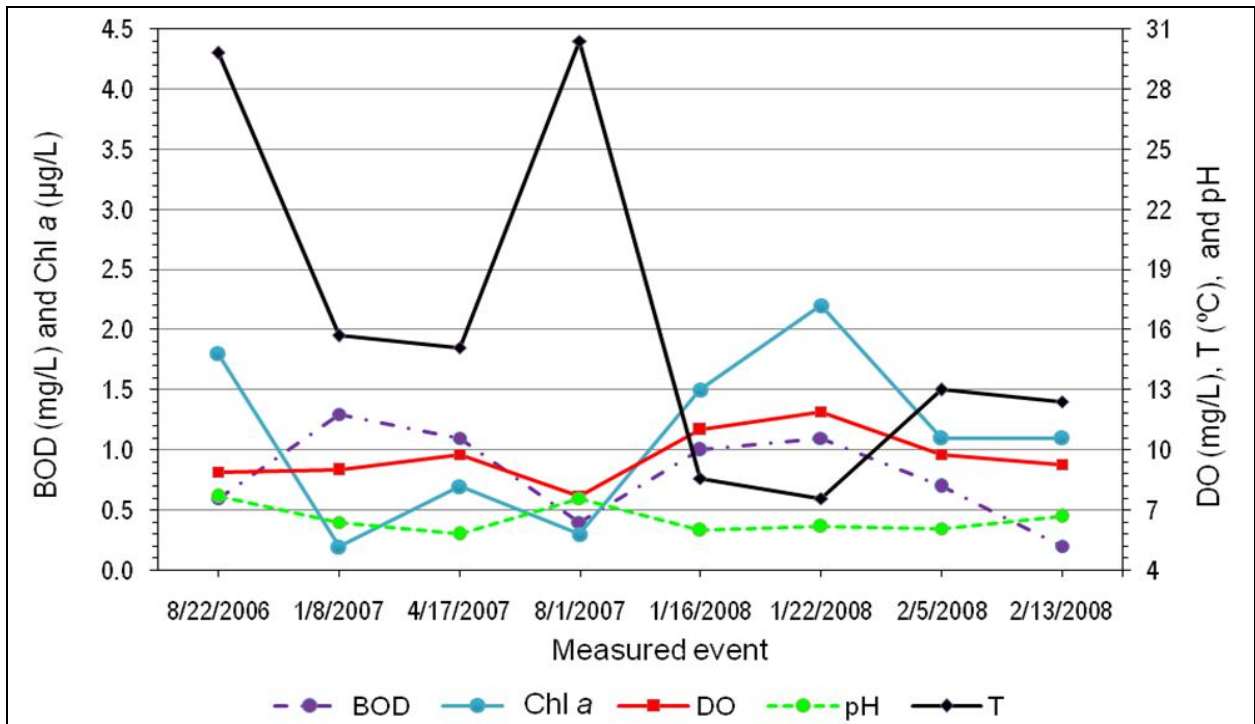


Figure 32.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site WCR.

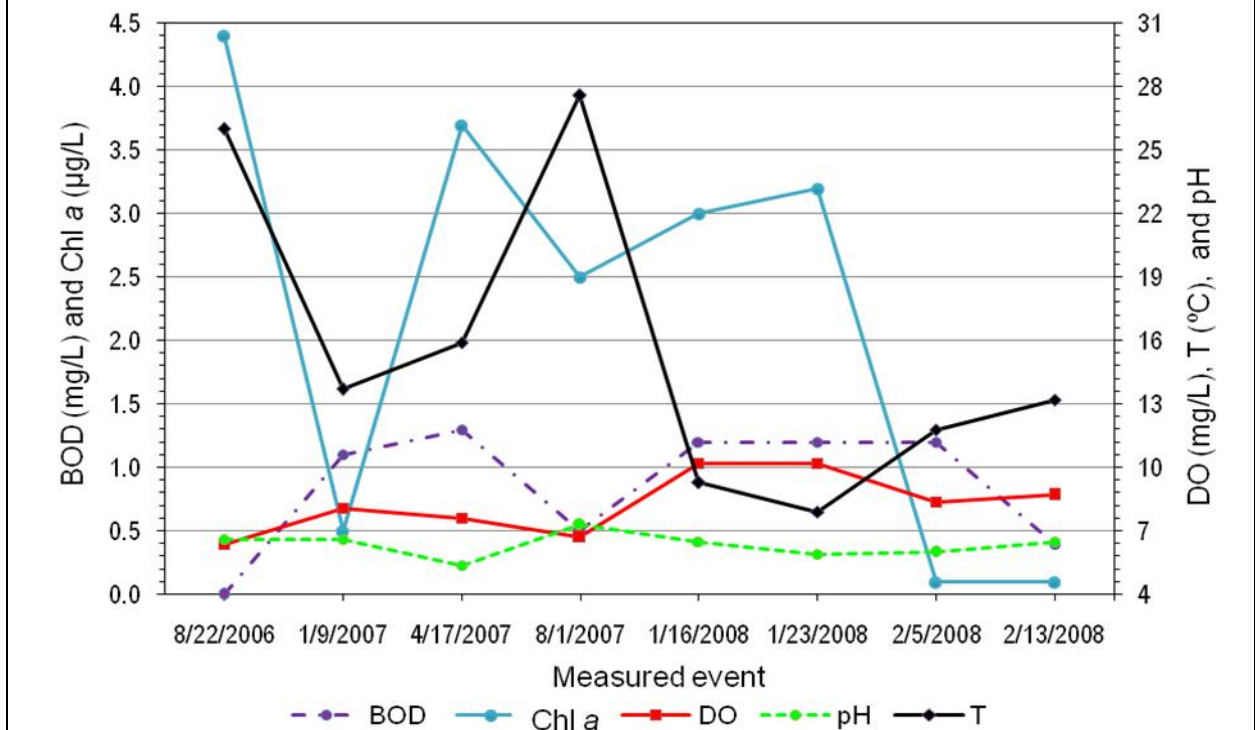


Figure 33.—Biochemical oxygen demand, chlorophyll a, dissolved oxygen, pH, and stream temperature at monitoring site CR1.

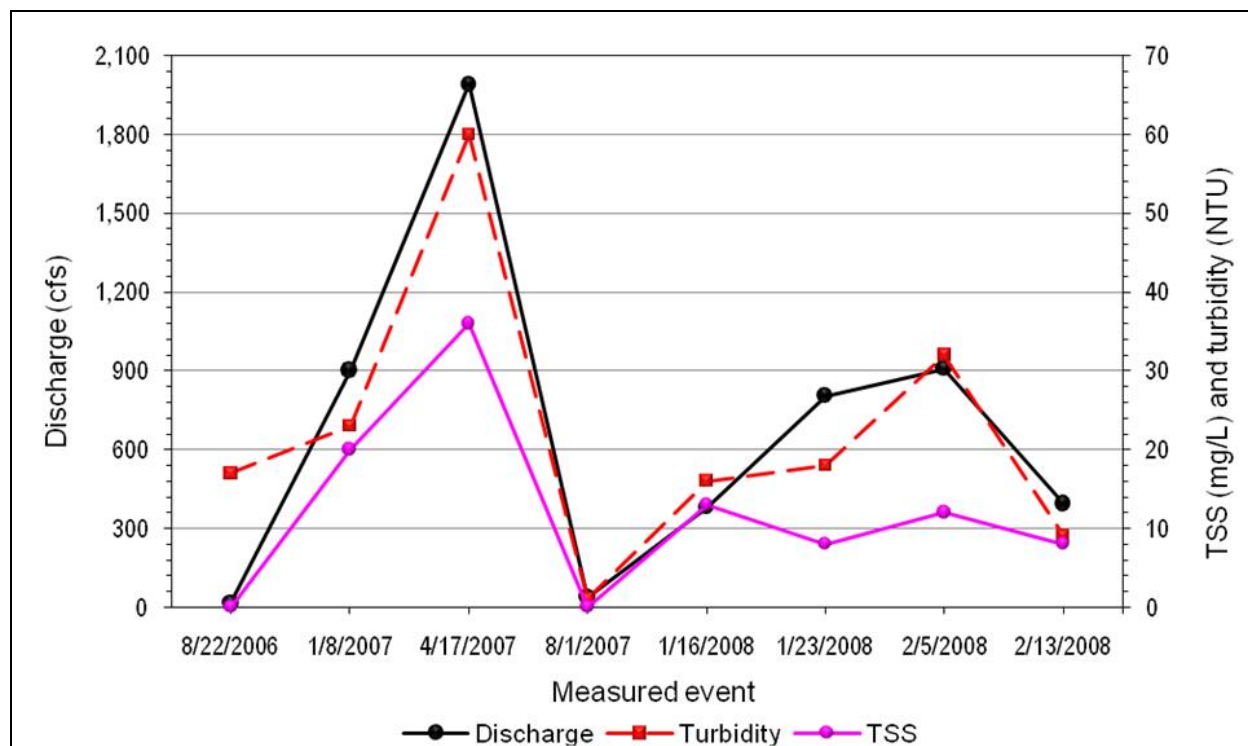


Figure 34.—Discharge, turbidity, and total suspended solids at monitoring site PR1.

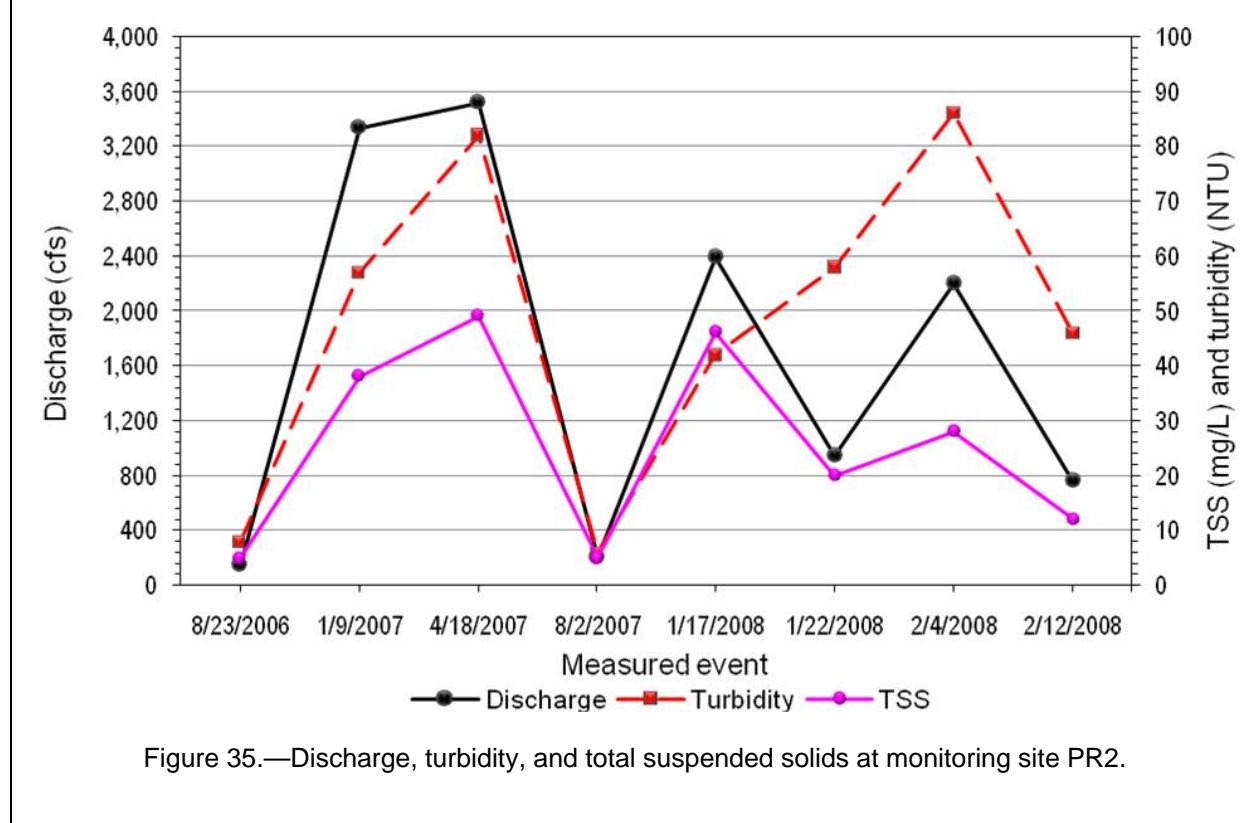


Figure 35.—Discharge, turbidity, and total suspended solids at monitoring site PR2.

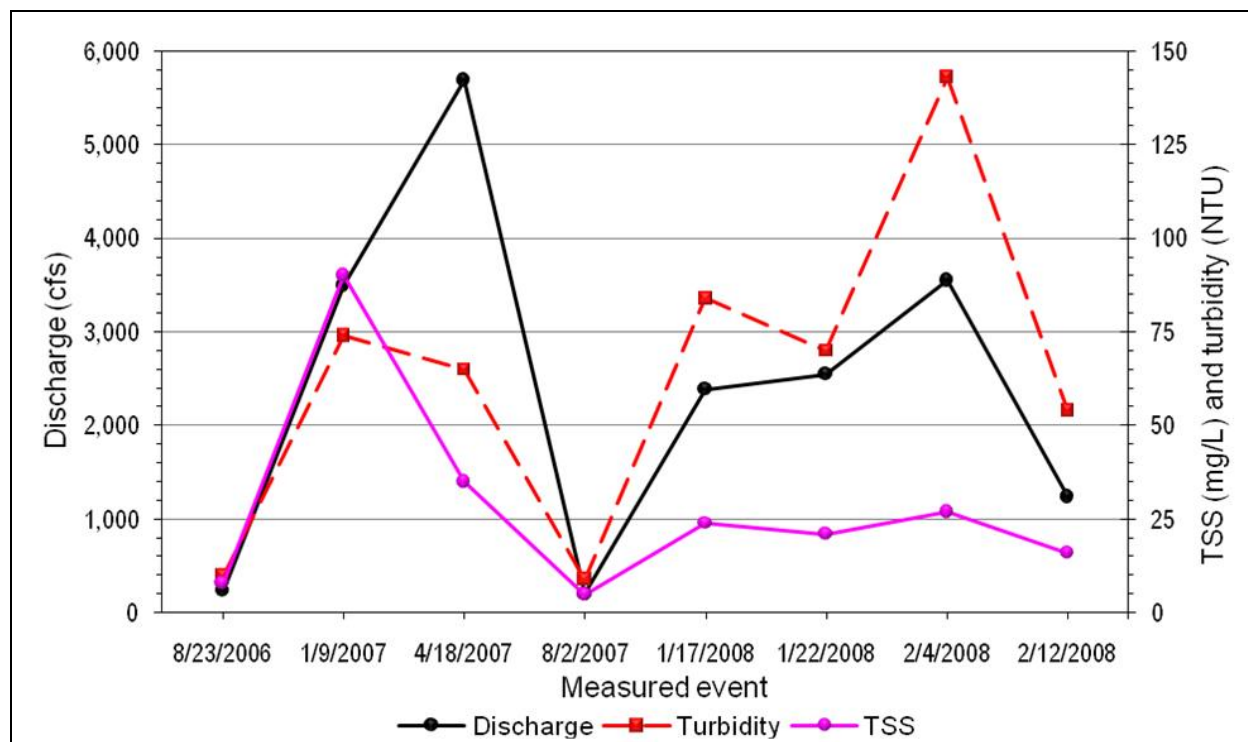


Figure 36.—Discharge, turbidity, and total suspended solids at monitoring site PR3.

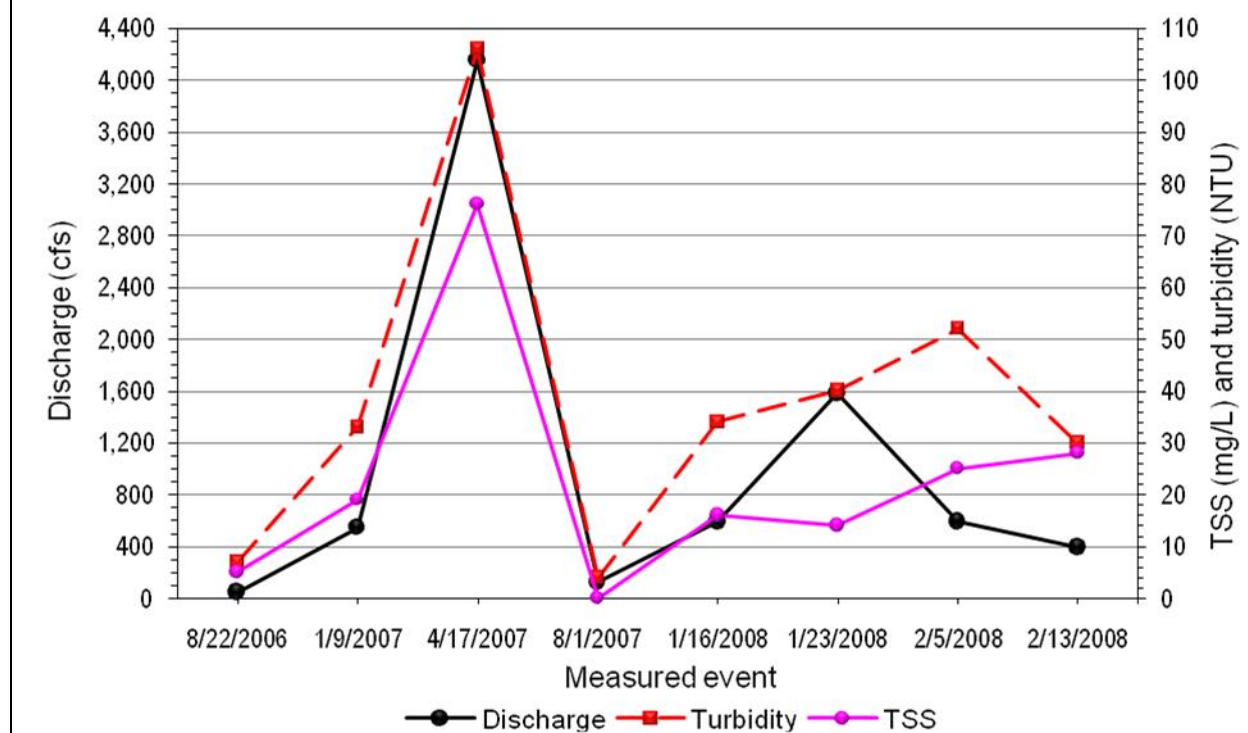


Figure 37.—Discharge, turbidity, and total suspended solids at monitoring site ECR.

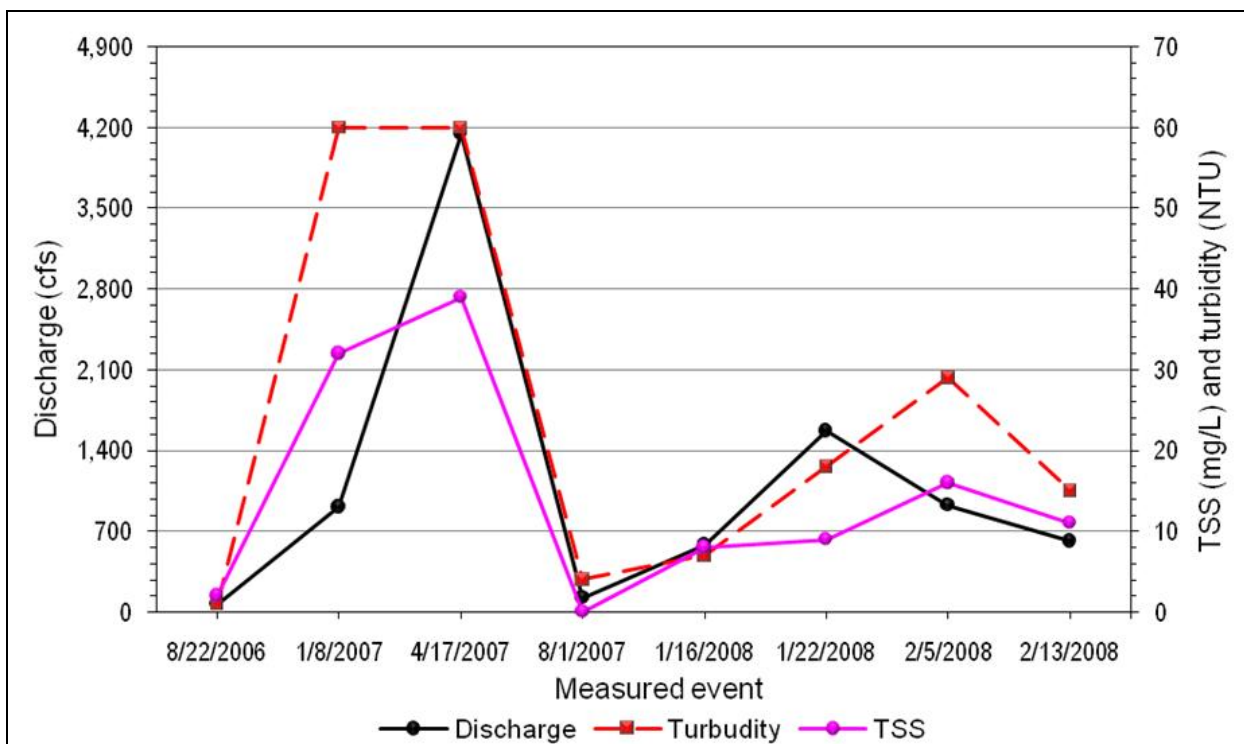


Figure 38.—Discharge, turbidity, and total suspended solids at monitoring site WCR.

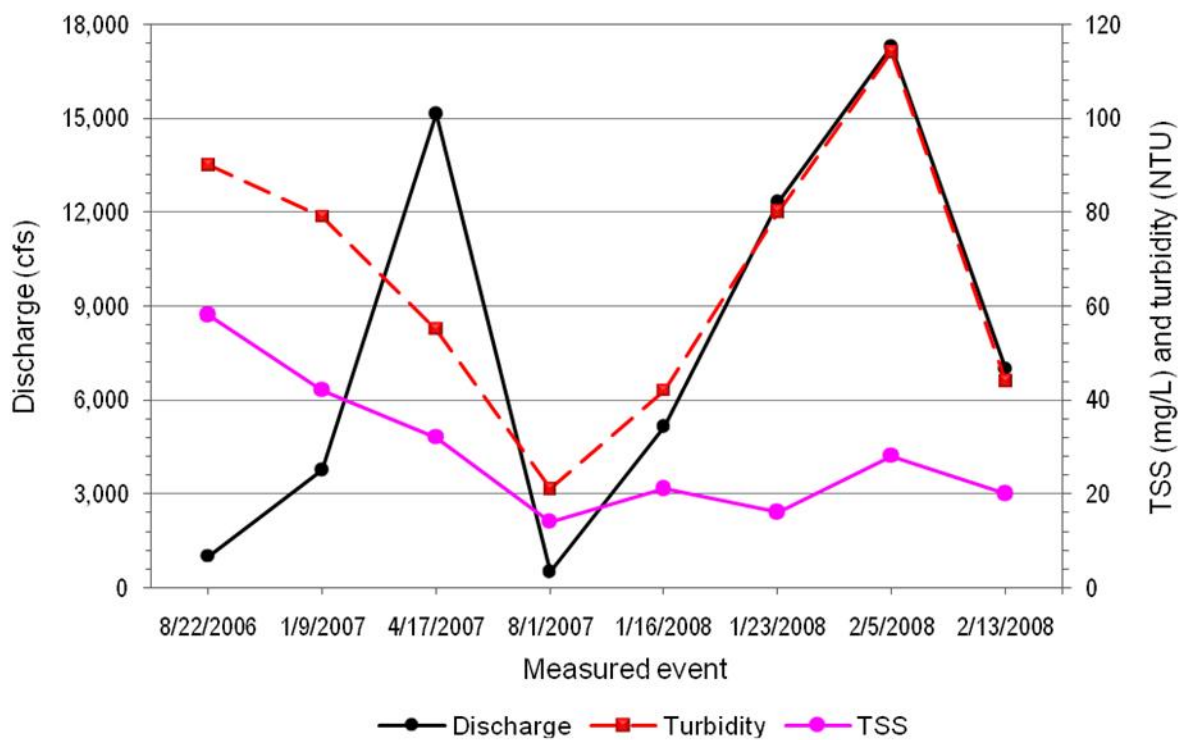


Figure 39.— Discharge, turbidity, and total suspended solids at monitoring site CR1.

An estimation of annual suspended sediment and nutrient (for example, nitrate and phosphorus) loading to the Choctawhatchee River as it enters Florida can be made using the load values of selected parameters at sites located further downstream in Alabama. Correspondingly, annual estimated loads of TSS, NO₃-N, and total-P concentrations entering Florida were estimated as being approximately equal to their values at sites PR3 and CR1.

SEDIMENTATION

Sedimentation, the most prevalent nonpoint source pollutant in streams, is a process by which eroded particles of rock are transported primarily by moving water from areas of relatively high elevation to areas of relatively low elevation, where the particles are deposited. Upland sediment transport is primarily accomplished by overland flow, and rill and gully development. Lowland or flood plain transport occurs in streams of varying order, where upland sediment joins sediment eroded from flood plains, stream banks, and stream beds. Erosion rates are accelerated by human activity related to agriculture, construction, timber harvesting, unimproved roadways, or any activity where soils or geologic units are exposed or disturbed. Excessive sedimentation is detrimental to water quality, destroys biological habitat, reduces storage volume of water impoundments, impedes the usability of aquatic recreational areas, and causes damage to structures. Sediment loads in streams are primarily composed of relatively small particles suspended in the water column (suspended solids) and larger particles that move on or near the stream bed (bed load).

SUSPENDED SEDIMENT

Suspended solids are defined as that portion of a water sample that is

separated from the water by filtering. This solid material may be composed of organic and inorganic material and includes algae, industrial and municipal wastes, urban and agricultural runoff, and eroded material from geologic formations. These materials are transported by overland storm-water runoff to stream channels. For the purposes of this investigation, TSS is synonymous with suspended sediment.

The concentrations of TSS in mg/L were determined by laboratory analysis of water samples. Samples were collected during a range of discharge events from low to high flow. Total suspended solids concentrations were strongly related to the discharge rates at most of the monitoring sites. Thus, the highest TSS concentrations were associated with large discharge events in April for sites PR1, PR2, ECR, and WCR (figs. 34, 35, 36, and 38, respectively). The southernmost (downstream) sites PR3 (fig. 36) and CR1 (fig. 39) exhibited lower TSS values in 2008 and seemed to be less impacted by changes in discharge rates. TSS concentrations and estimated suspended sediment loads for each monitoring site are included in table 10. On average, TSS concentrations were 5 to 20 times greater in samples collected during high flow compared to samples collected during low flow, except in samples collected at site CR1 (table 10).

Table 10.—Total suspended solids concentrations and estimated suspended sediment loads at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	TSS (mg/L)			TSS load	
	Maximum	Minimum	Average	tons/yr	tons/mi ² /yr
PR1	36	BDL*	13	2,572	7.1
PR2	49	5	25	21,247	22.0
PR3	90	5	28	30,631	19.7
ECR	76	BDL	26	2,344	10.0
WCR	39	BDL	19	4,267	12.0
CR1	52	14	29	29,611	9.6

*BDL=below detection limit of 4 mg/L

tons/yr = tons per year

tons/mi²/yr = tons per square mile per year

SUSPENDED SEDIMENT LOADS

Total suspended solids loads for each monitored stream were estimated using measured TSS concentrations and estimated mean daily discharge values and the regression with centering model, discussed previously in this report. Estimated annual suspended sediment loads are shown in figures 40 and 41. Total suspended solids loads are generally greater at downstream locations and larger drainage areas. Accordingly, the farthest downstream sites with the largest drainage areas, CR1 and PR3, exhibited the largest suspended sediment loads (29,611 and 30,631 tons/yr, respectively) (table 10, figs. 40, 41). However, when the loads were normalized with respect to unit watershed area, the largest suspended sediment loads were identified at sites PR2 and PR3 (22 and 19.7 tons/mi²/yr, respectively) (table 10, fig. 40).

Estimated annual suspended sediment loads transported to Florida are presented in figure 41. The largest suspended sediment

load transported to Florida was from the Pea River (30,631 tons/yr). Choctawhatchee River transports slightly less suspended sediment to Florida (29,611 tons/yr). The total suspended sediment loads transported from Alabama's Choctawhatchee watershed to Florida can be estimated as the sum of annual estimated loads at downstream sites PR3 and CR1. Thus, the total annual estimated suspended sediment load transported to Florida from Choctawhatchee River watershed is approximately 60,242 tons/yr. Annual estimated suspended solids loads as well as normalized annual estimated suspended solids loads were determined for three major rivers in south Alabama as part of previous investigations conducted by the Geological Survey of Alabama. A comparison of these estimates with those determined for this study (for example, Choctawhatchee and Pea Rivers) is depicted in figure 41. The largest exported load to Florida comes from Conecuh River (80,069 tons/yr), followed by Pea River (30,631 tons/yr), Choctawhatchee River (29,611 tons/yr), and Yellow River

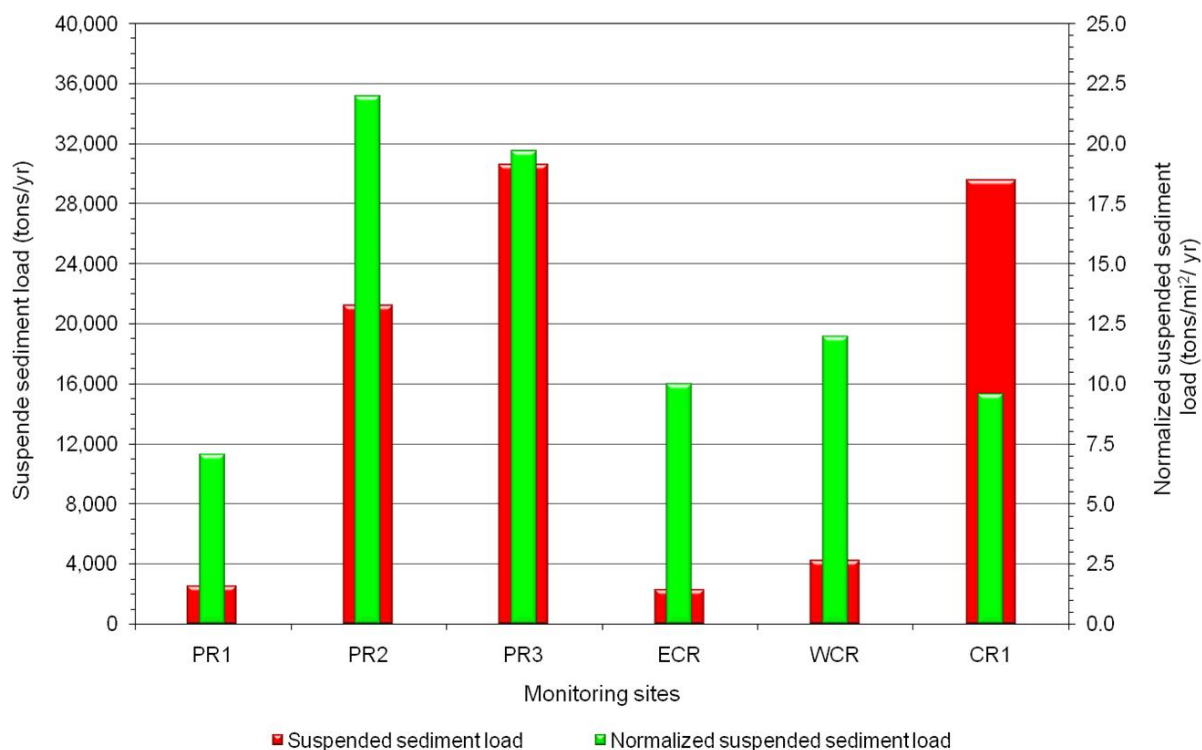


Figure 40.—Annual estimated suspended sediment and annual estimated normalized suspended sediment loads at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

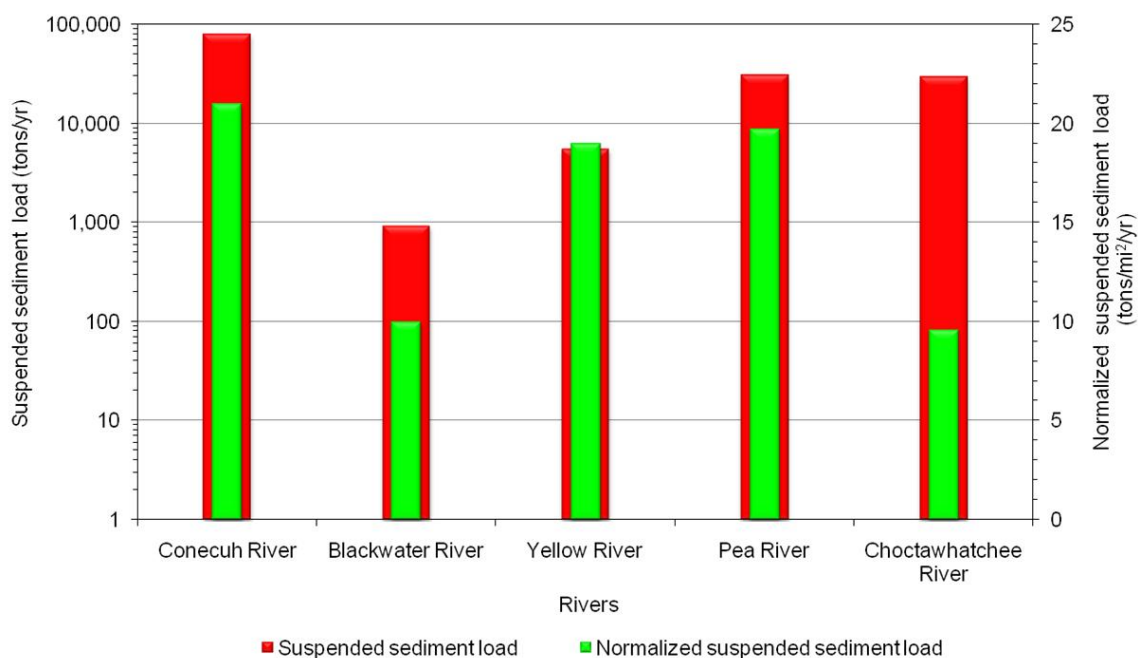


Figure 41.—Annual estimated total suspended sediment loads and normalized annual estimated suspended sediment loads transported from Alabama to Florida.

(5,546 tons/yr). The smallest load transported to Florida was estimated to come from Blackwater River (932 tons/yr). However, normalized estimated annual loads indicate that Choctawhatchee River contributes the smallest volume of suspended solids to Florida.

NUTRIENTS IN PROJECT STREAMS

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 the principal form of toxic ammonia. Elevated ammonia levels may adversely impact aquatic life. Concentrations of ammonia as N in uncontaminated streams may be as low as 0.01 mg/L ($\text{NH}_3\text{-N}$) (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 longer periods of time (up to six weeks) may also 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 $\text{NH}_3\text{-N}$, even relatively short exposures can lead to skin, eye, and gill damage (USEPA, 2004). For the purpose of this study $\text{NH}_3\text{-N}$ is referred to as NH_3 .

Analytical results for the investigated rivers indicated, on average, low NH_3 concentrations with just a few exceptions (table 11). Ammonia levels ranged from less than 0.02 to 0.23 mg/L. The highest concentrations were recorded in the West Fork Choctawhatchee River at site WCR (0.23 mg/L in August 2006 and 0.13 mg/L in 2007) and in Pea River at site PR2 (0.09 mg/L in August 2006 and 0.12 mg/L in January 2007) (fig. 42) and were generally associated with lowest discharge (except at site PR2 in January 2007). Sites PR1, PR3, and CR1 also exhibited high NH_3 levels (0.08, 0.07, and 0.07 mg/L, respectively) (fig. 42). Ammonia concentrations exceeded the background concentration level of 0.01 mg/L for uncontaminated streams (Maidment, 1993) at all monitoring sites. However, the toxicity limit (0.5 mg/L) was not exceeded in any of the samples (table 11).

Table 11.—Ammonia concentrations measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Ammonia as nitrogen (mg/L as $\text{NH}_3\text{-N}$)		
	Maximum	Minimum	Average
PR1	0.08	BDL*	0.04
PR2	0.12	0.03	0.05
PR3	0.07	0.02	0.04
ECR	0.04	BDL	0.03
WCR	0.23	0.03	0.08
CR1	0.07	0.03	0.04

*BDL = below detection limit of 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 proved to have the highest nitrate input to surface waters (Maidment, 1993). Hem (1985) stated that water from small- and medium-sized rivers that drain agricultural areas have nitrate concentrations that can exceed 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^- -N 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. 43). Nitrate values ranged from below the detection limit to 0.69 mg/L (table 12). The highest nitrate concentrations were exhibited at sites PR2 (0.69 mg/L) and CR1 (0.68 mg/L) in the Pea and Choctawhatchee Rivers, respectively (fig. 43, table 12). Moreover, the two sites had the highest average nitrate concentrations (table 12). The lowest nitrate concentrations for all monitoring sites were measured in April 2007. With just one exception (site CR1), the highest discharge events were recorded as well during this period (figs. 44-49). Conversely, high nitrate concentrations were measured during baseflow (August) (figs. 44-49). Therefore, generally, an inverse correlation between nitrate concentrations and discharge was observed (fig. 50). However, slightly elevated nitrate concentrations were recorded in January 2008, during higher flow events. Furthermore, higher nitrate concentrations (recorded at low discharge events) were associated with elevated chloride concentrations (table 12).

Table 12.—Nitrate and chloride concentrations and nitrate loads measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Nitrate concentrations (mg/L)			Nitrate load		Chloride concentrations (mg/L)		
	Maximum	Minimum	Average	tons/yr	tons/ mi ² /yr	Maximum	Minimum	Average
PR1	0.40	BDL*	0.16	265	0.7	7.0	3.3	5.7
PR2	0.69	0.20	0.25	1,446	1.5	8.8	3.3	5.8
PR3	0.37	0.11	0.23	1,376	0.9	5.6	3.1	4.9
ECR	0.39	0.10	0.21	340	1.5	6.6	2.4	5.6
WCR	0.16	0.07	0.13	193	0.5	4.8	3.2	4.5
CR1	0.68	0.11	0.38	5,494	1.8	6.1	3.1	5.2

*BDL = below detection limit of 0.02 mg/L

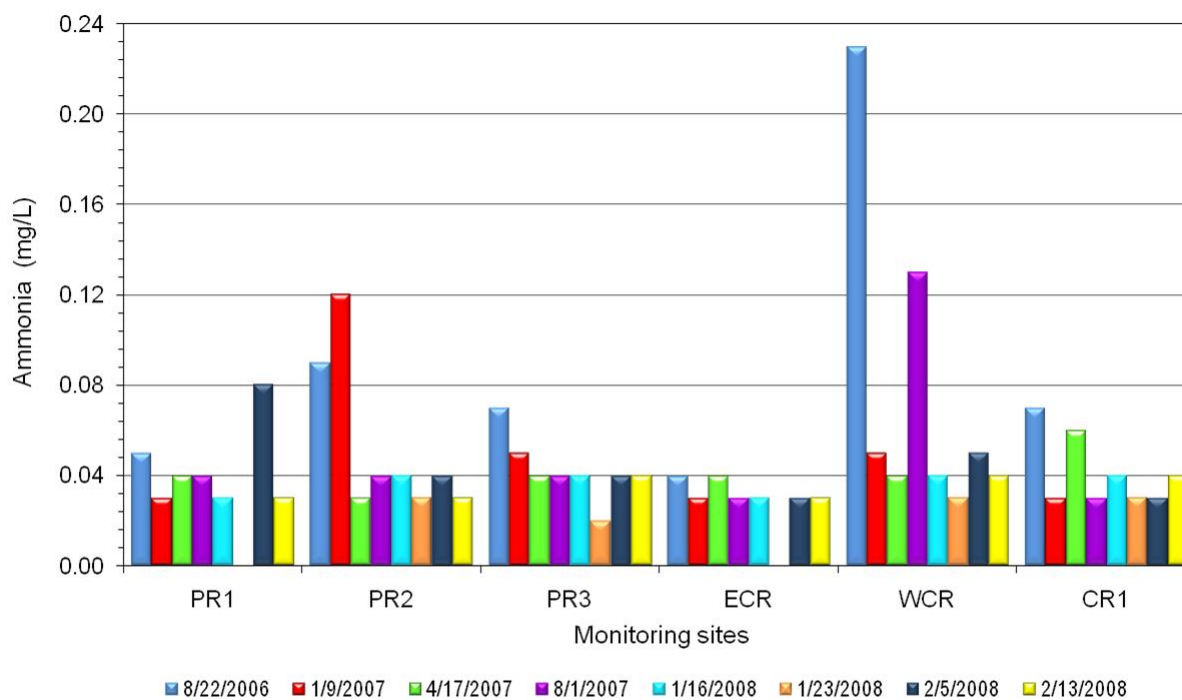


Figure 42.—Measured ammonia at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

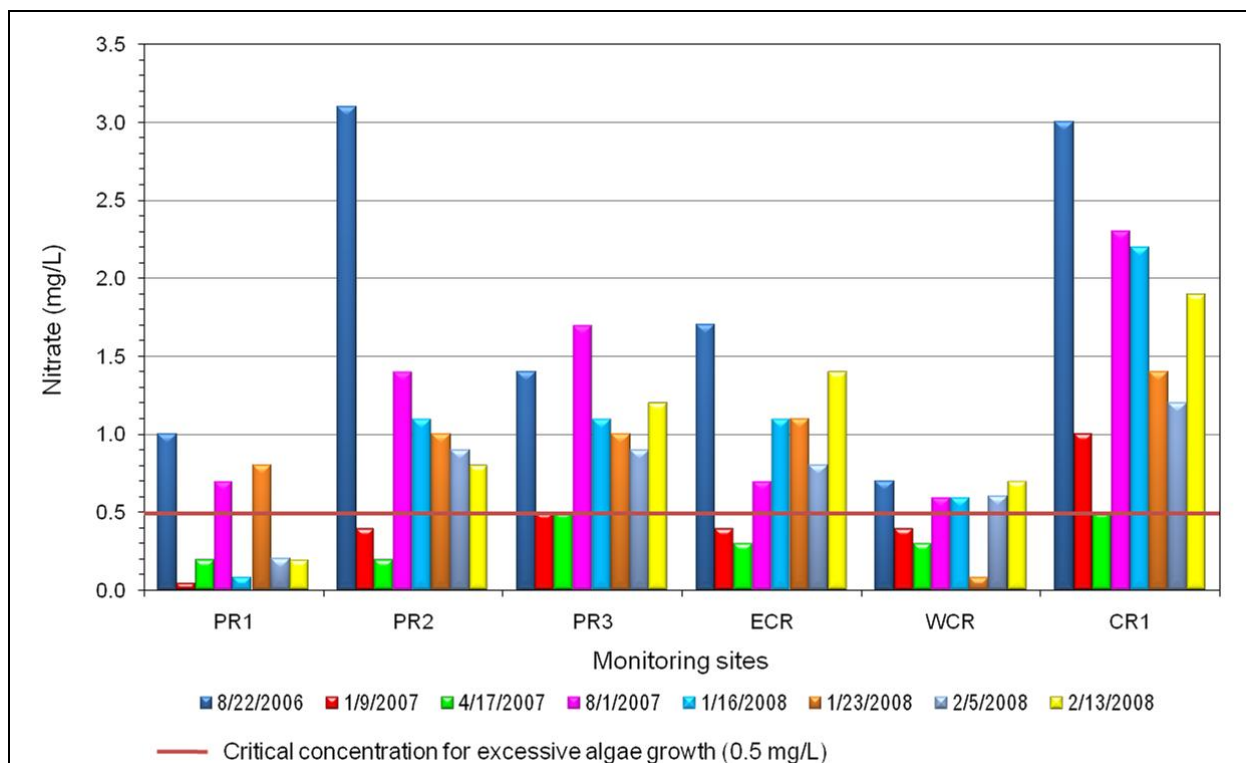


Figure 43.—Measured nitrate at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

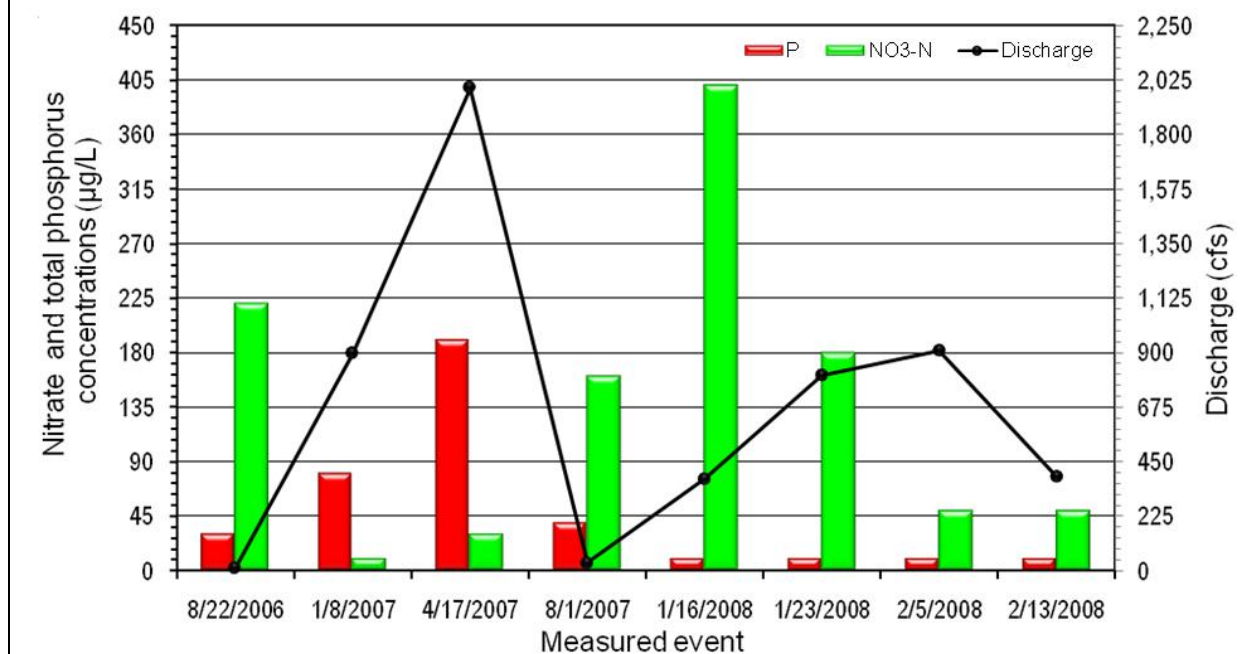


Figure 44.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site PR1.

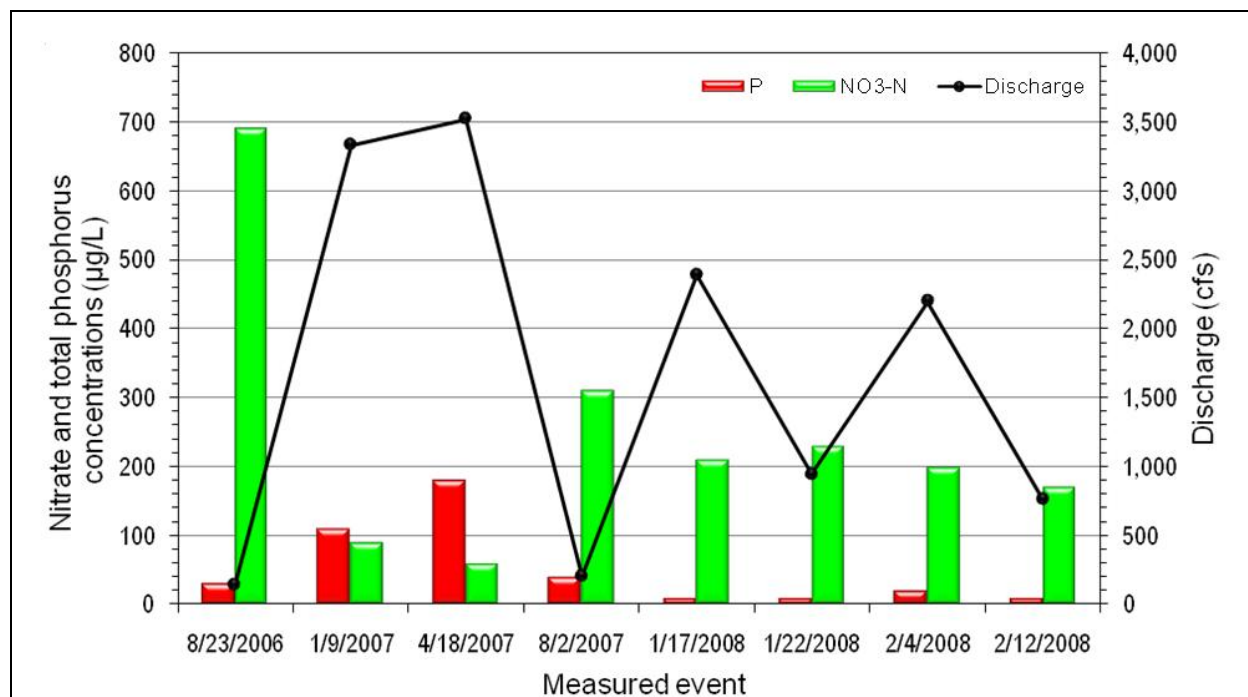


Figure 45.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site PR2.

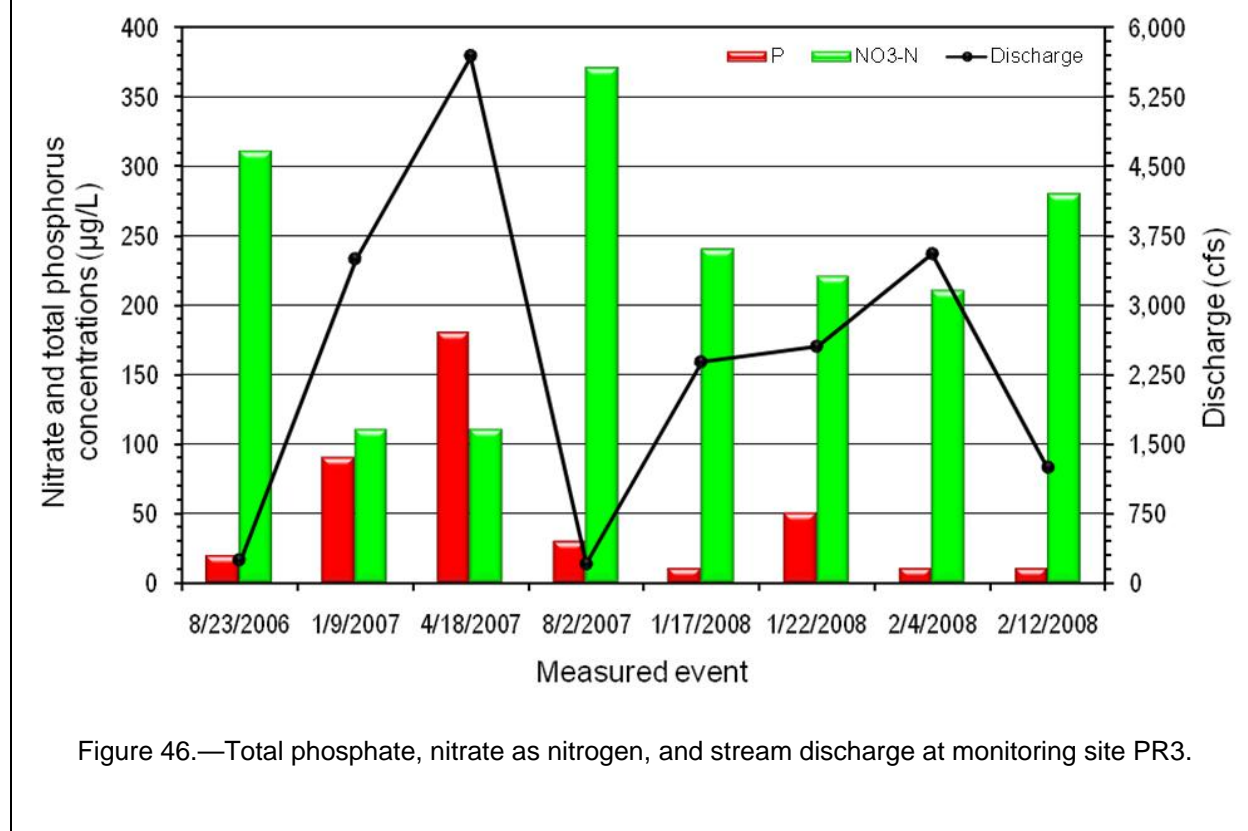


Figure 46.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site PR3.

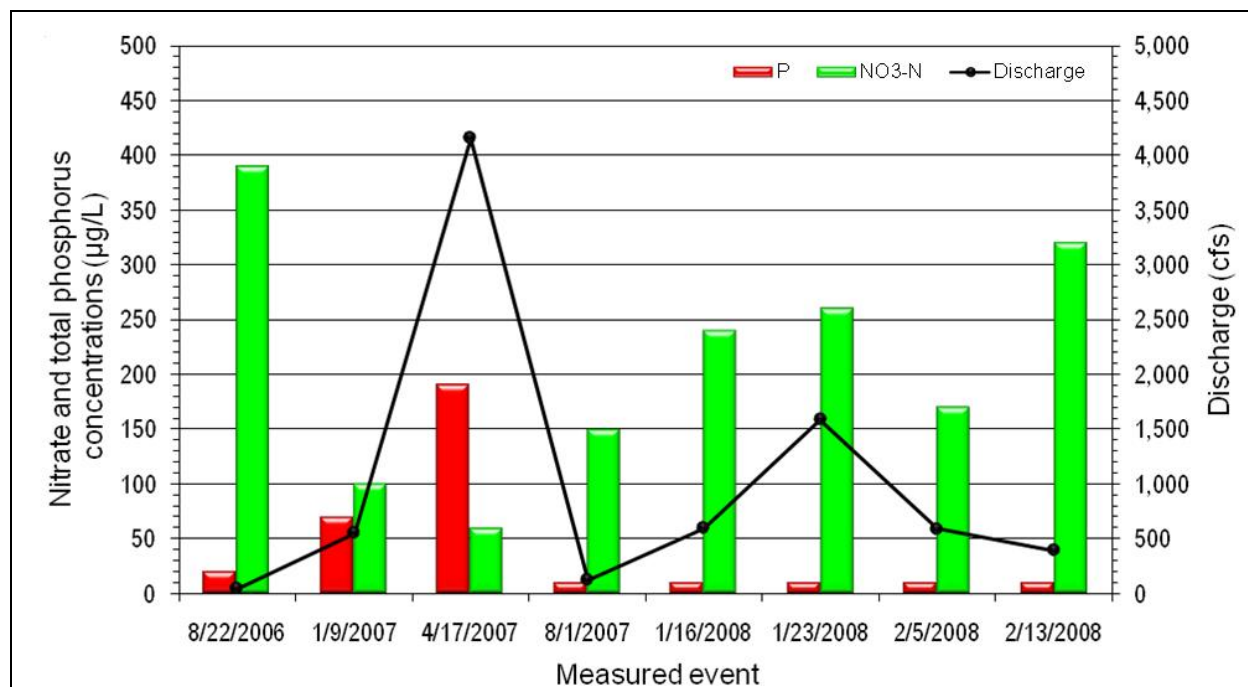


Figure 47.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site ECR.

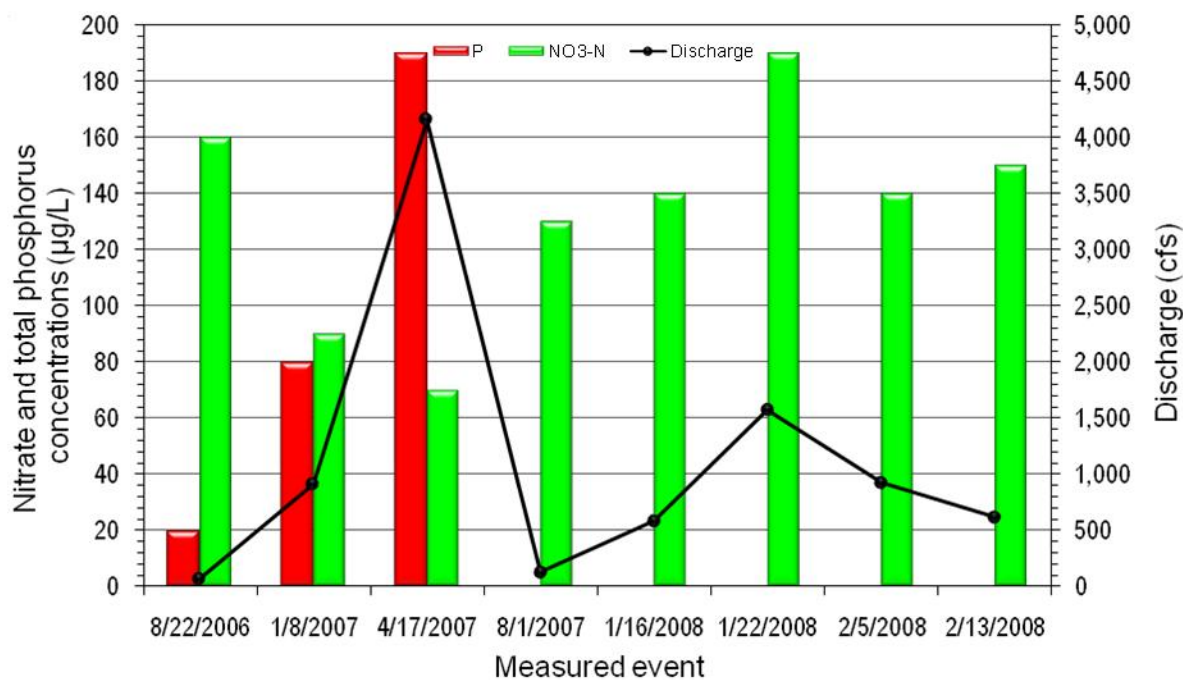


Figure 48.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site WCR.

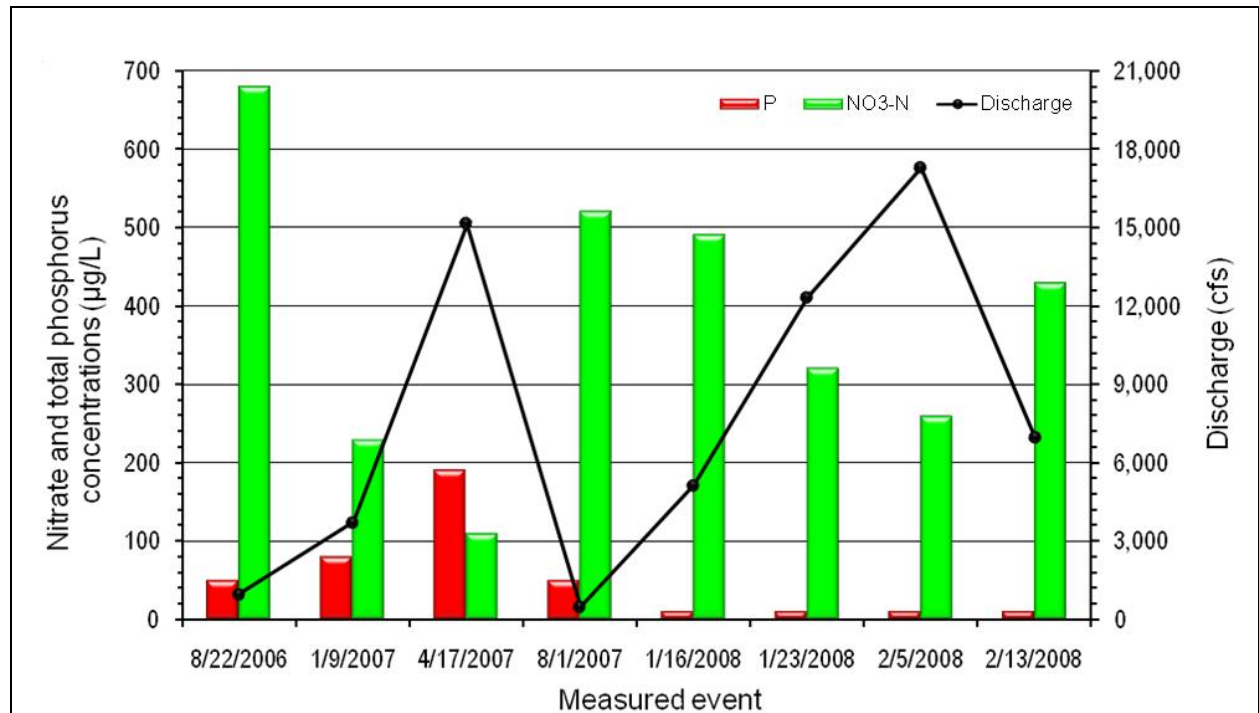


Figure 49.—Total phosphate, nitrate as nitrogen, and stream discharge at monitoring site CR1.

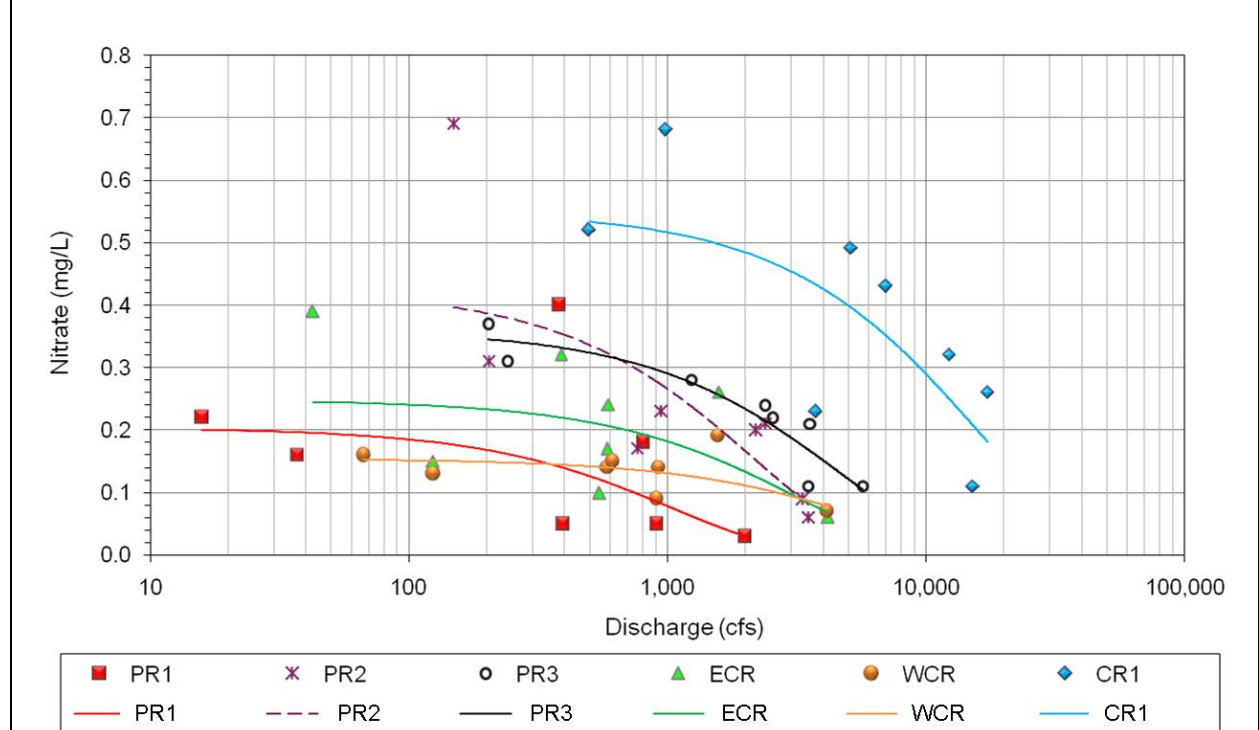


Figure 50.—Scatter-plot of nitrate concentrations and stream discharge rates at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

NITRATE LOADS

Total nitrate loads were determined by application of the regression with centering computer program to nitrate concentrations and mean daily discharge obtained for each monitoring stream during the project period (table 12, fig. 51). The Choctawhatchee River transports about 5,494 tons of nitrate per year at the downstream site CR1 (table 12, fig. 51). The largest nitrate load for the Pea River was estimated at sites PR2 (1,446 tons/yr) and PR3 (1,376 tons/yr). The largest normalized nitrate load (1.8 tons/mi²/yr) was measured in the Choctawhatchee River at site CR1 (fig. 51, table 12).

Estimated annual nitrate loads transported from Alabama to Florida are presented in figure 52. The total nitrate load transported from Choctawhatchee and Pea Rivers to Florida is about 6,860 tons/yr. Annual estimated nitrate loads as well as normalized annual estimated nitrate loads were determined for five major rivers in south Alabama as part of the current study (for example, Choctawhatchee and Pea Rivers) and

previous investigations conducted by the Geological Survey of Alabama. A comparison of these estimates is depicted in figure 52. The largest estimated nitrate load to Florida comes from Choctawhatchee River (5,494 tons/yr) followed by Pea River (1,376 tons/yr) (fig. 52). The smallest nitrate load transported to Florida was estimated to come from the Blackwater River (18.7 tons/yr). However, normalized annual estimated nitrate loads for the investigated rivers revealed that Yellow River contributes the least amount of this constituent to Florida (0.1 tons/mi²/yr) (fig. 52).

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 (PO₄) (Maidment, 1993). Orthophosphate is soluble and is the only biologically available form of phosphorus. The natural background

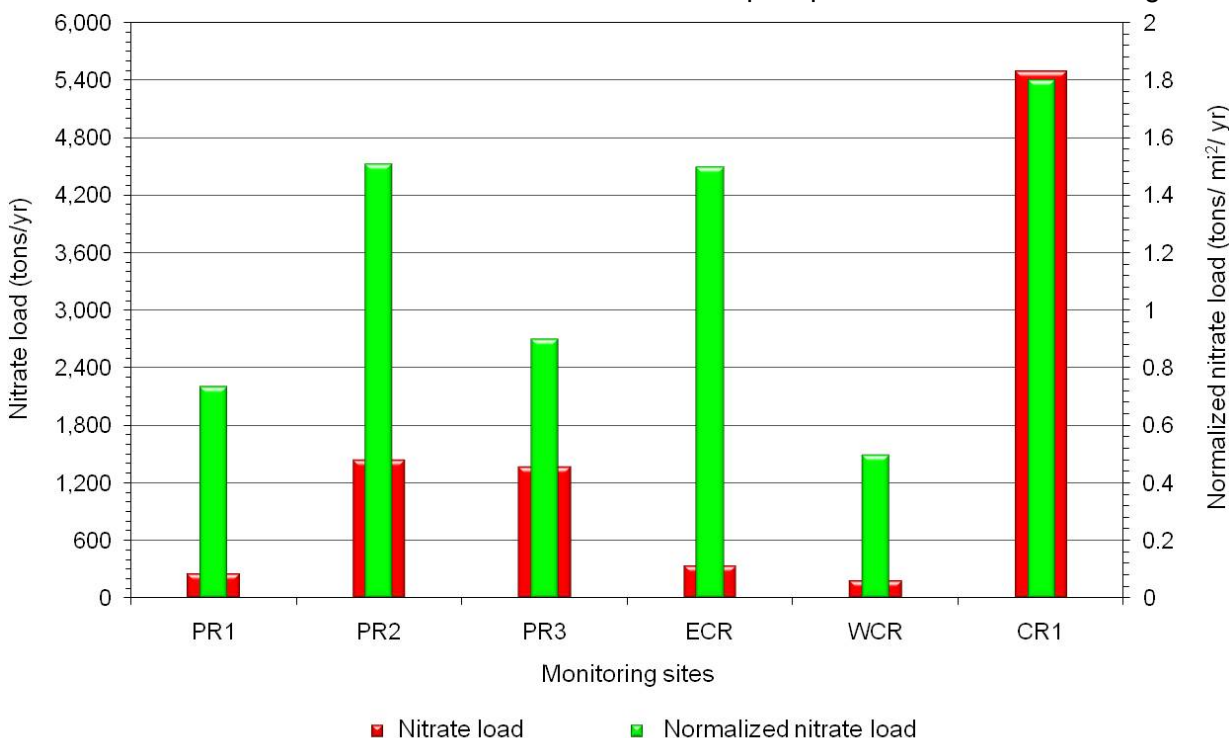


Figure 51.—Annual estimated nitrate loads and annual estimated normalized nitrate loads at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

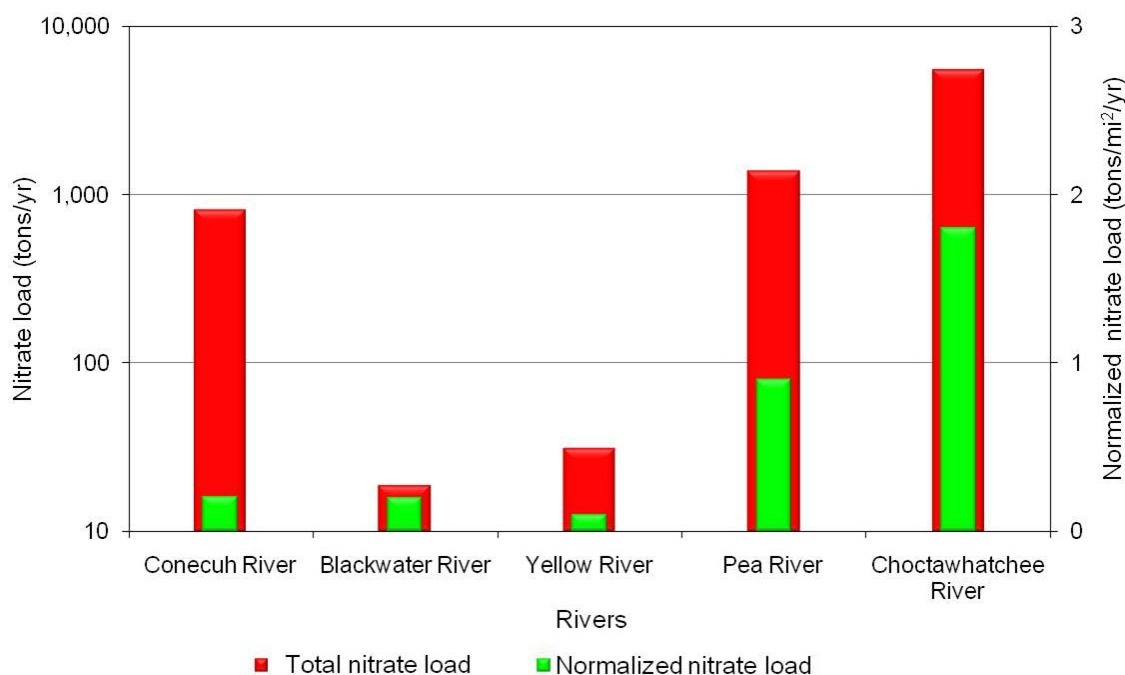


Figure 52.—Annual estimated nitrate loads and normalized annual estimated nitrate loads transported from Alabama to Florida.

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 in order 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 investigated watersheds exceeded the algal productivity limit (0.05 mg/L total-P) at all sites (table 13) but not for the entire monitoring period (fig. 53). At sites PR1, PR2, ECR, and WCR the limit of 0.05 mg/L was exceeded by 25 percent of the samples (fig.

Table 13.—Total phosphorus concentrations and loads measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	Total-P concentrations (mg/L)			Total-P load	
	Maximum	Minimum	Average	tons/yr	tons/mi ² /yr
PR1	0.19	BDL*	0.09	25.6	0.07
PR2	0.18	BDL	0.08	77.5	0.08
PR3	0.18	BDL	0.07	120	0.08
ECR	0.19	BDL	0.09	6.4	0.08
WCR	0.19	BDL	0.08	11	0.03
CR1	0.19	BDL	0.09	240.5	0.08

*BDL = below detection limit of 0.02 mg/L

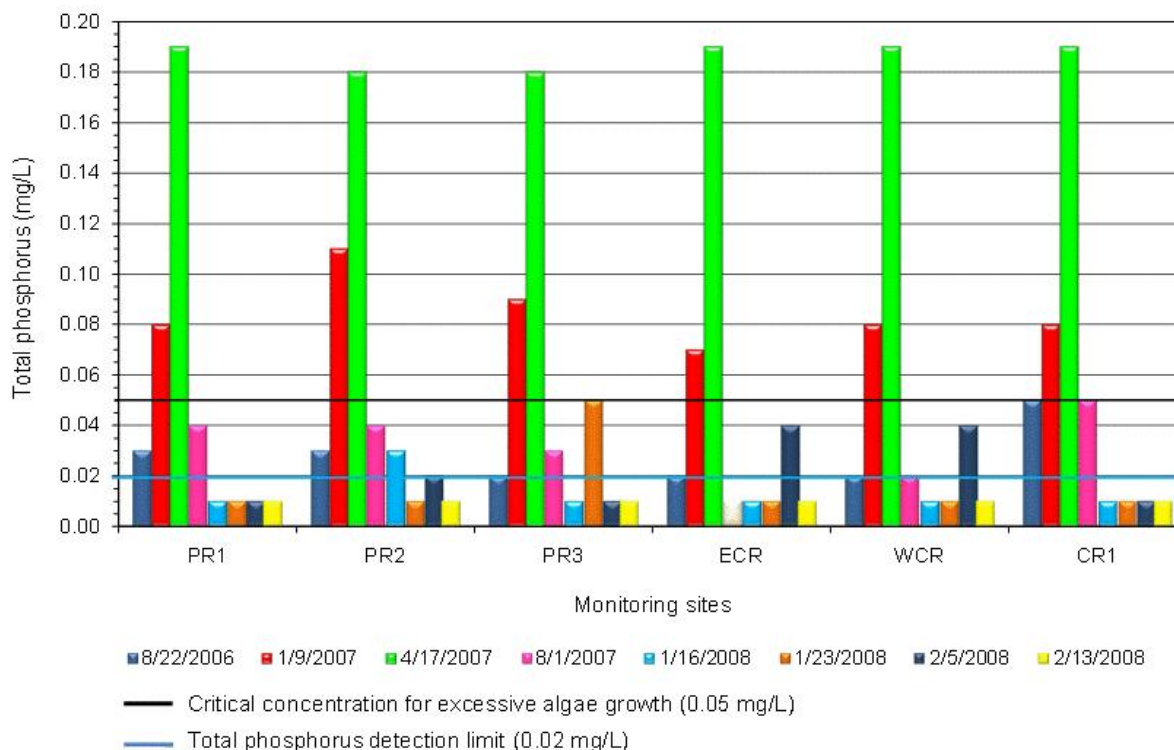


Figure 53.—Measured total phosphorus concentrations at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

53). At sites PR3 and CR1, 50 percent of the samples exhibit total-P concentrations greater than 0.05 mg/L (fig. 53). High concentrations (0.19 and 0.18 mg/L) were measured at each of the sites and were related with the highest flow event in April (2007) (figs. 44-49). However, total-P concentrations measured in January and February 2008 were lower or below detection limit and do not relate with discharge (figs. 44-49). Nevertheless, the relationship between total-P and discharge is positive (fig. 54). Furthermore, there is an inverse relationship between total-P and nitrate concentrations (figs. 44-49).

PHOSPHORUS LOADS

Total-P loads were determined by application of the regression with centering computer program to nitrate concentrations and mean daily discharge obtained for each monitoring stream during the project period (table 13, fig. 55). The Choctawhatchee River transports the largest total-P load (about 240.5 tons/yr) at the downstream site CR1 (table 13, fig. 55). However, normalized total-

P loads revealed three sites with the same annual load values per unit area. Thus, sites PR2, PR3, and CR1 contribute equally to phosphate loading to the Choctawhatchee River (table 13, fig. 55). Consequently, the largest nitrate loads transported to the Choctawhatchee River come from Pea River, sites PR2 (77.5 tons/yr or 0.08 tons/mi²/yr) and PR3 (120 tons/yr or 0.08 tons/mi²/yr) and from the downstream Choctawhatchee River site CR1 (240.5 tons/yr or 0.08 tons/mi²/yr) (table 13, fig. 55).

Estimated annual total-P loads exported to Florida are presented in figure 56. The total phosphorus loads exported from the Choctawhatchee and Pea Rivers to Florida is approximately 360.5 tons/yr. Annual estimated loads as well as normalized annual estimated total-P loads were determined for Yellow River in South Alabama as part of a previous investigation conducted by the Geological Survey of Alabama. Estimates of the Yellow River, Choctawhatchee River, and Pea River are compared in figure 56. The largest estimated annual total-P load

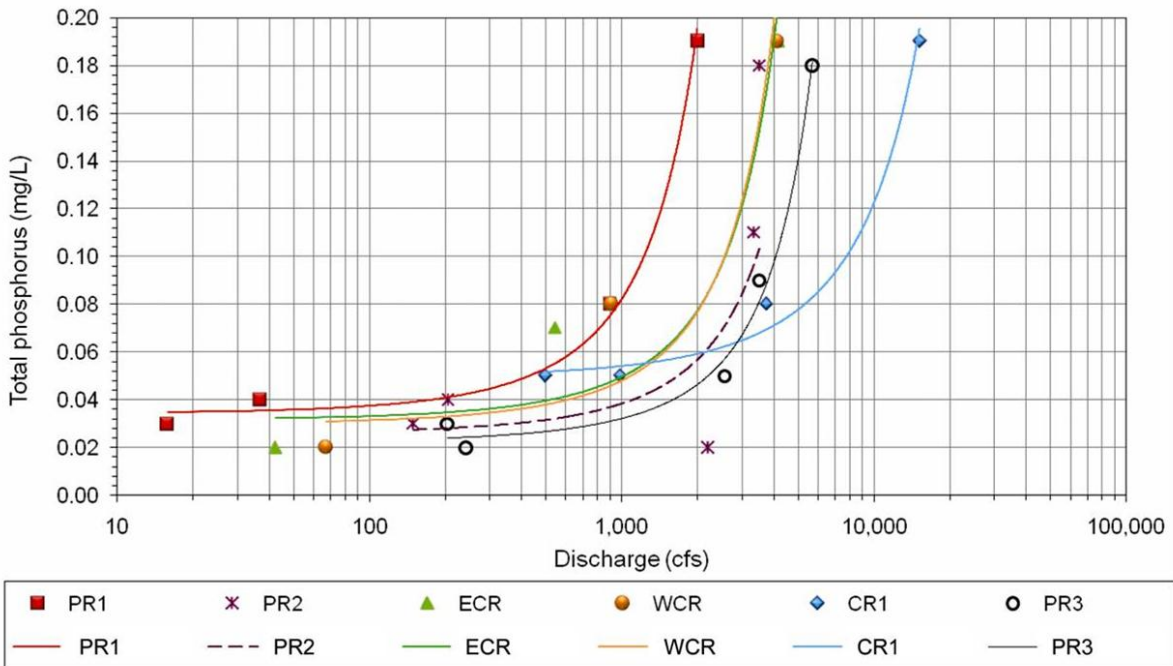


Figure 54.—Scatter-plot of total phosphorus concentrations and stream discharge rates at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

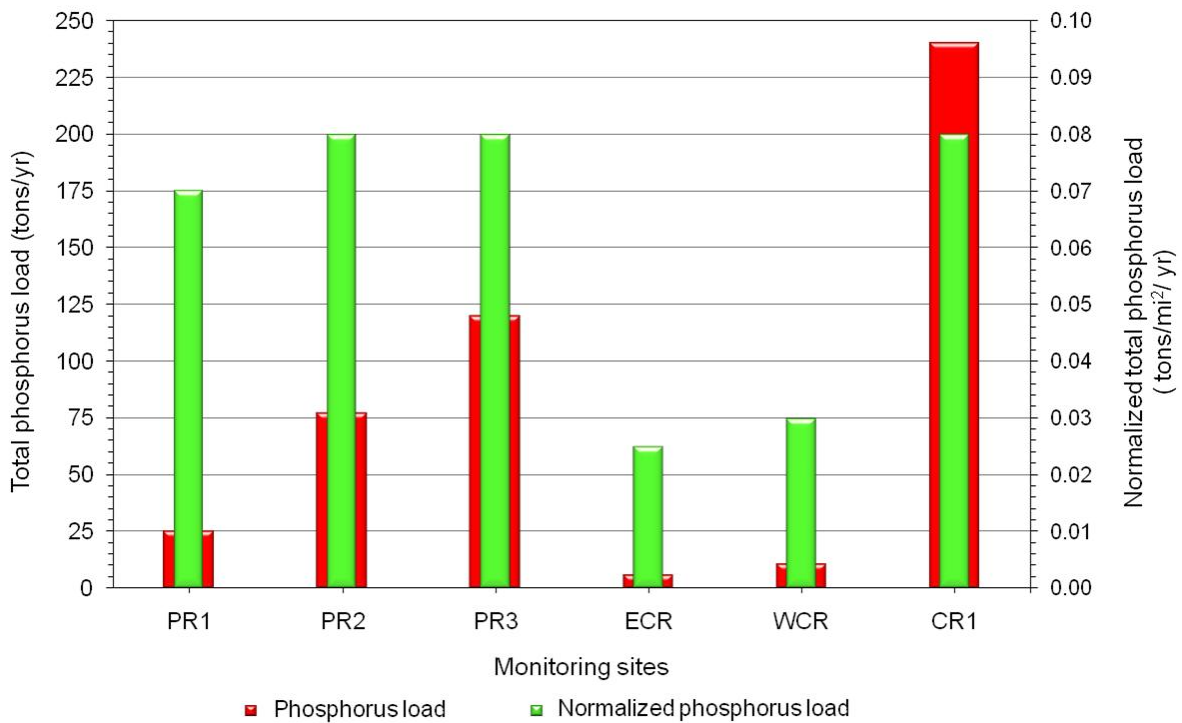


Figure 55.—Annual estimated total phosphorus loads and normalized annual estimated total phosphorus loads at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

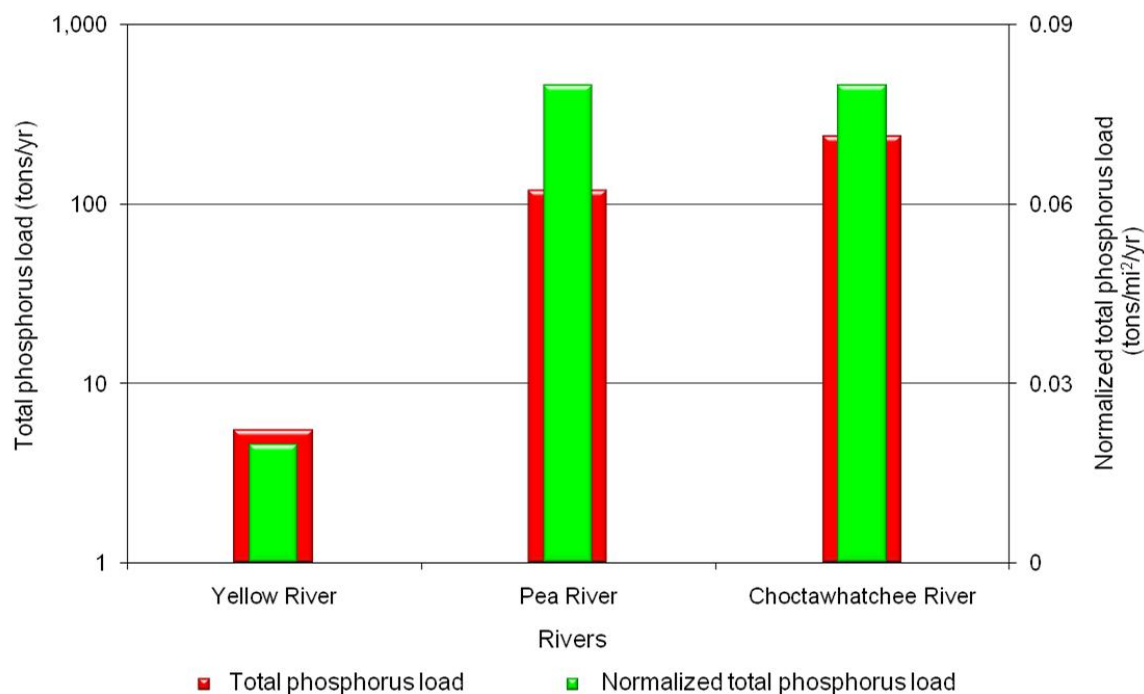


Figure 56.—Annual estimated total phosphorus loads and normalized annual estimated total phosphorus loads transported from Alabama to Florida.

exported to Florida is attributed to the Choctawhatchee River (240.5 tons/yr) and the smallest to Yellow River (fig. 56). Normalized estimated annual total-P loads for the investigated rivers revealed that both Choctawhatchee River and Pea River contribute the same amount of this constituent to Florida (0.8 tons/mi²/yr) (figs. 55, 56).

METALLIC CONSTITUENTS

Numerous metals are naturally present in streams in small concentrations. However, toxic metals in streams are usually a result of human activity. Recently, lead and mercury have received much attention. Detectable concentrations of lead are commonly found in streams and may originate from local sources or through atmospheric transport from more distant sources. Other toxic metals are sometimes found in relatively large concentrations that can be correlated with point sources. Biologically, there is a need for many trace elements, but both oversupply and undersupply are harmful. Consequently there are two circumstances: elements that

are essential can become toxic at elevated levels and elements that are not essential but are tolerated at low levels that may become toxic at high doses. Certain characteristics, such as the element's bioavailability to organisms, the residual or exchangeable phase of the metal, and its abundance in a system can affect the toxicity. The phase in which a metal is present is extremely important. Metals in the *residual* phase, such as silicates, are not toxic, simply because they are unavailable. Metals in the *exchangeable* phase are much more available and therefore are more toxic. Recently, lead and mercury have received much attention. Detectable concentrations of lead are commonly found in streams and may originate from local sources or through atmospheric deposition from sources that may be long distances from the site of deposition.

Water samples collected from the project streams were analyzed for selected metallic constituents. Table 14 shows average concentrations of metallic constituents (concentrations in red are above drinking

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

Metallic Constituent	USEPA primary/secondary drinking water standards (µg/L)	Aquatic life criteria (µg/L)		EPR1	PR2	PR3	ECR	WCR	CR1
		Freshwater acute	Freshwater chronic						
Aluminum	50-200	-	-	247	244	220	252	950	212
Arsenic	10	340	150	BDL*	BDL	BDL	BDL	BDL	BDL
Barium	60	-	-	65	55	56	51	49	45
Beryllium	4	-	-	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium**	5	0.47	0.09	BDL	BDL	BDL	BDL	BDL	BDL
Chromium	100	16	11	BDL	BDL	BDL	BDL	BDL	BDL
Copper**	1,300/1,000	3.27	2.48	BDL	BDL	BDL	BDL	BDL	BDL
Iron	300	-	-	732	572	440	672	744	585
Lead**	15	12.2	0.48	25	7	28	7	8	13
Manganese	50	-	-	157	56	27	47	39	16
Mercury	2	2.4	0.12	BDL	BDL	BDL	BDL	BDL	BDL
Selenium	50	-	-	BDL	BDL	BDL	BDL	BDL	BDL
Thallium	2	-	-	BDL	BDL	BDL	BDL	BDL	BDL
Zinc**	5,000	32.9	33.1	32	25	26	23	21	22

*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 CaCO₃) measured at each monitoring site. Numbers in red represent constituent concentrations exceeding the USEPA primary/secondary drinking water standards.

water standards) detected at monitored sites. Naturally occurring metals such as aluminum, barium, iron, manganese, and zinc are commonly found in small concentrations in coastal plain streams. Lead (Pb) is pervasive in the Choctawhatchee River watershed and occurred in 75 percent of samples from sites PR1, PR2 and WCR, 63 percent of samples from site ECR, and 88 percent of samples from sites CR1 and PR3. At two of the sites (PR1 and PR3), average lead concentrations exceeded the USEPA primary/secondary drinking water standard of 15 µg/L (USEPA, 1996) (fig. 57, table 14). The average lead concentrations exceeded the aquatic freshwater acute and chronic life criteria at sites PR1, PR3, and WCR and sites PR1, PR2, PR3, CR1, ECR, WCR, respectively (table 14). The largest concentration was measured at site PR3 (120 µg/L). The next highest lead concentration was recorded at site PR1 (80 µg/L) (fig. 57). The elevated concentrations were correlated with higher flow events (April 2007) and low pH values.

Moreover, an inverse relationship between Pb concentrations and pH was observed at all sites. 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). Aluminum (Al) and iron (Fe) concentrations exceed the USEPA (1996) primary/secondary drinking water standards of 0.05-0.2 and 0.3 mg/L, respectively (table 14), at all sites.

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

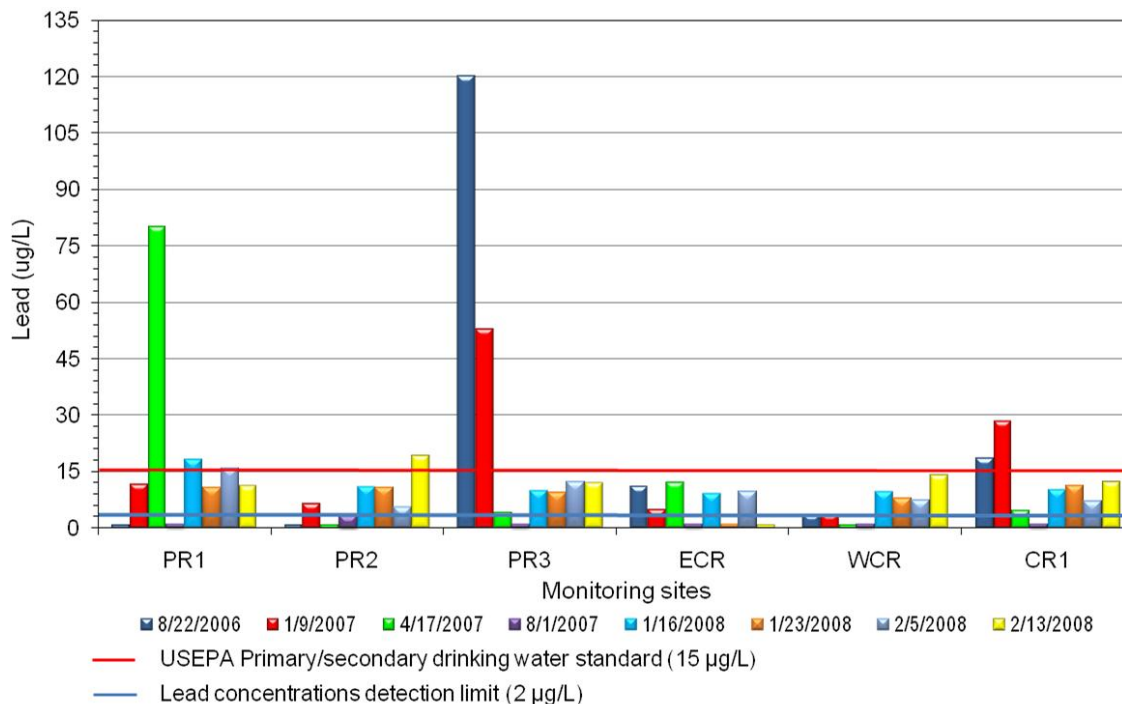


Figure 57.—Measured lead concentrations at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

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 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). Minimum, maximum, and average TOC values for monitoring sites are shown in table 15. The highest TOC concentration was measured in Pea River at site PR1 (table 15, fig. 58). The highest concentrations at each

site were associated with the maximum flow events, recorded in April during the monitoring period.

Phenols are used in the production of phenolic resins, germicides, herbicides, fungicides, pharmaceuticals, dyes, plastics, and explosives (Fenelon, 1996). They may occur in domestic and industrial wastewaters, natural waters, and potable water supplies and they are generally traceable to industrial

Table 15.—Total organic carbon concentrations measured at monitoring sites in the Choctawhatchee and Pea Rivers watersheds

Site	TOC concentrations (mg/L)		
	Maximum	Minimum	Average
PR1	13.1	3.9	7.9
PR2	10.5	3.5	3.9
PR3	7.7	1.1	4.7
ECR	10.4	BDL*	5.6
WCR	6.3	3.8	4.6
CR1	7.2	3.8	3.9

*BDL = below detection limit of 0.5 mg/L

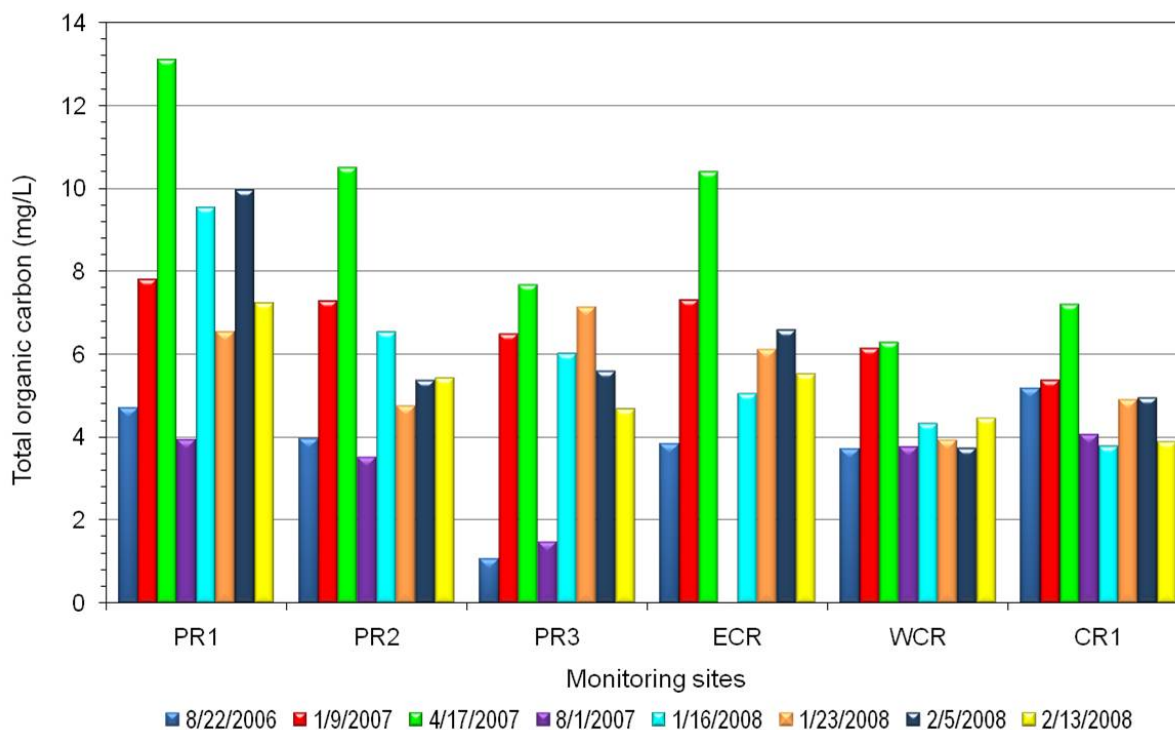


Figure 58.—Measured total organic carbon at monitoring sites in the Choctawhatchee and Pea Rivers watersheds.

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 streams should not exceed 0.3 mg/L. Phenols cause acute and chronic toxicity to freshwater aquatic life. Neither phenols nor oil and grease were detected in any samples collected during the project period.

SUMMARY OF FINDINGS

The Choctawhatchee and Pea Rivers watershed covers 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 has been 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 Choctawhatchee and

Pea Rivers watersheds. For this purpose land-use/land-cover analysis was combined with geochemical investigations of surface water samples collected from the study area. This combination of methods provides an understanding of the 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 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 forest (fig. 5). The southeasternmost corner of the study area (Houston County and parts of Henry, Dale, and Geneva Counties) is dominated by agriculture (fig. 5). Therefore, a greater input of contaminants from this area

to the Choctawhatchee River watershed is expected. Fertilizer and herbicide applications in these areas may cause an increase in the concentration of contaminants such as NO_3^- -N, total-P, TDS, and TSS, which, in turn, 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 (figs. 2, 3) and land uses associated with particular river reaches. Sites PR1, ECR, and WCR were considered as low-impact sites since they are located at river reaches that drain primarily forested lands and less-developed urban and agricultural areas. Sites PR2, CR1, and PR3 are located in river reaches that drain areas dominated by agricultural and higher density developed land uses. Additionally, sites CR1 and PR3 were expected to have the highest contamination impact as they are the most downstream sites and drain the largest agricultural and developed areas.

There are several impaired streams found on the ADEM 303(d) list that discharge into the Choctawhatchee River. The number of impaired streams in Choctawhatchee River watershed increased during the years from 1996 to 2008. 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. Low conductivity values associated with high flow events, such as occurred in April 2007, may indicate that the concentration of nonpoint source pollutants commonly flushed into streams during high discharge events was negligible. Generally, the highest conductivity values correspond to the lowest discharge events (in

August) when river levels decrease and ionic concentrations increase. Higher conductivities associated with lower discharge episodes may suggest that shallow groundwater has a greater contaminant input to the streams. 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. 7-12).

At sites PR1, PR3, and CR1, increasing discharge is associated with higher TDS concentrations, lower stream temperatures, and medium conductivity values (figs. 7, 9, 12). 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, suggesting that contamination to the streams may be continuous (for example, sewer breakthrough, leaching from livestock waste, etc.).

Waters in the investigated rivers are slightly acidic. The range of values and the slightly higher frequency of acidic pH values (table 6, fig. 12) indicate that the water is not very well buffered and has a higher potential for contamination. The general inverse relationship between pH and discharge for both rivers may reflect relatively acidic rainfall and/or dilution.

There was a positive correlation between DO and pH as well as DO and stream temperature, which may be the result of natural biological processes that take place in surface waters and/or the presence of contaminants. The relatively low DO concentrations observed at site PR2 (table 7) are possibly the result of contamination from surrounding urban and residential land uses (fig. 3). 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), when water temperatures were highest. Furthermore, higher BOD levels were accompanied by lower pH values and increased chlorophyll and DO levels. In April 2007, when discharge was highest, BOD concentrations were also highest but nitrate concentrations were lowest. This may be explained by the fact that in April, when temperatures are relatively warm, nitrate is used up by algae or other organisms whereas high nitrate concentrations and low chlorophyll observed in August may be explained by either algae decomposition resulting in nitrogen release and/or nitrate input from shallow groundwater. Biological oxygen demand in both Pea and Choctawhatchee Rivers exhibited a positive relationship with phosphorus and an inverse relationship with nitrate. Furthermore, a positive relationship between total-P and flow and an inverse relationship between nitrate concentrations and flow were observed for all six 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 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). The January and February 2008 nitrate data do not correlate with flow events. However, during this time, concentrations higher than 0.1 mg/L (average nitrate concentration recorded in January 2007 at all sites was 0.11 mg/L) were recorded. Furthermore, high nitrate

concentrations are associated with elevated chloride concentrations (table 12). Consequently, the presence of nitrate in monitoring streams 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 and Pea River watersheds. At two of the monitoring sites (PR1 and PR3), average lead concentrations exceeded the USEPA primary/secondary drinking water standard of 15 µg/L (USEPA, 1996) and the acute freshwater aquatic life criterion (fig. 57, table 14) (ADEM, 2008). The chronic freshwater aquatic life criterion was exceeded at all sites (table 14). The largest concentrations measured correlated with the higher flow events and lower pH values. Lead contamination may be attributed to sources such as atmospheric transport, industrial waste-water discharge, urban runoff, leaching batteries, and lead paint. Aluminum (Al) and iron (Fe) concentrations exceeding the USEPA primary/secondary drinking water standards may presumably be the result of surface weathering and erosion of clay minerals.

RIVER WATER-QUALITY RANKING

The primary constituents that affect water quality in streams in Alabama have nonpoint sources and consist of sediment, nutrients, bacteria, and metals (Hairston and Stribling, 1995). Evaluations of these constituents provide a good indication of overall water quality and stream health.

An effective method of comparing water quality at respective monitoring sites is to rank each site as to the magnitude of particular water-quality constituents. Tables 16, 17, and 18 show the ranking of project sites from highest (1) to lowest (6), according to the priority constituents. Table 16 shows rankings of normalized suspended sediment loads. Ranks for individual parameters were calculated based on the highest and lowest concentrations, with the highest impacted site

ranked as number 1 and the lowest impacted site ranked as number 6.

Rankings with respect to two or more parameters were determined based on the summation of the individual parameter's ranks used in analyses. The largest and smallest loads were estimated for Pea River at sites PR2 and PR1, respectively. Table 17 shows rankings of normalized nitrate and total-P loads. The largest nitrate loads were estimated for Choctawhatchee River at site CR1 and for Pea River at site PR2. The smallest nitrate loads were estimated for site WCR on the West Fork of Choctawhatchee River.

Site CR1, the most downstream site along Choctawhatchee River, receives waters draining a large agricultural area. Sites ECR and WCR are the most upstream sites located on Choctawhatchee River and water discharging at these locations is draining mainly wooded lands with sparse agricultural and residential uses. Nevertheless, suspended sediment loads at site WCR are larger compared to site ECR (table 16).

Water from the West Fork Choctawhatchee River discharging at the WCR site drains a larger area underlain by easily erodible formations (those composed, for example, of sand and clay) (figs. 4A, B). Thus, the larger suspended solids load at this site may be the result of sand erosion from the Tuscaloosa Sand formation. In contrast, nitrate loading is larger at site ECR (fig. 18). Water discharging at this location drains a larger agricultural area compared to that from the West Fork Choctawhatchee River. Furthermore, Dunham Creek, a tributary to the Choctawhatchee River in southern Henry County, receives waters from an EPA superfund site. The superfund site once contained a fertilizer manufacturing plant and a metals smelting operation plant. Cook (2004) determined that the superfund site contributed high concentrations of nitrate, phosphorus, and metals into Dunham Creek and eventually to the Choctawhatchee River. However, due to dilution, nitrate, phosphate, and metals concentrations at site ECR do not suggest the presence of point source contamination.

Table 16.—Water-quality ranking with respect to sediment loads

Site	Suspended sediment load tons/ mi ² /yr	Rank
PR1	7.1	6
PR2	22	1
PR3	19.7	2
ECR	10	4
WCR	12	3
CR1	9.6	5

Table 17.—Water-quality ranking with respect to nutrient and total phosphorus loads

Site	Nitrate Load (tons/mi ² /yr)	Total-P (tons/mi ² /yr)	Rank
PR1	0.74	0.07	4
PR2	1.51	0.08	2
PR3	0.90	0.80	3
ECR	1.50	0.03	5
WCR	0.50	0.03	6
CR1	1.80	0.08	1

Table 18.—Water-quality ranking based on key constituents

Site	Average BOD (mg/L)	Average lead (µg/L)	Suspended sediment load (tons/mi ² /yr)	Nitrate Load (tons/mi ² /yr)	Total-P Load (tons/mi ² /yr)	Rank
PR1	1.15	25	7.1	0.74	0.07	4
PR2	1.46	7	22	1.51	0.08	1
PR3	1.18	28	19.7	0.90	0.80	2
ECR	1.18	7	10	1.50	0.03	6
WCR	0.80	8	12	0.50	0.03	5
CR1	0.86	13	9.6	1.80	0.08	3

Consequently, the larger nitrate load may be explained by nitrate leaching from fertilizer and pesticides application.

Site PR2 is located at the confluence of Pea River with Big and Whitewater Creeks in the city of Elba. Big Creek has its headwaters in Pike County at the city of Troy. The largest loads of suspended solids and nitrate at this site may reflect the impact of developed and residential land uses. The downstream site PR3 receives waters that drain larger agricultural and smaller developed areas. The lower suspended solids load at this location may be explained by lower gradient and flow velocities of Pea River in Geneva County, caused by floodplain morphology (fig. 4A, B). Phosphorus (total-P) loads were the highest at downstream sites PR3 and CR1 (table 17). Overall, land-use practices correlate well with analytical data.

Average lead concentrations are tabulated in table 18. The highest average lead concentrations were measured in Pea River at site PR3 and the lowest in Choctawhatchee River and Pea River at sites ECR and PR2. BOD can be used to indicate the presence and magnitude of organic pollutants. Analytical data (table 18) indicate that Pea River had the highest average BOD concentration at site PR2. The highest average BOD concentration in Choctawhatchee River was measured at site ECR.

CONCLUSIONS

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.

When all priority constituents were considered, Pea River at sites PR2 and PR3

and Choctawhatchee River at site CR1 had the highest magnitude of impacted water quality (table 18). The lowest magnitudes of impacted water quality are estimated for sites PR1, WCR, and ECR (table 18). This correlates well with pollutant sources and land uses in the respective watersheds. Furthermore, the results reveal that the sites located farthest downstream, such as CR1, tend to be the most contaminated. In Pea River, site PR2 has the highest degree of contamination. However, the downstream site PR3 is the second most contaminated site in the study area (table 18). Based on the foregoing data, it is concluded that land-use practices adjacent to or upstream from an investigated site are useful indicators of downstream water quality.

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