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Prepared in cooperation with the St. Johns River Water Management District

Scientific Investigations Report 2004-5177

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

U.S. Department of the Interior

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Suggested citation: Kroening, S.E., 2004, Streamflow and Water-Quality Characteristics at Selected Sites of the St. Johns River in Central Florida, 1933 to 2002: U.S. Geological Survey Scientific Investigations Report 2004-5177, 102 p.

Contents

Abstract	1
Introduction	2
Previous Studies	4
Purpose and Scope	5
Description of the Study Area	5
Climate	5
Hydrogeologic Setting	6
Hydrologic Setting	7
Land Use and Land Cover	8
Wastewater	10
Approach and Methods	10
Streamflow Data	11
Retrospective Water-Quality Data	11
Data Collected for this Study	15
Sample Collection and Analysis Methods	16
Quality Assurance	17
Continuous Monitoring Data	19
Data Analysis Methods	19
Acknowledgments	21
Streamflow Characteristics	22
Temporal Trends	22
Seasonal Variation	25
Streamflow Reversals	25
Flow Duration	27
Low-Flow Frequency Statistics	28
Water-Quality Characteristics	
Water Temperature	31
Dissolved Oxygen	32
Water pH	36
Specific Conductance	38
Total Dissolved Solids	40
Major lons	42
Silica	52
Minor Inorganic Constituents	55
Sulfide	55
Iron	56
Bromide	56
Water Color and Organic Carbon	58
Nutrients	64

Total Nitrogen6	5 7
Ammonia Nitrogen6	6
Organic Plus Ammonia Nitrogen	0
Nitrate Nitrogen	0
Total Phosphorus7	4
Orthophosphate Phosphorus7	'5
Chlorophyll- <i>a</i>	8
Turbidity	80
Total Suspended Solids8	80
Human and Veterinary Antibiotics, Other Human Prescription and Nonprescrip- tion Drugs, Pesticides, and Organic and Wastewater Constituents8	31
Temporal Trends (1991-99)	36
Summary	6
References	39
Appendix A. Sites with retrospective water-quality data compiled for this report9)6
Appendix B. Water-quality constituents analyzed in stream water collected	
during this study9	17
Appendix C. Streamflow duration statistics at selected sites on the St. Johns,	
Econlockhatchee, and Wekiva Rivers and Blackwater Creek	12

Figures

1.	Map showing location of the St. Johns River Basin, central Florida			
2.	Graph showing mean monthly temperature and rainfall at the Orlando airport,			
	1961	-90	. 6	
3.	Мар	o showing generalized land use and land cover in the study area, 1999	. 9	
4.	Map	showing location of study area and stream sites	13	
5-11.	Grap	ohs showing:		
	5.	Seven-day annual minimum low-flow values plus 4,000, and the		
		corresponding fit by the Pearson Type III distribution for data from the St. Johns River near DeLand, Florida	20	
	6.	Annual minimum streamflow averaged over 7 consecutive days at the Econlockhatchee River near Chuluota, Florida	24	
	7.	Annual minimum streamflow averaged over 7 consecutive days at the Wekiva River near Sanford, Florida, 1935-2000	24	
	8.	Streamflow-duration hydrographs for sites on the St. Johns River and Blackwater Creek, water years 1985-2000	26	
	9.	Flow-duration curves for St. Johns River sites, water years 1957-2000	27	
	10.	Flow-duration curves for sites on the St. Johns River, Econlockhatchee River, Wekiva River, and Blackwater Creek, water years 1985-2000	28	
	11.	Streamflow characteristics and precipitation at St. Johns River sites, 2000-02	33	
12.	Box Rive	plots showing seasonal variations in water temperature in the St. Johns r upstream of Lake Harney near Geneva, Florida, 1991-99	34	

13.	Boxplots showing dissolved oxygen concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-1999 34			
14.	Graph showing dissolved oxygen concentration and streamflow at the St. Johns Biver near Christmas, Florida, 2000-02			
15.	Boxplots showing water pH in the St. Johns River and near the mouths of			
16	the Econlockhatchee and Wekiva Rivers, 1991-1999			
10. 17.	Graphs showing relation between specific conductance and streamflow at sites on the St. Johns River 1991-99			
18.	Boxplots showing specific conductance values at St. Johns River sites and near the mouths of the Econlockhatchee and Wekiva Rivers, May 1991-99 40			
19.	Graphs showing continuous specific conductance and stream discharge at St. Johns River sites, 2000-02			
20.	Graphs showing total dissolved solids concentration and streamflow at St. Johns River sites, 2000-02			
21.	Trilinear diagrams for water samples collected from St. Johns River sites, Wekiva River, Blackwater Creek, and Blue Springs, 2000-02			
22-24.	Graphs showing:			
	22.Sulfate concentration and streamflow at St. Johns River sites, 2000-022000-0249			
	23. Chloride concentration and streamflow at St. Johns River sites, 2000-02			
	24. Dissolved silica concentration and streamflow at St. Johns River sites, 2000-02			
25.	Map showing silica concentrations in the Floridan aquifer system, 1990-2002			
26-28.	Graphs showing:			
	26. Total iron concentrations and streamflow at St. Johns River sites, 2000-022000-0257			
	27. Percent of dissolved iron comprising the total iron concentration and streamflow at the St. Johns River near Sanford, Florida, 2000-02			
	28. Bromide concentration and streamflow at St. Johns River sites, 2000-02			
29.	Map showing bromide concentrations in the Floridan aquifer system, 1990-2002			
30.	Graphs showing water color values and streamflow at St. Johns River sites, 2000-02			
31.	Graphs showing dissolved organic carbon concentration, specific ultra- violet light absorbance, and streamflow at St. Johns River sites, 2000-02 65-6			
32.	Plots showing total nitrogen concentration and nitrogen speciation in the St. Johns River and near the mouths of the Econlockhatchee and Wekiya Rivers. 1991-99			
33.	Graphs showing dissolved ammonia nitrogen concentration and streamflow at St. Johns River sites. 2000-02			
34.	Boxplots showing nitrate nitrogen concentrations by seasonal period near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99			

Graphs showing dissolved nitrite plus nitrate nitrogen concentration and water temperature at St. Johns River sites, 2002-02			
Graphs showing total phosphorus concentration and streamflow at St. Johns River sites, 2002-02	76		
Boxplots showing chlorophyll- <i>a</i> concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99			
Boxplots showing seasonal variations in chlorophyll- <i>a</i> concentrations in the St. Johns River downstream of Blue Springs, Florida,1991-99			
Graph showing chlorophyll- <i>a</i> concentrations and streamflow at the St. Johns River site near Cocoa, Florida, 2000-02	79		
Boxplots showing seasonal variations in total suspended solids concentration in the St. Johns River near Hontoon Marina, Florida, 1991-9982			
Graphs showing:			
41. Total suspended solids concentration and streamflow at the St. Johns River site near Christmas, Florida, 2000-02	82		
42. Frequency of detection of human and veterinary antibiotics, othe human prescription and nonprescription drugs, pesticides, and o wastewater constituents at the St. Johns River sites near Cocoa Sanford, Florida, water years 2002-03	er organic and 84		
43. Number of human and veterinary antibiotics, other human presc and nonprescription drugs, pesticides, and organic wastewater constituents detected at selected St. Johns River sites near Coc and Sanford, Florida, water years 2002-03	ription oa 85		
	 water temperature at St. Johns River sites, 2002-02 Graphs showing total phosphorus concentration and streamflow at St. Johns River sites, 2002-02 Boxplots showing chlorophyll-<i>a</i> concentrations in the St. Johns River near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99 Boxplots showing seasonal variations in chlorophyll-<i>a</i> concentrations the St. Johns River downstream of Blue Springs, Florida, 1991-99. Graph showing chlorophyll-<i>a</i> concentrations and streamflow at the St. Johns River site near Cocoa, Florida, 2000-02 Boxplots showing seasonal variations in total suspended solids concentration in the St. Johns River near Hontoon Marina, Florida, 19 Graphs showing: 41. Total suspended solids concentration and streamflow at the St. Johns River site near Christmas, Florida, 2000-02 42. Frequency of detection of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and organic wastewater constituents at the St. Johns River sites near Cocoa Sanford, Florida, water years 2002-03 43. Number of human and veterinary antibiotics, other human prescription drugs, pesticides, and organic wastewater constituents detected at selected St. Johns River sites near Cocoa and Sanford, Florida, water years 2002-03 		

Tables

1.	Locations of sites with streamflow and water-quality data analyzed in this study
2.	Retrospective water-quality sites with paired field- and laboratory- determined water pH values and sign test results
3.	Remark codes associated with retrospective water-quality data collected by Florida Department of Environmental Protection, Orange County,
	Volusia County, and the St. Johns River Water Management District 14
4.	Censoring limits applied to retrospective water-quality data
5.	Land-use and land-cover percentages of the drainage area upstream of
	the sites sampled for this study
6.	Statistical summary of field-blank samples for water-quality data collected
	for this study
7.	Variability in constituent values for water-quality data collected for this study 19
8.	Temporal trends in daily-mean and N-day consecutive low-streamflow data
	from sites with more than 10 years of data on the St. Johns River,
	Econlockhatchee River, Wekiva River, and Blackwater Creek
9.	Low-flow frequency statistics for the St. Johns River near Cocoa, Florida 29
10	Low-flow frequency statistics for the St. Johns River near Christmas Florida 29
11	Low-flow frequency statistics for the Econlockhatchee River near
	Chuluota Florida 20
	onuluota, monua

12.	Low-flow frequency statistics for the St. Johns River upstream of Lake Harney near Geneva, Florida
13	Low-flow frequency statistics for the St. Johns River near Sanford Florida 30
14.	Low-flow frequency statistics for the Wekiya River near Sanford, Florida 30
15.	Low-flow frequency statistics for Blackwater Creek near Cassia. Florida 31
16.	Low-flow frequency statistics for the St. Johns River near DeLand, Florida
17.	Mean annual streamflow for sites in the study area
18.	Relations between dissolved oxygen concentration and water pH and
	streamflow at St. Johns River sites, 1991-2002
19.	Relations between specific conductance values and total dissolved solids
20	Relations between major dissolved inorganic constituent concentrations
20.	and streamflow at St. Johns River sites 2000-2002
21	Relations between dissolved silica total sulfide total iron dissolved iron
21.	and bromide concentrations and streamflow at St. Johns River sites.
	2000-02
22.	Descriptive statistics of total sulfide concentrations at St. Johns River,
	Wekiva River, and Blackwater Creek sites, 2000-0255
23.	Relations between water color values and dissolved organic carbon
	concentrations and streamflow at St. Johns River sites, 2000-2002
24.	Relations between total nitrogen, ammonia nitrogen, and organic plus
	ammonia nitrogen concentrations and streamflow at St. Johns River sites,
	1991-2002
25.	Descriptive statistics of nitrate nitrogen concentrations in the St. Johns,
	Econlockhatchee, and Wekiva Rivers, 1991-99
26.	Descriptive statistics of total phosphorus concentrations in the St. Johns,
07	Econiocknatchee, and vvekiva Rivers, 1991-99
27.	Relations between total phosphorus and orthophosphate concentrations
20	Descriptive statistics of orthonhosphete concentrations in the St. Johns
20.	Econlockhatchae, and Wekiya Biyers, 1991-99
29	Belations between turbidity values and total suspended solids
23.	concentrations and streamflow at St. Johns River sites 1991-2002 80
30	Descriptive statistics of total suspended solids concentrations in the
00.	St. Johns. Econlockhatchee, and Wekiva Rivers, 1991-99
31.	Kendall's tau correlation coefficients describing the relation between
	chlorophyll- <i>a</i> and total suspended solids concentration at sites on the
	St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99
32.	Temporal trends in selected physical properties, nutrients, and
	chlorophyll- <i>a</i> at St. Johns River sites, 1991-99

Multiply	Ву	To obtain
	Length	
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi ²)	2.59	square kilometer
	Mass	
ton, long (2,240 lb)	1.016	megagram
	Flow rate	
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second

Conversion Factors and Verical Datum

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: $^{\circ}C = (^{\circ}F - 32) / 1.8$

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

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

Acronyms and Abbreviations

ET	evapotranspiration
FDEP	Florida Department of Environmental Protection
FFWCC	Florida Fish and Wildlife Conservation Commission
LOWESS	locally-weighted scatterplot
MCL	maximum contaminant level
μg/L	micrograms per liter
μ	micron
μS/cm	microsiemens per centimeter
mg/L	milligrams per liter
mL	milliliter
nm	nanometer
NWIS	National Water Information System
NTU	nephelometric turbidity units
SJRWMD	St. Johns River Water Management District
SWIM	Surface Water Improvement and Management
TMDL	total maximum daily load
UV	ultraviolet light
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

By Sharon E. Kroening

Abstract

To meet water-supply needs in central Florida for 2020, the St. Johns River is being considered as a source of water supply to augment ground water from the Floridan aquifer system. Current (2004) information on streamflow and water-quality characteristics of the St. Johns River in east-central Florida is needed by water resources planners to assess the feasibility of using the river as an alternate source of water supply and to design water treatment facilities. To address this need, streamflow and water quality of the 90-mile-long middle reach of the St. Johns River, Florida, from downstream of Lake Poinsett to near DeLand, were characterized by using retrospective (1991-99) and recently collected data (2000-02). Streamflow characteristics were determined by using data from water years 1933-2000. Water-quality characteristics were described using data from 1991-99 at 15 sites on the St. Johns River and 1 site each near the mouths of the Econlockhatchee and Wekiva Rivers. Data were augmented with biweekly water-quality data and continuous physical properties data at four St. Johns River sites and quarterly data from sites on the Wekiva River, Blackwater Creek, and downstream of Blue Springs from 2000-02. Water-quality constituents described were limited to information on physical properties, major ions and other inorganic constituents, nutrients, organic carbon, suspended solids, and phytoplankton chlorophyll-a. The occurrence of antibiotics, human prescription and nonprescription drugs, pesticides, and a suite of organic constituents, which may indicate domestic or

industrial waste, were described at two St. Johns River sites using limited data collected in water years 2002-03. The occurrence of these same constituents in water from a pilot water treatment facility on Lake Monroe also was described using data from one sampling event conducted in March 2003.

Dissolved oxygen concentration and water pH values in the St. Johns River were significantly lower during high-flow conditions than during low-flow conditions. Low dissolved oxygen concentrations may have resulted from the input of water from marsh areas or the subsequent decomposition of organic matter transported to the river during high-flow events. Low water pH values during high-flow conditions likely resulted from the increased dissolved organic carbon concentrations in the river.

Concentrations of total dissolved solids and other inorganic constituents in the St. Johns River were inversely related with streamflow. Most major ion concentrations, total dissolved solids concentrations, and specific conductance values varied substantially at the Christmas, Sanford, and DeLand sites during low-flow periods in 2000-01 probably reflecting wind and tidal effects.

Sulfide concentrations as high as 6 milligrams per liter (mg/L) were measured in the St. Johns River during high-flow periods. Increased sulfide concentrations likely resulted from the decomposition of organic matter or the reduction of sulfate. Bromide concentrations as high as 17 mg/L were measured at the most upstream site on the St. Johns River during 2000-02. Temporal variations in bromide were characterized by sharp peaks in concentration during low-flow periods. Peaks in bromide concentrations tended to coincide with peaks in chloride concentrations because the likely source of both constituents is ground water affected by relict seawater.

Median dissolved organic carbon concentrations ranged from 15 to 26 mg/L during 2000-02, and concentrations as high as 42 mg/L were measured. Water color values and dissolved organic carbon concentrations generally were significantly greater during high-flow conditions than during low-flow conditions. Specific ultraviolet light absorbance data indicated the organic carbon during high-flow events was more aromatic in composition and likely originated from terrestrially derived sources compared to organic carbon in the river during other times of the year.

Detections of ammonia nitrogen and orthophosphate phosphorus in the St. Johns River indicated that bioavailable forms of nutrients generally are present. Ammonia nitrogen concentrations in the river generally were greater during high-flow conditions than during low-flow conditions. Nitrate nitrogen concentrations during 1991-99 were significantly lower in the upstream part of the river compared to other sites, which may be related to nitrate being used as a nutrient by terrestrial or aquatic plants or denitrification in wetland areas. High nitrate concentrations at sites downstream of the confluence with the Wekiva River may have been due to nitrogen-enriched ground-water inflow. Seasonal variations in nitrate concentrations from 2000-02 were characterized by sharp peaks in concentration from about October through February, which probably resulted from nitrification.

Chlorophyll-*a* and total suspended solids concentrations generally were greatest in May and June compared to other times of the year. Low chlorophyll-*a* concentrations in July and August may have resulted from light limitation due to increased concentrations of highly colored organic matter in the river. High total suspended solids concentrations during the May-June low-flow period indicate that runoff of soil eroded from the land surface is not the primary mechanism by which suspended solids are contributed to the St. Johns River, but rather that suspended solids are contributed by algal production or the resuspension of bottom sediments.

Pesticides, antibiotics, plasticizers, and detergent metabolites were detected in water from the St. Johns River. No constituent concentrations exceeded applicable Maximum Contaminant Levels established by the U.S. Environmental Protection Agency. Atrazine, metolachlor, and cholesterol were the most frequently detected compounds. More constituents were detected in water from the Sanford site (20) compared to the Cocoa site (5), which likely resulted because the Sanford site is downstream of point sources of municipal wastewater effluent to streams in the study area and urban-residential areas on septic systems. Limited data suggested these constituents are derived from runoff to the Cocoa site and from pointsource discharges or septic tank leachate at the Sanford site.

The most notable temporal trends in water-quality constituents during 1991-99 were increased concentrations of total phosphorus and dissolved orthophosphate at three sites on the St. Johns River upstream of Lake Harney. Increased fertilizer sales, increased livestock populations, or increased phosphorus concentrations in recently restored wetlands do not account for this trend.

Introduction

The St. Johns River Basin encompasses about 9,400 square miles (mi²) in east-central Florida (fig. 1). The river originates in the St. Johns River marsh, a vast wetlands area near Vero Beach, and flows northward about 275 miles (mi) , where it discharges to the Atlantic Ocean near Jacksonville. The St. Johns River Water Management District (SJRWMD) encompasses about 12,400 mi² in east-central Florida—about 21 percent of the land area in the State of Florida. The SJRWMD is responsible for managing the ground- and surface-water supplies in this region.

Sites along the St. Johns River are being considered as potential intake points for surface water to augment ground water from the Floridan aquifer system to meet future water-supply needs in central Florida (St. Johns River Water Management District and CH2MHILL, 1998). The population of the area managed by the SJRWMD is projected to increase from about 3.7 million in 1998 to 5.2 million in 2020 (St. Johns River Water Management District, 2000). With this projected population increase, there may not be sufficient water available from the Floridan aquifer system to supply all existing and projected water uses and to sustain the aquifer system and related natural systems, such as springs and lakes. Approximately 40 percent of the area managed by the SJRWMD was classified as Water Resource Caution Areas (St. Johns River Water Management District, 2000) as part of the 1998 water-supply assessment. Water Resource Caution Areas are places where water-supply problems exist or where proposed ground-water withdrawals have been projected to result in substantial harm to surface- or ground-water resources.



Figure 1. Location of the St. Johns River Basin, central Florida.

The middle St. Johns River Basin (defined as the part of the basin from the confluence with the Econlockhatchee River to the confluence with the Wekiva River, fig. 1) is being preserved and restored through the State of Florida's Surface Water Improvement and Management (SWIM) Act. The Florida Legislature enacted the SWIM Act in 1987 to preserve water bodies that were in good condition and to restore some of the State's most important water bodies. The SJRWMD developed a SWIM plan for the middle St. Johns River Basin that focuses on nutrient load reduction, lake protection, and stormwater management (St. Johns River Water Management District, 2002).

Under section 303(d) of the Clean Water Act, every 2 years the State of Florida must identify water bodies that do not meet applicable water-quality standards by developing an impaired waters or 303(d) list. The impaired waters list is developed using a detailed methodology described in section 62-303.300 of the Florida Administrative Code. In general, a water body is placed on the impaired waters list if: (1) water-quality criteria established to maintain the water body's designated use, such as drinking water supply or recreation, propagation and maintenance of a healthy and well-balanced population of fish and wildlife, are not met; (2) the water body does not meet biological assessment thresholds; (3) the water body is acutely or chronically toxic; or (4) the water body exceeds narrative nutrient thresholds established by the State of Florida. Within the study area, parts of the St. Johns River, Econlockhatchee River, Blackwater Creek, Wekiva Springs, and Lake Monroe are identified as impaired waters on the Florida Department of Environmental Protection's (FDEP) 1998 303(d) list (St. Johns River Water Management District, 2002).

A total maximum daily load (TMDL) may be developed for streams, springs, and lakes in the study area that are on the verified impaired waters list developed by the FDEP. A TMDL is defined as the maximum amount of a constituent that a water body can absorb and still maintain its designated uses, such as drinking, fishing, or swimming. TMDLs include all existing and future loads from point sources such as municipal wastewater treatment facilities and industry; nonpoint sources such as runoff from agricultural areas, urban areas, and forests; and natural sources such as decaying organic matter and nutrients in the soil. The verified list of impaired waters is used to prioritize development of TMDLs in the State of Florida. The verified list of impaired waters is different from the impaired waters list described in the previous paragraph. Some water bodies may be included on the impaired waters list because water-quality criteria are

exceeded due to natural conditions or physical alterations of the water body not related to contaminants. These water bodies are not included on the verified list of impaired waters. The methodology used to develop the verified list of impaired waters is described in detail in section 62-303.400 of the Florida Administrative Code. More than 80 water bodies were included in the draft verified impaired waters list released by the FDEP in June 2003 (Florida Department of Environmental Protection, 2003a) for the middle St. Johns River Basin, including the St. Johns River, Econlockhatchee River, Wekiva River, Blackwater Creek, Lake Harney, Lake Monroe, Lake Jesup, and Blue Springs.

In 2000, the U.S. Geological Survey (USGS) and the SJRWMD began a 4-year study to characterize the streamflow and water quality of the St. Johns River in east-central Florida. Current (2004) information on streamflow and water-quality characteristics of the St. Johns River is needed by water resources planners to assess the feasibility of using the river as an alternate source of water supply and to design water treatment facilities. This information also may be used by water resources planners to conduct water-quality monitoring or modeling studies associated with other activities, such as implementing the middle St. Johns River SWIM Plan or the development of TMDLs.

Previous Studies

Several reports have presented information on lowflow characteristics of the St. Johns River and its tributaries. Lichtler and others (1968) presented low-flow frequency curves and flow-duration curves for sites on the St. Johns and Econlockhatchee Rivers based on data collected from 1934-62. Snell and Anderson (1970) presented flow-duration curves for sites on the St. Johns and Wekiva Rivers based on data collected from 1934-65. Heath and Wimberly (1971) determined flow-duration and low-flow frequency statistics based on data collected from 1933-65. Hughes (1981) presented low-flow frequency statistics based on data collected from 1933-77. Rumenik and Grubbs (1996) presented low-flow frequency statistics based on data collected from 1933-87. These previously published low-flow frequency and flowduration curves can be improved by incorporating additional streamflow data that were collected as part of USGS stream-gaging activities since 1987. In addition, previously published low-flow frequency and flow-duration statistics may not represent current (2004) conditions due to the rapid urbanization in the middle St. Johns River Basin.

Information has been published on the water quality of the St. Johns River and its tributaries. Lichtler and others (1968) presented the range of major ion and nitrate concentrations near Cocoa and Christmas from 1953-63. Goolsby and McPherson (1970) described the chemical and biological characteristics in the St. Johns River south of Lake Harney, based on 1969-70 data. DeMort (1990) presented summary statistics of selected water-quality constituents, based on 1974-79 data.

Purpose and Scope

The purpose of this report is to describe the streamflow and water-quality characteristics of the St. Johns River from downstream of Lake Poinsett to near DeLand. Streamflow characteristics were determined by using data collected by the USGS. Streamflow characteristics described include temporal trends and seasonal variations in streamflow. Flow-duration curves and low-flow frequency statistics also are presented. Temporal trends in streamflow were determined at sites with at least 10 years of data using the longest period of record available, which ranged from 16 years (water years 1985-2000) to 68 years (water years 1933-2000). The water year is the 12-month period from October 1 to September 30 and is designated by the calendar year in which it ends. Thus, the water year ending on September 30, 2000, is called water year 2000. Low-flow frequency statistics were computed using the longest period of trend-free record. Seasonal variations in streamflow were determined using data from water years 1985-2000. Flow-duration curves for St. Johns River sites were determined using data from water years 1957-2000. Flow-duration curves also were determined using data from water years 1985-2000 to compare streamflow characteristics among sites on the St. Johns River, Econlockhatchee River, Wekiva River, and Blackwater Creek.

Water-quality characteristics are described using retrospective information from 1991-99 at 15 sites on the St. Johns River and 1 site each near the mouths of the Econlockhatchee and Wekiva Rivers. Water-quality constituents described in this report include physical properties (water temperature, specific conductance, turbidity, and water color); dissolved oxygen concentration and water pH; major ions and other inorganic constituents such as silica, bromide, and sulfide; nutrients; organic carbon and ultraviolet light absorbance; phytoplankton chlorophyll-a; and total suspended solids. The retrospective data were augmented with biweekly data collected by the USGS during water years 2000-02 at four St. Johns River sites; continuous field properties data collected primarily during water years 2001-02 at four St. Johns River sites; and quarterly data collected

during water years 2000-02 from the Wekiva River, Blackwater Creek, and downstream of Blue Springs (in the spring run). Retrospective water-quality data included information from the FDEP, Florida Fish and Wildlife Conservation Commission (formerly the Florida Game and Freshwater Fish Commission), Orange County Department of Environmental Protection, SJRWMD, Volusia County Health Department, and the USGS. The occurrence of antibiotics, human prescription and nonprescription drugs, pesticides, and organic wastewater constituents were described at two St. Johns River sites using limited data collected in water years 2002-03. The occurrence of antibiotics, prescription and nonprescription drugs, pesticides, and a suite of organic constituents that may indicate industrial or domestic waste in water from a pilot water treatment facility on Lake Monroe was described using data from one sampling event conducted in March 2003. Variations in water-quality constituent values among sites are presented by comparing boxplots and summary statistics. Seasonal variations in water-quality constituent values are presented by comparing boxplots and plots of constituent values over time. Correlation coefficients are presented to quantify the relation between water-quality constituent values and streamflow. Temporal trend test results are presented for water-quality constituents for 1991-99. Water-quality constituent values are compared to 2000 Federal and State of Florida regulations.

Description of the Study Area

The study area includes about 90 mi of the St. Johns River from downstream of Lake Poinsett to near DeLand (fig. 1). The St. Johns River Basin within and upstream of the study area encompasses about 3,000 mi² and includes all or part of Brevard, Indian River, Lake, Okeechobee, Orange, Osceola, Seminole, and Volusia Counties. In 2000, the population of these counties was about 2.7 million (U.S. Bureau of Census, 2004).

Climate

The climate of the study area is humid subtropical. The study area normally (1961-90) receives about 50 inches (in.) of rainfall per year at the Orlando airport (Southeast Regional Climate Center, 2001). Over onehalf of the rainfall occurs from June through September (fig. 2), typically as localized, brief afternoon thunderstorms. The June through September rainy period commonly is referred to as the wet season. Tropical storms and hurricanes also periodically contribute rainfall during



Figure 2. Mean monthly temperature and rainfall at the Orlando airport, 1961-90.

the summer. The air temperature in the study area normally (1961-90) is highest in July and August and lowest in January and February (fig. 2). The normal maximum air temperature ranges from about 92 degrees Fahrenheit (°F) in July and August to about 72 °F in January and February. The normal minimum air temperature ranges from about 50 °F in February to 74 °F in August. Evapotranspiration (ET) generally is about the same magnitude as rainfall, averaging from 27 to 57 in. per year, depending on the land cover (Sumner, 1996; Swancar and others, 2000). ET in central Florida generally is highest in July and August and lowest in January and February (D. Sumner, U.S. Geological Survey, written commun., 2003).

Hydrogeologic Setting

The study area is underlain by a thick sequence (greater than 5,000 feet (ft)) of sedimentary rocks (Lichtler and others, 1968). The principal water-bearing units in the study area are the surficial and Floridan aquifer systems. These two units are separated by an intermediate confining unit.

The surficial aquifer system generally consists of fine-to-medium grained quartz sands that contain varying amounts of silt, clay, and loose shell fragments (Tibbals, 1990). Recharge to the surficial aquifer system primarily occurs by the infiltration of rainfall. Other sources of recharge to the surficial aquifer system include the land application of wastewater and reclaimed water, irrigation water, lateral ground-water inflow from adjacent areas, and upward leakage from the Floridan aquifer system. Discharge from the surficial aquifer system occurs by seepage to lakes, canals, and streams, by evapotranspiration where the water table is near the land surface, by pumping, and by downward leakage to the Floridan aquifer system.

The Floridan aquifer system is composed primarily of calcite and dolomite, with minor amounts of gypsum, apatite, glauconite, quartz (or chert), clay minerals, and trace amounts of metallic oxides and sulfide (Sprinkle, 1989). The uppermost stratigraphic units in the aquifer system are characterized by fractures and vuggy and cavernous porosity. In central Florida, the Floridan aquifer system consists of the Upper Floridan aquifer and the Lower Floridan aquifer, separated by a middle semiconfining unit. Both recharge and discharge areas to the Floridan aquifer system are present within the study area (Tibbals, 1990). Discharge areas generally are in the vicinity of the St. Johns and Wekiva Rivers and along the lower part of the Econlockhatchee River. The remainder of the study area consists of recharge areas to the Floridan aquifer system. Recharge to the Floridan aquifer system occurs by downward leakage from the surficial aquifer system, by lateral inflow of ground water from adjacent areas, and through drainage wells. Drainage wells primarily are used for control of lake levels and disposal of storm water by emplacing surface water into the aquifer. Spring flow, pumpage, and upward leakage to the surficial aquifer system are additional sources of discharge from the Floridan aquifer.

The vicinity of the St. Johns River generally is classified as a discharge area from the Floridan aquifer system. However, the intermediate confining unit generally varies from less than 50 to 150 ft thick in the vicinity of the St. Johns River (Murray and Halford, 1996); the confining unit probably retards movement of water from the Upper Floridan aquifer to the surficial aquifer system. As a result, discharge of water from the Upper Floridan aquifer to the river probably occurs through fractures or other karstic features. The presence of faults parallel to the St. Johns River from the headwaters to near the northern border of Orange County, from Lake Harney to Lake Monroe, and from Lake Monroe northward to Lake George were reported by Pirkle (1971).

The quality of water from the Upper Floridan aquifer varies greatly in central Florida. Total dissolved solids concentrations are used as an indicator of the mineral content of water. In the Upper Floridan aquifer in central Florida, total dissolved solids concentrations were reported to vary from less than 150 to greater than 2,000 mg/L (Lichtler and others, 1968; Tibbals, 1990; Adamski and German, 2004). Chloride concentrations in the Upper Floridan aquifer in central Florida were reported to vary from less than 10 to greater than 5,000 mg/L (Lichtler and others, 1968; Tibbals, 1990; Spechler and Halford, 2001; Adamski and German, 2004). The highest chloride and total dissolved solids concentrations in the Upper Floridan aquifer occur along the St. Johns River, especially south of Lake Harney (Spechler and Halford, 2001). The higher mineral content of water in this part of the Upper Floridan aquifer generally is attributed to incomplete flushing of seawater that entered the aquifer in the geologic past (Lichtler and others, 1968; Tibbals, 1990; Boniol, 1996).

Hydrologic Setting

The St. Johns River originates in the St. Johns River marsh (fig. 1). The river channel is poorly defined in the headwaters of the St. Johns River. Water from the marsh sheetflows north about 30 mi before the St. Johns River forms a distinct channel in the vicinity of Lake Hellen Blazes. The St. Johns River flows northward through Lake Hellen Blazes, Sawgrass Lake, Lake Washington, Lake Winder, and Lake Poinsett and then northwestward through Lake Harney and Lake Monroe. These lakes likely are relicts of an ancient estuary (White, 1970) rather than depressions formed by the dissolution of limestone, which generally is how most of the lakes in Florida were formed (Schiffer, 1998).

The St. Johns River has a low gradient—the river falls only about 30 ft from the source to the mouth (DeMort, 1990). Within the study area, the river does not have daily streamflow reversals due to tides. Backwater from tides within the study area, however, affects streamflow in the St. Johns River, especially at sites downstream from Lake Monroe. As a result of the very low gradient, a strong tide combined with low-flow conditions can cause periodic streamflow reversals in the St. Johns River as far upstream as Lake Monroe (DeMort, 1990). A strong northerly wind during low-streamflow conditions also may cause flow reversals in the river.

The Econlockhatchee and Wekiva Rivers are the two largest tributaries to the St. Johns River within the study area. The Econlockhatchee River is 35.8 mi long and has a drainage area of 270 mi² (St. Johns River Water Management District, 2002). The Econlockhatchee River originates in a wetlands area in northern Osceola County. The drainage basin of the Econlockhatchee River is composed of poorly drained soils and a high water table

with few areas of high ground-water recharge. The Econlockhatchee River is characterized by highly colored, acidic, slow-moving water containing little sediment (St. Johns River Water Management District, 2002). In 1992, the Florida Legislature designated the Econlockhatchee River an Outstanding Florida Water. Generally, permits cannot be issued for new direct discharges of contaminants into an Outstanding Florida Water that would lower the existing water quality (Florida Department of Environmental Protection, 2002). Contaminant discharges from tributaries or adjacent waters also must not significantly degrade an Outstanding Florida Water (Florida Department of Environmental Protection, 2002).

The Little Econlockhatchee River is the largest stream tributary to the Econlockhatchee River. Many miles of the Little Econlockhatchee River and its tributaries have been channelized to lower ground-water levels, resulting in a network of drainage ditches (St. Johns River Water Management District, 2002). These ditches also convey stormwater runoff from the Orlando metropolitan area to the Little Econlockhatchee River. Prior to 1983, the Little Econlockhatchee River received substantial amounts of municipal wastewater effluent from up to 12 facilities (St. Johns River Water Management District, 2002). By 1984, the effluent from most of these facilities was diverted to regional municipal wastewater facilities, which currently (2004) provide tertiary treatment.

The Wekiva River forms at the confluence of Wekiwa Springs Run and Rock Springs Run. The river flows approximately 14.2 mi to the St. Johns River. The drainage basin of the Wekiva River contains both springfed and blackwater streams. The two major tributaries to the Wekiva River are the Little Wekiva River and Blackwater Creek. The Wekiva River drains an area of rolling hills interspersed with lakes and sinks. Soils in the drainage basin generally are very sandy; a large portion of the basin is an area of high ground-water recharge (St. Johns River Water Management District, 2002). The flow of the Wekiva River is maintained by springs that discharge from the Upper Floridan aquifer. The Wekiva River was designated as an Outstanding Florida Water. Part of the Wekiva River was designated as a Florida Scenic and Wild River in 1982, and as a National Wild and Scenic River by the Federal Government in 2000.

Blue Springs is located to the east of the St. Johns River in Volusia County. The spring does not flow directly into the river, but vents into a 100-ft-diameter spring pool. From the spring pool, the water flows about 0.4 mi in a spring run to the river (Rosenau and others, 1977). Modifications were made to the St. Johns River upstream and within the study area. The U.S. Army Corps of Engineers (USACE) maintains a navigation channel on part of the river. The river channel is maintained at a 5-ft depth from Lake Harney to Sanford, and at an 8-ft depth from Sanford to DeLand (Tibbals, 1990). Prior to the 1930s, Lake Jesup was hydraulically connected to the St. Johns River by at least four channels. In the 1930s, the USACE replaced these channels with one navigation channel to improve accessibility to the lake by barge traffic (Belleville, 2000).

Historically, most of the floodplain of the upper St. Johns River (the reach from the headwaters to the confluence with the Econlockhatchee River) was a broad, shallow marsh (Sterling and Padera, 1998). By about 1970, approximately 70 percent of the floodplain marsh of the upper St. Johns River was drained by an extensive canal system to support the production of citrus, row crops, and beef cattle (Sterling and Padera, 1998). Some of these canals diverted water outside of the St. Johns River Basin to the Indian River Lagoon. In addition, there were more than 40 private pumping stations throughout the upper St. Johns River Basin that discharged agricultural runoff directly into the river (U.S. Environmental Protection Agency, 2002). These modifications resulted in a reduction of water storage areas, increased nutrient concentrations in water and bottom sediments, altered hydroperiods, and excessive amounts of freshwater discharging to the Indian River Lagoon (St. Johns River Water Management District, 2003). In 1988, a construction project co-sponsored by the SJRWMD and the USACE began to restore part of the upper St. Johns River Basin-about 240 mi² of wetlands were enhanced or restored, nine canals were plugged (Sterling and Padera, 1998), and some of the agricultural pumping stations were eliminated (Fall, 1990). Restored wetlands consist of marsh conservation areas and water management areas. Marsh conservation areas provide temporary storage of floodwaters and reduce the need to discharge freshwater to the Indian River Lagoon (Sterling and Padera, 1998). Water management areas store and treat agricultural drainage and provide water supply for agricultural purposes (Sterling and Padera, 1998).

Land Use and Land Cover

Wetlands, agriculture, forests, and urban are the predominant land use and land covers in the study area (fig. 3). Wetlands make up about 31 percent of the study area and generally border the St. Johns River, especially in the upstream reaches. About 25 percent of the study

Introduction 9



Figure 3. Generalized land use and land cover in the study area, 1999.

area is agricultural land, mostly concentrated in the southern part of the area. The primary agricultural products are beef cattle, citrus, and vegetables. About 70 percent of the agricultural land is pasture-most of which is unimproved (according to 1995 land-use data from the St. Johns River Water Management District). In some areas of Florida, pastures are planted with grasses, such as Bahia grass, and are referred to as improved pasture. Citrus is the most important crop in the study area; citrus groves comprise about 13 percent of the agricultural land. About 70 percent of the citrus groves are located in the extreme southeastern part of Indian River County. Surface water primarily is used to irrigate citrus in Indian River County. In 1996, 158 million gallons per day (Mgal/d) was used for citrus irrigation in this county; 75 percent of the water was from surface-water sources (Florence and Moore, 1999). Citrus crops typically are fertilized one to two times per year using slow-release fertilizers (Ferguson, 1995). In 1992, approximately 80 percent of the growers surveyed reported that their crops were irrigated with microsprinklers or drip systems and 60 percent of these systems also were designed for fertigation (Ferguson, 1995). Fertigation systems deliver both irrigation water and liquid fertilizer.

Approximately 30,000 tons of nitrogen fertilizer and about 5,200 tons of phosphorus fertilizer were sold in 1997 in the counties within and upstream of the study area (D. Lorenz, U.S. Geological Survey, written commun., 1999). Approximately 18,700 tons of nitrogen and 5,400 tons of phosphorus in these counties were generated each year as part of livestock manure, based on 1997 data (B. Ruddy, U.S. Geological Survey, written commun., 1999). Fertilizer sales data were compiled based on State sales totals. County-level fertilizer sales data were estimated by disaggregating the State fertilizer sales totals based on agricultural land cover. As a result, these data underestimate fertilizer use in areas where non-agricultural fertilizer use may be substantial, such as the Orlando metropolitan area. The largest amounts of fertilizer sold, in terms of total amounts and amount per area, were in Indian River and Orange Counties. The largest amount of nitrogen and phosphorus generated as part of livestock manure, again in terms of total amounts and amount per area, were in Okeechobee and Orange Counties; however, Okeechobee County accounts for a small part of the study area (about 3 percent).

Forests cover about 16 percent of the study area, and are concentrated in the northern part of the study area. Urban land comprises about 14 percent of the study area, and is concentrated in the Orlando metropolitan area and in the cities of Cocoa and Titusville. St. Augustine grass is the most commonly planted turfgrass in the urban areas in Florida (Trenholm and others, 2000). Two to six fertilizer applications from March-October are recommended for St. Augustine grass (Trenholm and others, 2000). Fertilizer containing nitrogen (50 percent soluble and 50 percent slow release), phosphorus, and potassium is recommended to be applied in March and October.

Wastewater

In 1995, 240 Mgal/d of municipal wastewater was discharged in Brevard, Indian River, Lake, Okeechobee, Orange, Osceola, Seminole, and Volusia Counties (Marella, 1999). Approximately 65 percent of this wastewater was treated and discharged to the ground. Municipal wastewater is discharged to streams by a few facilities in the study area. The largest of these is a tertiary treatment facility located on the Little Econlockhatchee River. In 2003, this facility had a total permitted capacity of 40 Mgal/d (Florida Department of Environmental Protection, 2003b). About one-half of the treated wastewater from this facility is discharged to the Little Econlockhatchee River; the remaining effluent is discharged to a constructed wetlands area where it undergoes further nitrogen and phosphorus removal (City of Orlando, 2002). The effluent from the constructed wetlands flows through a State-owned reserve and discharges into the St. Johns River.

Septic tanks are prevalent in the study area (St. Johns River Water Management District, 2002) and also may be a source of contaminants to the St. Johns River. Within the middle St. Johns River Basin, there are approximately 176,000 septic systems (Florida Department of Environmental Protection, 2003c). When septic systems fail, inadequately treated wastewater may be transported to streams by runoff or as ground-water inflow.

Approach and Methods

Streamflow characteristics are described in this report by using flow-duration hydrographs, flow-duration statistics and curves, and low-flow frequency statistics. Flow-duration hydrographs show the general pattern and variability in streamflow that occurs during the year, based on a given period of record.

Flow-duration curves show the percent of time streamflows are equaled or exceeded during a given period (Searcy, 1959). The shape of the flow-duration curve provides information about the hydrologic characteristics and variability of streamflow in a drainage basin. A flow-duration curve with a steep slope results from a stream with highly variable flow, whereas a flowduration curve with a flat slope indicates the presence of surface- or ground-water storage that tends to minimize streamflow variations. The shape of the flow-duration curve may vary depending upon the period of record selected for analysis, particularly at the low-flow end. The longer the period of record selected for analysis, the more the flow-duration curve will represent long-term conditions.

Low-flow frequency statistics relate the magnitude of a low-flow event to its average frequency of occurrence. Low-flow frequency statistics commonly are used to evaluate the water-supply and waste-dilution potential of streams, and to establish minimum streamflows for regulatory purposes.

The water quality of the St. Johns River and selected tributaries was characterized by using several sources of information, including retrospective data, biweekly data at selected St. Johns River sites from 2000-02, and continuous physical properties data. The primary sources of water-quality data used in this report were the retrospective and biweekly data. Retrospective data from 1991-99 were used to document water-quality conditions at a greater number of sites than could be sampled on a biweekly basis from 2000-02, to characterize water-quality conditions over a wider range of hydrologic conditions compared to 2000-02, and to assess temporal trends in constituent values. Biweekly data from 2000-02 at selected St. Johns River sites were used to provide more frequent information to augment the retrospective data (which generally were collected monthly or bimonthly), and to provide information on a wider range of constituents compared to the retrospective data. Quarterly waterquality data also were collected from the Wekiva River and Blackwater Creek from 2000-02 to provide information on the quality of tributary inflow to the St. Johns River. Water-quality data were collected quarterly downstream of Blue Springs (in the spring run) from 2000-02 as part of USGS data collection activities (U.S. Geological Survey, 2000; 2001; 2002). These data were compiled to document the quality of springflow to the St. Johns River and to better explain the spatial variation in constituent values along the river.

Continuous specific conductance data were collected primarily in water years 2001 and 2002 at four sites to provide more detailed information on the variability of dissolved inorganic constituents in the St. Johns River. Specific conductance is an indicator of the concentration of dissolved inorganic constituents in the water. In the upstream part of the study area, highly mineralized water was reported in the river during drought conditions (Lichtler and others, 1968), which would influence water treatment strategies. Streamflow reversals occur in the St. Johns River as a result of wind and tidal effects, which also may influence inorganic constituent concentrations.

Streamflow Data

Streamflow data were compiled from the USGS National Water Information System (NWIS). Continuous data were obtained from eight sites on the St. Johns River, the Econlockhatchee River, Wekiva River, and Blackwater Creek (sites 1, 3, 6, 8, 12, 14, 15, and 21; fig. 4, table 1). Data were not compiled from other sites with continuous streamflow data because these sites generally had 2 years or less of data. This period is too short to develop flowduration curves, which are representative of long-term conditions, or accurate low-flow frequency statistics. Although there was less than 10 years of streamflow data from the Sanford site (site 12, fig. 4, table 1), these data were compiled and analyzed because the St. Johns River in the vicinity of the Sanford site may be used as an alternate source of water supply in central Florida.

Retrospective Water-Quality Data

Water-quality data were available from approximately 100 sites on the St. Johns River and its direct tributaries within the study area from the U.S. Environmental Protection Agency's STORET Legacy Data Center. At least 20 years of water-quality data collected on a regular frequency were available from some sites. Water-quality data also were available for periods spanning 20 to 30 years at other sites, but with large gaps in the period of record. Data were reported from only one sampling event at many sites. At other sites, no waterquality data had been collected recently; the most recent data were about 20 to 30 years old.

The criterion for inclusion of retrospective waterquality data for this study was that a minimum of 4 years of data collected at least quarterly were available at a site from 1991-99. This criterion was established to obtain data representing more recent conditions and to reduce the amount of data to be analyzed to a size manageable within the timeframe of this study. Thirty water-quality sites sampled by the FDEP, Florida Fish and Wildlife Conservation Commission (FFWCC), Orange County Department of Environmental Protection (hereinafter referred to as Orange County), SJRWMD, Volusia County Department of Environmental Health (hereinafter referred to as Volusia County), and USGS met this criterion (app. A). Data from Orange County, the SJRWMD, and Volusia

Table 1. Locations of sites with streamflow and water-quality data analyzed in this study.

Map ID (fig. 4)	Station name	Period of record for streamflow data (water years)	Stream- flow data	Period of record for retrospective data (calendar years)	Retrospective water-quality data	2000-02 water-quality data
1	St. Johns River near Cocoa	1953-2000	х	1979-99	х	Х
2	St. Johns River at Beeline Highway			1988-99	х	
3	St. Johns River near Christmas	1933-2000	х	1980-99	х	Х
4	St. Johns River at Orange Mound			1981-99	х	
5	St. Johns River at Puzzle Lake			1980-81, 1983-99	Х	
6	Econlockhatchee River near Chuluota	1935-2000	х			
7	Econlockhatchee River near the mouth			1973-99	х	
8	St. Johns River above Lake Harney near Geneva	1982-2000	х	1980-99	х	
9	St. Johns River at north end of Lake Harney			1981-99	х	
10	St. Johns River at Lemon Bluff			1991-99	Х	
11	St. Johns River at State Road 415 bridge			1991-99	х	
12	St. Johns River near Sanford	1987-1989, 1996-2000	х	1968-99	х	Х
13	St. Johns River south of the confluence with the Wekiva River			1987-99	Х	
14	Wekiva River near Sanford	1935-2000	х			Х
15	Blackwater Creek near Cassia	1968-1969, 1985-2000	х			х
16	Wekiva River near the mouth			1987-99	х	
17	St. Johns River north of the confluence			1987-99	х	
	with the Wekiva River					
18	St. Johns River downstream of Blue Springs			1991-99	х	
19	Blue Springs near Orange City					х
20	St. Johns River near Hontoon Marina			1991-99	Х	
21	St. Johns River near DeLand	1933-2000	х	1948-95	Х	Х

County were available from both the U.S. Environmental Protection Agency's STORET Legacy Data Center and the agency's internal database. Data from these three agencies were obtained from the internal databases instead of from the STORET Legacy Data Center because personnel of these agencies indicated their databases were the best sources of data.

Data were compiled on water pH, specific conductance, water temperature, and concentrations of nutrients, dissolved oxygen, phytoplankton chlorophyll-*a*, and total suspended solids because information on these constituents is necessary to assess the feasibility of using the St. Johns River as an alternate source of water supply. Information on water color and concentrations of major ions, organic carbon, and total dissolved solids also is needed to assess the feasibility of using the river as a source of water supply. Information on these constituents was not compiled, however, because the period of record for these data was limited. Water-quality samples collected by the FFWCC, Orange County, USGS, and Volusia County were analyzed by the respective agency's laboratory. Some samples collected by the SJRWMD were analyzed by the agency's laboratory. When the sample backlog at the SJRWMD laboratory became too great, however, waterquality samples were sent to several contract laboratories for analysis (S. Connors, Database Manager, St. Johns River Water Management District, written commun., 2001).

Specific conductance and water pH data were reported as determined in the field or laboratory. In this report, specific conductance and water pH values determined in the field were used as the primary source of information. For dates when no field-determined values were available, laboratory-determined values were used to supplement the record. There may be substantial differences between field- and laboratory-determined specific conductance and water pH values, especially for water pH values because biological processes can influence

Figure 4. Location of study area and stream sites.

streamwater pH. Paired field- and laboratory-determined water pH values were compiled and analyzed from the retrospective data to determine whether there was any significant difference between field- and laboratorydetermined values. Paired field- and laboratory-determined water pH values were available at three sites with retrospective data (table 2). The sign test (Helsel and Hirsch, 1992) was used to quantify differences between field- and laboratory-determined water pH values. The exact form of the test was used when comparing sample sizes less than 20. No statistically significant differences were found at the 0.05 significance level.

Nutrient data compiled for this report consisted of ammonia nitrogen, nitrate nitrogen, organic plus ammonia nitrogen (Kjeldahl), total phosphorus, and orthophosphate concentrations. Ammonia data were reported as "total" or "dissolved" concentrations. Throughout this report, the term "total" refers to a concentration determined on an

Table 2. Retrospective water-quality sites with paired field- and laboratory-determined water pH values and sign test results.

[FDEP, Florida Department of Environmental Protection; USGS, U.S. Geological Survey; p, p-value; n, number of samples]

Map ID (fig. 4)	Station name	Agency	Sign test results
8	St. Johns River upstream of Lake Harney, near Geneva	FDEP	p = 0.3036, n = 15
12	St. Johns River near Sanford	FDEP	p = 0.4018, n = 16
21	St. Johns River near DeLand	USGS	p = 0.4207, n = 24

unfiltered sample, and the term "dissolved" refers to a concentration determined on a filtered sample. Total ammonia concentration data were used as the primary source of retrospective data because most agencies reported total ammonia concentrations. Dissolved ammonia concentration data were used to supplement the record when total ammonia concentration data were not available.

Total nitrite-plus-nitrate, dissolved nitrite-plusnitrate, or total nitrate concentrations were reported by agencies having retrospective information. These three constituents were combined and are referred to collectively as nitrate concentrations throughout the remainder of this report. Aggregating these three constituents was considered valid because nitrite concentrations generally are small compared to nitrate, and nitrate generally occurs in the dissolved phase because nitrate as a negatively charged species does not sorb to sediment particles.

Total organic-plus-ammonia nitrogen (Kjeldahl) concentration data generally were available from all of the agencies having retrospective data, except the FFWCC. Water-quality data obtained from the FFWCC reported total ammonia nitrogen and total organic nitrogen concentrations separately. Total organic-plus-ammonia nitrogen concentrations were calculated at sites sampled by the FFWCC by summing total organic nitrogen and total ammonia nitrogen concentration data. In this calculation, censored values (values below the method reporting limit) were set to one-half the reporting limit.

Orthophosphate concentration data were reported as determined on filtered or unfiltered samples, depending on the agency. Total and dissolved concentrations of these two constituents were combined and are referred to as orthophosphate concentrations throughout this report. Preliminary analyses of the data indicated little difference between the total and dissolved forms of orthophosphate. Chlorophyll-*a* concentration data were reported as determined by using the spectrophotometric method or the trichromatic method. Only chlorophyll-*a* concentration data reported as determined by the spectrophotometric method were compiled because the trichromatic procedure does not correct measured concentrations for interferences caused by the presence of pheophytin-*a*, a chlorophyll degradation product (American Public Health Association, 1986).

Water-quality data were qualified by using several types of remark codes. USGS concentration data below the method reporting limit were qualified using a "<" (less-than) remark code. Water-quality data from the FDEP, Orange County, SJRWMD, and Volusia County were qualified by several remark codes (table 3). Data values with a remark code of "J," which indicated the value was estimated and not the result of a laboratory or field analysis, were not compiled in this report. Method detection limits associated with the remark codes "I," "T," "U," and "W" were obtained from the FDEP, FFWCC, Orange County, and Volusia County. Method detection limits associated with the SJRWMD data were not readily available. Method detection limits for SJRWMD data were assumed to be the highest concentration reported with the remark codes "K," "U," "I," "T," or "W."

Table 3. Remark codes associated with retrospective water-qualitydata collected by Florida Department of Environmental Protection,Orange County, Volusia County, and the St. Johns River WaterManagement District.

Remark code	Explanation
Ι	The value reported is less than the practical quantifi- cation limit and higher than or equal to the method detection limit.
J	Estimated. Value shown is not a result of analytical measurement.
K	Off-scale low. Actual value not known, but known to be lower than value shown.
L	Off-scale high. Actual value not known, but known to be higher than value shown.
Q	Sample held beyond normal holding time.
Т	Value reported is less than the criterion of detection.
U	Material was analyzed, but not detected. Value stored is the limit of detection for the process in use.
W	Value observed is less than the lowest value reportable under remark "T."

Table 4. Censoring limits applied to retrospective water-quality data.

[FDEP, Florida Department of Environmental Protection; FFWCC, Florida Fish and Wildlife Conservation Commission; Orange County, Orange County Department of Environmental Protection; SJRWMD, St. Johns River Water Management District; Volusia County, Volusia County Department of Environmental Health; USGS, U.S. Geological Survey. All units in milligrams per liter; N, nitrogen; P, phosphorus]

Agency Nitrate (as N)		Organic plus ammonia nitrogen (as N)	Total phosphorus	Orthophosphate (as P)	Total suspended solids	Ammonia (as N)
FDEP	0.01	0.12	0.01	Not compiled	Not compiled	0.02
FFWCC	.06	.08	No data	Not compiled	No data	.08
Orange County	.02	.4	.01	0.01	2	.02
SJRWMD	.02	.1	.01	.02	10	.01
Volusia County	.02	.3	.06	.006	4	Not analyzed
USGS	.05	No censored data	.01	.01	Not compiled	.01

Water-quality data from agencies other than the USGS were censored at twice the method detection limit to minimize the risk of utilizing false negative measurements. Table 4 shows the censoring limits used in this report. A false negative is defined as a constituent reported as not being present in the sample when it is present at a concentration greater than the method detection limit. Childress and others (1999) reported that a sample with a true concentration at the method detection limit calculated according to U.S. Environmental Protection Agency (USEPA) procedures has a 50-percent chance of being reported as a false negative. Chlorophyll-*a* data were analyzed as reported and not censored because no information was available on method detection limits.

Retrospective water-quality data were available from two or more agencies at several St. Johns River sites and near the mouths of the Econlockhatchee and Wekiva Rivers. Water-quality data from these sites were pooled; this resulted in data from a total of 17 sites (table 1, fig. 4). There may be differences in constituent values reported by the agencies as a result of differences in sampling, processing, and analytical methods. Differences in constituent concentrations reported among the various agencies were not assessed due to insufficient data.

Data Collected for this Study

From January 2000 to September 2002, biweekly water-quality data were collected at four St. Johns River sites (sites 1, 3, 12, and 21), and quarterly data were collected from sites on the Wekiva River near Sanford and Blackwater Creek sites (sites 14 and 15) (fig. 4). All sites sampled from 2000-02 were co-located with existing

USGS stream-gaging sites because water-quality constituent concentrations often vary with streamflow. Waterquality samples at each of these sites were analyzed to determine concentrations of about 40 inorganic constituents (app. B). Total calcium, total magnesium, total barium, total strontium, total nitrite-plus-nitrate, total nitrite, and total organic carbon concentrations were determined only during water years 2000-01. Total organic-plus-ammonia nitrogen concentrations were determined only in water year 2002. In addition, guarterly major ion, nutrient, and trace constituent data collected as part of the USGS network (U.S. Geological Survey, 2000; 2001; 2002) at Blue Springs (site 19, fig. 4) were included in some analyses. That site is in the spring run, downstream of the spring pool but upstream of backwater from the St. Johns River.

Limited sampling was conducted at two St. Johns River sites (sites 1 and 12, fig. 4) in water years 2002 and 2003 to determine the occurrence of human and veterinary antibiotics, other human prescription and nonprescription drugs, and a suite of organic constituents that may indicate domestic or industrial waste (app. B). More than 70 constituents were included in this suite of organic constituents, such as, pesticides, plasticizers, fragrances, fire retardants, detergent metabolites, and disinfectants. Site 1 was sampled three times from December 2001 to August 2002. Human and veterinary antibiotics and the suite of organic constituents that may indicate wastewater were analyzed at this site. Site 12 was sampled three times from June 2002 to March 2003. One set of samples also was collected in March 2003 at a pilot water treatment facility on Lake Monroe to determine the occurrence of these organic constituents: (1) in the influent water to the pilot

Map ID (fig. 4)	Station name	Urban	Agriculture	Range- land	Upland forests	Water	Wetlands	Barren land	Transportation, communication, and utilities	Not classified
1	St. Johns River near Cocoa	5.3	44.5	5.2	8.7	3.6	29.3	0.7	0.7	1.1
3	St. Johns River near Christmas	6.2	39.7	6.9	10.4	3.4	30.9	.6	.9	.9
12	St. Johns River near Sanford	11.0	27.5	7.1	14.7	5.2	32.2	.5	1.3	.5
14	Wekiva River near Sanford	45.5	9.0	6.2	15.0	4.4	18.0	.3	1.6	0
15	Blackwater Creek near Cassia	11.1	17.0	6.0	32.5	6.1	26.6	.4	.1	0
21	St. Johns River near DeLand	13.8	25.4	6.9	16.0	5.1	30.6	.5	1.2	.5

Table 5. Land-use and land-cover percentages of the drainage area upstream of the sites sampled for this study.[Percentages may not total 100 due to rounding]

plant; (2) at the point in the treatment process immediately before reverse osmosis; and (3) in the finished water. Human and veterinary antibiotics were not analyzed in these samples because none were detected at sites 1 and 12. The March low-flow period was selected because preliminary results from sampling at sites 1 and 12 indicated more constituents generally were detected at greater concentrations during low-flow periods.

Land use and land cover varied among the sites sampled, based on 1995 data from the SJRWMD. The drainage areas of the Cocoa and Christmas sites (sites 1 and 3, fig. 4) contained the greatest percentage of agricultural land, about 40 percent (table 5). The area surrounding the Wekiva River near Sanford site (site 14) had the greatest percentage of urban land of the sites sampled; almost one-half of the drainage area of this site was composed of urban land.

Sample Collection and Analysis Methods

For this study, most water-quality data were collected in accordance with USGS protocol (U.S. Geological Survey, 1997-99). Stream velocities generally were too low to use isokinetic depth-integrating samplers (U.S. Geological Survey, 1997-99); water samples were collected at three points across the stream using a weighted glass bottle. The glass bottle was lowered from the surface to the bottom of the water column at each point to obtain a depth-integrated sample. Field measurements of water temperature, specific conductance, water pH, and dissolved oxygen concentration also were made at the time of sampling. Prior to sampling, water-quality equipment was decontaminated by soaking in a 2 percent solution of LiquinoxTM and tap water, rinsed with tap water, then rinsed with deionized water, and allowed to air dry. Equipment used to collect and process samples

that were analyzed to determine concentrations of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and the suite of organic constituents that may indicate domestic or industrial waste also were rinsed with pesticide-grade methanol to remove any trace amounts of these constituents prior to sampling. Decontaminated sampling equipment was stored in clean plastic bags prior to use. Prior to sample collection, all equipment was rinsed with native stream water. Samples analyzed for dissolved inorganic constituents were filtered through a 0.45-micron (μ) encapsulated filter. Samples analyzed for human and veterinary antibiotics and other human prescription and nonprescription drugs were filtered through a 0.7-µ nominal pore size glass-fiber filter (precombusted at 450 degrees Celsius (°C)). Dissolved and total organic carbon samples were collected at the center of the stream by using a weighted glass bottle (precombusted at 450 °C). The protocol for processing dissolved organic carbon samples changed during this study from filtering through a 0.45-µ silver filter to filtering through a 0.45-µ encapsulated filter due to the decreasing availability of silver filters. There is no significant difference between the results obtained using silver filters and encapsulated filters (U.S. Geological Survey Office of Water Quality Technical Memorandum 2000.08). Dissolved organic carbon samples collected from January 2000 through February 2001 were filtered through a 0.45-µ silver filter. From March 2001 to September 2002, dissolved organic carbon samples were filtered through a 0.45-µ encapsulated filter and preserved with 1 milliliter (mL) of 4.5N sulfuric acid. Equipment used to filter dissolved organic carbon samples was rinsed with water certified to be free of carbon and wrapped in aluminum foil in accordance with USGS protocol (U.S. Geological Survey, 1997-99). Sulfide samples were collected as surface grab samples at the center of the

stream and were preserved immediately with sodium hydroxide and 0.5 gram of zinc acetate. Samples analyzed for major cations, such as calcium and magnesium, were preserved with 2 mL of 6N nitric acid. Samples analyzed to determine total phosphorus concentrations were preserved with 1 mL of 4.5N sulfuric acid. Chlorophyll-*a* samples were filtered through a 0.7- μ glass-fiber filter which was wrapped in aluminum foil and kept frozen until shipped to the laboratory.

Most water-quality samples were analyzed at the USGS Water Quality and Research Laboratory in Ocala, Florida. Samples were analyzed at the USGS National Water-Quality Laboratory in Denver, Colorado, to determine human prescription and nonprescription drugs and the suite of organic constituents that may indicate domestic or industrial waste. Analytical methods used to determine constituent concentrations are listed in appendix B.

Quality Assurance

Information on the bias and variability in a data set is necessary to correctly interpret water-quality data. Bias and variability may exist in a data set as a result of sample collection, processing, or analytical procedures. Bias is the systematic error inherent in a method and may be either positive or negative. Positive bias may result from the introduction of contaminants into the sample during sampling or processing procedures, laboratory analysis, exposure to airborne gases and particulates, or due to inadequately cleaned sample collection or analytical equipment. Variability is the random error in independent measures of the same quantity.

Contamination bias was assessed in the data collected as part of this study by collecting 16 field blank samples. A field blank is a water sample that is intended to be free of the analytes of interest and is prepared at the sampling location. No field blank samples were analyzed to determine concentrations of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, or the suite of organic constituents that may indicate domestic or industrial waste. Field blank samples were prepared as described by Mueller and others (1997). Briefly, field blank samples were prepared by pouring water, certified by the USGS to be free of the constituents listed in table 6, through all of the sample collection and splitting equipment as if an environmental sample were being processed. These samples were filtered, preserved, and shipped to the laboratory according to USGS protocol (U.S. Geological Survey, 1997-99).

Contamination bias in the water-quality data was quantified by constructing an upper tolerance bound on the field-blank concentration data. A tolerance bound is a statistical interval that contains a specified proportion of a sampled population. In analyses of water-quality data, an upper tolerance bound is constructed to determine a limiting concentration that most values do not exceed. Because the distributions of the field-blank concentration data were highly skewed, distribution-free methods (Hahn and Meeker, 1991) were used to calculate upper tolerance bounds. Upper tolerance bounds, which 85 percent of the concentrations generally did not exceed, were calculated with a 70-percent confidence level (table 6). The 70percent confidence level was selected because there were not sufficient field-blank data to calculate upper tolerance bounds with a greater confidence level.

Variability was assessed in the data collected as part of this study by collecting 12 concurrent replicate samples. Concurrent replicate samples are used to assess the variability introduced by sample collection, processing, handling, and laboratory analysis procedures. Concurrent replicate samples were prepared by collecting two waterquality samples at approximately the same time. Each of the samples was processed and analyzed separately. No concurrent replicate samples were analyzed to determine concentrations of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, or the suite of organic constituents that may indicate domestic or industrial waste.

The variability in constituent concentrations was quantified by calculating the mean relative standard deviation for each of the constituents. The relative standard deviation is defined as the standard deviation divided by the mean concentration. Censored values were handled in the calculation by arbitrarily setting each censored value to one-half the method reporting limit.

The constituents with the widest variability were chlorophyll-*a*, turbidity, total suspended solids, total ammonia nitrogen, and sulfide (table 7). The mean relative standard deviation was greater than 10 percent for these constituents. The large variability in chlorophyll-*a* concentrations (38 percent) primarily resulted from four pairs of replicate samples in which chlorophyll-*a* was detected in one sample but not in the other. When these four pairs were eliminated from the analysis, the variability in chlorophyll-*a* concentrations was 11.1 percent for the remaining eight pairs. Wider variability in chlorophyll-*a*, turbidity, total dissolved solids, total ammonia nitrogen, and sulfide concentrations was consistent with the precision of the laboratory analytical methods.

Table 6. Statistical summary of field-blank samples for water-quality data collected for this study.

[mg/L, milligrams per liter; <, less than; µg/L, micrograms per liter; NTU, nephelometric turbidity units; µS/cm, microsiemen per centimeter; °C, degrees Celcius; nm, nanometers; cm, centimeters]

Constituent	Number of field- blank samples	Method reporting limit	Upper tolerance bound for 85 percent of the samples
Total sulfide, mg/L	13	1	<1*
Dissolved calcium, mg/L	16	.02	.06
Dissolved magnesium, mg/L	16	.03	<.03
Dissolved sodium, mg/L	16	.1	<.1
Dissolved potassium, mg/L	16	.1	<.1
Dissolved chloride, mg/L	16	.05	.06
Dissolved sulfate, mg/L	16	.07	<.07
Dissolved silica, mg/L	16	.01	.04
Dissolved barium, µg/L	16	.5	<.5
Dissolved iron, µg/L	16	2	<2.0
Total iron, µg/L	16	2	2.9
Dissolved strontium, µg/L	16	.5	<.5
Dissolved bromide, mg/L	16	.05	<.05
Dissolved ammonia nitrogen, mg/L as nitrogen	16	.01	<.01
Total ammonia nitrogen, mg/L as nitrogen	16	.01	.01
Dissolved nitrite nitrogen, mg/L as nitrogen	16	.01	<.01
Dissolved nitrite plus nitrate nitrogen, mg/L as nitrogen	16	.02	<.02
Total phosphorus, mg/L	16	.02	<.02
Dissolved orthophosphate phosphorus, mg/L as phosphorus	16	.01	.02
Total orthophosphate phosphorus, mg/L as phosphorus	16	.01	.02
Dissolved organic carbon, mg/L	16	.1	3.2
Turbidity, NTU	16	.05	.40
Color, platinum-cobalt units	16	5	<5
Laboratory specific conductance, µS/cm	16	1	2
Total nonfilterable residue at 105 °C (total suspended solids), mg/L	16	1	1
Dissolved residue at 180 °C (total dissolved solids), mg/L	16	1	6
Phytoplankton chlorophyll <i>a</i> , µg/L	13	.1	<.1*
Acid-neutralizing capacity, mg/L	16	1	5.50
Ultraviolet absorbance at 254 nanometers, cm ⁻¹	16	.001	.004

*70-percent upper tolerance bound for 60 percent of the samples.

Table 7. Variability in constituent values for water-quality data collected for this study.

[°C, degrees Celcius; nm, nanometers]

Constituent	Mean relative standard deviation (in percent)
Total sulfide	10.2
Dissolved calcium	.4
Dissolved magnesium	1.1
Dissolved sodium	1.6
Dissolved potassium	.8
Dissolved chloride	1.2
Dissolved sulfate	1.0
Dissolved silica	.3
Dissolved barium	1.4
Dissolved iron	4.6
Total iron	4.3
Dissolved strontium	1.2
Dissolved bromide	9.7
Dissolved ammonia nitrogen	4.9
Total ammonia nitrogen	11.9
Dissolved nitrite nitrogen	3.9
Dissolved nitrite plus nitrate nitrogen	4.9
Total phosphorus	6.3
Dissolved orthophosphate phosphorus	5.7
Total orthophosphate phosphorus	7.8
Dissolved organic carbon	4.5
Turbidity	12.2
Color	8.3
Laboratory specific conductance	.6
Total nonfilterable residue at 105 °C (total suspended solids)	11.7
Dissolved residue at 180 °C (total dissolved solids)	1.1
Phytoplankton chlorophyll-a	38.0*
Acid-neutralizing capacity	.5
Ultraviolet absorbance at 254 nm	0

*Mean relative standard deviation was 11.1 percent when four pairs of replicate samples were eliminated from the analysis.

The laboratory reported a relative standard deviation of 13.9 percent for chlorophyll-*a*, 15.8 percent for turbidity, 9.2 percent for total suspended solids, 8.7 to 12.2 percent for total ammonia nitrogen depending upon the concentration range measured, and 18.6 percent for sulfide (U.S. Geological Survey, 1999). The variability in the other constituents was reported to range from 0.5 to 8.7 percent (U.S. Geological Survey, 1999).

Continuous Monitoring Data

Four St. Johns River sites (sites 1, 3, 12, and 21) were monitored continuously primarily in water years 2001-02 using a YSI model 600XL sonde to determine water temperature and specific conductance. Fouling and calibration drift affects data from continuous monitors. Continuous monitors at all sites were inspected, cleaned, and calibrated according to USGS protocol (Wagner and others, 2000) to ensure verifiable results. Sensors on the YSI model 600XL sondes generally were cleaned biweekly.

Data Analysis Methods

Low-flow frequency statistics and flow-duration curves determined from data with significant temporal trends do not represent current conditions. Temporal trends in streamflow were determined using Kendall's tau (Helsel and Hirsch, 1992) to select the longest period of record of trend-free data. The 0.05 significance level was used as the criterion for statistical significance. Locallyweighted scatterplot (LOWESS) smoothing, a robust smoothing technique (Helsel and Hirsch, 1992), also provided information on significant trends in streamflows.

Flow-duration curves were constructed as described by Searcy (1959). Briefly, daily-mean streamflows were ranked according to magnitude and placed into about 30 class intervals. Each class interval represented an incremental range in daily-mean streamflow. The percentage of time daily-mean streamflows in each class interval were equaled or exceeded was computed. The lower limit of each class interval was plotted on the y-axis, and the percentage of time daily-mean streamflows in each class interval were equaled or exceeded was plotted on the x-axis (on a probability scale), and a smooth curve was drawn through the data. From this smooth curve, dailymean streamflows that were equaled or exceeded 99, 98, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 2, and 1 percent of the time were determined.

To compare streamflow characteristics among sites, flow-duration curves were constructed for the same time period. Flow-duration curves constructed with data from different time periods may be substantially different because one time period used in the analyses may not have included an important high- or low-flow event. At least 40 years of daily-mean streamflow data were available at most of the St. Johns River sites (table 1). A shorter period of record (less than 20 years) was available at two St. Johns River sites (sites 8 and 12) and at the Blackwater Creek near Cassia (site 15). For the two St. Johns River sites, flow-duration curves were adjusted to longer time periods by using the graphical-correlation method described by Searcy (1959). In this method, a relation was

established between the flow-duration curve for the site with the shorter record and the site with the longer record (termed an index site). This relation was used to estimate the duration curve (based on the longer period of record) at the site with the shorter streamflow record. In this report, the 1-, 2-, 5-, 10-, 15-, 20-, 25-, 30-, 35-, 40-, 45-, 50-, 55-, 60-, 65-, 70-, 75-, 80-, 85-, 90-, 95-, 98-, and 99-percent durations were used to establish the relation between the short-term and index sites. The smooth line establishing the relation was computed using locallyweighted regression (Helsel and Hirsch, 1992).

Low-flow frequency statistics were determined by fitting low-flow data to a Pearson Type III distribution (Riggs, 1972). In cases where the data did not fit a Pearson Type III distribution, low-flow frequency statistics were determined using graphical methods. Time series of annual minimum low flows over 1, 2, 3, 7, 10, 30, 60, 90, 183, and 365 consecutive-day periods, commonly referred to as N-day annual minimum low-flow values, were used to determine low-flow frequency statistics. N-day annual minimum low flows typically are determined using a climatic year, which usually begins on April 1 or October 1, to ensure all low-flow data related to a particular drought are contained in the same climatic year. In this report, Nday annual minimum low flows were computed by using a climatic year beginning on October 1 because the lowest streamflows in the study area typically occur from April through June. N-day annual low-flow values were fit to a Pearson Type III distribution by solving the equation

$$Q_{N,T} = Q_N + S_N x K_T$$

where,

- Q_{N,T} is an estimate of the N-day annual minimum low-flow at the T-year recurrence interval;
 - Q_N is the mean of the N-day annual minimum low flows;
 - S_N is the standard deviation of the N-day annual minimum low flows; and
 - K_T is a frequency factor that is a function of the skewness of the data and recurrence interval.

Typically, the logarithms of the N-day annual minimum low flow are fit to a Pearson Type III distribution. A slight variation of this procedure was used to determine low-flow frequency statistics at selected sites where streamflow reversals, which are reported as negative numbers, occur as a result of tidal and wind effects. Fitting logarithms of the N-day annual minimum low flows to a Pearson Type III distribution could not be done at these sites because the logarithm of a negative number is not defined. At these sites, a factor was added to all N-day annual minimum low flows to make all values positive. The resulting time series of positive numbers were fit to a Pearson Type III distribution. All N-day annual minimum low flows calculated in this manner fit the Pearson Type III distribution well as shown with 7-day annual minimum low flows from the St. Johns River near DeLand (fig. 5).

Figure 5. Seven-day annual minimum low-flow values plus 4,000, and the corresponding fit by the Pearson Type III distribution for data from the St. Johns River near DeLand, Florida.

Low-flow frequency statistics for the original time series were determined by subtracting the factor from the lowflow frequency statistics computed by using the modified time series. In the graphical technique, N-day annual minimum low-flow values were ranked and assigned a recurrence interval by using the Weibull plotting position (Riggs, 1972). These data were plotted and a smooth curve was fit through the plotted values. The resulting graph was used to determine low-flow frequency values at selected recurrence intervals.

The accuracy of low-flow frequency statistics is dependent upon the period of record used in the analysis, the variability and skewness in the data, and the recurrence interval. Standard error was calculated according to Hardison (1969) for selected low-flow frequency statistics when the statistics were determined using a Pearson Type III distribution. This procedure assumes the error in the estimation of frequency statistics is a function of the uncertainty in estimating the mean, standard deviation, and skewness of the data.

Variations in water-quality constituent values among sites were shown by using boxplots or summary statistics. Seasonal variations in constituent values in the retrospective data were shown by using boxplots for six periods (January-February, March-April, May-June, July-August, September-October, and November-December). Data were divided into six periods because some sites were sampled on a bimonthly frequency from 1991-99. Variations in water-quality constituent values among sites or by seasonal period were quantified by using a one-way analysis of variance (Devore and Peck, 1986, chapter 13) and Tukey multiple comparison (Tukey, 1953, unpublished report, Princeton University). Data were transformed when necessary to make the values more normally distributed and variances more homogeneous among groups. Relations between water-quality constituent values and streamflow were quantified using Kendall's tau (Helsel and Hirsch, 1992) at selected sites where both water-quality and continuous streamflow data were available (fig. 4). For all statistical tests in this report, the criterion for statistical significance was the 0.05 significance level.

Censored values were present in some of the waterquality data analyzed. Aggregating data from multiple agencies also resulted in water-quality data with multiple reporting limits. One common approach to handling censored water-quality data in statistical analyses is to arbitrarily substitute a value, such as one-half the reporting limit, zero, or the reporting limit, for each censored value. This method has no theoretical basis and produced biased estimates of summary statistics (Helsel, 1990). In this report, summary statistics for data with greater than 5 percent censored values were estimated by using a probability plotting procedure adapted for data with multiple reporting limits (Helsel and Cohn, 1988).

Temporal trends in water-quality constituent values were determined by using the Seasonal-Kendall test or Tobit regression (Helsel and Hirsch, 1992). The Seasonal-Kendall test is a nonparametric test for monotonic trend. This test reduces seasonal variability by making comparisons of data only from similar seasons. In this report, six seasonal periods were used when applying the Seasonal-Kendall test because some sites were sampled only bimonthly during part of the 1991-99 period. Streamflowrelated variability in the water-quality data was removed by first determining the relation between water-quality constituent values and streamflow by using locallyweighted regression. The residuals (predicted minus the observed values) from this regression were tested for temporal trend by using the Seasonal-Kendall test. Locally-weighted regression was selected because this is a more robust method of flow adjustment compared to simple linear regression.

Tobit regression (Helsel and Hirsch, 1992) was used to determine temporal trends in water-quality values when more than 5 percent of the observed values were censored. Tobit regression is a parametric approach that assumes normally distributed errors. This technique also may be used to determine temporal trends when there are several reporting limits in the data. Flow- and seasonal-variability in water-quality constituent values were taken into account by including flow and cyclical terms in the regression model. In this report, temporal trends in both streamflow and water-quality data were considered statistically significant at the 0.05 significance level.

Acknowledgments

The author thanks Mike Gately from the Volusia County Department of Environmental Health; Sue Connors and Steve Winkler from the St. Johns River Water Management District; Ken Cossin from the Orange County Department of Environmental Protection; Ted Lange from the Florida Fish and Wildlife Conservation Commission; and Patrick Detscher, Eric Pluchino, and Donald Smith from the Florida Department of Environmental Protection for providing water-quality data or information on method detection limits. The author expresses appreciation to Bill Kirby of the U.S. Geological Survey for his advice on the determination of lowstreamflow characteristics at sites with reverse streamflows. The author also expresses appreciation to Ed Furlong of the U.S. Geological Survey for providing pharmaceuticals analyses and Mike Meyer of the U.S. Geological Survey for providing antibiotics analyses and for their advice on interpretation of those respective data.

Streamflow Characteristics

The streamflow characteristics of the St. Johns River will affect the amount of water that can be withdrawn for public supply and the amount of storage necessary to maintain the water demand throughout the year. Mean annual streamflow in the St. Johns River increases from 1,030 cubic feet per second (ft³/s) downstream of Lake Poinsett (site 1, fig. 4) to 2,850 ft³/s near DeLand (site 21, fig. 4), based on data from water years 1985-2000. The greatest increase in mean annual streamflow occurs between Lake Harney and DeLand. Mean annual streamflow increases by 940 ft³/s along this reach; the majority of this increase can be attributed to inflow from the Wekiva River, Blackwater Creek, and Blue Springs.

Temporal Trends

Temporal trends in streamflow were determined at seven sites that had at least 10 years of data (sites 1, 3, 6, 8, 14, 15, and 21) on the St. Johns River, Econlockhatchee River, Wekiva River, and Blackwater Creek (table 8, fig. 4). Only data from water years 1957-2000 were analyzed to determine temporal trends at the DeLand site (site 21) on the St. Johns River because data collected prior to water year 1957 were not considered representative for use in developing flow-duration curves or low-flow frequency statistics. Daily-mean streamflow data at the DeLand site begin in 1933; streamflow at this site, however, often is reversed as a result of wind and tidal effects. Examination of paper records archived in the USGS Altamonte Springs office showed that instrumentation capable of measuring reverse streamflows was not installed at this site until 1956. As a result, all streamflow data collected at this site prior to water year 1957 is biased toward positive values and probably did not accurately represent streamflow conditions.

No significant temporal trends were detected in the daily-mean or N-day low-flow time series from the St. Johns River or Blackwater Creek sites (table 8, fig. 4). These results generally were consistent with those reported by Rumenik and Grubbs (1996), who determined temporal trends in N-day low flows at most of these sites from the beginning of record to 1987. Significant temporal trends were detected in most of the N-day annual minimum low flows from the Econlockhatchee River. Significant increases in N-day annual minimum low flows in the Econlockhatchee River are consistent with a study by Wanielista and others (1992) that determined streamflow volumes in the Econlockhatchee River increased during 1970-90. Increased 7-day annual minimum low flows in the Econlockhatchee River primarily occurred from about 1950-84 (fig. 6). From about 1985-2000, there were no readily apparent increases in the 7-day annual minimum low streamflows at this site. Similar temporal patterns were found in most of the other N-day annual minimum low flows at this site.

Increased low flows at the Econlockhatchee River site from about 1950-84 probably resulted from wastewater discharges to the Little Econlockhatchee River or modifications to the Little Econlockhatchee River Basin. Residential development in the Little Econlockhatchee River Basin increased substantially in the 1950's (Michaels and others, 1960). Prior to 1940, most development in the Little Econlockhatchee River Basin was for agricultural purposes and consisted primarily of improved pasture (Michaels and others, 1960). By 1960, there were about six municipal wastewater treatment plants discharging to the Little Econlockhatchee River (Michaels and others, 1960). The Little Econlockhatchee River received substantial amounts of municipal wastewater effluent from about 12 facilities by 1983 (St. Johns River Water Management District, 2002). In 1984, wastewater effluent from most of the municipal wastewater treatment facilities on the Little Econlockhatchee River were diverted to regional municipal wastewater facilities (Miller & Miller, 1984). Major modifications to Little Econlockhatchee River Basin also have occurred since the 1960's. Many reaches of the Little Econlockhatchee River and its tributaries were deepened and channelized to lower the water table (St. Johns River Water Management District, 2002), creating a network of drainage ditches in the basin. Streamflow in the Little Econlockhatchee River also is controlled by 13 major water control structures (Miller & Miller, 1984). One purpose for installing these structures was to prevent water loss from the river system during dry periods (Michaels and others, 1960). Changes in evapotranspiration rates resulting from increased urban land use also may have affected low streamflows in the Econlockhatchee River Basin. Evapotranspiration rates may change with increasing urban land use as a result of a loss of vegetation as impervious areas increase. In addition, different types of vegetation may be planted by property owners in newly developed urban areas, which may

Table 8. Temporal trends in daily-mean and N-day consecutive low-streamflow data from sites with more than 10 years of data on the St. Johns River, Econlockhatchee River, Wekiva River, and Blackwater Creek.

		Pariod of			N-day low-streamflow						Daily mean		
Map ID (fig. 4)	Station name	record (water years)	1	2	3	7	10	30	60	90	183	365 (annual mean)	in cubic feet per second
1	St. Johns River near Cocoa	1953-2000	-0.124 (.223)	-0.119 (.240)	-0.118 (.244)	-0.114 (.263)	-0.117 (.248)	-0.112 (.271)	-0.099 (.331)	-0.095 (.350)	-0.084 (.409)	-0.084 (.409)	-0.110 (.274)
3	St. Johns River near Christmas	1933-2000	026 (.762)	026 (.762)	022 (.795)	019 (.820)	014 (.875)	013 (.880)	019 (.829)	009 (.922)	013 (.880)	065 (.442)	067 (.424)
6	Econlockhatchee River near Chuluota	1935-2000	.593 (0)	.603 (0)	.609 (0)	.618 (0)	.620 (0)	.584 (0)	.469 (0)	.364 (0)	.205 (.016)	.089 (.295)	.067 (.432)
8	St. Johns River upstream of Lake Harney, near Geneva	1982-2000	135 (.441)	099 (.576)	088 (.624)	076 (.675)	053 (.780)	029 (.889)	064 (.726)	076 (.675)	099 (.576)	.029 (.889)	.072 (.704)
14	Wekiva River near Sanford	1935-2000	.337 (0)	.329 (0)	.324 (0)	.298 (0)	.287 (.001)	.267 (.002)	.185 (.030)	.155 (.069)	.093 (.284)	.120 (.159)	.166 (.052)
15	Blackwater Creek near Cassia	1986-2000	200 (.321)	219 (.276)	210 (.298)	200 (.322)	219 (.276)	200 (.322)	200 (.322)	181 (.373)	162 (.428)	124 (.553)	029 (.921)
21	St. Johns River near DeLand	1957-2000	.118 (.256)	.128 (.218)	.103 (.323)	.026 (.807)	.046 (.660)	.018 (.868)	018 (.868)	055 (.604)	022 (.837)	121 (.244)	0.057 (.591)

[Top number, Kendall's tau; number in parenthesis, p-value; trends significant at the 0.05 significance level are shown in bold]

influence evapotranspiration rates. Water not evaporated from the land surface may seep into the ground and eventually be returned to streams as baseflow. In the eastern United States, decreasing trends in evaporation were found in watersheds with increased urban land use (Dow and DeWalle, 2000). A LOWESS smooth line through the 7-day annual minimum low streamflows indicates low streamflows in the Wekiva River near Sanford generally increased between 1935-68 (fig. 7). There did not appear to be any increase in 7-day annual minimum low flows at this site from 1968-2000. Subsequent temporal trend analyses on

Figure 6. Annual minimum streamflow averaged over 7 consecutive days at the Econlockhatchee River near Chuluota, Florida.

Figure 7. Annual minimum streamflow averaged over 7 consecutive days at the Wekiva River near Sanford, Florida, 1935-2000.

the 1968-2000 portion of the 7-day annual minimum low-flow time series did not detect any significant trend (Kendall's tau = -0.1458, p = 0.2389). Similar results were noted in the other N-day low-flow time series at this site.

Increased low streamflows at this site may be attributed to basin modifications that began around 1926, especially in the Little Wekiva River Basin. The headwaters of the Little Wekiva River originally were near the Seminole/Orange County border, but were extended farther south by the construction of ditches to Lake Lawne (CDM, 2003) (fig. 4). Originally, the land cover in the Little Wekiva River Basin was subtropical forest (Woodward-Clyde and others, 1998). Around 1926, the basin began to be developed for citrus farming. By the 1950's, most of the subtropical forest in the basin was replaced by orange groves (Woodward-Clyde and others, 1998). To promote agriculture, reaches of the Little Wekiva River were ditched to lower the water table (Woodward-Clyde and others, 1998). Ditches drain ground water into streams at a faster rate than under undisturbed conditions and act to increase low streamflows for a short period of time. The Little Wekiva River Basin began to be urbanized in the 1950's (Woodward-Clyde and others, 1998). Much of the development was done prior to the enactment of stormwater management regulations, which resulted in periodic flooding problems (CDM, 2003). To alleviate flooding, water control structures were placed on the outlets of several lakes within and outside of the basin to transport water from otherwise closed basins to the Little Wekiva River (CDM, 2003). In addition, a canal was constructed in the mid-1960's to connect Lake Lawne to Lake Orlando.

Increased low streamflows in the Wekiva River also could have resulted from increased springflow; however, the data indicate that springflows have not increased. On the contrary, flow from Wekiva Springs, which contributes about one-third of the baseflow to the Wekiva River, has decreased from 1970-2000 (Spechler and Halford, 2001). Springflow from Palm Springs, which also discharges to the Wekiva River, has decreased from 1970-2000 (Spechler and Halford, 2001).

Seasonal Variation

Streamflows in the St. Johns River near Christmas and Blackwater Creek generally are lowest in May (fig. 8). Streamflows also were lowest in May at the other St. Johns River sites and in the Econlockhatchee and Wekiva Rivers. Low streamflows in May probably result from several factors. There is less antecedent rainfall in May compared to the June-September wet season, resulting in decreased water storage in lakes and wetlands. Also, evapotranspiration rates are greater in May compared to January-April due to the high air temperatures and high solar radiation. Streamflows in the St. Johns, Econlockhatchee, and Wekiva Rivers generally were highest in September and October. Higher streamflows in September and October probably result from increased rainfall combined with less available storage in the lakes and wetlands due to increased rainfall during the wet season. In contrast to the results for the St. Johns, Econlockhatchee, and Wekiva Rivers, median streamflows in Blackwater Creek generally were highest in February and March, a period when rainfall amounts typically are about 2 to 3 in. lower per month compared to June through September (fig. 2). High median streamflows in Blackwater Creek during February and March may have resulted from differences in water storage between this basin and the other basins described in this report.

Streamflow Reversals

Streamflow reversals were observed at all St. Johns River sites in the study area. At the Sanford and DeLand sites (sites 12 and 21, fig. 4), reverse streamflows typically are measured at least once every year and result from wind and tidal effects. Examination of hourly streamflow and stage data from these two sites showed no tidal signal was present at streamflows greater than 3,000 ft³/s at the Sanford site and at streamflows greater than 4,000 ft³/s at the DeLand site. Reverse streamflows at the DeLand site occurred, on average, about 4 percent of the time based on streamflow data from water years 1957-2000. Reverse streamflows occurred at the Sanford site, on average, about 13 percent of the time, but this percentage is based on a shorter period of record (water years 1996-2000). The percentage of time reverse flows occurred in an individual year at the DeLand site ranged from zero to about 18 percent. At the Sanford site, the percentage of time reverse flows occurred in an individual year ranged from 5 to 22 percent. The greatest percentage of zero or reverse daily mean streamflow observations at the DeLand site tended to occur during years with less than average mean annual streamflow. There is a significant correlation between the annual percentage of zero or reverse streamflow and mean annual streamflow (Kendall's tau = -0.36, p = 0.001).

Streamflow reversals were measured sporadically during periods of extreme low flow at the Cocoa, Christmas, and upstream of Lake Harney sites (sites 1, 3, and 8, respectively; fig. 4). Instrumentation capable of measuring reverse streamflows was installed at these three sites in

Figure 8. Streamflow-duration hydrographs for sites on the St. Johns River and Blackwater Creek, water years 1985-2000.

1993 and 1994. Prior to 1993, it is likely that reverse streamflows occurred but were not reported. Streamflow reversals at these sites resulted from wind moving the water upstream because this reach of the river is not affected by tides from the Atlantic Ocean. At the Cocoa and upstream of Lake Harney sites, streamflow reversals were reported only in water year 2000. At the Christmas site, streamflow reversals were reported in water years 1997, 1999, and 2000. Daily-mean streamflows were zero or reverse flow about 9 percent of the time at the Cocoa site and about 6 percent of the time at the upstream of Lake Harney site in water year 2000. At the Christmas site, daily-mean streamflows were zero or reverse flow about 3 percent of the time in water year 1997; about 9 percent of the time in water year 1999; and about 6 percent of the time in water year 2000.

Figure 9. Flow-duration curves for St. Johns River sites, water years 1957-2000.

Flow Duration

Flow-duration statistics were developed using data from water years 1957-2000 for the St. Johns River, and the longest period of trend-free data for the Econlockhatchee River, Wekiva River, and Blackwater Creek. Flow-duration curves also were developed using data from water years 1985-2000 to compare streamflow characteristics among these four streams. Flow-duration statistics for both of these periods are listed in appendix C. The longest common period of record of trend-free data for most of the St. Johns River sites was from water years 1957-2000. Streamflow records from the site upstream of Lake Harney and the Sanford site (sites 8 and 12, respectively, fig. 4) exist only from water year 1982 to the present (2004). At these two sites, flow-duration curves were extended to the water year 1957-2000 period. The Christmas site (site 3, fig. 4) was used as an index site to extend the flow-duration curve for the site upstream of Lake Harney. The DeLand site (site 21, fig. 4) was used as an index site to extend the flow-duration curve for the Sanford site. For tributaries to the St. Johns River, the longest period of record of trend-free data ranged from water years 1968-2000 for the Wekiva River site to water years 1985-2000 for the Econlockhatchee River site. Flow-duration curves for the Econlockhatchee River,

Wekiva River, and Blackwater Creek were not extended to water years 1957-2000 because suitable index sites were not available.

Flow-duration curves for the St. Johns River sites show that streamflows at the Sanford and DeLand sites decreased rapidly to below zero during low-flow conditions because of streamflow reversals (fig. 9). Streamflows also were expressed on a unit area basis (fig. 10) to eliminate drainage-area size effects in order to better compare the flow characteristics at selected sites. Flowduration curves for the Cocoa, Christmas, and upstream of Lake Harney sites have the same general shape. The flowduration curve for the Econlockhatchee River site flattens during low-flow conditions due to the effects of upstream wastewater discharges. For this same reason, streamflows at the upstream of Lake Harney site did not decrease as rapidly during low-flow conditions compared to the Cocoa and Christmas sites. At all St. Johns River sites, the slope of the flow-duration curves flattens slightly during high-flow conditions because of storage in lakes and wetlands. Streamflows in the Wekiva River are substantially less variable compared to those in the St. Johns and Econlockhatchee Rivers and Blackwater Creek because flow in the Wekiva River depends substantially upon springflow from the Floridan aquifer system.

Figure 10. Flow-duration curves (expressed on a unit area basis) for sites on the St. Johns River, Econlockhatchee River, Wekiva River, and Blackwater Creek, water years 1985-2000.

Low-Flow Frequency Statistics

Low-flow frequency statistics are presented in tables 9 to 16. Statistics for the Econlockhatchee and the Wekiva River sites were not determined using the entire period of record because there were significant temporal trends in low streamflows at these two sites. Water years 1957-2000 were used to determine low-flow frequency statistics for the DeLand site because of the change in streamflow-computation methods in 1956, which resulted in the reporting of reverse flows at this site.

Low-flow frequency statistics at the St. Johns River sites should be interpreted with caution, especially at the Sanford and DeLand sites, because N-day annual minimum low flows may represent the sum of positive and reverse flows. The low-flow frequency statistics presented in this report for the Cocoa and Christmas sites on the St. Johns River differ substantially from those reported by Rumenik and Grubbs (1996). Low-flow frequency statistics at these sites were greatly influenced by reverse streamflows. Rumenik and Grubbs (1996) used the streamflow data collected from 1933-87 to determine low-flow frequency statistics at these sites; however, equipment capable of measuring reverse streamflows was not installed at these locations until 1994.

Water-Quality Characteristics

The 1991-99 data documented a wide range of hydrologic conditions from below to above average streamflow (table 17). The 2000-02 period documented extreme high- and low-flow conditions (fig. 11). Yearly rainfall totals measured at the Orlando airport were substantially below the long-term average (about 50 in.) in water year 2000 (38.99 in.). Totals were near average in water year 2001 (55.76 in.) and water year 2002 (54.35 in.), although more than one-half of the months during water years 2001-02 had a rainfall deficit. This deficit resulted in streamflows in the St. Johns River at or below the 25th percentile during parts of water years 2000, 2001, and 2002, based on a 43-year period of record. Rainfall totals were substantially above average in July 2001, September 2001, and June through September 2002. During these months, rainfall totals were 2.7 to 10.8 in. above the 30-year average, based on the 1972-2001 period of record. This increased rainfall resulted in streamflows greater than the 75th percentile in the latter parts of 2001 and 2002, based on a 43-year period of record.
Table 9. Low-flow frequency statistics for the St. Johns River near Cocoa, Florida.

[Site 1, fig. 4. Period of record analyzed was from water years 1953 to 2000; NA, not available. Accuracy not determined because statistics determined graphically]

Recurrence		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)					
2	95	96	97.5	99.9	112.5	124	159.2	187.2	327.0	995.5					
5	34	37	34.5	38.8	41	45.5	54.8	74.7	126.9	563.9					
10	13	17.5	12.5	18.7	18	23.2	30.2	44.0	84.9	375.1					
20	3	8	2	8.5	6	10.3	13.1	21.6	53.4	193.4					
50	-63	-41	-30	-17.5	-7.5	1.06	NA	NA	NA	NA					

Table 10. Low-flow frequency statistics for the St. Johns River near Christmas, Florida.

[Site 3, fig. 4. Period of record analyzed was from water years 1933 to 2000. Accuracy not determined because statistics determined graphically]

Recurrence interval		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days														
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)						
2	112	115	113.7	122	121.2	158	192.6	229.2	427.8	1,281.3						
5	35.5	37.5	36.9	37	40.5	59	62.2	85.8	175.1	751.8						
10	9	11	11.9	11	15.2	29	37.2	49.1	110.5	566.7						
20	-27	-24	-20	0	-7	7	17.9	33.9	77.5	358.6						
50	-125	-107.5	-84	-77	-66.5	-17	5.2	25.7	57.4	164.0						

Table 11. Low-flow frequency statistics for the Econlockhatchee River near Chuluota, Florida.

[Site 6, fig. 4. Period of record analyzed was from water years 1985 to 2000; SE_{x,y}, standard error of the x-day annual minimum flow with a recurrence interval of y years. Accuracy, SE_{7,2} = 2.1 ft³/s; SE_{7,10} = 2.0 ft³/s; SE_{30,2} = 3.5 ft³/s; SE_{30,10} = 2.9 ft³/s]

Recurrence		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)					
2	39.9	40.7	41.3	42.8	44.3	50.4	58.1	69.0	121	304					
5	33.4	34.6	35.1	36.2	37.3	40.5	44.5	50.2	79.3	217					
10	30.6	32.0	32.5	33.7	34.5	36.7	39.6	44.6	64.8	178					
20	28.5	30.2	30.6	32.0	32.6	34.1	36.4	41.2	55.3	149					
50	26.4	28.3	28.8	30.3	30.8	31.6	33.5	38.5	46.8	120					

statistics determ	inicu grapi	lically								
Recurrence			А	nnual minir for indi	num low flo cated numb	w, in cubic er of conse	: feet per se ecutive day	econd, s		
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)
2	235	225	234	254.5	298.8	366	463	533	728	1,846
5	87.5	95	109	107.5	126.8	152	180	211	335	1,167
10	57.5	56.5	57	66	70	101	158	172	290	926

-35

-98.2

-10

-64

12.4

NA

31.9

NA

101

NA

819

NA

Table 12. Low-flow frequency statistics for the St. Johns River upstream of Lake Harney near Geneva, Florida.

[Site 8, fig. 4. Period of record analyzed was from water years 1982 to 2000; NA, not available. Accuracy not determined because statistics determined graphically]

Table 13. Low-flow frequency statistics for the St. Johns River near Sanford, Florida.

-43

-109.5

-63

-146

-68

-142

-77

-171

20

50

[Site 12, fig. 4. Period of record analyzed was from water years 1988 to 1989 and water years 1996 to 2000; SE_{x,y}, standard error of the x-day annual minimum flow with a y-year recurrence interval. Accuracy, SE_{7,2} = 328 ft³/s; SE_{7,10} = 341 ft³/s; SE_{30,2} = 237 ft³/s; SE_{30,10} = 301 ft³/s]

Recurrence		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)					
2	-1,100	-820	-658	-287	-174	186	392	518	670	1,910					
5	-1,750	-1,540	-1,410	-1,030	-812	-321	-140	-47	204	1,240					
10	-2,010	-1,880	-1,780	-1,420	-1,140	-568	-385	-305	102	990					
20	-2,200	-2,140	-2,080	-1,740	-1,400	-764	-570	-499	56	822					
50	-2,370	-2,410	-2,420	-2,110	-1,690	-974	-761	-698	27	666					

Table 14. Low-flow frequency statistics for the Wekiva River near Sanford, Florida.

[Site 14, fig. 4. Period of record analyzed was from water years 1968 to 2000; $SE_{x,y}$, standard error of the x-day annual minimum flow with a y-year recurrence interval. Accuracy, $SE_{7,2} = 4.1$ ft³/s; $SE_{7,10} = 5.3$ ft³/s; $SE_{30,2} = 6.3$ ft³/s; $SE_{30,10} = 7.2$ ft³/s]

Recurrence	Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)				
2	202	202	203	204	205	210	217	223	246	290				
5	182	182	183	184	185	189	194	199	215	255				
10	172	173	173	175	176	180	184	188	201	239				
20	165	165	166	167	168	173	176	180	190	227				
50	156	157	157	159	160	165	168	172	179	214				

Table 15. Low-flow frequency statistics for Blackwater Creek near Cassia, Florida.

[Site 15, fig. 4. Period of record analyzed was from water years 1968 to 1969 and water years 1985 to 2000; SE_{x,y}, standard error of the x-day annual minimum flow with a y-year recurrence interval. Accuracy, SE_{7,2} = 1.3 ft³/s; SE_{7,10} = 0.5 ft³/s; SE_{30,2} = 1.7 ft³/s; SE_{30,10} = 0.7 ft³/s]

Recurrence		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)					
2	7.0	7.1	7.2	7.6	7.9	9.3	12	14	25	51					
5	3.8	3.8	3.9	4.1	4.2	4.9	5.9	6.9	13	30					
10	2.7	2.7	2.7	2.8	3.0	3.4	3.9	4.6	8.5	22					
20	2.0	2.0	2.0	2.1	2.2	2.5	2.7	3.3	6.0	17					
50	1.4	1.4	1.4	1.4	1.5	1.7	1.8	2.1	3.9	13					

Table 16. Low-flow frequency statistics for the St. Johns River near DeLand, Florida.

[Site 21, fig. 4. Period of record analyzed was from water years 1957 to 2000; SE_{x,y}, standard error of the x-day annual minimum flow with a y-year recurrence interval. Accuracy, SE_{7,2} = 138 ft³/s; SE_{7,10} = 195 ft³/s; SE_{30,2} = 98 ft³/s; SE_{30,10} = 148 ft³/s]

Recurrence		Annual minimum low flow, in cubic feet per second, for indicated number of consecutive days													
interval (in years)	1	2	3	7	10	30	60	90	183	365 (annual mean)					
2	-934	-757	-583	86	303	819	1,064	1,216	1,655	2,870					
5	-1,921	-1,741	-1,551	-733	-407	298	543	669	972	2,030					
10	-2,454	-2,278	-2,083	-1,191	-787	44.3	315	439	702	1,645					
20	-2,903	-2,733	-2,537	-1,585	-1,106	-156	148	275	519	1,353					
50	-3,418	-3,259	-3,062	-2,046	-1,469	-371	-17	117	353	1,052					

Water Temperature

Water temperature affects many of the chemical and biological processes in streams. Growth rates of phytoplankton and other aquatic plants also are influenced by temperature and tend to increase with greater water temperatures. Oxygen, which is essential for the survival of fish and other aquatic life, is less soluble in warmer water. As a result, oxygen concentrations naturally are lower in warmer water compared to cooler water.

The water temperature generally ranged from about 10 to 35 °C in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, based on the 1991-99 data. Data collected from the St. Johns River from 2000-02 showed a similar range in water temperatures. The greatest median water temperatures in the

St. Johns River upstream of Lake Harney typically occurred during July-August; the lowest median temperatures typically occurred from December-January (fig. 12). Similar seasonal variations were observed at the other sites on the St. Johns, Econlockhatchee, and Wekiva Rivers. The seasonal variations in water temperature coincide with the general seasonal distribution of air temperatures in the study area (fig. 2). Water temperatures in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers were more variable from November through March compared to other times of the year, as shown by the wider interquartile range on the boxplots in figure 12. Wider variations in water temperatures from November through March resulted from the wider variations in air temperature that occurred during this period.

Table 17. Mean annual streamflow for sites in the study area.

[Units are cubic feet per second; NA, not available]

Мар	Map ID Station name						Wate	er year						Mean (water
ID (fig. 4)	Station name	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	years 1985-2000)
1	St. Johns River near Cocoa	1,228	1,132	973	653	2,059	1,380	759	2,007	497	1,120	753	1,746	1,028
3	St. Johns River near Christmas	1,685	1,603	1,479	891	2,319	1,847	710	2,221	621	1,174	780	2,012	1,261
6	Econlockhatchee River near Chuluota	378	320	358	354	492	438	247	450	170	183	266	390	313
8	St. Johns River upstream of Lake Harney, near Geneva	2,340	2,148	2,239	1,718	3,784	2,586	1,280	3,056	858	1,583	1,155	2,686	1,909
12	St. Johns River near Sanford	NA	NA	NA	NA	NA	3,499	1,275	3,509	951	2,092	1,258	3,930	NA
14	Wekiva River near Sanford	274	260	285	310	376	382	271	368	254	246	228	293	290
15	Blackwater Creek near Cassia	48	16	56	53	118	102	29	100	31	27	37	65	54
21	St. Johns River near Deland	2,925	2,716	3,251	2,382	4,937	4,445	2,111	4,356	1,551	2,368	1,809	4,137	2,847

Water temperatures did not vary as widely in the Wekiva River near Sanford (located about 7 mi upstream from the mouth), Blackwater Creek, and Blue Springs sites compared to the St. Johns River. At the Wekiva River near Sanford and Blackwater Creek, water temperatures ranged from about 16 to 26 °C from 2000-02. At Blue Springs, the water temperature ranged from about 23 to 24 °C from 2000-02. Water temperatures in the Wekiva River near Sanford and Blue Springs probably were not as variable compared to those in the St. Johns River because a substantial amount of the flow at these sites is contributed by springflow from the Floridan aquifer system.

Dissolved Oxygen

Dissolved oxygen in the water is necessary for the survival of fish and other higher forms of aquatic life. The equilibrium concentration of dissolved oxygen in streams is a function of temperature and pressure, and to a lesser extent, the concentration of other solutes. Dissolved oxygen in streams may be depleted by processes that consume organic matter; values above equilibrium can be produced in streams containing actively photosynthesizing biota. The USEPA recommends that the 7-day average dissolved oxygen concentration in streams not be less than 5 mg/L to protect sensitive species of fish and other aquatic life (U.S. Environmental Protection Agency, 1986). The State of Florida recommends that dissolved oxygen concentrations not be less than 5 mg/L for streams designated as potable water supplies, designated as shellfish propagation and harvesting areas, or designated for recreational use and the maintenance of healthy fish communities (Florida Administrative Code, 2003a).

Dissolved oxygen concentrations equal to or less than 5 mg/L were reported at all sites during 1991-99 and 2000-02. Concentrations equal to or less than 5 mg/L were reported most frequently at the Beeline Highway, Christmas, and Orange Mound sites on the St. Johns River, and near the mouth of the Wekiva River during 1991-99 (fig. 13). Concentrations less than 5 mg/L were measured in Blackwater Creek and Blue Springs during 2000-02; median concentrations were 4.8 and 1.1 mg/L, respectively.

Median dissolved oxygen concentrations in the St. Johns River during 1991-99 were slightly greater at the Cocoa, downstream of Lake Harney, Sanford, upstream of the Wekiva River, and downstream of the Wekiva River sites compared to other sites on the river (fig. 13). All of these sites are located downstream of large lakes on the St. Johns River—Lake Poinsett, Lake Harney, and Lake Monroe. Increased dissolved oxygen concentrations at these sites may have been the result of algal production in the lakes; the quiescent lake conditions may have provided more optimal conditions for algal growth.



Figure 11. Streamflow characteristics and precipitation at St. Johns River sites, 2000-02.

Dissolved oxygen concentrations had a significant inverse relation with streamflow based on Kendall's tau at all St. Johns River sites (table 18). All correlations between dissolved oxygen concentration and discharge were significant at the 95-percent confidence level. Data collected during 2000-02 at the Christmas site show the relation between dissolved oxygen concentrations and streamflow (fig. 14); at this site, dissolved oxygen concentrations approached zero during high-flow periods in 2001 and 2002. One likely source of water with low dissolved oxygen concentrations to the St. Johns River is runoff from wetland areas. For 1989-98, limited SJRWMD data from wetlands in the upper St. Johns River Basin showed dissolved oxygen concentrations ranging from 0.70 to 6.3 mg/L, with a median concentration of 3.1 mg/L. Lower dissolved oxygen concentrations during high-flow conditions also may have resulted from the decomposition of organic matter in the river. The distribution of dissolved organic carbon concentrations in the St. Johns River will be discussed in detail later in this report; however, dissolved organic carbon concentrations generally increased during high-streamflow conditions.



Figure 12. Seasonal variations in water temperature in the St. Johns River upstream of Lake Harney near Geneva, Florida, 1991-99.



Sites shown in downstream order; map identifier shown in figure 4; data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, U.S. Geological Survey, and Volusia County.

Figure 13. Dissolved oxygen concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99.

Table 18. Relations between dissolved oxygen concentration and water pH and streamflow at St. Johns River sites, 1991-2002.

[Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations. Retrospective data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

			Dissolved oxyge	n concentration	Water pH values	
Map ID (fig. 4)	Station name	Explanation of values	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)
1	St. Johns River near Cocoa	tau p n	-0.1835 .0269 68	-0.1709 .0335 72	-0.5020 0 64	4644 0 72
3	St. Johns River near Christmas	tau p n	4342 0 121	3292 0 72	4409 0 121	5184 0 72
8	St. Johns River upstream of Lake Harney, near Geneva	tau p n	3196 0 245	Not sampled	3442 0 240	Not sampled
12	St. Johns River near Sanford	tau p n	Not determined	1992 .0140 71	Not determined	3662 0 72
21	St. Johns River near DeLand	tau p n	3611 0 126	3199 .0001 71	4798 0 124	4941 0 72



Figure 14. Dissolved oxygen concentration and streamflow at the St. Johns River near Christmas, Florida, 2000-02 (reverse flow not shown).

Water pH

The pH is the hydrogen ion activity in water and is an indicator of the acidity of the water. The pH of water is controlled by interrelated chemical and biological reactions that produce or consume hydrogen ions. The USEPA recommends a water pH between 6.5 and 9 to protect freshwater aquatic life, and a water pH between 5 and 9 for waters to be used as domestic water supplies (U.S. Environmental Protection Agency, 1986). For waters designated as public water supplies, the State of Florida generally recommends a water pH between 6 and 8.5 (Florida Administrative Code, 2003b).

Median water pH values in the St. Johns River ranged from 6.8 to 7.5 from 1991-99 (fig. 15). Water pH values were slightly greater at the Cocoa, downstream of Lake Harney, Sanford, upstream of Wekiva River, and downstream of Wekiva River sites compared to the other sites. Increased water pH values at these sites may have resulted from algal activity in Lake Poinsett, Lake Harney, and Lake Monroe. Carbon dioxide (CO₂) in the water is utilized by algae during photosynthesis, which tends to reduce the CO₂ concentration of the water and thus, shifts the carbonate equilibrium to more basic conditions (Wetzel, 1983, p. 211). Water pH values at the Cocoa and Sanford sites had a significant inverse relation with streamflow, based on 1991-2002 data (table 18, fig. 16). Significant inverse relations between water pH and streamflow also were observed at other St. Johns River sites (table 18). All correlations between water pH values and streamflow were significant at the 95-percent confidence level. Lower water pH values during high-flow conditions resulted from the increased dissolved organic carbon concentrations that also occur in the river during high-flow conditions. Dissolved organic carbon in natural waters generally is composed of aquatic fulvic and hydrophilic acids (Aiken and Cotsaris, 1995), which lower the water pH. During high-flow events, the water pH typically decreased to less than 7.0.

The 2000-02 data showed a noticeable seasonality in the water pH values at the Cocoa and Sanford sites (fig. 16). Water pH values at these sites were greater than 8.5 standard units from about May through June in water years 2000 and 2001. Higher water pH values at these two sites during these periods also probably resulted from algal activity in the St. Johns River or upstream lakes. The distribution of chlorophyll-*a*, an indicator of the amount



Sites shown in downstream order; map identifier shown in figure 4; data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, U.S. Geological Survey, and Volusia County.

Figure 15. Water pH in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99.



Figure 16. Water pH and streamflow at St. Johns River sites, 2000-02.

of phytoplankton, will be discussed in more detail later in the report; however, chlorophyll-*a* concentrations in the river generally were highest in May and June.

Specific Conductance

Specific conductance, or the ability of water to conduct an electric current, is related to the presence of charged ionic species in water, thus providing an indication of the ion concentration of water. The State of Florida has established criteria for the specific conductance values in surface waters based on designated uses. Stream water designated to be used as potable water supplies, for recreational purposes, or for the propagation and maintenance of healthy populations of fish and wildlife should not have specific conductance values increased by more than 50 percent above background levels or 1,275 microsiemens per centimeter (μ S/cm), whichever is greater (Florida Administrative Code, 2003a). Stream water designated for navigational or industrial use should not have specific conductance values greater than 4,000 µS/cm (Florida Administrative Code, 2003a).

Specific conductance values in the St. Johns River had an inverse relation with streamflow, based on both the 1991-99 retrospective and 2000-02 data (table 19). All correlations were significant at the 95-percent confidence level; however, the relation between specific conductance values and streamflow varied among the sites. LOWESS smooth lines for the 1991-99 data show the relation between specific conductance values and streamflow at selected sites (fig. 17). Data points are not shown in figure 17 to reduce clutter and to make the smooth lines distinguishable. Although not shown, specific conductance values tracked the LOWESS smooth line fairly closely. The relation between specific conductance and streamflow based on the 2000-02 data (not shown) was similar to the 1991-99 data. Specific conductance values from 1991-99 varied considerably at the Cocoa, Christmas, and upstream of Lake Harney sites when streamflows were less than about 3,000 ft³/s. Values at these three sites varied most dramatically when streamflows were less than about 1,000 ft^3 /s. During such conditions, specific conductance values at these three sites ranged from less than 600 μ S/cm to greater than 2,000 µS/cm. In contrast, specific conductance values at the DeLand site did not vary as widely during lowflow conditions compared to the other three sites. At the DeLand site, specific conductance values generally ranged from about 1,200 to 1,500 µS/cm when streamflows were less than $1,000 \text{ ft}^3/\text{s}$.

Table 19. Relations between specific conductance values and total dissolved solids concentration and streamflow at

 St. Johns River sites, 1991-2002.

[Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations. Retrospective data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

			Specific co	nductance	Total dissolved solids
Map ID (fig. 4)	Station name	Explanation of values	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)	U.S. Geological Survey data (2000-02)
1	St. Johns River near Cocoa	tau p n	-0.6370 0 68	-0.6698 0 72	-0.6616 0 72
3	St. Johns River near Christmas	tau p n	5563 0 123	7782 0 72	7782 0 72
8	St. Johns River upstream of Lake Harney, near Geneva	tau p n	5795 0 246	Not sampled	Not determined
12	St. Johns River near Sanford	tau p n	Not determined	3875 0 71	3928 0 72
21	St. Johns River near DeLand	tau P n	5738 0 126	4413 0 72	3967 0 72



Data from the Florida Department of Environmental Protection, Florida Fish and Wildlife, Conservation Commission, Orange County, St. Johns River Water Management District, U.S. Geological Survey, and Volusia County.

Figure 17. Relation between specific conductance and streamflow at sites on the St. Johns River, 1991-99.

The LOWESS smooth lines also show that the spatial variation in specific conductance values among the St. Johns River sites was different under low- and high-flow conditions. When streamflows were less than about 1,000 ft³/s, specific conductance values at the Christmas and upstream of Lake Harney sites generally were about 300 to 800 μ S/cm greater than values at the DeLand site. In contrast, when streamflows were greater than about 1,000 ft³/s, specific conductance values at the DeLand site were about 200 to 400 μ S/cm greater than those at the Christmas and upstream of Lake Harney sites.

To further examine the influence that low-flow conditions had on specific conductance values at a greater number of sites along the St. Johns River, boxplots of retrospective data from May 1991-99 were constructed by site (fig. 18). Data for the Orange Mound site are not shown because only one measurement was reported for May 1991-99. During the May 1991-99 low-flow conditions, median specific conductance values were greater at the Puzzle Lake site and the sites from downstream of Lake Harney to State Road 415 compared to the other St. Johns River sites. Increased specific conductance values during the May low-flow period at sites from Puzzle Lake to State Road 415 are consistent with a study by DeMort (1990), which reported saline water and the presence of plants more tolerant of saline conditions in the Puzzle Lake and Mullet Lake areas of the St. Johns River. High specific conductance values at these locations on the river are due to the inflow of brackish water from the Floridan aquifer system. Specific conductance values in the Upper Floridan aquifer in the vicinity of the St. Johns River from upstream of Puzzle Lake to Lake Jesup ranged from about 2,000 to 15,000 µS/cm (Spechler and Halford, 2001). The reach of the St. Johns River from Puzzle Lake to State Road 415 also coincides with areas where faults or subsidence features—which probably extend into the Floridan aquifer system-were reported, and known or suspected springflow from the Floridan aquifer system to the St. Johns River occurs (Tibbals, 1990).

Higher specific conductance values at the Cocoa and Christmas sites during the May low-flow period also indicate the Floridan aquifer system discharges to the St. Johns River in the vicinity of these two sites. The total amount of inflow from the Floridan aquifer system between the Cocoa and Christmas sites is not known (Tibbals, 1990).



U.S. Geological Survey, and Volusia County.

Figure 18. Specific conductance values at St. Johns River sites and near the mouths of the Econlockhatchee and Wekiva Rivers, May 1991-99.

Continuous data from 2001-02 show the variations in specific conductance values with streamflow at the Christmas and Sanford sites (fig. 19). At the Christmas site, specific conductance had several large spikes in values during low-streamflow conditions in water year 2001. It is unlikely that variations in ground-water quality caused these spikes in specific conductance values. One explanation, however, is that the wind pushed water with greater specific conductance values from the vicinity of the Puzzle Lake site upstream to the Christmas site. Specific conductance values fluctuated considerably at the Sanford and DeLand sites (not shown) during lowstreamflow conditions in water year 2001, which also probably resulted from wind and tidal effects.

Total Dissolved Solids

Total dissolved solids concentration (also termed residue on evaporation) is a measure of the dissolved material in water. Total dissolved solids concentrations are determined by measuring the weight of the dry residue remaining from an aliquot of sample after removing the water by evaporation. The results of total dissolved solids concentration analyses may not solely represent the amount of inorganic constituents in the water, which can make interpretation of the results difficult. Dissolved organic matter in the water can contribute to the total dissolved solids concentration because organic matter is not completely removed from the sample unless strongly ignited. Water is retained by some types of residues, such as sulfate, and therefore, may not be completely removed at the temperature used for evaporation (Hem, 1992). Other inorganic constituents, such as nitrate, bicarbonate, and boron, are partly volatile and may or may not be present as part of the total dissolved solids concentration (Hem, 1992). Despite these difficulties in interpreting the data, total dissolved solids concentrations are widely used in evaluating water quality. The USEPA (2000a) and the State of Florida (Florida Administrative Code, 2003b) have established a secondary drinking water regulation of 500 mg/L for total dissolved solids concentrations.



Figure 19. Continuous specific conductance and stream discharge at St. Johns River sites, 2000-02.

Total dissolved solids concentrations greater than the secondary drinking water regulation of 500 mg/L were measured at all sites sampled during 2000-02, except the Wekiva River site near Sanford where the maximum concentration measured was 336 mg/L. In the St. Johns River, more than 50 percent of the samples collected at each of the sites had concentrations exceeding 500 mg/L. The Cocoa site had the lowest percentage of samples exceeding 500 mg/L (58.3 percent); the DeLand site had the highest percentage of samples exceeding 500 mg/L (80.6 percent).

Total dissolved solids concentrations in the St. Johns River had a significant inverse relation with streamflow (table 19). All correlations were significant at the 95-percent confidence level. Relations between concentration and streamflow generally were stronger at the Cocoa and Christmas sites compared to the Sanford and DeLand sites, as indicated by the larger absolute value of Kendall's tau (table 19). Variations in total dissolved solids concentrations at selected sites from 2000-02 are shown in figure 20. Concentrations greater than the secondary drinking water regulation of 500 mg/L occurred during low-flow periods at each of the sites.

Major lons

The predominant inorganic species in stream water typically are calcium, magnesium, sodium, potassium, bicarbonate, chloride, and sulfate. Secondary drinking water regulations established by the USEPA and the State of Florida for chloride and sulfate concentrations in drinking water recommend that concentrations not exceed 250 mg/L (U.S. Environmental Protection Agency, 2000a; Florida Administrative Code, 2003b). The major source of inorganic constituents to the streams in the study area is ground-water inflow from the Floridan aquifer system. Water from the surficial aquifer system typically is low in dissolved mineral content compared to the Floridan aquifer system (Lichtler and others, 1968; Boniol, 1996).

A specific water type is based on the types of cations or anions that predominate in the water (50 percent or greater). For example, a water type in which calcium is the dominant cation and bicarbonate is the dominate anion is called calcium-bicarbonate water. A water type in which neither cation or anion predominate is referred to as mixed-ion type water. The major ion composition at the Cocoa and Christmas sites was more variable compared to the Sanford and DeLand sites, as indicated by the greater scatter of values plotted on the trilinear diagrams in figure 21. At times, the water at the Cocoa and Christmas sites was a mixed-ion type; this occurred during periods of increased streamflow. Chloride was the predominant anion at the Sanford and DeLand sites and was the predominant anion at the Cocoa and Christmas sites during low-flow periods. The major ion composition at the Wekiva River near Sanford and Blackwater Creek sites was substantially different compared to the St. Johns River. The water from the Wekiva River near Sanford was a mixed-ion type; the water from Blackwater Creek generally was a calcium-sulfate type. The water from Blue Springs generally was a sodium-chloride type.

Chloride and sulfate concentrations greater than 250 mg/L were measured in the St. Johns River. Chloride concentrations greater than 250 mg/L were measured most frequently at the Sanford site (62.5 percent) and least frequently at the Cocoa site (36.1 percent). About one-half of the chloride concentrations measured at the Christmas (54.2 percent) and DeLand sites (50 percent) were higher than 250 mg/L. Sulfate concentrations periodically exceeded 250 mg/L at the Cocoa and Christmas sites. Approximately 14 percent of the samples collected from the Cocoa site and about 20 percent of the samples collected from the Christmas site had sulfate concentrations exceeding 250 mg/L. No sulfate concentrations exceeded 250 mg/L at the Sanford and DeLand sites.

Figures 22 and 23 show variations in sulfate and chloride concentrations with streamflow at selected St. Johns River sites, respectively, during 2000-02. Variations in calcium, magnesium, sodium, and potassium concentrations (not shown) generally were similar to those for chloride. Chloride concentrations generally exceeded 250 mg/L for a greater period of time in water years 2000-01, when rainfall amounts were below average, compared to water year 2002. Sulfate concentrations greater than 250 mg/L were measured at the Cocoa site during water year 2001. Sulfate concentrations greater than 250 mg/L were measured at the Christmas site during water years 2000-01.

During low-flow conditions, chloride concentrations, as well as concentrations of the other major ions, were greater at the Cocoa and Christmas sites compared to the Sanford and DeLand sites. Higher major ion concentrations at the Cocoa and Christmas sites during low-flow periods resulted from the inflow of mineralized water from the Floridan aquifer system underlying the St. Johns River in the vicinity of these two sites. The highest concentrations of chloride and the other major ions were measured at the Christmas site during 2000-02. Chloride concentrations of nearly 1,200 mg/L were measured at this site during low-flow conditions in 2000. The maximum chloride concentration measured at the Cocoa site was 647 mg/L.



Figure 20. Total dissolved solids concentration and streamflow at St. Johns River sites, 2000-02.



Figure 20. Total dissolved solids concentration and streamflow at St. Johns River sites, 2000-02. (Continued)



Figure 21. Trilinear diagrams for water samples collected from St. Johns River sites, Wekiva River, Blackwater Creek, and Blue Springs, 2000-02.



46 Streamflow and Water-Quality Characteristics at Selected Sites of the St. Johns River in Central Florida, 1933 to 2002

Figure 21. Trilinear diagrams for water samples collected from St. Johns River sites, Wekiva River, Blackwater Creek, and Blue Springs, 2000-02. (Continued)



Figure 21. Trilinear diagrams for water samples collected from St. Johns River sites, Wekiva River, Blackwater Creek, and Blue Springs, 2000-02. (Continued)



Figure 21. Trilinear diagrams for water samples collected from St. Johns River sites, Wekiva River, Blackwater Creek, and Blue Springs, 2000-02. (Continued)

Chloride and sulfate concentrations at the Christmas site varied greatly from about March through June 2001. Variations in most major ion concentrations, total dissolved solids concentrations (fig. 20), and specific conductance values (fig. 19) also were measured during this same period. These variations in constituent concentrations likely resulted from periodic streamflow reversals, which may have moved more mineralized water from the vicinity of the Puzzle Lake site (fig. 4) upstream. Increased specific conductance values at the Puzzle Lake site indicated increased major ion concentrations at this site as well.

Slight variations in chloride concentrations (as well as most major ion concentrations, total dissolved solids concentrations, and specific conductance values) were observed at the Sanford and DeLand sites from about March 2000 to July 2001. Variations in chloride concentrations likely resulted from wind and tidal effects.

In the St. Johns River, major ion concentrations had a significant inverse relation with streamflow (table 20). Correlations between constituent concentrations and streamflow were stronger at the Cocoa and Christmas sites compared to the Sanford and DeLand sites, as indicated by the larger absolute value of Kendall's tau (table 20). All of the correlations were significant at the 95-percent confidence level.



Figure 22. Sulfate concentration and streamflow at St. Johns River sites, 2000-02.



Figure 23. Chloride concentration and streamflow at St. Johns River sites, 2000-02.



Figure 23. Chloride concentration and streamflow at St. Johns River sites, 2000-02. (Continued)

Table 20. Relations between major dissolved inorganic constituent concentrations and streamflow at St. Johns River sites, 2000-2002.[Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations]

Map ID (fig. 4)	Station name	Explanation of values	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate
1	St. Johns River near Cocoa	tau p n	-0.6804 0 72	-0.6667 0 66	-0.6820 0 61	-0.4770 0 61	-0.6831 0 72	-0.6663 0 72
3	St. Johns River near Christmas	tau p n	7715 0 72	7692 0 66	8055 0 61	7295 0 61	8032 0 72	7054 0 72
12	St. Johns River near Sanford	tau p n	4781 0 72	3697 0 65	3825 0 61	2842 .0012 61	3854 0 72	3897 0 72
21	St. Johns River near DeLand	tau p n	4570 0 72	3907 0 66	4093 0 61	3180 .0003 61	4264 0 72	3803 0 72

Silica

Unlike the major ions, silica concentrations in the St. Johns River were significantly greater during high-flow conditions compared to other times of the year (table 21; fig. 24). All correlation coefficients were significant at the 95-percent confidence level. During high-flow conditions, silica concentrations in the river generally were at least 10 mg/L. During low-flow conditions, however, silica concentrations generally were less than 5 mg/L. At the Cocoa, Christmas, and Sanford sites, silica concentrations generally were 1 mg/L or less during low-flow conditions. One possible explanation for increased silica concentrations

during high-flow periods might be that water from the Floridan aquifer system, which contributes proportionally more inorganic constituents to the river during low-flow conditions than during high flow, contains little silica because the aquifer is composed primarily of limestone and dolomite. This explanation, however, is not consistent with silica concentration data for water from the Floridan aquifer system collected by the FDEP and the USGS from 1990-2002. Silica concentrations in the Floridan aquifer system generally ranged from about 8 to 30 mg/L, which is substantially greater than concentrations generally measured in the St. Johns River during low-flow conditions (fig. 25). Also, silica concentrations in water from the surficial

Table 21. Relations between dissolved silica, total sulfide, total iron, dissolved iron, and bromide concentrations and streamflow at St. Johns River sites, 2000-02.

[Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations]

Map ID (fig. 4)	Station name	Explanation of values	Silica	Sulfide	Total iron	Dissolved iron	Bromide
1	St. Johns River near Cocoa	tau p n	0.3779 0 72	0.3903 0 49	0.3889 0 72	0.6228 0 72	-0.6451 0 72
3	St. Johns River near Christmas	tau p n	.4593 0 72	.4762 0 49	.3811 0 72	.6052 0 72	7410 0 72
12	St. Johns River near Sanford	tau p n	.3087 .0001 72	.3690 0 49	.5458 0 72	.5575 0 72	3744 0 72
21	St. Johns River near DeLand	tau p n	.3772 .0006 72	.3644 0 48	.6123 0 72	.5806 0 72	3556 0 72



Figure 24. Dissolved silica concentration and streamflow at St. Johns River sites, 2000-02.



Figure 25. Silica concentrations in the Floridan aquifer system, 1990-2002.

aquifer system generally were greater than concentrations in the river during low-flow periods. Data collected by the FDEP and USGS showed silica concentrations in the surficial aquifer system ranged from about 3 to 28 mg/L during 1990-2000. Another explanation for reduced silica concentrations during low-flow conditions is that silica was utilized by the biota. Some types of algae, primarily diatoms, use silicon to construct a frustule or shell that surrounds the organism (Wetzel, 1983). In eutrophic lakes, silica concentrations commonly are near method reporting limits due to intensive assimilation by diatoms (Wetzel, 1983). Silica concentrations are high during high-flow conditions due to less utilization by algae. Chlorophyll-a concentrations are discussed in detail later in this report. Concentrations typically are low during high-flow conditions, which indicates that algal abundances also are low during low-flow conditions.

Minor Inorganic Constituents

Sulfide, iron, and bromide typically are present at lower concentrations in stream water compared to the major inorganic constituents. Sulfide imparts an unpleasant odor in the water and is produced by the reduction of sulfate, which occurs under anaerobic conditions. Sources of iron in water include the oxidation of pyrite (which generally is not present in large quantities in the study area), the oxidation of humic materials, and the dissolution of iron oxides and silicate minerals. The reduction of the relatively insoluble ferric iron (Fe³⁺) compounds to the relatively soluble ferrous iron (Fe²⁺) compounds is dependent upon the pH and oxidationreduction potential of the water. Increased concentrations of iron may cause discoloration problems if the water is used for domestic purposes. To prevent discoloration problems, the USEPA (U.S. Environmental Protection Agency, 2000a) and the State of Florida (Florida Administrative Code, 2003b) established a secondary drinking water regulation of 300 micrograms per liter (μ g/L) for the concentration of iron in water.

Bromide is an important constituent in seawater and occurs naturally in the Floridan aquifer system because the aquifer originally formed in a marine environment; bromide also could have been introduced during subsequent advances of the sea in the geologic past. Elevated concentrations of bromide in water may lead to the formation of bromate or other brominated disinfection byproducts if the water is disinfected using either ozone or chlorine. Some of these disinfection byproducts, such as bromate, bromodichloromethane, and bromoform, are known carcinogens (U.S. Environmental Protection Agency, 1998). A Maximum Contaminant Level (MCL) of 0.010 mg/L was established by the USEPA (U.S. Environmental Protection Agency, 1998) for the concentration of bromate in drinking water.

Sulfide

Sulfide concentrations in the St. Johns River, the Wekiva River near Sanford, and Blackwater Creek were determined from November 2000 to September 2002. Summary statistics of sulfide concentrations are presented in table 22. Sulfide concentrations were not analyzed in Blue Springs. In the St. Johns River, sulfide was detected most frequently in samples from the Cocoa site and least frequently in samples from the DeLand site.

 Table 22. Descriptive statistics of total sulfide concentrations at St. Johns River, Wekiva River, and Blackwater Creek sites, 2000-02.

[Units are milligrams per liter; N, number of samples; <, less than. No data available for 02235500, Blue Springs near Orange City]

Map ID (fig. 4)	Station number	Station name	N	Percent of samples with detectable concentrations	Minimum	25 th percentile	Median	75 th percentile	Maximum
1	02232400	St. Johns River near Cocoa	49	57.1	<1.0	1.0	1.0	2.0	4.0
3	02232500	St. Johns River near Christmas	49	55.1	<1.0	1.0	1.0	2.0	6.0
12	02234500	St. Johns River near Sanford	49	51.0	<1.0	1.0	1.0	2.0	3.0
14	02235000	Wekiva River near Sanford	7	14.3	<1.0	<1.0	<1.0	<1.0	2.0
15	02235200	Blackwater Creek near Cassia	7	57.1	<1.0	1.0	3.0	3.5	5.0
21	02236000	St. Johns River near DeLand	48	41.7	<1.0	<1.0	<1.0	2.0	4.0

In the St. Johns River, sulfide concentrations increased during high-flow conditions. All correlations between sulfide concentrations and streamflow were significant and positive (table 21). Concentrations as great as 6 mg/L were measured during high-flow conditions. During low-flow conditions, sulfide concentrations generally were near method reporting limits (1 mg/L). One potential source of sulfide is ground-water inflow from the Floridan aquifer system. Sulfide was reported in water from wells in the Floridan aquifer system in Orange County (Lichtler and others, 1968), particularly in flowing wells in the eastern part of the county. Lower sulfide concentrations in the St. Johns River during low-flow conditions, however, is inconsistent with ground-water inflow as the predominant source of sulfide to the river. Sulfide also may be produced by the decomposition of organic matter (Wetzel, 1983, p. 319). Sulfate may be reduced to sulfide when the oxidation-reduction potential declines to less than 100 millivolts (Wetzel, 1983, p. 320). It is likely that these processes strongly influence sulfide concentrations in the St. Johns River.

Iron

Total iron concentrations greater than 300 μ g/L were measured at all sites on the St. Johns River, Wekiva River, and Blackwater Creek. In the St. Johns River, concentrations exceeded 300 μ g/L most frequently at the Christmas site (88.9 percent of the samples) and least frequently at the DeLand site (27.8 percent of the samples). Total iron concentrations in 75 percent of the samples from Blackwater Creek exceeded 300 μ g/L. In contrast, concentrations in less than 10 percent of the samples from the Wekiva River near Sanford exceeded 300 μ g/L.

In the St. Johns River, total iron concentrations had a significant positive relation with streamflow (table 21, fig. 26). Total iron concentrations greater than 300 μ g/L generally were measured at the Cocoa, Sanford, and DeLand sites only during periods of increased streamflow. Total iron concentrations at the Christmas site generally were greater than 300 μ g/L at all times of the year.

Dissolved iron ranged from 5 to 83 percent of the total iron concentration. The percentage of dissolved iron in the river water was dependent upon streamflow conditions, as indicated by data from the Sanford site (fig. 27). During low-flow conditions, dissolved iron generally was, at most, about 20 percent of the total iron concentration at each of the St. Johns River sites. The increased percentage of dissolved iron at the Sanford site from October 2000 through January 2001 resulted from

upstream inputs. Concentrations were high from October through November 2001 at the Cocoa and Christmas sites due to increased streamflows. In contrast, dissolved iron accounted for 70 percent or more of the total iron concentration at each of the sites during high-flow conditions. Ferrous iron (Fe²⁺) is a soluble form of iron in water. Water pH, temperature, and oxidation-reduction potential influence the reduction of ferric iron (Fe³⁺) to ferrous iron. In the St. Johns River, water pH and dissolved oxygen concentrations are lower during high-flow conditions. It is possible that during high-flow events, iron was reduced to the ferrous form, resulting in a greater percentage of dissolved iron in the river.

Bromide

Bromide concentrations had temporal variations unlike any of the other inorganic constituents. Concentrations ranged from 0.19 to 17 mg/L during 2000-02 and had a significant inverse relation with streamflow (table 21). All correlations were significant at the 95-percent confidence level. Temporal variations in bromide concentration were characterized by sharp peaks in concentration during low-flow periods at all St. Johns River sites (fig. 28), especially in water year 2001 when concentrations as great as 17 mg/L were measured at the Cocoa site. Maximum bromide concentrations at the other sites were substantially lower than those at the Cocoa site; concentrations at these sites did not exceed 9.0 mg/L. Increased concentrations during water year 2001 may have resulted from less dilution due to the low-streamflow conditions. Mean annual streamflows were less in water year 2001 compared to water years 2000 and 2002 (table 17). Periods of increased bromide concentrations generally were of a shorter duration compared to the other inorganic constituents, such as chloride (fig. 23), especially in water year 2001. There also was an increase in bromide concentrations at the Cocoa and Christmas sites during water year 2000 that was not observed at the Sanford and DeLand sites.

Like most of the inorganic constituents, maximum bromide concentrations in the St. Johns River occur during low-flow conditions because the source of bromide to the river is ground water affected by relict seawater. Limited data were available from USGS files on bromide concentrations in water from the Floridan or surficial aquifer systems within the study area; a majority of the data were collected in the late 1990's west of St. Johns River in the central part of the study area. Bromide concentrations in water from the Floridan aquifer system ranged from below the method reporting limit (0.05 mg/L) to 22 mg/L (fig. 29).



Figure 26. Total iron concentrations and streamflow at St. Johns River sites, 2000-02.



Figure 27. Percent of dissolved iron comprising the total iron concentration and streamflow at the St. Johns River near Sanford, Florida, 2000-02.

Concentrations generally were lower in water from the surficial aquifer system compared to the Floridan aquifer system; concentrations ranged from below the method reporting limit (0.05 mg/L) to 3.2 mg/L. The highest concentrations in the surficial and Floridan aquifer systems generally were reported in the discharge areas for the Floridan aquifer system in the vicinity of the Econlockhatchee and St. Johns Rivers in the central part of the study area.

Peaks in bromide concentrations were expected to be concomitant with maximum chloride concentrations at the Cocoa and Christmas sites. Both chloride and bromide in ground water in the study area likely originated from relict seawater. The limited ground-water-quality data also showed significant correlations between bromide and chloride concentrations in water from the Floridan aquifer system (Kendall's tau = 0.6990, p = 0). Peaks in bromide concentrations that were not coincident with maximum chloride concentrations measured during water year 2001 were unexpected, suggesting different sources of bromide and chloride to the St. Johns River. Agricultural canals in the Upper St. Johns River Basin may be a source of bromide to the Cocoa site. Goolsby and McPherson (1970) reported that an increase in dissolved solids concentrations in the St. Johns River downstream of Lake Washington was due to the inflow of mineralized water from agricultural drainage canals. Although chloride and bromide concentrations in agricultural canal

water were not reported by Goolsby and McPherson (1970), it is possible that agricultural drainage water contains chloride and bromide.

Water Color and Organic Carbon

The yellowish-brown color of some Florida streams is due in part to organic matter in the water. Organic matter in streams serves many functions. Organic matter may serve as a carbon substrate in microbially mediated reactions and also may influence the water pH because organic acids makeup most of the organic matter in natural waters. Colored organic matter in the water absorbs light. As a result, the depth of the photic zone (area in which photosynthesis occurs) potentially may be controlled by the amount of organic matter present in highly colored waters. Organic matter in water also has some undesirable effects. If water is disinfected with chlorine during treatment, the presence of organic matter in the water may lead to the formation of disinfection byproducts, some of which are known carcinogens. Organic matter in the water also may transport contaminants. Contaminants such as hydrophobic organic compounds and metals, which are relatively immobile in the environment, may interact with organic matter and be transported considerable distances downstream.



Figure 28. Bromide concentration and streamflow at St. Johns River sites, 2000-02.



Figure 28. Bromide concentration and streamflow at St. Johns River sites, 2000-02. (Continued)



Figure 29. Bromide concentrations in the Floridan aquifer system, 1990-2002.

Sources of organic carbon can be categorized as entering the stream from a terrestrial watershed (allochthonous) or being derived from biota in the water body (autochthonous). Organic matter derived from different source materials has distinctive characteristics. Organic matter derived from lignin, a component of woody plants such as shrubs and trees, has relatively large amounts of aromatic carbon and is low in nitrogen content (Aiken and Cotsaris, 1995). In contrast, microbially derived organic matter has relatively low amounts of aromatic carbon and a high nitrogen content (Aiken and Cotsaris, 1995). The aromatic carbon content of organic matter also may influence water treatment strategies. In water treatment, there is a strong correlation between chlorine consumption and the aromatic carbon content of the source water (Reckhow and others, 1990), so the generation of disinfection byproducts may be greater during periods when organic carbon concentrations and the aromatic carbon content are high.

Water color is determined by matching dilutions of a standard solution of cobalt chloride and potassium chloroplatinate. The intensity of color is rated numerically. For example, a color of 5 is equal to a 1:100 dilution of the standard solution. The numerical value assigned to the color has no direct connection with the amount of organic material in the water. For aesthetic purposes, the USEPA and the State of Florida established a secondary drinking water regulation of 15 color units (U.S. Environmental Protection Agency, 2000a; Florida Administrative Code, 2003b).

Ultraviolet light (UV) absorbance is a surrogate measure of the aromaticity of organic carbon. Specific UV absorbance is defined as the UV absorbance divided by the dissolved organic carbon concentration. Specific UV absorbance values are used to indicate the source of organic matter because algal-derived organic carbon has a lower molar absorptivity than terrestrially derived organic matter (McKnight and others, 1994). Specific UV absorbance also was proposed as a predictor of the disinfectant byproduct formation potential of the water (Edzwald and others, 1985).

The color of the St. Johns River water varied substantially. Water color values ranged from 10 to 400 platinum-cobalt units. More than 95 percent of the samples had water color values exceeding 15 platinumcobalt units. Median water color values were greater at the Cocoa and Christmas sites (120 and 140 platinumcobalt units, respectively) than at the Sanford and DeLand sites (100 and 75 platinum-cobalt units, respectively).

Water color values generally increased substantially with increasing streamflow at each of the sites, as shown by data from the Christmas and DeLand sites (fig. 30). Correlations between water color values and streamflow at each of the sites also were significant and positive (table 23). During low-flow conditions, water color values generally were greater at the Cocoa and Christmas sites (about 50 to 100 platinum-cobalt units) compared to the Sanford and DeLand sites (about 25 to 50 platinum cobalt units); these lower water color values may be due to inputs from spring-fed streams or ground-water inflow. Data from the Wekiva River near Sanford, which receives a substantial amount of flow from Wekiva Springs, and Blue Springs documented that water from these sources is less colored compared to the St. Johns River. Median water color values in the Wekiva River near Sanford and Blue Springs were 10 and less than 5 platinum-cobalt units, respectively. Water color values at each St. Johns River site remained high for about a month after high flows receded. These continued high water color values may be due to the storage of water in lakes and wetlands.

Dissolved organic carbon concentrations ranged from 1.6 to 42 mg/L during 2000-02. Median dissolved organic carbon concentrations ranged from 15.0 at the DeLand site to 26.0 mg/L at the Cocoa site. Median concentrations at the Christmas and Sanford sites were 25.0 and 19.5 mg/L, respectively. Lower median dissolved organic carbon concentrations at the DeLand site compared to the Cocoa and Christmas sites probably result from dilution by inflow from the Wekiva River (which had a median dissolved organic carbon concentration of 2.7 mg/L during 2000-02) and by ground-water inflow.

Dissolved organic carbon concentrations were not related to streamflow at the Cocoa site during 2000-02 (fig. 31, table 23); however, specific UV absorbance values at this site increased substantially during high-flow conditions (fig. 31). High specific UV absorbance values indicated that the dissolved organic matter was more aromatic in composition and probably originated from terrestrially derived sources. Low specific UV absorbance values during low-flow conditions indicated the organic matter was less aromatic in composition and probably originated from algal-derived sources. One likely source of algal production in the vicinity of the Cocoa site is Lake Poinsett.

At the Christmas, Sanford, and DeLand sites, dissolved organic carbon concentrations were positively correlated with streamflow, as indicated by data from the Sanford site (fig. 31, table 23). Relations between dissolved organic carbon concentrations and streamflow were stronger at the Sanford and DeLand sites compared



Figure 30. Water color values and streamflow at St. Johns River sites, 2000-02.

Table 23. Relations between water color values and dissolved organic carbon concentrations and streamflow at St. Johns River sites, 2000-2002.

[Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations]

Map ID (fig. 4)	Station name	Explanation of values	Water color	Dissolved organic carbon
1	St. Johns River near Cocoa	tau p n	0.5900 0 72	0.0704 .3781 72
3	St. Johns River near Christmas	tau p n	.7230 0 72	.3466 0 72
12	St. Johns River near Sanford	tau p n	.5595 0 72	.5008 0 72
21	St. Johns River near DeLand	tau p n	.5293 0 72	.5278 0 72

to the Christmas site, as indicated by the larger absolute values of Kendall's tau shown in table 23. Specific UV absorbance values also increased substantially at these three sites during high-flow periods, indicating that increased dissolved organic carbon concentrations resulted from inputs of organic matter from terrestrial sources.

Nutrients

Nutrients (defined in this report as nitrogen and phosphorus compounds) are essential for plant and animal growth. In streams and lakes, nitrogen primarily occurs as nitrite (NO_2^{-}) , nitrate (NO_3^{-}) , ammonium (NH_4^{+}) , or as part of particulate or dissolved organic matter. Phosphorus in streams and lakes primarily occurs as orthophosphate (PO_4^{-3-}) or as part of particulate or dissolved organic matter or inorganic complexes. Nitrate nitrogen concentrations greater than 10 mg/L in drinking water can cause a potentially fatal condition, primarily in infants, called methemoglobinemia. Unionized ammonia in water can be toxic to fish and other aquatic life.

Elevated concentrations of nutrients in slower moving reaches of streams and lakes can result in eutrophication, which is the excessive growth of aquatic plants and algae. This excessive growth can result in the water smelling or tasting foul, which may ultimately increase water treatment costs if the water is used as a source of drinking water. In addition, when these plants and animals die, dissolved oxygen may be depleted in the water, ultimately resulting in fish kills. Within the study area, Lake Monroe is known to exhibit eutrophication and reaches of the St. Johns, Wekiva, and Econlockhatchee Rivers are listed by the State of Florida as being impacted by nutrients (St. Johns River Water Management District, 2002).

Sources of nitrogen and phosphorus include fertilizer, animal manure, phosphatic rock, dishwashing detergents, and human waste. Nitrogen and phosphorus may enter streams and lakes through runoff from the land surface, inputs from springs or ground-water inflow, point discharges such as municipal wastewater effluent, or atmospheric deposition. To prevent methemoglobinemia, the USEPA and the State of Florida established a MCL for nitrate of 10 mg/L as nitrogen in drinking water (U.S. Environmental Protection Agency, 2000a; Florida Administrative Code, 2003b). The USEPA also recommends that total nitrogen concentrations not exceed 0.9 mg/L and total phosphorus concentrations not exceed 0.04 mg/L in aggregate ecoregion XII (which includes the State of Florida) to prevent eutrophication in streams (U.S. Environmental Protection Agency, 2000b).

Nitrogen is dynamic in the environment. Ammonium is the most readily available form of nitrogen to plants and is readily converted to organic nitrogen after assimilation. Organically bound nitrogen also may be converted to ammonium through a series of biological transformations as the organic matter is decomposed and degraded. Under high pH conditions (pH greater than 8), which can occur with excessive algal blooms, ammonium can be converted to ammonia (NH₃) that is released to the atmosphere through volatilization. Ammonium also can be immobilized through ion exchange onto negatively charged soil particles, which makes ammonium less mobile in the environment compared to other forms of nitrogen.

Ammonium can be oxidized to nitrate in an aerobic environment through the microbially mediated process of nitrification. Nitrite is formed as an intermediate product in the nitrification process and typically is not found in large concentrations in the environment. Plants and microbes may assimilate nitrate through assimilatory nitrate reduction. Unlike ammonium, nitrate as a negatively charged compound is not subject to immobilization by negatively charged soil particles and is more mobile in the environment. Under anaerobic conditions, nitrate may be reduced to molecular nitrogen (N_2) and nitrous oxide (N_2O) by microorganisms. Denitrification is an important pathway for nitrogen loss from most kinds of wetlands (Mitsch and Gosselink, 2000). Molecular nitrogen also may be converted to organic nitrogen by certain aerobic and anaerobic bacteria and blue-green algae, a process known as nitrogen fixation.


Figure 31. Dissolved organic carbon concentration, specific ultraviolet light absorbance, and streamflow at St. Johns River sites, 2000-02.



Figure 31. Dissolved organic carbon concentration, specific ultraviolet light absorbance, and streamflow at St. Johns River sites, 2000-02. (Continued)

Phosphorus often is the most limiting nutrient in streams and lakes. Phosphorus occurs as dissolved and particulate inorganic and organic forms in water. Orthophosphate is the most common inorganic form of phosphorus in streams and is readily available to biota. Phosphorus has an affinity for calcium, iron, and aluminum and forms complexes with these elements. Phosphate also may sorb onto clay particles, organic matter, and ferric and aluminum oxides and hydroxides. Changes in environmental conditions may cause phosphate to be released from streambed sediments and soils. Under anaerobic conditions, ferric iron may be reduced to the more soluble ferrous iron, resulting in the release of phosphorus that was associated with the ferric iron. Phosphorus also can be released from insoluble salts when the pH of the water is lowered.

Total Nitrogen

Median total nitrogen concentrations in the St. Johns River ranged from 1.2 to 1.7 mg/L as nitrogen during 1991-99 (fig. 32). Concentrations at most sites were not significantly related to streamflow (table 24). Median concentrations were slightly lower at sites 17-18 and 20-21 (1.2-1.3 mg/L as nitrogen) compared to sites 1-5 (1.6-1.7 mg/L as nitrogen). Low concentrations may have resulted from dilution by the Wekiva River and Blue Springs. Concentrations near the mouth of the Wekiva River (site 16) during 1991-99 were lower than concentrations at all of the St. Johns River sites. The USEPA's recommended ecoregional nutrient criterion for total nitrogen of 0.9 mg/L as nitrogen was exceeded in about 90 percent or more of the samples collected from the



Figure 32. Total nitrogen concentration and nitrogen speciation in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99.

Table 24. Relations between total nitrogen, ammonia nitrogen, and organic plus ammonia nitrogen concentrations and streamflow at

 St. Johns River sites, 1991-2002.

[Correlations statistically significant at the 0.05 significance level are shown in bold. Explanation of values: tau, Kendall's tau; p. p-value; n, number of observations. Retrospective data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

Map ID		Explanation	Total nitrogen	Ammoni	Total organic plus ammonia nitrogen	
(fig. 4)	Station name	of values	Retrospective data (1991-99)	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)*	Retrospective data (1991-99)
1	St. Johns River near Cocoa	tau p n	-0.0503 .5410 69	0.2420 .0038 67	0.2355 .0034 72	-0.0618 .4525 69
3	St. Johns River near Christmas	tau p n	2411 .0001 123	3900 0 123	2907 .0003 72	2088 .0005 126
8	St. Johns River upstream of Lake Harney, near Geneva	tau p n	0543 .2082 242	3141 0 143	Not determined	0274 .5190 250
12	St. Johns River near Sanford	tau p n	Not determined	Not determined	.2879 .0003 72	Not determined
21	St. Johns River near DeLand	tau p n	.0699 .2473 125	.1723 .2121 26	.0837 .2964 72	.0781 .1888 130

*Dissolved ammonia nitrogen data.

St. Johns River during 1991-99. Fewer samples (about 65 percent) collected near the mouth of the Wekiva River exceeded 0.9 mg/L.

Ammonia Nitrogen

More than 75 percent of the ammonia concentrations reported at each of the St. Johns River sites during 1991-99 were greater than 0.02 mg/L. Ammonia also generally was detected in the river during 2000-02. Ninety percent or more of the concentrations measured from 2000-02 were at or greater than the method reporting limit for ammonia. Detections of ammonia nitrogen indicated that bioavailable nitrogen generally was present in the St. Johns River from 1991-2002. Ammonia concentrations generally increased during high-flow conditions at the Cocoa and Sanford sites, based on the 1991-99 data (table 24) and the 2000-02 data (table 24 and fig. 33). Higher ammonia concentrations during high-flow conditions may have resulted from less uptake of ammonia by phytoplankton or from runoff of animal wastes. During high-flow conditions, chlorophyll-a concentrations

rapidly decreased to below method reporting limits, indicating phytoplankton were less prevalent compared to other times of the year.

In contrast, ammonia concentrations generally were greater during low-flow conditions at the Christmas and above Lake Harney sites on the St. Johns River, based on the 1991-2002 data (fig. 33, table 24). One source of ammonia nitrogen to streams during low-flow conditions is ground-water inflow. The FDEP's data showed ammonia nitrogen concentrations as high as 1.2 mg/L in the Floridan aquifer system. There was a substantial increase in ammonia nitrogen concentrations at the Cocoa site during lowflow conditions in May 2000-values as high as 0.35 mg/L as nitrogen were measured. Increased concentrations during May 2000 likely did not result from ground-water inflow because ammonia nitrogen concentrations generally were not increased during low-flow conditions in water years 2001 and 2002 at this site. Another explanation for increased ammonia nitrogen concentrations is that decomposition of organic matter occurred, resulting in the production of ammonia.



Figure 33. Dissolved ammonia nitrogen concentration and streamflow at St. Johns River sites, 2000-02.

Organic Plus Ammonia Nitrogen

Most of the nitrogen in the St. Johns and Econlockhatchee Rivers was in the form of organic plus ammonia nitrogen. In the St. Johns River, more than 90 percent of the nitrogen in the water during 1991-99 was in the form of organic plus ammonia nitrogen. More than 80 percent of the nitrogen near the mouth of the Econlockhatchee River was in the form of organic plus ammonia nitrogen. Near the mouth of the Wekiva River, the percentage of organic plus ammonia nitrogen in the water was less compared to the St. Johns and Econlockhatchee Rivers. At this site, generally about one-half of the nitrogen in the water during 1991-99 was in the form of organic plus ammonia nitrogen.

The distribution of total organic plus ammonia nitrogen concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers during 1991-99 were similar to those for total nitrogen concentrations (fig. 32) because organic plus ammonia nitrogen made up more than one-half of the nitrogen in the streams. Total organic plus ammonia nitrogen concentrations generally were not significantly correlated with streamflow at the St. Johns River sites during 1991-99 (table 24).

Nitrate Nitrogen

Nitrate concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers generally were less than 0.5 mg/L during 1991-99 (table 25). The distribution of nitrate concentrations in the St. Johns River was not similar to the distribution of total nitrogen. Nitrate generally comprised less than 10 percent of the total nitrogen concentration in the river. Nitrate concentrations in the St. Johns River were significantly greater at sites downstream of the Wekiva River compared to the other sites (table 25). High median nitrate concentrations at these sites may be due in part to nitrogen-enriched ground-water inflow. Nitrate concentrations exceeding 1.0 mg/L were reported in water from the

Table 25. Descriptive statistics of nitrate nitrogen concentrations in the St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99.

[N, number of samples; IQR, interquartile range; the IQR may not equal the 75th percentile minus the 25th percentile due to rounding. The a, b, c, letters next to the IQR indicates whether concentrations were significantly different among sites at the 0.05 significance level. IQRs denoted with the same letter indicate concentrations were not significantly different]

Map ID (fig. 4)	Station name	Ν	Percent censored data	25 th percentile	Median	75 th percentile	IQR
1	St. Johns River near Cocoa	69	49.3	0.010*	0.020	0.057	0.048 a
2	St. Johns River at Beeline Highway	77	40.3	.014*	.023	.056	.043 a
3	St. Johns River near Christmas	123	41.5	.013*	.027	.070	.057 ab
4	St. Johns River at Orange Mound	30	53.3	.010*	.024*	.062	.052 a
5	St. Johns River at Puzzle Lake	79	67.1	.010*	.017*	.030	.020 a
7	Econlockhatchee River near the mouth	73	15.1	.052	.15	.23	.178 d
8	St. Johns River upstream of Lake Harney, near Geneva	248	11.3	.030	.048	.075	.045 ab
9	St. Johns River at north end of Lake Harney	127	47.2	.019*	.030	.060	.041 ab
10	St. Johns River at Lemon Bluff	107	35.5	.023*	.040	.060	.037 ab
11	St. Johns River at State Road 415 Bridge	107	38.3	.024*	.040	.060	.036 ab
12	St. Johns River near Sanford	150	36.7	.020*	.040	.097	.077 ab
13	St. Johns River south of the confluence with the Wekiva River	125	29.6	.020*	.060	.10	.080 b
16	Wekiva River near the mouth	124	2.4	.245	.40	.500	.255 e
17	St. Johns River north of the confluence with the Wekiva River	124	15.3	.060	.091	.120	.060 c
18	St. Johns River downstream of Blue Springs	106	5.7	.079	.10	.200	.121 c
20	St. Johns River near Hontoon Marina	107	10.3	.070	.10	.147	.077 c
21	St. Johns River near DeLand	131	9.2	.062	.10	.170	.108 c

*Percentile estimated using the probability plotting procedure described by Helsel and Cohn, 1988.

Upper Floridan aquifer in the Wekiva Springs groundwater basin (Toth and Fortich, 2002). Wekiva Springs, with an average flow of about 56 ft³/s, forms the headwaters of the Wekiva River. Median nitrate concentrations near the mouth of the Wekiva River during 1991-99 were significantly greater during the January-June lowflow period compared to the September-October highflow period (fig. 34). These results indicate that nitrateenriched ground water affected the Wekiva River and probably affected the St. Johns River downstream of its confluence with the Wekiva River. Low median nitrate concentrations in the upstream part of the St. Johns River, may be related to: (1) nitrate being used as a nutrient by terrestrial and aquatic plants; (2) denitrification in wetland areas; or (3) the fact that much of the agricultural land is pasture, which generally is not fertilized.

Median nitrate concentrations near the mouth of the Econlockhatchee River were greater than those in the St. Johns River during 1991-99. At this site, nitrate concentrations were significantly greater during the January-February and May-June low-flow periods compared to the September-October high-low period (fig. 34). These results indicate that increased nitrate concentrations in the Econlockhatchee River were related to discharges of municipal wastewater or to ground-water inflow.

Seasonal variations in nitrate concentrations in the St. Johns River were characterized by sharp peaks in concentration from about October-February during 2000-02, most notably at the Cocoa, Sanford, and DeLand sites (fig. 35). Nitrate concentrations from about October-February at the Cocoa and DeLand sites increased to values as high as 0.44 mg/L. During most other times of



Figure 34. Nitrate nitrogen concentrations by seasonal period near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99.



Figure 35. Dissolved nitrite plus nitrate nitrogen concentration and water temperature at St. Johns River sites, 2000-02.



Figure 35. Dissolved nitrite plus nitrate nitrogen concentration and water temperature at St. Johns River sites, 2000-02. (Continued)

the year, concentrations were at or below method reporting limits (0.02 mg/L) at the Cocoa and DeLand sites. Increased concentrations from October-February probably did not result from wastewater discharges or ground-water inflow. There are few wastewater discharges upstream of the Cocoa site. Increased concentrations from wastewater discharges or ground-water inflow also are expected to occur during low-flow conditions. The October-February period, however, encompassed both high- and low-flow conditions. If variations in concentrations were primarily the result of wastewater discharges or ground-water inflow, increased concentrations also would be expected during the March-June low-flow period, which did not occur. Nitrate can be used as a nutrient by plants, which could explain lower concentrations from March-June. Ammonium nitrogen, which generally is used preferentially by plants before nitrate is used, typically was detected at all St. Johns River sites; this indicates that nitrate may not have been assimilated by plants from March-June. Another explanation for increased nitrate concentrations from October-February is that conditions may have been more favorable for nitrification of ammonium in the St. Johns River or floodplain sediments. The main factors that limit nitrification include the

availability of ammonium nitrogen, dissolved oxygen concentration, and water temperature (Schmidt, 1982). Nitrate nitrogen concentrations at the Cocoa, Christmas, Sanford, and DeLand sites were inversely correlated to water temperature (fig. 35). During periods of low water temperatures, conditions may have been favorable for nitrification because of reduced uptake of ammonium nitrogen by plants and the greater solubility of oxygen in the water.

At the Sanford and DeLand sites, increased nitrate concentrations also were measured during high-flow conditions in water years 2001 and 2002. Nitrate concentrations were as high as 0.27 mg/L and occurred on the rising limb of the streamflow hydrograph. Increased concentrations at these two sites may have resulted from the runoff of fertilizers or animal wastes from urban land.

Total Phosphorus

Median total phosphorus concentrations in the St. Johns River ranged from about 0.03 to 0.09 mg/L during 1991-99 (table 26). Increased total phosphorus concentrations at sites downstream of the Wekiva River may have resulted from phosphorus-enriched ground-

 Table 26. Descriptive statistics of total phosphorus concentrations in the St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99.

[Map identifier refers to fig. 4. N, number of samples; IQR, interquartile range; the IQR may not equal the 75th percentile minus the 25th percentile in some cases due to rounding]

Map ID (fig. 4)	Station name	Ν	Percent censored data	25 th percentile	Median	75 th percentile	IQR
1	St. Johns River near Cocoa	67	0	0.050	0.066	0.099	0.049
2	St. Johns River at Beeline Highway	71	0	.058	.083	.118	.060
3	St. Johns River near Christmas	122	1.6	.049	.072	.110	.062
4	St. Johns River at Orange Mound	29	3.4	.036	.053	.091	.055
5	St. Johns River at Puzzle Lake	78	2.6	.018	.032	.065	.047
7	Econlockhatchee River near the mouth	52	0	.065	.083	.091	.029
8	St. Johns River upstream of Lake Harney, near Geneva	250	52.0	.040*	.060*	.087	.047
9	St. Johns River at north end of Lake Harney	102	65.0	.040*	.053*	.069	.029
10	St. Johns River at Lemon Bluff	103	53.4	.050*	.062*	.081	.032
11	St. Johns River at State Road 415 Bridge	104	41.3	.050*	.069*	.095	.045
12	St. Johns River near Sanford	146	31.0	.054*	.080	.100	.046
13	St. Johns River south of the confluence with the Wekiva River	100	17.0	.068	.082	.107	.039
16	Wekiva River near the mouth	103	4.9	.076	.091	.113	.037
17	St. Johns River north of the confluence with the Wekiva River	104	15.4	.067	.085	.101	.035
18	St. Johns River downstream of Blue Springs	103	17.5	.066	.080	.097	.031
20	St. Johns River near Hontoon Marina	104	16.3	.067	.080	.101	.034
21	St. Johns River near DeLand	129	12.4	.065	.078	.095	.030

*Percentile estimated using the probability plotting procedure described by Helsel and Cohn, 1988.

water inflow. Phosphorus concentrations as high as 0.35 mg/L were reported in water from the Upper Floridan aquifer in the Wekiva Springs ground-water basin (Toth and Fortich, 2002). Phosphorus concentrations in the Wekiva River were greater than those in the St. Johns River. The 1991-99 data showed a median total phosphorus concentration of 0.091 mg/L near the mouth of the Wekiva River; the 2000-02 data showed a median total phosphorus concentration of 0.10 mg/L at the Wekiva River near Sanford.

More than 80 percent of the total phosphorus concentrations from the St. Johns River, Econlockhatchee River, Wekiva River, and Blue Springs exceeded the recommended ecoregional nutrient criterion of 0.04 mg/L established by the USEPA, based on 1991-99 and 2000-02 data. In the St. Johns River, the fewest exceedances of the recommended ecoregional nutrient criterion were at the Orange Mound and Puzzle Lake sites (sites 4-5, fig. 4). At these two sites, 72 and 44 percent of the concentrations exceeded the recommended ecoregional nutrient criterion, respectively.

The 2000-02 data showed increased total phosphorus concentrations in the St. Johns River on the rising limb of the hydrograph, especially in water years 2001 and 2002 (fig. 36). Increased phosphorus concentrations generally coincided with increased total iron concentration, suggesting that phosphorus was associated with iron. There was one occurrence of a pronounced increase in total phosphorus concentrations in the St. Johns River during low-flow conditions. At the Cocoa site, total phosphorus concentrations increased to 0.25 mg/L in May-June 2000. This pattern is not consistent with inputs by ground water because concentrations did not increase to these levels during low-flow periods in 2001 and 2002. A major process in the cycling of phosphorus in lakes and rivers is the interaction of phosphorus with bottom sediments (Correll, 1998; House and Denison, 2002). One explanation for increased concentrations from May-July 2000 is that conditions were conducive for phosphorus release from sediments in the St. Johns River or riverine lakes.

Relations between total phosphorus concentrations and streamflow were not consistent between the 1991-99 and 2000-02 data at the St. Johns River sites (table 27), suggesting that relations determined using the 2000-02 data may be due to the extreme high- and low-flow conditions of this period. The 1991-99 data showed total phosphorus concentrations generally increased during high streamflow conditions at the Cocoa site. Detection of a significant relation between total phosphorus concentration and streamflow at this site during 2000-02 may have been masked by the increased total phosphorus concentrations during May-July 2000, which did not occur during other low-flow periods. The 1991-99 data also showed that total phosphorus concentrations at the Christmas and upstream of Lake Harney sites generally decreased with increasing streamflow; the data showed no relation between total phosphorus concentration and streamflow at the DeLand site. The positive relation between total phosphorus concentrations and streamflow at the Christmas site (2000-02 data) may have resulted from increased phosphorus accumulation on the land surface during the drought conditions in 2000 and 2001 that washed off during the high-flow events.

Orthophosphate Phosphorus

At most of the sites on the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, orthophosphate was reported in more than 90 percent of the samples from 1991-99 (table 28), indicating that bioavailable phosphorus generally is present in the St. Johns River. Orthophosphate made up about 35 to 66 percent of the median total phosphorus concentration at the St. Johns River sites. Orthophosphate made up about 69 percent of the median total phosphorus concentration near the mouth of the Econlockhatchee River, and about 78 percent of the median total phosphorus concentration near the mouth of the Wekiva River.

The 1991-2002 data showed orthophosphate concentrations were significantly greater during high-flow conditions at the Cocoa, Sanford, and DeLand sites (table 27). Increased orthophosphate concentrations during high-flow periods may indicate the runoff of phosphorus fertilizer applied to the land surface. In contrast, little fertilizer is applied to the agricultural land in the vicinity of the Cocoa and Christmas sites because most of this land is unimproved pasture. It is likely that increased orthophosphate concentrations at these sites during highflow conditions resulted from the mineralization of livestock manures or organic soils, which may have occurred during drier conditions.

Relations between orthophosphate concentrations and streamflow determined using the 1991-99 and 2000-02 data were not consistent at the Christmas site. The 1991-99 data showed orthophosphate concentrations at the Christmas site had no relation with streamflow. The 2000-02 data, however, showed that orthophosphate concentrations significantly increased during high-flow conditions.



Figure 36. Total phosphorus concentration and streamflow at St. Johns River sites, 2000-02.

 Table 27. Relations between total phosphorus and orthophosphate concentrations and streamflow at St. Johns River sites, 1991-2002.

[Correlations statistically significant at the 0.05 significance level are shown in bold. Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations. Retrospective data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

		Total pho	osphorus	Orthophosphate phosphorus		
Map ID (fig. 4)	Station name	Explanation of values	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)
1	St. Johns River near Cocoa	tau p n	0.2415 .0038 67	0.0395 .6218 72	0.3107 .0001 69	0.3760 0 72
3	St. Johns River near Christmas	tau p n	1600 .009 122	.1941 .0151 72	0569 .3478 123	.3772 0 72
8	St. Johns River upstream of Lake Harney, near Geneva	tau p n	1002 .0177 250	Not determined	0695 .1099 238	Not determined
12	St. Johns River near Sanford	tau p n	Not determined	.1342 .0926 72	Not determined	.3290 0 72
21	St. Johns River near DeLand	tau p n	.0329 .579 129	.2516 .0016 72	.3544 0 131	.4433 0 72

Table 28. Descriptive statistics of orthophosphate concentrations in the St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99.

[All concentrations are expressed as phosphorus; N, number of samples; IQR, interquartile range; the IQR may not equal the 75th percentile minus the 25th percentile due to rounding. Data from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

Map ID (fig. 4)	Station name	Ν	Percent censored data	Maximum reporting limit	25 th percentile	Median	75 th percentile	IQR
1	St. Johns River near Cocoa	69	22	0.02	0.015*	0.030	0.059	0.044
2	St. Johns River at Beeline Highway	75	2.7	.02	.034	.049	.087	.053
3	St. Johns River near Christmas	123	22	.02	.023	.038	.059	.036
4	St. Johns River at Orange Mound	27	18.5	.01	.015	.026	.060	.045
5	St. Johns River at Puzzle Lake	81	35.8	.01	.006*	.014	.027	.020
7	Econlockhatchee River near the mouth	54	3.7	.01	.040	.057	.068	.028
8	St. Johns River upstream of Lake Harney, near Geneva	238	28	.02	.020	.035	.049	.029
9	St. Johns River at north end of Lake Harney	105	1.9	.006	.014	.023	.037	.023
10	St. Johns River at Lemon Bluff	107	1.9	.006	.020	.028	.039	.019
11	St. Johns River at State Road 415 bridge	107	3.7	.006	.024	.024	.036	.025
12	St. Johns River near Sanford	133	12.8	.02	.011	.028	.046	.035
13	St. Johns River south of the confluence with the Wekiva River	105	5.7	.006	.011	.030	.054	.043
16	Wekiva River near the mouth	105	0		.071	.084	.093	.022
17	St. Johns River north of the confluence with the Wekiva River	105	1.0	.006	.020	.037	.059	.039
18	St. Johns River downstream of Blue Springs	106	1.9	.006	.026	.042	.058	.033
20	St. Johns River near Hontoon Marina	107	0		.020	.040	.055	.035
21	St. Johns River near DeLand	131	3.8	.01	.020	.040	.060	.040

*Percentile was estimated using a probability plotting procedure.

Total phosphorus concentration data (fig. 36) showed increased concentrations at the Cocoa site during May-June 2000. An increase in orthophosphate concentrations at this site during the same period was not measured. It is likely that any orthophosphate present at this site was utilized by phytoplankton and converted into organic phosphorus.

Chlorophyll-a

Chlorophyll-*a* is a photosynthetic pigment whose concentration is commonly used as a surrogate for the amount of algae in the water. To prevent eutrophication in streams, the USEPA recommends that chlorophyll-*a* concentrations not exceed 0.40 μ g/L in aggregate ecoregion XII, which includes the State of Florida. Retrospective chlorophyll-*a* concentration data were available from the FFWCC, Orange County, SJRWMD, and Volusia County. No retrospective data were available from the FDEP and the USGS.

Chlorophyll-*a* concentrations generally were greater than 0.4 μ g/L in more than 90 percent of the samples from the St. Johns, Econlockhatchee, and Wekiva Rivers, based on the 1991-2002 data. In the St. Johns River, chlorophyll-*a* concentrations during 1991-99 (fig. 37) generally were greater at sites downstream of Lake Monroe compared to the other sites. Total phosphorus concentrations in the St. Johns River also generally were greater at sites downstream of Lake Monroe compared to the other sites (table 26), which suggests that increased chlorophyll-a concentrations at these same locations may have resulted in part from increased phosphorus concentrations. Chlorophyll-a concentrations also were greater at the downstream of Lake Harney site compared to the upstream of Lake Harney site, although total phosphorus concentrations were not substantially different at these two sites (table 26). This suggests that increased chlorophyll-a concentrations downstream of the lake may not be the result of increased phosphorus inputs to the river. Another explanation for increased chlorophyll-a concentrations at the downstream of Lake Harney site is that the quiescent conditions in the lake provide more optimal conditions for algal growth.

Chlorophyll-*a* concentrations in the St. Johns River generally were greater during the spring and summer low-flow periods. The 1991-99 data generally showed that concentrations were greater during the May-June low-flow period compared to other times of the year at sites downstream of site 11 (fig. 4). For example, in the St. Johns River downstream of Blue Springs (site 18), median concentrations in May-June were about 29 μ g/L compared to about 2 μ g/L in November-December (fig. 38).



Figure 37. Chlorophyll-*a* concentrations in the St. Johns River and near the mouths of the Econlockhatchee and Wekiva Rivers, 1991-99.



Figure 38. Seasonal variations in chlorophyll-*a* concentrations in the St. Johns River downstream of Blue Springs, Florida, 1991-99.

During 2000-02, chlorophyll-*a* concentrations at the Cocoa site generally were high during the spring and summer low-flow periods, from about April through August (fig. 39).Concentrations were high from about April through August at the other sites as well. Concentrations likely increased during the spring and summer low-flow periods in response to increased water temperatures. Chlorophyll-*a* concentrations generally remained elevated during the summer until high-flow events occurred in response to the wet-season rainfall.

Decreases in chlorophyll-*a* concentrations during highflow events likely resulted from light limitation of phytoplankton growth due to inputs of highly colored organic matter into the St. Johns River (fig. 30). Chlorophyll-*a* concentrations and water color were inversely related (Kendall's tau = -0.5041, p = 0). This hypothesis is consistent with studies (Aldridge and others, 1998; Phlips and others, 2000), indicating that light availability strongly affects phytoplankton crops in the lower St. Johns River.



Figure 39. Chlorophyll-*a* concentrations and streamflow at the St. Johns River site near Cocoa, Florida, 2000-02.

Turbidity

Turbidity is a measure of the scattering of light and is interpreted as a measure of the clarity of water. Increased water turbidity may result from algal growth or inorganic sediment suspended in the water. To protect streams from over-enrichment of nitrogen and phosphorus, the USEPA has established a recommended ecoregional criterion for turbidity of 1.9 nephelometric turbidity units (NTU) for aggregate ecoregion XII, which includes the State of Florida.

More than 80 percent of the turbidity values in the St. Johns River from 2000-02 exceeded 1.9 NTU. In contrast, less than 10 percent of the turbidity values from the Wekiva River near Sanford and 33 percent of the values from Blackwater Creek exceeded the recommended criterion of 1.9 NTU. Median turbidity values in the St. Johns River were greater at the Cocoa and Christmas sites (4.8 and 6.1 NTU, respectively) than at the Sanford and DeLand sites (3.9 and 2.9 NTU, respectively). Turbidity values had a significant inverse relation with streamflow at each of the sites (table 29). High turbidity values during low-flow periods were not consistent with inputs of sediment by soil erosion, but suggests

that algal growth or the resuspension of bottom sediments during the spring and summer low-flow period contributes turbidity in the St. Johns River.

Total Suspended Solids

Total suspended solids concentration is an indicator of the amount of particulate matter in water and is measured as the amount of particulates that remains on a glass-fiber filter after an aliquot of sample has passed through a filtration apparatus. Particulate matter may be transported to a stream by erosion or through the resuspension of settled particulate matter in the streambed. Photosynthetic activity also can convert carbon and nutrients dissolved in the water into biomass.

Spatial, seasonal, and temporal variations in total suspended solids concentrations were similar to those for chlorophyll-*a*. Median total suspended solids concentrations in the St. Johns River during 1991-99 (table 30) were highest at sites downstream of State Road 415, generally where the highest chlorophyll-*a* concentrations occur in the river (fig. 37). Similar to the results for chlorophyll-*a*, total suspended solids concentrations generally

 Table 29. Relations between turbidity values and total suspended solids concentrations and streamflow at St. Johns

 River sites, 1991-2002.

[Correlations statistically significant at the 0.05 significance level are shown in bold. Explanation of values: tau, Kendall's tau; p, p-value; n, number of observations. Retrospective data were compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

			Turbidity	Total suspe	ended solids
Map ID (fig. 4)	Station name	Explanation of values	U.S. Geological Survey data (2000-02)	Retrospective data (1991-99)	U.S. Geological Survey data (2000-02)
1	St. Johns River near Cocoa	tau p n	-0.5172 0 72	Not determined	-0.5708 0 72
3	St. Johns River near Christmas	tau p n	3799 0 72	2465 0 126	4710 0 72
8	St. Johns River upstream of Lake Harney, near Geneva	tau p n	Not sampled	2393 0 249	Not determined
12	St. Johns River near Sanford	tau p n	3282 0 72	Not determined	3009 .0002 72
21	St. Johns River near DeLand	tau p n	3282 0 72	2132 .0009 108	2825 .0005 72

Table 30. Descriptive statistics of total suspended solids concentrations in the St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99.

[N, number of samples; IQR, interquartile range; the IQR may not equal the 75th percentile minus the 25th percentile due to rounding. Data not analyzed for St. Johns River at Puzzle Lake]

Map ID (fig. 4)	Station name	Ν	Percent censored data	25 th percentile	Median	75 th percentile	IQR
1	St. Johns River near Cocoa	69	91.3		Not co	mputed	
2	St. Johns River at Beeline Highway	77	55.8	1.62*	3.59*	7.46	5.84
3	St. Johns River near Christmas	126	67.5	1.77*	3.51*	6.89	5.12
4	St. Johns River at Orange Mound	29	20.7	3.00	4.00	6.00	3.00
7	Econlockhatchee River near the mouth	57	57.9	.86*	1.93*	4.00	3.14
8	St. Johns River upstream of Lake Harney, near Geneva	249	59.8	2.13*	3.47*	6.00	3.87
9	St. Johns River at north end of Lake Harney	103	61.2	2.54*	4.13*	7.00	4.46
10	St. Johns River at Lemon Bluff	105	56.2	1.93*	3.94*	9.00	7.07
11	St. Johns River at State Road 415 Bridge	106	35.8	3.74*	6.50	11.25	7.51
12	St. Johns River near Sanford	133	27.8	5.00*	8.00	14.50	9.50
13	St. Johns River south of the confluence with the Wekiva River	104	14.4	5.00	11.0	14.75	9.75
16	Wekiva River near the mouth	103	53.4	2.94*	4.44*	6.50	3.56
17	St. Johns River north of the confluence with the Wekiva River	104	23.1	5.00	8.50	12.00	7.00
18	St. Johns River downstream of Blue Springs	105	26.7	7.50*	4.57	12.00	7.43
20	St. Johns River near Hontoon Marina	106	21.7	5.00	8.00	13.25	8.25
21	St. Johns River near DeLand	106	28.3	4.60*	7.00	11.40	6.80

*Percentile estimated using a probability plotting procedure.

were greater during the May-June low-flow period compared to the other periods at sites downstream of Lake Harney, as indicated by data from the Hontoon Marina site (fig. 40). Data from the Christmas site from 2000-02 (fig. 41) further illustrate that the highest total suspended solids concentrations occurred during lowflow conditions.

Higher total suspended solids concentrations during low-flow periods combined with similar spatial, seasonal, and temporal patterns between chlorophyll-*a* and total suspended solids concentrations suggest that chlorophyll-*a* probably contributes a substantial portion of the suspended solids in the river. Correlations between chlorophyll-*a* and total suspended solids concentrations at all of the St. Johns River sites were significant and positive, except for the Cocoa, Christmas, and Orange Mound sites from 1991-99 (table 31). The strongest correlations between chlorophyll-*a* and total suspended solids concentrations generally were observed at sites downstream of State Road 415. These also were the sites where the highest concentrations of chlorophyll-*a* generally were observed (fig. 37).

Human and Veterinary Antibiotics, Other Human Prescription and Nonprescription Drugs, Pesticides, and Organic Wastewater Constituents

Limited sampling was conducted at the Cocoa (site 1, fig. 4) and Sanford (site 12, fig. 4) sites on the St. Johns River in 2002 and 2003 to determine the occurrence of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and a suite of organic constituents which may indicate domestic or industrial waste (app. B). Human prescription and nonprescription drugs analyzed included antacids, antibiotics, a stimulant, and anticoagulant, antihypertensive, and antiinflammatory drugs. A limited number (11) of pesticides and pesticide degradates were analyzed, including atrazine, bromacil, carbaryl, chlorpyrifos, diazinon, metalaxyl, metolachor, and prometon. Method reporting limits for pesticides were relatively high $(0.5 \,\mu g/L)$ compared to other methods (Furlong and others, 2001). Some of the pesticides analyzed, such as bromacil, atrazine, and metolachlor, may be applied to agricultural land in the study



Figure 40. Seasonal variations in total suspended solids concentration in the St. Johns River near Hontoon Marina, Florida, 1991-99.



Figure 41. Total suspended solids concentration and streamflow at the St. Johns River site near Christmas, Florida, 2000-02.

area. Caffeine, cotinine, and sulfamethoxazole were analyzed by two methods; two reporting limits are listed for these constituents in appendix B.

A total of 20 compounds was detected, including pesticides, antibiotics, plasticizers, and detergent metabolites (fig. 42). Atrazine, metolachlor, and cholesterol were the most frequently detected compounds. No pesticide concentrations exceeded applicable MCLs established by the USEPA. Atrazine and metolachlor are pesticides used to control broadleaf and grassy weeds on corn and vegetable crops in Florida (Shahane, 1999). Atrazine also is used to control weeds in St. Augustine grass (McCarty, 1995). Cholesterol is a steroid and can originate from both animal and plant sources (Zaugg and others, 2002). The frequent detection of cholesterol is consistent with a nationwide study on the occurrence of pharmaceuticals, hormones, and organic wastewater contaminants in streams in which steroids were detected in over 80 percent of the samples analyzed (Kolpin and others, 2002). Atrazine was detected in 83 percent of the **Table 31.** Kendall's tau correlation coefficients describing the relation between chlorophyll-*a* and total suspended solids concentration at sites on the St. Johns, Econlockhatchee, and Wekiva Rivers, 1991-99.

[N, number of observations; p-value, probability value. Correlations statistically significant at the 0.05 significance level are shown in bold. Retrospective data compiled from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

Map ID	Station name		letrospective d (1991-99)	ata	U.S. Geological Survey data (2000-02)		
(fig. 4)	Station name	Ν	Kendall's tau	p-value	Ν	Kendall's tau	p-value
1	St. Johns River near Cocoa	59	0.0158	0.7353	72	0.4887	0.0
2	St. Johns River at Beeline Highway	29	.4433	.0006		Not sample	d
3	St. Johns River near Christmas	76	.01789	.8022	72	.4636	0
4	St. Johns River at Orange Mound	28	.2154	.1167	Not sampled		
5	St. Johns River at Puzzle Lake	Total s	suspended so not compile	lids data d		Not sample	d
7	Econlockhatchee River near the mouth	37	.2628	.0096		Not sample	d
8	St. Johns River upstream of Lake Harney, near Geneva	178	.1074	.0278		Not sample	d
9	St. Johns River at north end of Lake Harney	iver at north end of Lake Harney 105 .3463 0			Not sampled		
10	St. Johns River at Lemon Bluff	107	.3226	0		Not sample	d
11	St. Johns River at State Road 415 Bridge	106	.5332	0		Not sample	d
12	St. Johns River near Sanford	129	.4250	0	71	.6103	0
13	St. Johns River south of the confluence with the Wekiva River	106	.4947	0		Not sample	d
14	Wekiva River near Sanford		-Not sample	d	12	Not deter	rmined
15	Blackwater Creek near Cassia		-Not sample	d	12	Not deter	rmined
16	Wekiva River near the mouth	101	.1525	0		Not sample	d
17	St. Johns River north of the confluence with the Wekiva River	103	.5393	0		Not sample	d
18	St. Johns River downstream of Blue Springs	103	.5517	0		Not sample	d
20	St. Johns River near Hontoon Marina	105	.5456	0		Not sample	d
21	St. Johns River near DeLand	105	.5110	0	72	.5919	0

samples analyzed from the Cocoa and Sanford sites; metolachlor and cholesterol were detected in 57 percent of the samples analyzed. In most cases, concentrations were less than the method reporting limits; however, the presence of these constituents was confirmed in the laboratory by using mass spectrometry. Reported concentrations less than the method reporting limit are estimated concentrations.

More constituents were detected in water from the Sanford site compared to the Cocoa site, which likely reflects that the Sanford site is downstream from (1) point sources delivering municipal wastewater effluent to streams in the study area and (2) urban-residential areas on septic systems. A total of 20 constituents was detected at the Sanford site. The most frequently detected constituents at this site were atrazine, cholesterol, coprostanol, and cotinine. Coprostanol is produced almost exclusively in the digestive tracts of higher mammals and is often correlated with the presence of other sewage-derived contaminants (Zaugg and others, 2002). Cotinine is a nicotine metabolite. Atrazine was detected in 75 percent of the samples analyzed from this site, and cotinine was detected in 67 percent samples analyzed. Coprostanol and cholesterol were detected in 50 percent of the samples



Figure 42. Frequency of detection of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and organic wastewater constituents at the St. Johns River sites near Cocoa and Sanford, Florida, water years 2002-03.

analyzed. The other constituents detected at the Sanford site, including the antibiotic azithromycin and anhydroerythromycin, were each measured only once.

Atrazine, metolachlor, cholesterol, bromacil, and phenol were detected at the Cocoa site. Bromacil is a pesticide commonly applied to citrus in Florida. Phenol is used as a disinfectant (Zaugg and others, 2002) and was reported at oncentrations near reporting limits in field blank samples (Kolpin and others, 2002). Atrazine and metolachlor were detected in all of the samples analyzed from this site; cholesterol was detected in 67 percent of the samples analyzed. Bromacil and phenol were each detected once. The greatest concentration of atrazine, 0.77 ug/L, was measured in April 2002.

Although limited, the data at the Cocoa site suggest that a greater number of constituents were detected during high-flow conditions than during low-flow conditions, which suggests these constituents probably are transported by runoff (fig. 43). At this site, five constituents were detected during high-flow conditions in August 2002. In contrast, only one constituent (metolachlor) was detected during low-flow conditions in December 2001.

At the Sanford site, the limited data indicate that a greater number of constituents generally were detected during low-flow conditions, which suggests constituents measured at this site resulted from point-source discharges or septic tank leachate. Constituent concentrations are expected to be more concentrated during lowflow conditions if point-source discharges and septic tank leachate are the sources of constituents because these comprise a greater percentage of the streamflow during such conditions. At the Sanford site, 12 constituents were detected during low-flow conditions in June 2002; 10 constituents were detected during low-flow conditions in December 2002; and 4 constituents (not including human prescription and nonprescription drugs) were detected in March 2002. In contrast, only one constituent (2-butoxy-phosphate ethanol) was detected at this site during high-flow conditions in September 2002.

Sampling was conducted once in March 2003 to determine the occurrence of the suite of organic constituents that may indicate domestic or industrial waste, pesticides, and human prescription and nonprescription drugs at three points in the water treatment process at a pilot facility on Lake Monroe. Removal of iron and organic matter was necessary at this facility because iron concentrations in the St. Johns River were greater than the secondary drinking water regulation established by the USEPA during high-flow conditions and because dissolved organic carbon concentrations were relatively high (the median concentration at the Sanford site was 19.5 mg/L). Removal of dissolved solids and chloride



Figure 43. Number of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and organic wastewater constituents detected at selected St. Johns River sites near Cocoa and Sanford, Florida, water years 2000-02.

also was necessary because concentrations of these two constituents exceeded secondary drinking water regulations established by the USEPA during low-flow conditions. Conventional water treatment (coagulation/ flocculation, high-rate clarification, and filtration) was used at the pilot facility to remove iron and organic matter from the water, and reverse osmosis was used to remove dissolved solids and chloride. Disinfectant (chloramine) was applied prior to the reverse-osmosis process to reduce biological fouling of the reverse-osmosis membranes.

Water samples were collected to document the quality of the untreated influent or raw water to the facility, finished water after conventional treatment, and the finished water after the reverse-osmosis process. Fewer constituents were detected in the reverse-osmosis filtered sample than in the raw water or conventionally treated water samples. Only one constituent (bromoform) was detected in the reverse-osmosis treated water sample, which suggests this process removed most of the trace organic contaminants from the water. In the raw water sample, seven constituents were detected (atrazine; cotinine; caffeine; bromacil; phenol; 3,4-dichlorophenol isocyanate; and 2-butoxy-phosphate ethanol).

Ten constituents were detected in the conventionally treated water sample (anthraquinone, atrazine, cotinine, caffeine, bromacil, bromoform, 2-butoxy-phosphate ethanol, carbamazepine, fluoranthene, pentachlorophenol). Bromoform, a disinfection byproduct, likely was formed in the conventionally treated water after the disinfectant was applied. The fact that other constituents were detected in finished water that were not detected in raw water may have resulted from the removal of matrix components in the raw water by the conventional water-treatment process. Matrix interferences in raw water samples can preclude getting a sufficiently good-quality spectral match to be confident of making an identification, particularly if the concentration of the interferent is much greater than the compound of interest. This can be a particular problem with samples that may contain substantial amounts of wastewater effluent (E. Furlong, U.S. Geological Survey, written commun., 2003).

Anthraquinone is used as a bird repellent and is used in manufacturing textiles (Zaugg and others, 2002). Fluoranthene is a combustion product of coal, oil, gas, or wood (Zaugg and others, 2002). Pentachlorophenol is used as a wood preservative. Carbamazepine is an anticonvulsant drug, which has been reported as a persistent indicator of wastewater contamination in Europe. Ternes (1998) reported that carbamazepine was ubiquitously present in the aquatic environment in Germany with median concentrations of 2.1 µg/L in wastewater effluent and 0.25 µg/L in streams. These ubiquitous and high concentrations were attributed to the extremely low removal rate in wastewater treatment facilities. Only about 7 percent of the carbamazepine was removed in a wastewater treatment facility near Frankfurt, Germany (Ternes, 1998). Investigations in Germany and Switzerland (Ternes, 1998; Tixier and others, 2003) have shown that of the pharmaceuticals studied, carbamazepine had the highest daily loads in wastewater effluent. Subsequent sampling and collection of field-blank and replicate data would be useful to better define the occurrence of these constituents in the conventionally treated water. Five constituents (atrazine, cotinine, caffeine, bromacil, and 2-butoxy-phosphate ethanol) were detected in both the raw and conventionally treated water samples, which suggests that the conventional water-treatment process used at the pilot facility on Lake Monroe may not remove these constituents.

Temporal Trends (1991-99)

Temporal trends in constituent values during 1991-99 were determined at the Cocoa, Christmas, upstream of Lake Harney, and DeLand sites (fig. 4, table 32). Temporal trends were not determined at the Sanford site because continuous streamflow data were not available from 1991-95. Most temporal trends were determined using the Seasonal-Kendall test. Temporal trends in nitrate, ammonia nitrogen, total phosphorus, and orthophosphate concentrations were determined using Tobit regression because at each site there generally were greater than 5 percent censored data and two reporting limits. All Tobit regression models included terms accounting for flow- and seasonal-related variability. Temporal trends in ammonia nitrogen were not determined at the DeLand site because concentrations were not reported from 1996-99. Temporal trends in chlorophyll-a concentrations were not calculated for the Cocoa site because there were too few observations in the beginning of the period of record.

The criteria for significance of temporal trends were that each trend was significant at the 0.05-significance level during the 1991-98, 1991-99, and/or 1992-99 periods.

Increased total phosphorus and orthophosphate concentrations at the Cocoa, Christmas, and upstream of Lake Harney sites were the most notable temporal trends in water-quality constituents from 1991-99. The reason for the increases in phosphorus concentrations was not readily apparent. Higher phosphorus concentrations from 1991-99 likely were not the result of increased fertilizer applications or greater cattle numbers. County-level fertilizer-sales data compiled by the USGS (D. Lorenz, U.S. Geological Survey, written commun., 1999) showed no increase in the tons of phosphorus fertilizer sold in Brevard, Indian River, Lake, Okeechobee, Orange, Osceola, Seminole, or Volusia Counties from 1991-98. Livestock counts obtained from the Florida Agricultural Statistics Service also showed no increase in the number of beef cows in these same counties from 1991-99 (Florida Agricultural Statistics Service, 2004). Flooding former agricultural lands to create wetlands in the upper St. Johns River Basin may have influenced phosphorus concentrations in the river. Phosphorus that accumulated on the land surface as a result of fertilizer application or livestock manure generation may have remobilized once the land was reflooded. In addition, organic phosphorus in the soil may have mineralized when the wetland was drained. Several studies in Florida (Reddy, 1983; Olila and others, 1997) demonstrate that drying and reflooding organic soils release phosphorus into the water column. However, analyses of wetland data from the upper St. Johns River Basin (Marzolf, 2000) generally show no significant temporal trends from 1979-98 in total phosphorus or orthophosphate concentrations in the water.

Summary

Streamflow and water quality of the 90-mile-long middle reach of the St. Johns River from downstream of Lake Poinsett to near DeLand, Florida, was characterized using retrospective (1991-99) and recently collected data (2000-02). The Econlockhatchee and Wekiva Rivers are the two largest tributaries to the St. Johns River within the study area. Upstream and within the study area, much of the St. Johns River is characterized by flow through shallow lakes. Wetlands, agriculture, upland forests, and urban areas are the predominant land use and land covers. Agricultural land is concentrated in the southern part of the study area and consists mainly of unimproved pasture.

Table 32. Temporal trends in selected physical properties, nutrients, and chlorophyll-a at St. Johns River sites, 1991-99.

[Correlations statistically significant at the 0.05 significance level are shown in bold. %, percent; p, p-value; N, number of observations. Sites are shown in downstream order. Retrospective data were obtained from the Florida Department of Environmental Protection, Florida Fish and Wildlife Conservation Commission, Orange County, St. Johns River Water Management District, Volusia County, and the U.S. Geological Survey]

Map ID (fig. 4)	Site	Specific conductance	Dissolved oxygen	рН	Nitrate nitrogen	Total organic plus ammonia nitrogen	Ammonia nitrogen	Total phosphorus	Orthophosphate phosphorus	Chlorophyll- <i>a</i>
1	St. Johns River near Cocoa	trend = -2.1% p = .1415 N = 51	trend = -1.7% p = .4156 N = 51	trend = 0.8% p = .0148 N = 49	trend = -1.9% p = .7207 N = 69	trend = 2.4% p = .3139 N = 50	trend = -2.4% p = .4853 N = 67	trend = 11.7% p = 0 N = 67	trend = 12.1% p = .0004 N = 69	Not calculated
4	St. Johns River near Christmas	trend = -3.7% p = .0543 N = 53	trend = 2.3% p = .1695 N = 53	trend =1.2%* p = .0446 N = 52	trend = 6.4% p = .0501 N = 121	trend = 1.3% p = .5840 N=54	trend = 9.1%** p = .0002 N = 121	trend = 15.0% p = 0 N = 120	trend = 17.5% p = 0 N = 121	trend = -1.5% p = .9522 N = 46
8	St. Johns River upstream of Lake Harney, near Geneva	trend = -2.1% p =1994 N = 54	trend =1% p = .8876 N = 54	trend =3% p = .4.95 N = 54	trend = -2.0% p = .2074 N = 248	trend = 2.7% p = .1739 N = 54	trend = 6.5%*** p = .0022 N = 143	trend = 10.9% p = 0 N = 250	trend = 11.5% p = 0 N = 238	trend = 6.0% p = .3626 N = 54
21	St. Johns River near DeLand	trend = -1.0% p = .3900 N = 54	trend = -1.8% p = .2175 N = 54	trend =04% p = .7323 N = 54	trend = -1.9% p = .4503 N = 128	trend =03% p = .1502 N = 54	Not calculated	trend = .04% p = .9719 N = 126	trend = 1.1% p = .0590 N = 128	trend = -11.2% p = .0952 N = 54

*There was no significant temporal trend from 1991-98. Trend = 1.1%, p = 0.1166.

**There was no significant temporal trend from 1991-98. Trend = 3.1%, p = 0.3042.

***There was no significant temporal trend from 1991-98. Trend = 4.8%, p = 0.0646.

Urban land is concentrated in the Orlando metropolitan area and in the cities of Cocoa and Titusville. Many of the original wetlands in the Upper St. Johns River Basin were drained to support the production of citrus, row crops, and beef cattle. A large construction project began in 1988 to restore wetlands in the Upper St. Johns River Basin; about 240 square miles of wetlands have been enhanced or restored.

Streamflow characteristics of the St. Johns River were determined using data collected by the U.S. Geological Survey (USGS) from water years 1933-2000. Waterquality characteristics were described using 1991-99 retrospective data at 15 sites on the St. Johns River and 1 site each near the mouths of the Econlockhatchee and Wekiva Rivers. Water-quality constituents evaluated included physical properties, major ions and other inorganic constituents, nutrients, organic carbon, suspended solids, and phytoplankton chlorophyll-a. The 1991-99 data were augmented with: (1) biweekly water-quality data collected at four St. Johns River sites during water years 2000-02; (2) continuous field properties data collected at these same four sites primarily during water years 2001-02; (3) quarterly water-quality data collected from sites on the Wekiva River and Blackwater Creek from water years 2000-02; and (4) quarterly water-quality data collected at Blue Springs from water years 2000-02.

Mean annual streamflow in the St. Johns River increased from 1,030 cubic feet per second (ft³/s) downstream of Lake Poinsett to 2,850 ft³/s near DeLand, based on data from water years 1985 to 2000. Streamflow in the St. Johns River generally was lowest in May and highest in September and October. Lower streamflows in May probably resulted from less rainfall combined with greater evapotranspiration rates due to the high air temperatures. High streamflow in September and October probably resulted from increased rainfall combined with less available storage in lakes and wetlands. Rainfall from June through August may fill the lakes and wetlands, leaving less available storage for rainfall in September and October. The reach of the St. Johns River described in this report does not have daily tidal reversals of streamflow; however, periodic streamflow reversals were observed in the studied reach of the river. Reverse streamflows typically were measured at least once a year at the most downstream sites due to wind and tidal effects. Streamflow reversals were measured infrequently during periods of extreme low flow at upstream sites as a result of wind effects.

The highest dissolved oxygen concentrations were at sites downstream from Lake Poinsett, Lake Harney, and Lake Monroe. Higher concentrations at these sites may have resulted from algal production in the lakes. Dissolved oxygen concentrations and water pH values were substantially lower during high-flow conditions than during low-flow conditions. Low dissolved oxygen concentrations may have resulted from the input of water from marsh areas or from the subsequent decomposition of organic matter transported to the river during high-flow events. Low water pH values during high-flow conditions likely resulted from the increased dissolved organic carbon concentrations in the river. Dissolved organic carbon primarily is composed of fulvic and hydrophilic acids that lower the pH of the water.

More than 50 percent of the samples collected from the St. Johns River from 2000-02 had total dissolved solids concentrations greater than the secondary drinking water regulation of 500 milligrams per liter (mg/L) established by the U.S. Environmental Protection Agency (USEPA) and the State of Florida. Chloride and sulfate concentrations also exceeded the secondary drinking water regulation of 250 mg/L established by the USEPA and the State of Florida, primarily during summer lowflow periods. Chloride concentrations exceeded 250 mg/L at all sites; sulfate concentrations exceeded 250 mg/L only at the two most upstream sites.

Concentrations of total dissolved solids and other inorganic constituents in the St. Johns River were inversely related with streamflow. Most major ion concentrations, total dissolved solids concentrations, and specific conductance values varied substantially at the Christmas, Sanford, and DeLand sites during low-flow periods in 2000-01, probably reflecting wind and tidal effects. Bromide concentrations as high as 17 mg/L were measured at the most upstream site from 2000-02. Temporal variations in bromide were characterized by sharp peaks in concentration during low-flow periods. Peaks in bromide concentrations tended to coincide with peaks in chloride concentrations (except during 2001) because ground water affected by relict seawater likely was the source of both constituents.

Other constituents varied directly with streamflow. Sulfide concentrations as high as 6 mg/L were measured during high-flow periods. Increased sulfide concentrations likely resulted from the decomposition of organic matter or the reduction of sulfate. Total iron concentrations greater than the secondary drinking water regulation of 300 micrograms per liter (μ g/L) established by the USEPA and the State of Florida were measured at all St. Johns River sites from 2000-02. Total iron concentrations exceeded 300 μ g/L most frequently at the Christmas site, located in the upstream part of the study area. Total and dissolved iron concentrations also increased substantially during high-flow conditions in the St. Johns River.

During 2000-02, more than 95 percent of the samples from the St. Johns River sites had water color values that exceeded the secondary drinking water regulation of 15 platinum-cobalt units established by the USEPA and the State of Florida. Median dissolved organic carbon concentrations ranged from 15 to 26 mg/L during 2000-02; concentrations as high as 42 mg/L were measured. Water color values and dissolved organic carbon concentrations were significantly greater during high-flow conditions than during low-flow conditions. Specific ultraviolet light absorbance data indicated the organic carbon in the river during high-flow conditions was aromatic in composition and likely originated from terrestrially derived sources compared to other times of the year when organic carbon was likely derived from algae.

Ammonia nitrogen and orthophosphate phosphorus were present in the St. Johns River, indicating that bioavailable forms of nutrients generally were present. Ammonia nitrogen concentrations generally were greater during high-flow conditions than during low-flow conditions. Nitrate nitrogen concentrations during 1991-99 were lower in the upstream part of the river compared to other sites, which may be related to nitrate being used as a nutrient by terrestrial or aquatic plants or denitrification in wetland areas. High nitrate concentrations at sites downstream of the confluence with the Wekiva River may be due to nitrogen-enriched ground-water inflow. Seasonal variations in nitrate concentrations during 2000-02 were characterized by sharp peaks in concentration from about October through February, likely resulting from nitrification.

Chlorophyll-*a* and total suspended solids concentrations in the St. Johns River generally were highest in May and June compared to other times of the year. Low chlorophyll-*a* concentrations in July and August may have resulted from light limitation because of increased concentrations of highly colored organic matter in the river. High total suspended solids concentrations during the May and June low-flow period suggest that runoff of soil eroded from the land surface is not the primary mechanism in which suspended solids are contributed to the river, but rather that suspended solids primarily are contributed by algal production or the resuspension of bottom sediments.

The occurrence of human and veterinary antibiotics, other human prescription and nonprescription drugs, pesticides, and a suite of organic constituents that may indicate domestic or industrial waste were described at two sites using limited data collected in water years 2002-03 and at a pilot water-treatment facility on Lake Monroe using data from one sampling event conducted in March 2003. A total of 20 constituents was detected in water from the St. Johns River, which included pesticides. antibiotics, plasticizers, and detergent metabolites. No constituent concentrations exceeded applicable Maximum Contaminant Levels established by the USEPA. Atrazine, metolachlor, and cholesterol were the most frequently detected compounds. More constituents were detected in water from the Sanford site (20) compared to the Cocoa site (5), which likely reflects the location of the Sanford site downstream from point sources delivering municipal wastewater effluent to streams in the study area and downstream from urban-residential areas on septic systems. Limited data suggest these constituents are derived from runoff to the Cocoa site and from pointsource discharges or septic tank leachate at the Sanford site.

The most notable temporal trend in water-quality constituents during 1991-99 was increased concentrations of total phosphorus and dissolved orthophosphate at three upstream sites on the St. Johns River. The reason for the increases in phosphorus concentrations at these sites was not apparent. Increased fertilizer sales, increased livestock populations, or increased phosphorus concentrations in recently restored wetlands do not account for this trend.

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Appendixes

Appendix A. Sites with retrospective water-quality data compiled for this report

[FDEP, Florida Department of Environmental Protection; FFWCC, Florida Fish and Wildlife Conservation Commission; Orange County, Orange County Department of Environmental Protection; SJRWMD, St. Johns River Water Management District; Volusia County, Volusia County Department of Environmental Health; USGS, U.S. Geological Survey]

Agency station identifier	Station name	Sampling agency	Period of record
LPO SJ19A SJR528 SJ21 SRS	Lake Poinsett Outlet at State Road 520 St. Johns River at Beeline Highway St. Johns River at bridge on 528 St. Johns River at State Road 50, west Seminole Ranch south boundary at State Road 50 along St. Johns River	SJRWMD Orange County SJRWMD Orange County SJRWMD	1979-1999 1988-1999 1996-1999 1980-1999 1991-1999
SJ24	St. Johns River at Orange Mound	Orange County	1981-1999
SJ25	St. Johns River at south Puzzle Lake	Orange County	1980-1981, 1983-1999
GFCCR0173	Econlockhatchee River at Tree Line	FFWCC	1973-1996
SJ26	Econlockhatchee River at mouth	Orange County	1980-1999
20010012	St. Johns River at Florida Highway No. 46	FDEP	1968-1973, 1975-1995
SJ27 SRN SJ02 SJ04 GFCCR0188	 St. Johns River at State Road 46 Seminole Ranch north boundary at State Road 46 along St. Johns River St. Johns River at south end Lake Harney St. Johns River at north end Lake Harney St. Johns River exit to Lake Harney 	Orange County SJRWMD Volusia County Volusia County FFWCC	1980-1999 1982-1989, 1991-1999 1991-1999 1991-1999 1981-1996
SJ05	St. Johns River at Lemon BluffSt. Johns River south of State Road 415 bridgeSt. Johns River at U.S. Highway 17-92St. Johns River at U.S. Highway 17-92St. Johns River at U.S. Highway 17-92	Volusia County	1991-1999
SJ08		Volusia County	1991-1999
20010003		FDEP	1968-1995
20010003		SJRWMD	1995-1999
SJ12		Volusia County	1991-1999
GFCCR0197	St. Johns River ½ mile south of Wekiva River	FFWCC	1987-1996
SJ13	St. Johns River at channel marker 101	Volusia County	1991-1999
SJ14	Wekiva River 1 mi. upstream from St. Johns	Volusia County	1991-1999
GFCCR0196	Wekiva River part first sharp turn to right	FFWCC	1987-1996
GFCCR0199	St. Johns River north of Wekiva River	FFWCC	1987-1996
SJ15	St. Johns River at channel marker 93St. Johns River at channel marker 69St. Johns River at channel marker 53St. Johns River 50 yds. south of State Road 44 bridgeSt. Johns River near DeLand	Volusia County	1991-1999
SJ16		Volusia County	1991-1999
SJ18		Volusia County	1991-1999
SJ19		Volusia County	1991-1999
02236000		USGS	1948-1995

Appendix B. Water-quality constituents analyzed in stream water collected during this study

Constituent	Use of organic constituent	Method reporting limit	Analytical method
Total sulfide, mg/L		1	Iodometric titration (Fishman and Friedman, 1989)
Dissolved calcium, mg/L		.02	USEPA method 200.7 (USEPA, 1994)
Total calcium, mg/L		.02	Do.
Dissolved magnesium, mg/L		.03	Do.
Total magnesium, mg/L		.03	Do.
Dissolved sodium, mg/L		.1	Atomic absorption spectrometry (Fishman and Friedman, 1989)
Dissolved potassium, mg/L		.1	Do.
Dissolved chloride, mg/L		.05	USEPA method 300.0 (USEPA, 1993)
Dissolved sulfate, mg/L		.07	Do.
Dissolved silica, mg/L		.01	USEPA method 200.7 (USEPA, 1994)
Dissolved barium, µg/L		.5	Do.
Total barium, μg/L		.5	Do.
Dissolved iron, µg/L		2	Do.
Total iron, µg/L		2	Do.
Dissolved strontium, µg/L		.5	Do.
Total strontium, µg/L		.5	Do.
Dissolved bromide, mg/L		.05	USEPA method 300.0 (USEPA, 1993)
Dissolved ammonia nitrogen, mg/L as N		.01	Colorimetry (Fishman and Friedman, 1989)
Total ammonia nitrogen, mg/L as N		.01	Do.
Dissolved nitrite nitrogen, mg/L as N		.01	Do.
Total nitrite nitrogen, mg/L as N		.01	Do.
Total organic plus ammonia nitrogen, mg/L as N		.2	Do.
Total nitrite plus nitrate nitrogen, mg/L as N		.02	Do.
Dissolved nitrite plus nitrate nitrogen, mg/L as N		.02	Do.
Total phosphorus, mg/L		.02	Do.
Dissolved orthophosphorus, mg/L as P		.01	Do.
Total orthophosphorus, mg/L as P		.01	Do.
Total organic carbon, mg/L		.1	USEPA method 415.1 (USEPA, 1979)
Dissolved organic carbon, mg/L		.1	Do.
Turbidity, NTU		.05	Turbidimeter (Fishman and Friedman, 1989)
Color, platinum-cobalt units		5	Visual comparison (Fishman and Friedman, 1989)
Specific conductance, µS/cm		1	Wheatstone Bridge (Fishman and Friedman, 1989)
Water pH, pH units		.1	Glass electrode (Fishman and Friedman, 1989)
Total non-filterable residue at 105 °C (total suspended solids), mg/L		1	Gravimetric (Fishman and Friedman, 1989)
Dissolved residue at 180 °C (total dissolved solids), mg/L		1	Do.
Phytoplankton chlorophyll- <i>a</i> , µg/L		.1	Standard Methods SM10200H (American Public Health Association, 1986)
Acid-neutralizing capacity, mg/L		1	Titration (Fishman and Friedman, 1989)

Appendix B. Water-quality constituents analyzed in stream water collected during this study (Continued)

Constituent	Use of organic constituent	Method reporting limit	Analytical method
UV absorbance at 254 nm		.001	Standard Methods SM5910B (American Public Health Association, 1986)
Sulfamethizole, µg/L	antibiotic	.05	Liquid chromatography/mass spectrometry (Kolpin and others, 2002)
Sulfathiazole, µg/L	antibiotic	.05	Do.
Sulfamerazine, µg/L	antibiotic	.05	Do.
Sulfamethazine, µg/L	antibiotic	.05	Do.
Sulfachlorpyridazine, µg/L	antibiotic	.05	Do.
Sulfamethoxazole, µg/L	antibiotic	.05	Do.
Sulfamethoxazole, µg/L	antibiotic	.064*	Liquid chromatography/mass spectrometry (Cahill and others, 2004)
Sulfadimethoxine, µg/L	antibiotic	.05	Liquid chromatography/mass spectrometry (Kolpin and others, 2002)
Tylosin, µg/L	antibiotic	.02	Do.
Roxithromycin, µg/L	antibiotic	.02	Do.
Erthromycin-H2O, µg/L	erthromycin metabolite	.02	Do.
Tetracycline, µg/L	antibiotic	.05	Do.
Oxytetracycline, µg/L	antibiotic	.05	Do.
Chlortetracycline, µg/L	antibiotic	.05	Do.
Doxycycline, µg/L	antibiotic	.05	Do.
Norfloxaxin, µg/L	antibiotic	.02	Do.
Enrofloxaxin, µg/L	antibiotic	.02	Do.
Ciprofloxaxin, µg/L	antibiotic	.02	Do.
Sarafloxacin, µg/L	antibiotic	.02	Do.
Lincomycin, µg/L	antibiotic	.02	Do.
Carbadox, µg/L	antibiotic	.05	Do.
Trimethoprim, µg/L	antibiotic	.02	Do.
Virginiamycin, µg/L	antibiotic	.2	Do.
Methotrexate, µg/L	antibiotic	.05	Do.
Demeclocycline, µg/L	antibiotic	.05	Do.
Minocycline, µg/L	antibiotic	.05	Do.
Metformin	antidiabetic	not determined	Liquid chromatography/mass spectrometry (Cahill and others, 2004)
Cotinine, µg/L	nicotine metabolite	.014	Do.
Cotinine, µg/L	nicotine metabolite	1.0	Gas chromatography/mass spectrometry (Kolpin and others, 2002)
Albuterol (Salbutamol), µg/L	antiasthmatic	.023	Liquid chromatography/mass spectrometry (Cahill and others, 2004)
Cimetidine, µg/L	antacid	.012*	Do.
Acetaminophen, µg/L	antipyretic	.036	Do.
Ranitidine, µg/L	antacid	.013*	Do.
1,7-dimethylxanthine, µg/L	caffeine metabolite	.144	Do.
Trimethoprim, µg/L	antibiotic	.013	Do.
Diltiazem, µg/L	antihypertensive	.016*	Do.
Fluoxetine, µg/L	antidepressant	$.014^{*}$	Do.

Appendix B. Water-quality constituents analyzed in stream water collected during this study (Continued)

Constituent	Use of organic constituent	Method reporting limit	Analytical method
Warfarin, µg/L	anticoagulant	.011	Liquid chromatography/mass spectrometry (Cahill and others, 2004)
Ibuprofen, µg/L	anti-inflammatory	.042*	Do.
Gemfibrozil, µg/L	antihyperlipidemic	.013*	Do.
Caffeine, µg/L	stimulant	.016	Do.
Caffeine, µg/L	stimulant	.5	Gas chromatography/mass spectrometry (Kolpin and others, 2002)
Dehydronifedipine, µg/L	antianginal	.015	Liquid chromatography/mass spectrometry (Cahill and others, 2004)
Codeine, µg/L	analgesic	.015	Do.
Thiabendazole, µg/L	pesticide	.011	Do.
Diphenhydramine, µg/L	antihistamine	.015*	Do.
Azithromycin, µg/L	antibiotic	.005	Do.
Erythromycin, µg/L	antibiotic	.009	Do.
Carbamazapine, µg/L	anticonvulsant	.011	Do.
Miconazole, µg/L	antifungal	.018	Do.
Tetrachloroethylene, μg/L	solvent, degreaser	.5	Gas chromatography/mass spectrometry (Kolpin and others, 2002)
Bromoform, µg/L	disinfection byproduct	.5	Do.
Isopropyl benzene (cumene), µg/L	manufacturing phenol/acetone, fuels, and paint thinner	.5	Do.
Phenol, µg/L	disinfectant	.5	Do.
1,4-dichlorobenzene, µg/L	deodorizer	.5	Do.
d-limonene, µg/L	fungicide, antimicrobial, antiviral, fragrance in aerosols	.5	Do.
acetophenone, µg/L	fragrance	.5	Do.
para-cresol, µg/L	wood preservative	.5	Do.
Isophorone, µg/L	solvent for lacquer, plastic, oil, silicon, resin	.5	Do.
Camphor, µg/L	flavor, odorant, ointments	.5	Do.
Isoborneol, µg/L	fragrance in perfumery, disinfectants	.5	Do.
Menthol, µg/L	cigarettes, cough drops, liniments, mouthwash	.5	Do.
Napthalene, µg/L	polycyclic aromatic hydrocarbon	.5	Do.
Methyl salicylate, µg/L	liniment, food, beverage, UV-absorbing liquids	.5	Do.
Dichlorvos, µg/L	insecticide	1.0	Do.
Isoquinoline, µg/L	flavors and fragrances	.5	Do.
2-methylnapthalene, µg/L	2-5 percent of gasoline, diesel fuel, or crude oil	.5	Do.
Indole, µg/L	pesticide inert ingredient, fragrance in coffee	.5	Do.
3,4-dichlorophenyl isocyanate, µg/L	diuron degradate	.5	Do.
1-methylnapthalene, μg/L	2-5percent of gasoline, diesel fuel, or crude oil	.5	Do.

Appendix B. Water-quality constituents analyzed in stream water collected during this study (Continued)

Constituent	Use of organic constituent	Method reporting limit	Analytical method
3-methyl-1H-indole (skatol), µg/L	fragrance, stench in feces and coal tar	1.0	Gas chromatography/mass spectrometry (Kolpin and others, 2002)
2,6-dimethylnapthalene, µg/L	diesel, kerosene	.5	Do.
3- <i>tert</i> -butyl-4-hydroxyanisole (BHA), µg/L	antioxidant, general preservative	5.0	Do.
N,N-diethyltoluamide (DEET), µg/L	insect repellent	.5	Do.
5-methyl-1H-benzotriazle, µg/L	anticorrosive	2.0	Do.
Diethyl phthalate, µg/L	plasticizer	.5	Do.
4-tert-octylphenol, µg/L	nonionic detergent metabolite	1.0	Do.
Benzophenone, µg/L	fixative for perfumes and soaps	.5	Do.
Tributyl phosphate, µg/L	antifoaming agent, flame retardant	.5	Do.
Triethyl citrate (ethyl citrate), µg/L	cosmetics, pharmaceuticals	.5	Do.
Total para-nonylphenol, µg/L	nonionic detergent	5.0	Do.
Prometon, µg/L	herbicide (noncrop only)	.5	Do.
Pentachlorophenol, µg/L	herbicide, fungicide, wood preservative, termite control	2.0	Do.
Atrazine, µg/L	herbicide	.5	Do.
tri(2-chloroethyl) phosphate, µg/L	fire retardant	.5	Do.
4-n-octylphenol, μg/L	nonionic detergent metabolite	1.0	Do.
Diazinon, µg/L	insecticide	.5	Do.
Phenanthrene, µg/L	polycyclic aromatic hydrocarbon	.5	Do.
Anthracene, µg/L	polycyclic aromatic hydrocarbon	.5	Do.
Tonalide (AHTN), µg/L	musk fragrance	.5	Do.
Carbazole, µg/L	insecticide, manufacture of dyes, explosives, and lubricant	.5	Do.
Galaxolide (HHCB), µg/L	musk fragrance	.5	Do.
Monoethoxyl octylphenol (OPEO1), μ g/L	nonionic detergent metabolite	1.0	Do.
4-cumylphenol, μg/L	nonionic detergent metabolite	1.0	Do.
Carbaryl, µg/L	insecticide	1.0	Do.
Metalaxyl, µg/L	herbicide, fungicide	.5	Do.
Bromacil, µg/L	herbicide	.5	Do.
Metolachlor, µg/L	herbicide	.5	Do.
Chlorpyrifos, µg/L	insecticide	.5	Do.
Anthraquinone, µg/L	manufacture dyes/textiles	.5	Do.
Total nonylphenol ethoxylates (NPEO1), μg/L	nonionic detergent metabolite	5.0	Do.
Fluoranthene, µg/L	component of coal tar and asphalt, combustion product	.5	Do.
Triclosan, µg/L	antimicrobial disinfectant	1.0	Do.
Pyrene, µg/L	polycyclic aromatic hydrocarbon	.5	Do.
Diethoxyl octylphenol OPEO2, µg/L	nonionic detergent metabolite	1.0	Do.
Bisphenol A, µg/L	plasticizer	1.0	Do.
Total nonylphenol ethoxylates (NPEO2), ug/L	nonionic detergent metabolite	5.0	Do.
Appendix B. Water-quality constituents analyzed in stream water collected during this study (Continued)

[mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemen per centimeter; °C, degrees Celcius; NTU, nephelometric turbidity units; UV, ultraviolet; nm, nanometers; N, nitrogen; P, phosphorus; USEPA, U.S. Environmental Protection Agency. Concentrations denoted with an asterisk are estimates]

Constituent	Use of organic constituent	Method reporting limit	Analytical method
Tri(dichloroisopropyl) phosphate, $\mu g/L$	fire retardant	.5	Gas chromatography/mass spectrometry (Kolpin and others, 2002)
Triphenyl phosphate, µg/L	plasticizer	.5	Do.
2-butoxy-phosphate ethano,1 µg/L	plasticizer	.5	Do.
Polybrominated diphenyl ether (PBDE4-1), µg/L	plastics	10	Do.
Polybrominated diphenyl ether (PBDE4-2), µg/L	plastics	10	Do.
Diethylhexyl phthalate, µg/L	plasticizer	.5	Do.
Polybrominated diphenyl ether (PBDE4-3), µg/L	plastics	10	Do.
Polybrominated diphenyl ether (PBDE5-1), µg/L	plastics	10	Do.
Polybrominated diphenyl ether (PBDE5-2), µg/L	plastics	10	Do.
Benzo(a) pyrene, µg/L	polycyclic aromatic hydrocarbon	.5	Do.
Polybrominated diphenyl ether (PBDE5-3), µg/L	plastics	10	Do.
Polybrominated diphenyl ether (PBDE6-1), µg/L	plastics	10	Do.
Polybrominated diphenyl ether (PBDE6-2), µg/L	plastics	10	Do.
3- <i>beta</i> -coprostanol, µg/L	fecal steroid	2	Do.
Cholesterol, µg/L	plant/animal steroid	2	Do.
beta-sitosterol, µg/L	plant steroid	2	Do.
Stigmastanol, µg/L	plant steroid	2	Do.

Appendix C. Streamflow duration statistics at selected sites on the St. Johns, Econlockhatchee, and Wekiva Rivers and Blackwater Creek

[NA, not available]

Map ID (fig. 4)	Station number	Station name	Drainage area (square miles)	Period of record (water years)	Flow, in cubic feet per second, which was equaled or exceeded for percentage of time indicated						
					99	95	90	50	10	5	1
1	02232400	St. Johns River near Cocoa	1,331	1985-2000 1957-2000	4.8 7.4	51 45	105 92	595 591	2,560 2,400	3,640 3,390	5,310 5,300
3	02232500	St. Johns River near Christmas	1,539	1985-2000 1957-2000	-8.3 7.2	76 56	148 115	833 802	3,270 3,200	4,090 4,130	5,140 6,240
6	02233500	Econlockhatchee River near Chuluota	241	1985-2000	35	44	52	152	782	1,170	2,010
8	02234000	St. Johns River upstream of Lake Harney, near Geneva	2,043	1985-2000 1957-2000	39 56	176 136	282 233	1,220 1,210	4,770 4,750	6,070 6,120	7,830 NA
12	02234500	St. Johns River near Sanford			-979	-156	236	1,530	5,720	7,900	NA
14	02235000	Wekiva River near Sanford	189	1985-2000 1968-2000	156 156	179 181	202 203	255 263	411 433	528 541	821 804
15	02235200	Black Water Creek near Cassia	126	1985-2000 1968-1969 and 1985-2000	2.4 2.49	5.1 5.55	8.2 8.64	30 31.2	135 144	196 215	332 366
21	02236000	St. Johns River near Deland	3,066	1985-2000 1957-2000	-808 -1,035	294 162	760 688	2,250 2,460	6,140 6,370	7,450 7,560	9,590 10,750