

# Sampling Design and Procedures for Fixed Surface-Water Sites in the Georgia-Florida Coastal Plain Study Unit, 1993

By Hilda H. Hatzell, Edward T. Oaksford, and Clyde E. Asbury

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# FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.

- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch  
Chief Hydrologist



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## CONVERSION FACTORS, ACRONYMS, AND ADDITIONAL ABBREVIATIONS

Multiply	By	To obtain
milliliter (mL)	0.03382	ounce, fluid
liter (L)	33.82	ounce, fluid
square kilometer (km <sup>2</sup> )	0.3861	square mile

### ACRONYMS

- GAFL = Georgia-Florida Coastal Plain study unit  
 NAWQA = National Water-Quality Assessment Program  
 NASQAN = National Stream Quality Accounting Network

### ADDITIONAL ABBREVIATIONS

- EDI = Equal depth increment  
 EWI = Equal width increment  
 FA = Filtered, acidified; designation for bottles sent for chemical analysis  
 FC = Filtered, chilled; designation for bottles sent for chemical analysis  
 FM = Field measurements; constituent group of chemical and physical constituents analyzed in surface-water samples  
 Lf = Liter-fired; designation for a new, fired, 1-liter, brown glass bottle  
 Ls = Liter-sediment; designation for a wide-mouth, 1-liter, plastic bottle used for suspended sediment analyses  
 MI = Major ions and metals; constituent group of chemical constituents analyzed in surface-water samples  
 NT = Nutrients; constituent group of chemical constituents analyzed in surface-water samples  
 OC = Organic carbon; constituent group of chemical constituents analyzed in surface-water samples  
 PS = Pesticides; constituent group of chemical constituents analyzed in surface-water samples  
 QA = Quality assurance  
 RC = Raw, chilled; designation for bottles sent for chemical analyses  
 RU = Raw, untreated; designation for bottles sent for chemical analyses  
 SPE = Solid phase extraction  
 SS = Suspended sediments; constituent group of chemical and physical constituents analyzed in surface-water samples

# Sampling Design and Procedures for Fixed Surface-Water Sites in the Georgia-Florida Coastal Plain Study Unit, 1993

By Hilda H. Hatzell, Edward T. Oaksford, and Clyde E. Asbury

## Abstract

The implementation of design guidelines for the National Water-Quality Assessment (NAWQA) Program has resulted in the development of new sampling procedures and the modification of existing procedures commonly used in the Water Resources Division of the U.S. Geological Survey. The Georgia-Florida Coastal Plain (GAFL) study unit began the intensive data collection phase of the program in October 1992. This report documents the implementation of the NAWQA guidelines by describing the sampling design and procedures for collecting surface-water samples in the GAFL study unit in 1993. This documentation is provided for agencies that use water-quality data and for future study units that will be entering the intensive phase of data collection.

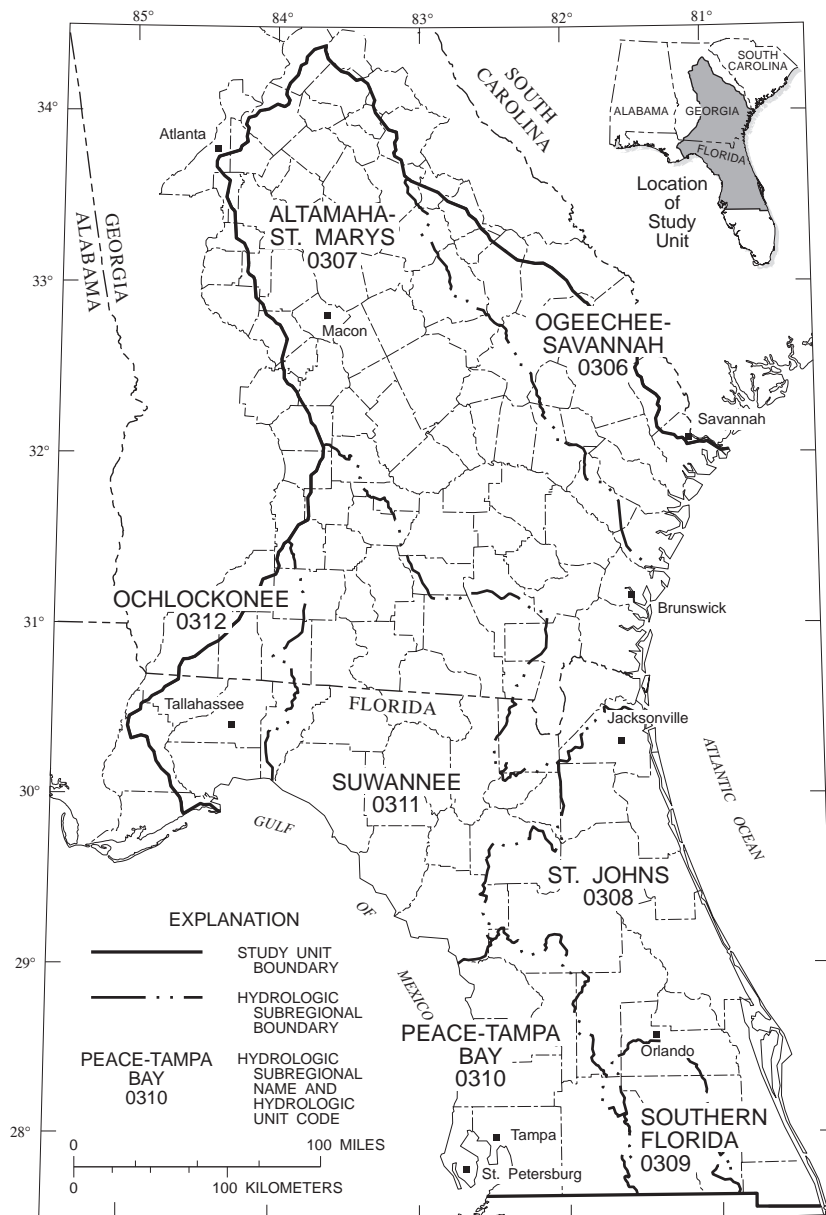
The sampling design is intended to account for large- and small-scale spatial variations, and temporal variations in water quality for the study area. Nine fixed sites were selected in drainage basins of different sizes and different land-use characteristics located in different land-resource provinces. Each of the nine fixed sites was sampled regularly for a combination of six constituent groups composed of physical and chemical constituents: field measurements, major ions and metals, nutrients, organic carbon, pesticides, and suspended sediments. Some sites were also sampled during high-flow conditions and storm events. Discussion of the sampling procedure is divided into three phases: sample collection, sample splitting, and sample

processing. A cone splitter was used to split water samples for the analysis of the sampling constituent groups except organic carbon from approximately nine liters of stream water collected at four fixed sites that were sampled intensively. An example of the sample splitting schemes designed to provide the sample volumes required for each sample constituent group is described in detail. Information about onsite sample processing has been organized into a flowchart that describes a pathway for each of the constituent groups.

## INTRODUCTION

The Georgia-Florida Coastal Plain (GAFL) study unit is one of 20 NAWQA study units that was selected to begin assessment activities in 1991. This study unit is located on the eastern coast of the United States and encompasses all or part of seven major hydrologic subregions (fig. 1). The GAFL study area covers 158,800 km<sup>2</sup> and is representative of an area where most of the population relies on ground water as the primary source of public water supply.

NAWQA activities within each study unit are based on an agenda of specified tasks that are repeated in 9-year cycles. These study-unit activities include 1 year of planning (for the start-up cycle only), 1 year of analyzing existing data, 3 years of intensive data collection and interpretation, 1 year of report writing, and 4 years of low-intensity data collection. The GAFL study unit entered the period of intensive data collection in fiscal year 1993.



**Figure 1.** Location of major hydrologic subregions in the Georgia-Florida Coastal Plain study unit of the National Water-Quality Assessment Program.

During the first year of intensive data collection in the GAFL study area, surface-water activities focused on the collection of surface-water samples at fixed sites and synoptic sites. Fixed sites are sites that are sampled at regular intervals throughout the 3-year period of intensive data collection. Synoptic sites are sampled either to assess specific chemical constituents during key hydrologic events or to evaluate conditions specific to the study area. Fixed and synoptic sites met NAWQA design guidelines for the collection of

data to determine how surface-water quality varies spatially and temporally in the study area.

The implementation of the design guidelines for fixed sites included changes in existing sampling procedures, analytical schedules, and equipment used by the U.S. Geological Survey (USGS). The implementation of these design guidelines in the GAFL study unit has been documented for agencies that use USGS water-quality data, and for all personnel responsible for completing sampling activities related to NAWQA and other Water Resources Division programs.



## Purpose and scope

The purpose of this report is to provide a detailed description of the sampling design and procedures for the nine fixed surface-water sites in the GAFL study unit of the NAWQA Program. The report describes the site-selection and sampling-scheme components of the sampling design and the collection, splitting, and processing components of the sampling procedure.

## Acknowledgments

The authors appreciate the suggestions and improvements contributed by Jonathan Martin, Christy Crandall, Lori Peed, and Mark Stephens of the GAFL study unit during the field testing of the cone splitting schemes. Their efforts greatly improved the effectiveness of the sampling procedures.

## SAMPLING DESIGN

The objective of the surface-water sampling design for the GAFL study unit was to examine the effects of land-use activities on surface-water quality in the context of designated hydrogeomorphic regions within the GAFL study area. Hydrogeomorphic regions were created by dividing the study unit into the following land-resource provinces: Central Florida Ridge, Coastal Flatwoods, Sand Hills, Southern Coastal Plain, and Southern Piedmont (fig. 2). These provinces are derived from major land resource areas that are geographic areas of land characterized by similar patterns of soil, climate, water resources, land use, and type of farming (Austin, 1965; Perkins and Shaffer, 1977; Caldwell and Johnson, 1982).

The goal of the sampling design was to locate and sample fixed sites to collect data that will be used to compare the effects of land use on surface-water quality among the land-resource provinces. Full implementation of this design would have required that sites be located in all of the various combinations of land-use types and provinces within the study unit. However, the number of fixed sites that could be sampled was limited by budget constraints and by the number of sites that met selection criteria.

The sampling design consisted of two parts: site selection and sampling scheme. The selection of fixed sites accounted for both large-scale and small-scale spatial variations within the study area.

The sampling scheme accounted for temporal variations related to land-use activities within the study area.

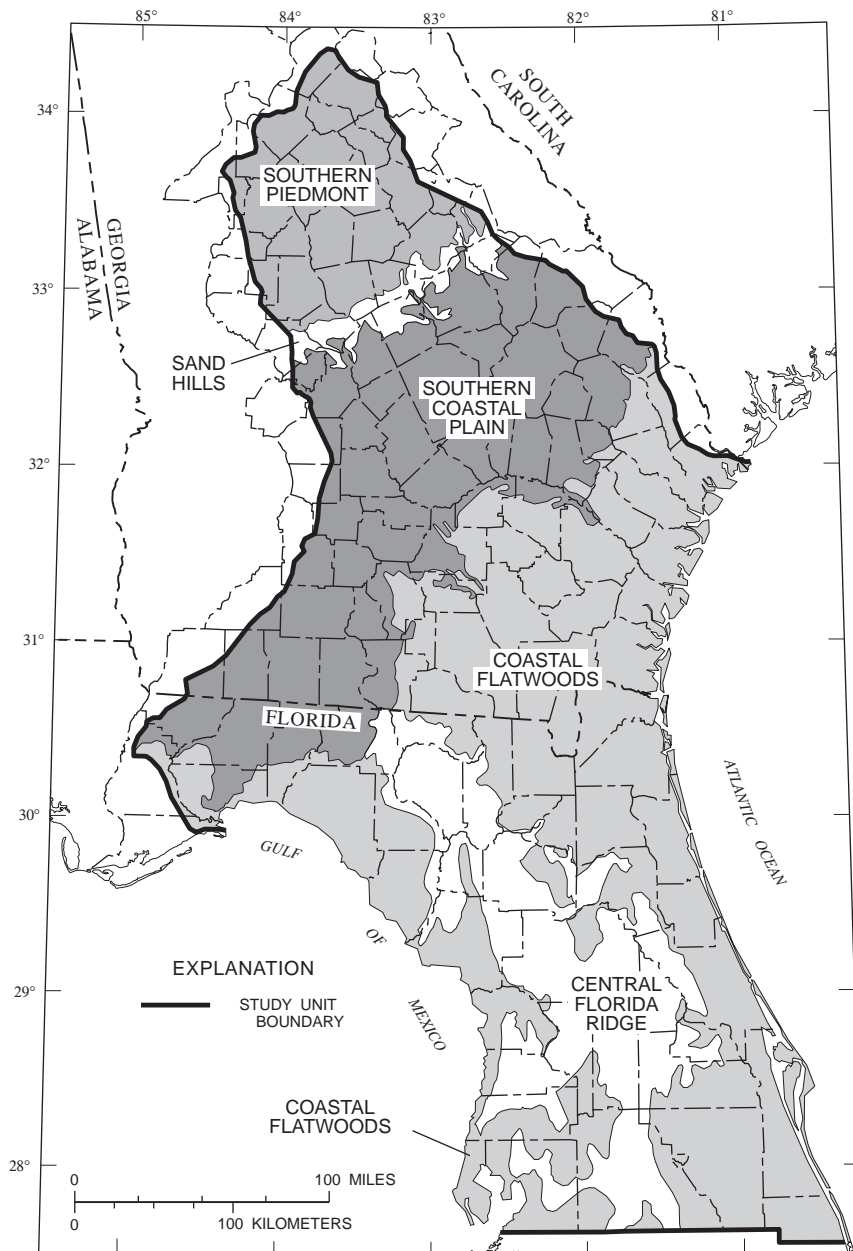
## Site Selection

Several criteria were used in the selection of fixed surface-water sites in the GAFL study area. A primary criterion was the presence of a stream-gaging station that could provide a reliable rating curve. Discharge values from the rating curve are needed along with concentrations to calculate constituent loads. Other selection criteria included the relative drainage density of basins in the land-resource provinces, the needs of the NAWQA national and regional synthesis of study-unit data, and the existing data-collection efforts of other agencies within the study area.

The two types of fixed sites selected for surface-water sampling in the NAWQA Program were integrator and indicator fixed sites. Integrator fixed sites are located in large drainage basins that cover broad, relatively heterogeneous geographic areas. Integrator fixed sites are large-scale sites that are intended to assess water quality affected by complex combinations of land-use settings, point sources, and natural influences (R.J. Gilliom, U.S. Geological Survey, written commun., 1992). These sites provide the broad spatial coverage needed to synthesize data at the national level of the NAWQA Program.

Indicator fixed sites are located in small drainage basins that cover relatively small homogeneous geographic areas. Each of these drainage basins is contained within a single land-resource province. Indicator fixed sites are small-scale sites selected to assess water quality affected by a specific land use, such as agriculture, or by a land use at the inception of a transition, such as agriculture changing to suburban.

Three integrator fixed sites, the Altamaha River, the Suwannee River, and the Withlacoochee River, were selected in the GAFL study area (table 1). The drainage basin for the Altamaha River is the largest basin of the integrator sites and contains parts of four land-resource provinces found in the study area. The drainage basin for the Suwannee River site contains parts of the Central Florida Ridge, the Coastal Flatwoods, and the Southern Coastal Plain provinces. The drainage basin for the Withlacoochee River site is the smallest basin of the integrator sites and is located within the Southern Coastal Plain province. The location of the sampling station for each integrator fixed site is shown in figure 3.



**Figure 2.** Land-resource provinces in the Georgia-Florida Coastal Plain study area.

The Suwannee River and Altamaha River fixed sites are also sampling sites in the National Stream Quality Accounting Network (NASQAN). NASQAN sites were established in 1975 by the U.S. Geological Survey to detect long-term trends in stream-water quality and provide a basis for future assessments of stream-water quality (Ficke and Hawkinson, 1975). The GAFL sampling at these sites is intended to supplement the NASQAN sampling and build on the long-term data available from these sites.

The six indicator fixed sites selected by the GAFL study unit are Bullfrog Creek, Lafayette

Creek, Little River, Middle Prong, Tucsawhatchee Creek, and Turnpike Creek (table 1 and fig. 3). No indicator sites were located in the Central Florida Ridge province because this province has a poorly developed stream network. The land uses of the indicator sites are representative of the land uses found in the study unit. In addition, two long-term transitions in land use were represented: a shift from agriculture to silviculture at the Turnpike Creek site, and a shift from agriculture to suburban at the Bullfrog Creek site.

**Table 1.** Site descriptions for nine fixed surface-water sampling sites in the Georgia-Florida Coastal Plain study area [km<sup>2</sup>, square kilometers; CFW, Coastal Flatwoods; SCP, Southern Coastal Plain; SH, Sand Hills; SP, Southern Piedmont; CFR, Central Florida Ridge]

Site name and station location	Station number	Station drainage area (km <sup>2</sup> )	Land resource province	Land-use description	Fixed-site type
Altamaha River near Everett City, Ga.	02226160	36,260	CFW, SCP, SH, SP	varied land uses	integrator
Bullfrog Creek near Wimauma, Fla.	02300700	75	CFW	agriculture changing to suburban	indicator
Lafayette Creek near Tallahassee, Fla.	02326838	27	SCP	suburban	indicator
Little River near Ty Ty, Ga.	02317797	334	SCP	agriculture (mixed row crops)	indicator
Middle Prong St. Marys River near Taylor, Fla.	02229000	324	CFW	silviculture	indicator
Tucsawhatchee Creek near Hawkinsville, Ga.	02215100	422	SCP	agriculture (cotton)	indicator
Turnpike Creek near McRae, Ga.	02216180	127	SCP	agriculture changing to silviculture	indicator
Suwannee River near Branford, Fla.	02320500	20,409	CFR, CFW, SCP	varied land uses	integrator
Withlacoochee River near Quitman, Ga.	02318500	3,833	SCP	varied land uses	integrator

Large-scale and small-scale spatial variations within the study unit were assessed in two ways in the sampling design. The first way was the selection of basins with different areas. This concept is embodied in the selection of integrator and indicator sites described above. The second way was the selection of smaller basins within larger basins wherever possible (fig. 3). For example, the drainage basin for the Little River site, an indicator fixed site, is located within the basin of the Withlacoochee River site, an integrator fixed site. In turn, the basin of the Withlacoochee River site is located within the basin of the Suwannee River site, which is another integrator site. The basins for two indicator fixed sites, the Tucsawhatchee River site and the Turnpike Creek site, are located within the basin for the Altamaha River site, an integrator fixed site.

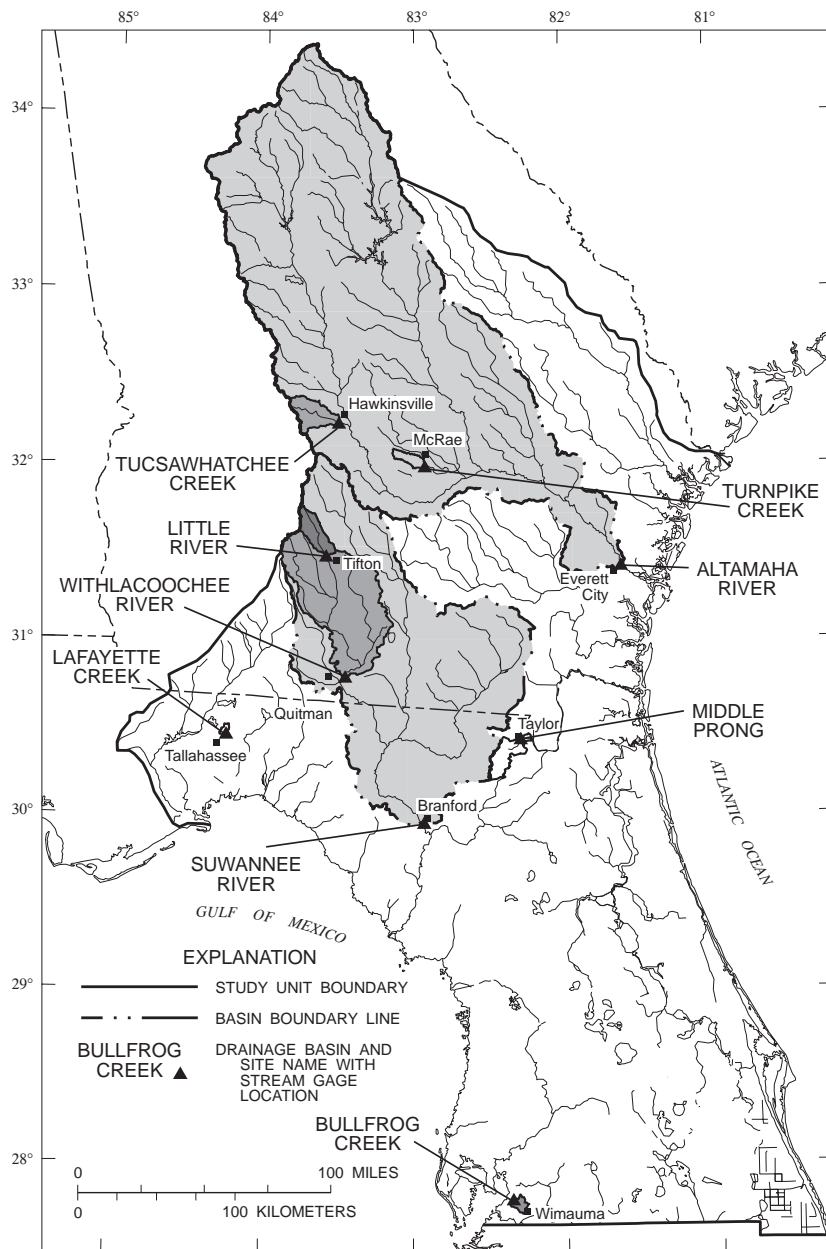
## Sampling Scheme

The sampling scheme for fixed surface-water sites is a combination of the constituents sampled and the sampling intensity. The chemical and physical characteristics analyzed in surface-water samples from the GAFL study area were divided into six constituent groups that were based on similar characteristics for laboratory analysis or the onsite collection of data. These six constituent groups are field measurements (FM), major ions and metals (MI), nutrients (NT), organic carbon (OC), pesticides (PS), and suspended sediments (SS). The pesticides and pesticide degradation products in the pesticide constituent group in table

2 are listed by chemical classes (Shelton, 1994). Constituents in the five other constituent groups are listed in table 3.

The NAWQA Program defined two sampling intensities for fixed surface-water sites: basic fixed and intensive fixed (R.J. Gilliom, U.S. Geological Survey, written commun., 1992). Sampling intensity refers to the frequency of sampling at regular intervals. Basic fixed sites were sampled less frequently and for fewer constituent groups than intensive fixed sites. These differences are related to the differences in the sampling purpose for the two types of intensities. Basic fixed sites were sampled to assess the general water-quality and hydrologic conditions of the study unit. Intensive fixed sites were sampled to assess seasonal and short-term temporal variability of stream-water quality and to determine the occurrence and seasonality of dissolved pesticides in streams in the study area.

The GAFL study unit selected three indicator fixed sites and one integrator fixed site as intensive fixed sites (tables 1 and 4). The three intensive fixed sites that are indicator sites were sampled weekly for four (FM, NT, PS, SS) of the six constituent groups and monthly for all constituent groups from March through October 1993 (table 4). The Withlacoochee River site is an intensive fixed site that is an integrator site and was sampled biweekly and monthly for the same constituent groups as the intensive fixed indicator sites.



**Figure 3.** Site names, basin boundaries, and stream gage locations for nine fixed surface-water sites in the Georgia-Florida Coastal Plain study area.

The remaining three indicator sites and two integrator sites were classified as basic fixed sites. The basic fixed sites that are indicator sites were sampled monthly for five (FM, MI, NT, OC, SS) of the six groups. The basic fixed sites that are integrator sites were both NASQAN sites and were sampled on the NASQAN schedule for each site. The NASQAN sampling constituents were supplemented to include the constituents listed in table 3.

In addition to the regular interval sampling at fixed sites, an automatic water-quality monitoring unit was placed near the stream gage at each fixed site for several 2-week intervals during a 1-year period within the intensive data collection interval. During each interval, the unit made hourly measurements of temperature, pH, specific conductance, and dissolved oxygen. The purpose of this monitoring was to collect additional data for the evaluation of the short-term variability at each site.

**Table 2.** Pesticides and pesticide degradation products analyzed in the pesticide constituent group for surface-water samples from intensive fixed sites in the Georgia-Florida Coastal Plain study area (Modified from Shelton, 1994.)

Pesticides and pesticide degradation products by chemical classes			
Amides			
Alachlor	Napropamide	Propachlor	
Metolachlor	Pronamide	Propanil	
Carbamates			
Aldicarb	Carbofuran	Molinate	Thiobencarb
Aldicarb sulfone	Carbofuran, 3-Hydroxy	Oxamyl	Triallate
Aldicarb sulfoxide	EPTC	Pebulate	
Butylate	Methiocarb	Propham	
Carbaryl	Methomyl	Propoxure	
Chloropheoxy herbicides			
2,4-D (acid)	2,4,5-T	MCPA	Silvex (2,4,5-TP)
2,4-DB	Dichlorprop (2,4-DP)	MCPB	Triclopyr
Dinitroanalins			
Benfluralin	Oryzalin	Trifluralin	
Ethafluralin	Pendimethalin		
Organochlorines			
Chlorothalonil	<i>p,p</i> -DDE	Dieldrin	gamma-HCH (lindane)
Dacthal (DCPA)	Dichlobenil	alpha-HCH	
Organophosphates			
Azinphos-methyl	Dimethoate	Ethyl-parathion	Methyl parathion
Chlorpyrifos	Disulfoton	Fonofos	Phorate
Diazinon	Ethoprop	Malathion	Terbufos
Pyrethroids			
<i>cis</i> -Permethrin			
Triazines			
Atrazine	Cyanazine	Prometon	
Atrazine, des-ethyl	Metribuzin	Simazine	
Uracils			
Bromacil	Terbacil		
Ureas			
Fenuron	Fluometuron	Neburon	
Diuron	Linuron	Tebuthiuron	
Miscellaneous			
Acifluorfen	Clopyralid	DNOC	Picloram
Bentazon	Dicamba	Esfenvalerate	Propargite
Bromoxynil	2,6-Diethylana-line	1-Naphthol	
Chloramben	Dinoseb	Norflurazon	

Sampling events for both high-flow conditions and storm events at fixed sites were included in the sampling scheme for the GAFL study unit (table 4). High-flow sampling was defined as the collection of a water sample when the stream discharge at the site was greater than a discharge that was exceeded 25 percent of the time. High-flow sampling events were determined from the station flow-duration curve and were included in the design because regular interval sampling did not ensure that samples would be collected during high flow. High-flow sampling was used to quantify the high export rate of constituents typically associated with periods of high flow.

Storm-event sampling at a site was defined as the collection of a series of samples during the increase and decrease of discharge associated with a rainstorm. Storm-event sampling was included in the sampling design to provide information about changes in field constituents and the concentrations of pesticides and nutrients during a single storm event. This sampling provided information about the pattern of variation of the constituent concentrations.

Quality assurance (QA) sampling in the GAFL study area in 1993 followed the general quality assurance/quality control plan for NAWQA surface-water sampling (Patrick Leahy, U.S. Geological Survey, written commun., 1993). However, the number of QA samples for the GAFL study unit was greater than the 15 percent of total number of surface-water samples that was required in the NAWQA guidelines. The additional QA samples were needed to evaluate the cleaning and sampling procedures associated with using the cone splitter at intensive fixed sites and to determine if the differences in sampling methods and equipment used at basic and intensive fixed sites affected the chemical analysis of the water samples. Types of QA samples for both intensive and basic fixed sites included field blanks and replicates. Field matrix spikes for the pesticide constituent group were used at intensive fixed sites.

## SAMPLING PROCEDURE

The general guidelines for the sampling procedures used for the surface-water part of the NAWQA Program have been described by Shelton (1994). The implementation of those guidelines in the GAFL study area were divided into three phases: sample collection, sample splitting, and sample processing.

**Table 3.** Chemical and physical constituents analyzed in five of the six constituent groups for surface-water samples from fixed sites in the Georgia-Florida Coastal Plain study area

Constituent group	Abbreviation	Chemical and physical constituents analyzed
Field measurements	FM	Temperature; pH; alkalinity; dissolved oxygen; specific conductance
Major ions and metals	MI	Dissolved calcium; dissolved iron; dissolved magnesium; dissolved manganese; dissolved potassium; dissolved sodium; dissolved chloride; dissolved fluoride; dissolved sulfate; dissolved silica; pH; alkalinity; specific conductance; residue on evaporation
Nutrients	NT	Dissolved ammonia-plus-organic nitrogen; dissolved ammonia nitrogen; dissolved nitrite-nitrogen; dissolved nitrite-plus-nitrate nitrogen; dissolved phosphorus; dissolved orthophosphorus; total ammonia-plus-organic nitrogen; total phosphorus
Organic carbon	OC	Dissolved organic carbon; suspended organic carbon
Suspended sediments	SS	Concentration; percent finer than 0.062 millimeters

### Sample Collection

The initial phase of the sampling procedure included the collection of the water sample and the measurements made prior to or during sample collection. Measurements were made for water temperature, stream-gage height, and dissolved oxygen (fig. 4), and are included in the field constituent group (table 3). Site conditions, such as the weather and stream debris, were also noted. Prior to sampling, all sampling equipment was cleaned using procedures recommended in the NAWQA guidelines (Shelton, 1994).

Water samples for the analysis of the organic-carbon constituent group were collected by the mid-stream single vertical sampling method (Edwards and Glysson, 1988) at all fixed-sites. In this method, water was sampled from approximately the middle of the stream channel with a weighted sampler containing a fired glass bottle. Although the single-vertical method is the recommended NAWQA procedure for sampling dissolved and suspended organic carbon, Shelton (1994) notes in the NAWQA guidelines that this method is not flow proportional and can affect the measurement of suspended organic carbon. The organic-carbon water sample was collected separately from other constituents because the sample could not be passed through the cone splitter. The methanol used in the cleaning procedure for the cone splitter is a potential contaminant in the organic-carbon analyses (Shelton, 1994).

Water samples for the analysis of all other chemical and physical constituents were collected from multiple verticals located along a cross section of the stream. The two methods that were used for

obtaining water samples from multiple verticals were equal-width increments (EWI) and equal-discharge increments (EDI) (Guy and Norman, 1982; Edwards and Glysson, 1988). Both methods are depth integrated and provide a representative sample for dissolved and suspended constituents. Although the EWI method is recommended for the NAWQA Program, the EDI method is acceptable for large streams where the stream flow distribution is known (Shelton, 1994). The EWI method was used for seven of the nine fixed surface-water sites in the GAFL study area (table 5) and was always used for regular interval sampling at intensive fixed sites.

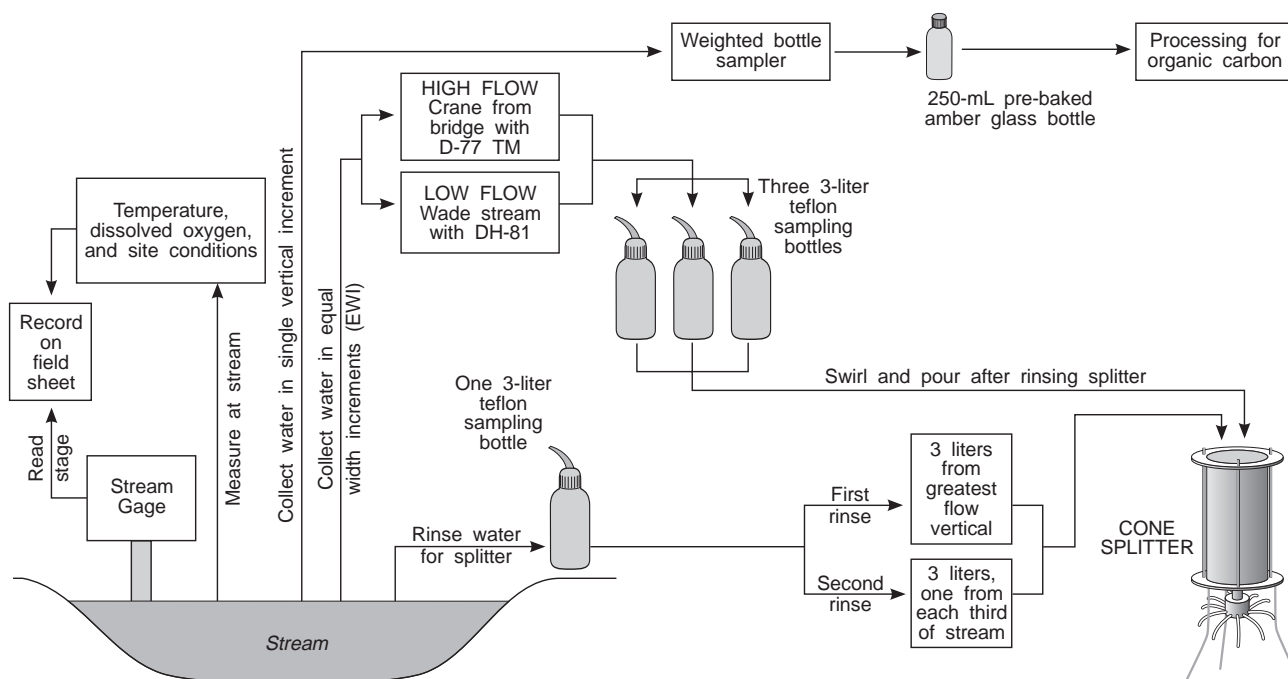
Since the Altamaha River and the Suwannee River basic fixed sites are also NASQAN sites and were sampled by the EDI method prior to the commencement of the NAWQA Program, sampling by the EDI method was continued at these sites to maintain the continuity of the data. Measurements of pH, temperature, dissolved oxygen, and specific conductance along the sampling cross section at both sites had been used to determine that the sites were suitable for the EDI sampling method. The constituents analyzed in the NASQAN Program at these two sites were supplemented by the GAFL study unit to include all constituents analyzed for basic fixed sites in the NAWQA Program.

The EWI procedure used to collect water samples for dissolved constituents and suspended sediment at intensive fixed sites consisted of dividing the cross section of the stream into 10 equal increments and sampling from each increment to collect approximately 9 L (liters) of stream water. Sampling equipment used for wadeable and nonwadeable conditions at intensive fixed sites is described in table 5.

**Table 4.** Sampling schedule showing frequency of sample collection and constituent groups for analysis of surface-water samples from the nine fixed-sites in the Georgia-Florida Coastal Plain study area, 1993

[FM, field measurements; MI, major ions and metals; NT, nutrients; OC, organic carbon; PS, pesticides; SS, suspended sediments; --, not sampled]

Site name	Station number	Fixed-site type	Sampling intensity	Constituent groups						
				Weekly	Biweekly	Monthly	Bimonthly	Quarterly	High flow	Storm event
Altamaha River	02226160	integrator	basic fixed	--	--	--	FM, MI, NT, OC, SS	--	FM, MI, NT, OC, SS	--
Bullfrog Creek	02300700	indicator	basic fixed	--	--	FM, MI, NT, OC, SS	--	--	FM, MI, NT, OC, SS	--
Lafayette Creek	02326838	indicator	intensive fixed	FM, NT, PS, SS	--	FM, MI, NT, OC, PS, SS	--	--	FM, MI, NT, OC, PS, SS	FM, NT, PS
Little River	02317797	indicator	intensive fixed	FM, NT, PS, SS	--	FM, MI, NT, OC, PS, SS	--	--	FM, MI, NT, OC, PS, SS	FM, NT, PS
Middle Prong	02229000	indicator	basic fixed	--	--	FM, MI, NT, OC, SS	--	--	FM, MI, NT, OC, SS	--
Tucsawhatchee Creek	02215100	indicator	intensive fixed	FM, NT, PS, SS	--	FM, MI, NT, OC, PS, SS	--	--	FM, MI, NT, OC, PS, SS	--
Turnpike Creek	02216180	indicator	basic fixed	--	--	FM, MI, NT, OC, SS	--	--	FM, MI, NT, OC, SS	--
Suwannee River	02320500	integrator	basic fixed	--	--	--	--	FM, MI, NT, OC, SS	FM, MI, NT, OC, SS	--
Withlacoochee River	02318500	integrator	intensive fixed	--	FM, NT, PS, SS	FM, MI, NT, OC, PS, SS	--	--	FM, MI, NT, OC, PS, SS	--



**Figure 4.** Sample collection procedure used at intensive fixed sites in the Georgia-Florida Coastal Plain study area, 1993.

When intensive fixed sites were nonwadeable, stream water was sampled from a bridge. Before the actual sample collection began, the rate at which the sampler should be lowered and raised in all of the verticals was determined by lowering a 3-L sampling bottle in the equal-width vertical estimated as having the greatest flow. At the initiation of sample collection, three 3-L Teflon sampling bottles were rinsed with stream water. One of the 3-L Teflon bottles was filled and replaced with a second bottle. When the second sampling bottle was filled, it was replaced with a third bottle that was filled (fig. 4). Each 3-L Teflon bottle was filled to or slightly below the 3-L mark to prevent overflowing. Overflowing the bottles could result in a nonrepresentative sample because water can spill as the bottle is raised from the stream. The three 3-L Teflon bottles were used to store the sample for processing through the cone splitter. This storing technique avoided compositing the sample before splitting.

The EWI procedure used for basic fixed sites in the GAFL study area required approximately 3 L of sample water collected from three or more verticals. Sampling equipment used for wadeable and nonwadeable conditions at basic fixed sites is described in table 5. If the site were nonwadeable,

then the sample water was collected from a bridge. The sample was composited in a churn splitter.

### Sample Splitting

Sample splitting refers to dividing a sample into smaller portions or subsamples that retain the chemical and physical characteristics of the original sample. Sample splitting was required to provide water samples for chemical and physical analyses. Two types of sample splitters were used in the GAFL study area in 1993. A cone splitter was used to divide water samples at intensive fixed sites and a churn splitter was used at basic fixed sites (table 5).

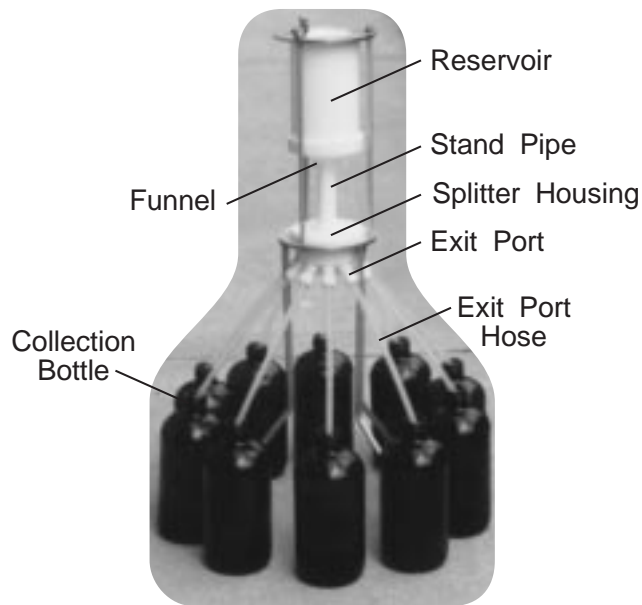
The use of the cone splitter at the intensive fixed sites required the GAFL study unit to design splitting schemes. The splitting schemes describe both the order in which sample water is poured through the cone splitter and the placement of collection bottles beneath the exit ports of the splitter. A discussion of the cone splitter and an example of a sampling scheme used in the GAFL data collection are provided in the following paragraphs.



**Table 5.** Methods and equipment for collecting and splitting water samples from the nine fixed surface-water sites in the Georgia-Florida Coastal Plain study area, 1993  
IFS, intensive fixed site; BFS, basic fixed site; EWI, equal-width increment; EDI, equal-depth increment; WBS, weighted-bottle sampler; L, liter; pt, pint (0.473 mL)]

Site name	Station number	Sampling intensity	Sample collection method	Sampling conditions	Dissolved constituents <sup>1</sup>		Suspended sediments		Type of sample splitter
					Sampler	Sampling bottle	Sampler	Sampling bottle	
Altamaha River	02226160	BFS	EDI	nonwadeable	WBS	1-L fired glass	DH-59	1-pt glass	churn
Bullfrog Creek	02300700	BFS	EWI	wadeable	DH-48	1-pt glass	DH-48	1-pt glass	churn
				nonwadeable	WBS	1-L fired glass	DH-59	1-pt glass	
Lafayette Creek	02326838	IFS	EWI	wadeable	DH-81	3-L Teflon	DH-81	3-L Teflon	cone
				nonwadeable	DH-77	3-L Teflon	DH-77	3-L Teflon	
Little River	02317797	IFS	EWI	wadeable	DH-81	3-L Teflon	DH-81	3-L Teflon	cone
				nonwadeable	DH-77	3-L Teflon	DH-77	3-L Teflon	
Middle Prong	02229000	BFS	EWI	wadeable	DH-81	1-L Teflon	DH-48	1-pt glass	churn
				nonwadeable	WBS	1-L fired glass	DH-59	1-pt glass	
Tucsawhatchee Creek	02215100	IFS	EWI	wadeable	DH-81	3-L Teflon	DH-81	3-L Teflon	cone
				nonwadeable	DH-77	3-L Teflon	DH-77	3-L Teflon	
Turnpike Creek	02216180	BFS	EWI	wadeable	DH-81	1-L Teflon	DH-48	1-pt glass	churn
				nonwadeable	WBS	1-L fired glass	DH-59	1-pt glass	
Suwannee River	02320500	BFS	EDI	nonwadeable	WBS	1-L fired glass	P-72	1-pt glass	churn
Withlacoochee River	02318500	IFS	EWI	wadeable	DH-81	3-L Teflon	DH-81	3-L Teflon	cone
					DH-77	3-L Teflon	DH-77	3-L Teflon	

<sup>1</sup>Does not include organic carbon.



**Figure 5.** Parts of a cone splitter.

The cone splitter is constructed of Teflon and consists of a cylindrical reservoir, funnel, stand pipe, and cone-splitter housing that contains 10 exit ports (fig. 5) (Pickering, 1980; Paul Capel, U.S. Geological Survey, written commun., 1993). The cone-splitter housing consists of a single block of Teflon that has 10 equally spaced holes drilled in the circumference. Each hole extends upward at a 45 degree angle from the horizontal. These holes meet at the center of the housing to create a single point for splitting. Sample water is poured into the top of the reservoir and passes through the funnel and stand pipe into the splitter housing. In the cone-splitter housing, the water sample is divided or split into 10 equal-volume subsamples that pass into 10 exit ports. The subsamples of water are delivered from the exit ports through Teflon hoses to sample-collection bottles placed at the base of the splitter.

The purposes of the splitting schemes for the cone splitter were to provide the correct final volumes of sample water needed for analysis of chemical and physical constituents and to minimize the number of times that subsamples were split into smaller volumes. Because the final volumes of water needed for the analysis of the various constituents were not the same, providing the correct final volume required that some

of the subsamples be poured through the splitter, or split, one or more times.

Two types of final volumes of sample water were obtained from the splitter: unfiltered and filtered. In the unfiltered type, the final volume of water needed for analysis was obtained directly from the cone splitter. Water from this type was analyzed for unfiltered constituents such as total nutrients and suspended sediments. The term, total, in this report refers to the sum of the ions of a specific constituent in solution and adsorbed onto solids. In the filtered type, the final volume of water needed for analysis was obtained by filtering a subsample taken from the splitter. Water for this type was analyzed for dissolved constituents, or those constituents in solution. For example, the nutrients constituent group (NT) (table 3) required an unfiltered and a filtered final volume. The unfiltered final volume consisted of approximately 108 mL of water taken directly from the cone splitter for analysis of total ammonia-plus-organic nitrogen, and total phosphorus. The filtered final volume consisted of approximately 108 mL of water that was filtered from a 1-L subsample taken from the cone splitter. The filtered sample was analyzed for dissolved nitrogen and phosphorus species (table 3).

The final volume of sample water needed for analyses of constituents, such as those in the NT group mentioned above, required sequential splitting of some subsamples. Splitting a subsample involved removing a bottle from the exit-port hose of the splitter and pouring its contents back through the cone splitter to obtain smaller subsamples. Two requirements were needed to obtain a final volume of sample that was representative of the stream water. The first requirement was that the entire volume of each sample be poured through the cone splitter because the sample water might not be uniformly mixed in the sample container. Since heavier particles settle at faster rates than lighter particles, pouring only part of a subsample through the cone splitter would have increased the possibility of leaving the coarser particles in the sample bottle. Under these conditions, the final volume of water from the splitter would not be representative of the particle size distribution of the stream water. The second requirement was that the number of times that subsamples were sequentially split be minimized because of the potential error associated with repeated splitting. The cone splitter splits suspended particles in a water sample with a relative standard deviation of about 5 percent (Paul Capel, U.S. Geological Survey,

written commun., 1993). Each subsequent split of a subsample would add to the error in the final volume.

Before the cone splitter was used to divide a water sample, it was rinsed with sample water to remove any residual materials from the cleaning procedure. In the GAFL study unit, the cone splitter was rinsed twice prior to sample collection (fig. 4). For the first rinse, a 3-L sampling bottle was filled with water during the time that the sampler was lowered into the EWV vertical with the greatest flow for the purpose of determining the rate of filling. The water in this bottle was swirled, poured into the cone splitter, and allowed to pass through the splitter ports. To obtain water for the second rinse, the stream was divided into three sections and one of the 3-L sampling bottles was filled by collecting about 1 L from each section. This second rinse was included to obtain water that was more representative of the stream. During the latter part of the second rinse, any sample-collection bottles that required rinsing before filling were rinsed with water from the ports of the cone splitter.

The splitting scheme for the monthly collection of water samples at intensive fixed sites is the most complex of the schemes because it accounts for all of the constituent groups that are processed through the cone splitter. The constituent groups that were analyzed in water samples obtained from this scheme were FM, MI, NT, PS, and SS (table 4). Other schemes, such as the one for the weekly collection at intensive fixed sites, account for fewer constituent groups and are variations of the monthly scheme.

The steps in the monthly splitting scheme are summarized in figure 6. In step 1, the water in the three 3-L sampling bottles that were collected with the EWV method was poured through the splitter to fill one 1-L plastic bottle and nine 1-L fired glass bottles with approximately 900 mL (milliliters) of sample water each. The plastic bottle contained the final volume for the suspended sediments (SS) constituent group. Of the nine fired glass bottles, seven were used in the filtering process, one was kept as an optional backup bottle in case of breakage, and one was poured in the subsequent splitting step. All of the bottles were removed from the exit-port tubes of the splitter. In step 2, one 125-mL brown plastic bottle labeled RC (raw, chilled), one 250-mL plastic bottle labeled RU (raw, untreated), and two 1-L fired glass bottles were placed in the arrangement shown in figure 6. A 1-L

fired glass bottle from step 1 was then poured through the splitter to provide approximately 90 mL of sample water per exit port. In step 3, one of the 1-L fired glass bottles containing approximately 180 mL of sample water from step 2 was poured through the splitter to fill the RC and RU bottles to a total of approximately 108 mL. The RC bottle contained the final volume for total ammonia-plus-organic nitrogen and total phosphorus. The RU bottle contained the final volume required by the laboratory for the analysis of pH and specific conductance in an unfiltered sample.

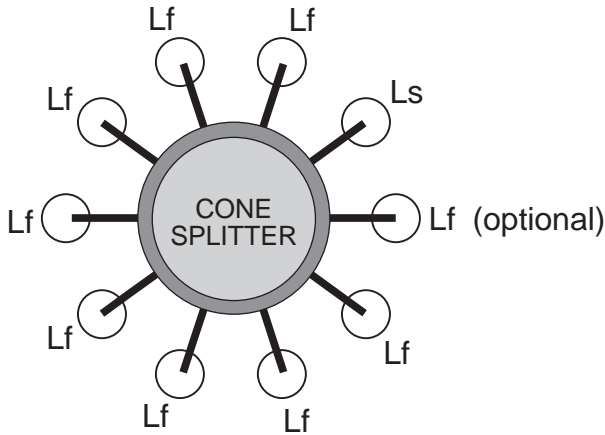
When the NAWQA surface-water sampling program began, the expense and limited availability of Teflon cone splitters resulted in the use of the churn splitter at basic fixed sites in the GAFL study area (table 5). The churn splitter, which has been used in the NASQAN Program since 1977 (Pickering, 1978), consists of a polyethylene bucket with an outlet valve at the base (Ward and Harr, 1990). Sample water is composited in the bucket and mixed, or churned, with a perforated-plate churning disk. Sample water is split into subsamples by withdrawing water through the outlet valve while churning (Pickering, 1976). The churn splitter was used to split water samples for the FM, MI, and NT constituent groups (table 3). The churn splitter is not recommended for splitting water samples used in the analysis of pesticides and organic-carbon (Pickering, 1978) and is recommended with limitations for samples used in the analysis of suspended sediments (Ward and Harr, 1990). Pesticides were not analyzed at basic fixed sites and water samples for analysis of organic carbon and suspended sediments were not passed through the churn splitter. Organic carbon was analyzed in samples collected with a weighted bottle sampler as described earlier. Suspended sediment samples were collected in 1-pint (0.473 L) glass bottles from multiple verticals (table 5).

## Sample Processing

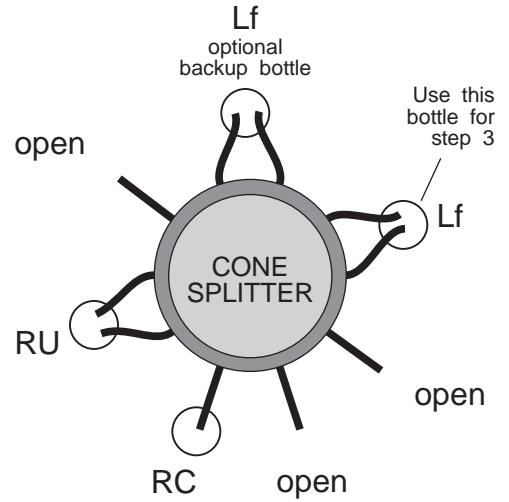
Sample processing at fixed sites in the GAFL study area consisted of measuring pH, specific conductance, and alkalinity, filtering subsamples, adding preservatives, and preparing samples for shipping. The sample processing procedures used in the GAFL study area generally followed the NAWQA surface-water sampling guidelines (Shelton, 1994). However, two variations were made to accommodate the long distances between sampling sites in the GAFL study area (fig. 3). First, water samples for

## STEPS FOR USING CONE SPLITTER

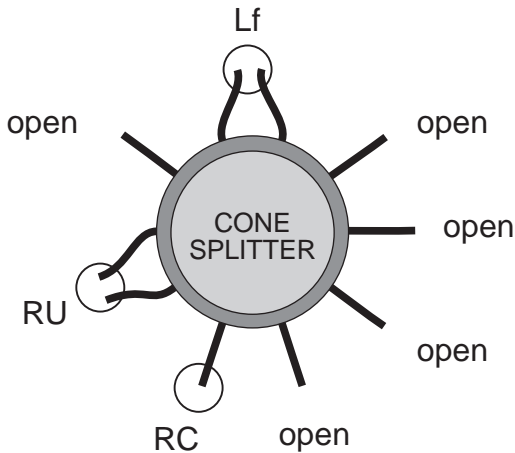
Step 1: Pour sample from each of three 3-L teflon bottles. Save 3 Lf bottles for pesticide filtration. Save 3 Lf bottles for filtering nutrients, majors, and alkalinity. Save 1 Lf bottle for field specific conductance and pH. Save Ls bottle for suspended sediments. Save 1 Lf bottle for subsequent splitting. Save 1 Lf bottle as a backup (optional).



Step 2: Remove bottles from step 1. Set new bottles as shown. Pour Lf bottle from step 1.





Step 3: Remove 1 Lf bottle from step 2. Pour the Lf bottle that was removed. Save RC and RU bottles. Save optional Lf bottle to use if needed.



### EXPLANATION

- Lf Fired, liter, amber glass bottle
- Ls Liter plastic sediment bottle
- RU 250 ml black top bottle
- RC 125 ml brown plastic bottle

-  1 hose placed in 1 bottle.
-  2 hoses placed in 1 bottle.

**Figure 6.** Steps in the splitting scheme for the monthly sampling of intensive fixed sites in the Georgia-Florida Coastal Plain study area.

organic carbon and nutrients were shipped in the same coolers rather than separate coolers. This combined shipping reduced the number of coolers and amounts of ice stored in the sampling vehicles. Second, the extraction of pesticides from water samples onto solid phase extraction (SPE) cartridges was completed in the GAFL laboratory and not in the field as recommended (Shelton, 1994). The water samples were sent to the GAFL laboratory in the Florida District office, extracted, and shipped to the national laboratory for analysis. The laboratory extraction of pesticides reduced the amount of time required to sample and process at each site.

A flowchart for the processing of water samples collected monthly from intensive fixed sites and QA samples is shown in figure 7 (in pocket on inside back cover). The flowchart includes the pathway for the six constituent groups and provides information about the types of sample collection bottles needed, filtering requirements, addition of sample preservatives, and shipping destinations. The flowchart can be modified to accommodate different sampling intensities by deleting pathways that are not needed. Subsamples from either the cone splitter or the churn splitter were processed through the same pathways (fig. 7).

## SUMMARY

The National Water-Quality Assessment (NAWQA) Program is a combination of study unit investigations that address regional and local water-quality issues, and the national synthesis of those study-unit investigations. The Georgia-Florida Coastal Plain (GAFL) study unit is located on the eastern coast of the United States and was 1 of 20 study units selected to begin assessment activities in 1991. In fiscal year 1993, the GAFL study unit entered a 3-year period of intensive data-collection and interpretation that initially focused on the collection of surface-water samples. The implementation of NAWQA design guidelines at the study-unit level required some modifications of the generic national sampling procedures. These modifications needed to be documented for agencies that use water-quality data and for other study units that would be entering the intensive data-collection period. The purpose of this report was to describe the sampling design and sampling procedures used in surface-water sampling at fixed sites in the GAFL study area in 1993.

The surface-water sampling design for the GAFL study area accounted for spatial variation in the study area through the selection of sites and for temporal variations in water quality through the sampling scheme for those sites. Nine fixed sites in the GAFL study area were selected to represent drainage basins of different sizes and different land uses. In the sampling scheme, chemical and physical constituents were divided into six constituent groups: field measurements, major ions and metals, nutrients, organic carbon, pesticides, and suspended sediments. The nine fixed sites were sampled at regular intervals for a combination of constituent groups. Sampling events for high flow conditions and storm events were also included in the sampling scheme.

Water samples for the analysis of all chemical and physical constituents except those in the organic carbon constituent group were collected by the equal-width-increment method (EWI) or by the equal-discharge-increment method (EDI). The EWI method was used at seven of the sites and the EDI was used at two sites. Water samples were split or divided into smaller volumes with one of two devices, the cone splitter or the churn splitter. The cone splitter was used at sites in which water samples were collected for pesticide analysis. The use of the cone splitter required the GAFL study-unit staff to design splitting schemes, an example of which is described in detail. Information about the processing of samples was organized into a flowchart that describes a pathway for each constituent group and provides information about the filtration, preservation, and shipping of samples.

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