THE HYDROLOGIC BENCH-MARK PROGRAM: A STANDARD TO

EVALUATE TIME-SERIES TRENDS IN SELECTED WATER-QUALITY

CONSTITUENTS FOR STREAMS IN GEORGIA

By Gary R. Buell and Susan C. Grams

U.S. GEOLOGICAL SURVEY

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CONVERSION OF INTERNATIONAL SYSTEM UNITS (SI) TO INCH-POUND UNITS

To convert SI units to inch-pound units, the following conversion factors are used:

Multiply SI units	<u>By</u>	To obtain inch-pound units
millimeter (mm)	8.83937	inch (in.)
kilometer (km)	0.62150	mile (mi)
square kilometer (km^2)	0.38618	square mile (mi^2)
milligram per liter , (mg/L)	1.00000	part per million (ppm)
cubic meter per second (m^3/s)	35.31073	<pre>cubic foot per second (ft³/s)</pre>
kilogram per day (kg/d)	0.00110	ton (short) per day
microsiemens per centimeter (µS/cm) at 25°C	1.00000	micromho per centimeter (µmho/cm) at 25°C

Temperature, in degrees Fahrenheit (°F), can be converted to temperature, in degrees Celsius (°C) as follows:

 $^{\circ}F = 1.8^{\circ}C + 32.$

THE HYDROLOGIC BENCH-MARK PROGRAM: A STANDARD TO EVALUATE TIME-SERIES TRENDS IN SELECTED WATER-QUALITY CONSTITUENTS FOR STREAMS IN GEORGIA

By Gary R. Buell and Susan C. Grams

ABSTRACT

Significant temporal trends in monthly pH, specific conductance, total alkalinity, hardness, total nitrite-plus-nitrate nitrogen, and total phosphorus measurements at five stream sites in Georgia were identified using a rank correlation technique, the seasonal Kendall test and slope estimator. These sites include a U.S. Geological Survey Hydrologic Bench-Mark site, Falling Creek near Juliette, and four periodic water-quality monitoring sites. parison of raw data trends with streamflow-residual trends and, where applicable, with chemical-discharge trends (instantaneous fluxes) shows that some of these trends are responses to factors other than changing streamflow. Percentages of forested, agricultural, and urban cover within each basin did not change much during the periods of water-quality record and therefore these non-flow-related trends are not obviously related to changes in land Flow-residual water-quality trends at the Hydrologic cover or land use. Bench-Mark site and at the Chattooga River site probably indicate basin responses to changes in the chemical quality of atmospheric deposition. These two basins are predominantly forested and have received little recent human use. Observed trends at the other three sites probably indicate basin responses to various land uses and water uses associated with agricultural and urban land or to changes in specific uses.

INTRODUCTION

U.S. Geological Survey Hydrologic Bench-Mark Program

The usefulness of Hydrologic Bench-Mark data in evaluating changes in surface-water-quality conditions in basins modified by human activity is examined in this study. The U.S. Geological Survey initiated the Hydrologic Bench-Mark Program in 1958 to provide a data base of hydrologic data on stream basins which are minimally affected by human impact (Cobb and Biesecker, 1971). Interpretation and analysis of these data can provide information which may be used to address water-quality-related objectives such as:

- to document baseline water-quality conditions in basins where little or no cultural use has occurred or where an equilibrium with respect to basin use has been reached;
- 2) to analyze relations between basin characteristics and water-quality characteristics; and
- 3) to measure and evaluate the effects of basin use on water quality by comparing water-quality data from modified basins with water-quality data from Hydrologic Bench-Mark basins.

Identification and quantification of hydrologic processes in Bench-Mark basins can provide a baseline against which effects of human basin use can be measured. Data from relatively undisturbed basins also provide an opportunity to measure the impact of regional influences on hydrology if those influences are the only disturbing factors affecting the basins. One method to assess the possible impact of basin use on water quality is to identify the time-dependent water-quality processes in modified basins and to statistically compare those processes with the same processes that occur in Hydrologic Bench-Mark basins.

Factors that define the surface-water quality in a watershed are basin geology, soil characteristics, precipitation quantity and quality, runoff characteristics, ground-water discharge, soil-water and ground-water residence times, land use, and water use. The synergistic effects of these factors may result in stream-quality trends. Interbasin comparisons of water-quality time-series trends can provide useful information on the importance of one or more of these influencing factors if the "extraneous" factors can be isolated.

Objective

The objective of this study is to identify the possible effects of land use on surface-water quality by comparing water-quality time-series trends and land-cover data in four basins with water-quality time-series trends and land-cover data from a Geological Survey Hydrologic Bench-Mark basin. The use of a control basin to evaluate the effects of land use on water quality in modified basins relates to several objectives of the Hydrologic Bench-Mark Program as previously discussed.

STUDY METHODOLOGY

The effects of land-cover type and land use on water quality should be more visible if the effects of other intervening factors (geology, soils, precipitation, streamflow variation) can be removed. A combination of techniques is used in this study to remove variance in the data caused by some of the effects other than land use. Modified basins that have similar geologic characteristics were selected to minimize possible interbasin differences related to different geologic and soil characteristics. Linear regression of selected water-quality variables on water discharge was used to remove streamflow-related variance in the water-quality data. Time series of flow-residual water-quality data were then tested for temporal trend using a rank correlation analysis, the seasonal Kendall test and seasonal Kendall slope estimator (Smith and others, 1982). Relations between water quality and land use in each basin were then examined by comparing time-series trends in residual water-quality data with time trends in land-cover distributions.

Techniques for surface-water-quality data analysis

Water-quality data used in this study were retrieved from the Geological Survey WATSTORE (National WATer Data STOrage and REtrieval System) water-quality file and analyzed with statistical software available through SAS Institute Inc. The Statistical Analysis System (SAS) software is documented in SAS Institute Inc. (1982a and 1982b). The initial characterization of each basin with respect to the water-quality variables chosen for study involved computation of the mean, median, minimum, maximum, standard deviation, and standard error of the mean for values of specific conductance, and for concentrations of total alkalinity, hardness, total nitrite-plus-nitrate nitrogen, and total phosphorus. The pH data used in this report are characterized by the median, minimum, and maximum values. These statistics were used to provide information about underlying chemical differences between the five basins.

Variance associated with water-discharge was removed from the waterquality data with one of the following linear regression models:

$$f(c) = \beta_0 + \beta_1 \cdot f(Q) + \epsilon, \qquad (1)$$
where $f(c) = c$ (a1) LINEAR or
$$f(c) = \ln(c) \qquad (a2) \qquad \text{LOGARITHMIC}$$
and $f(Q) = Q$ (b1) LINEAR
$$f(Q) = 1/Q \qquad (b2) \qquad \text{INVERSE}$$

$$f(Q) = \ln(Q) \qquad (b3) \qquad \text{LOGARITHMIC or}$$

$$f(Q) = 1/(1 + \beta \cdot Q) \qquad (b4) \qquad \text{HYPERBOLIC.}$$

The variable c is the instantaneous value of the water-quality variable, Q is the instantaneous water discharge, $\beta_{\rm O}$ and $\beta_{\rm I}$ are regression parameters, and ϵ is the error term. In general, the linear and logarithmic forms of the model describe the behavior of constituents adsorbed onto silt or clay particles that can be resuspended from the stream-channel bottom during periods of high velocities associated with increasing water discharge. The inverse form of the model describes a dilution/concentration process applicable to dissolved constituents.

The hyperbolic form of the model is derived from a mass balance equation proposed by Johnson and others (1969) to describe the mixing of baseflow ground water with storm-water runoff:

$$C_0 \cdot V_0 + C_a \cdot V_a = C \cdot (V_0 + V_a), \qquad (2)$$

where C_0 = soil-water (ground water) constituent concentration,

V_o = soil-water volume,

 C_a = storm-water constituent concentration,

 $V_a = storm-water volume,$

and c = constituent concentration of the resultant streamflow.

Equation (2) reduces to the equivalent linear model

$$C = \beta_0 + \beta_1 \cdot (1/(1 + \beta \cdot Q)) + \varepsilon$$
 (3)

In the hyperbolic discharge function, equation (b4), the coefficient β is related to the water discharge according to the formula,

$$\beta = 10(-2.5 \cdot [\log 10(Q)] + X), \tag{4}$$

where X varies from $10^{0.0}$ to $10^{3.5}$. Eight iterative hyperbolic models are thus generated for testing with the SAS procedure STEPWISE.

The hyperbolic model assumes that the watershed is a closed system and, through the coefficient β , takes into account the soil-water residence time in the basin. Because this model explains the physical mixing of chemically distinct waters, it has an added advantage over the other models. The model selection procedure based on equation (4) was used by Smith and others (1982) to remove discharge-related variance in total phosphorus data from 303 streamflow and charical-quality stations in the Geological Survey National Stream Quality Accounting Network (NASQAN).

The MAXR option of the SAS procedure STEPWISE was used to select the "best" one-variable model based on the highest correlation coefficient (SAS Institute Inc., 1982b, p. 102). Only models associated with at least 10 percent of the variance (r-squared greater than or equal to 0.10) and significant at the 0.05 level were used for flow adjustment. Once appropriate models were selected for each of the water-quality variables, those models were re-run using the SAS procedure REG (SAS Institute Inc., 1982b, p. 39-83) to obtain an output data set of predicted and residual values based on the selected regression models. The REG procedure was chosen over other SAS regression procedures because of its overall flexibility in writing comprehensive output data sets, residuals analysis options, and facility for testing timeseries data for first-order autocorrelation (Durbin-Watson statistic).

The following procedure was used to test for trend in time series of (1) the raw constituent data, (2) regression residuals, and, where applicable, (3) chemical-discharge values (instantaneous chemical loads). In the first procedure, a nonparametric rank correlation analysis was done on the time series using the seasonal Kendall test, a modified form of Kendall's tau statistic developed by Hirsch and others (1982). The seasonal Kendall test was applied to the three categories of time series using an experimental SAS procedure, SEASKEN (Crawford and others, 1983). This procedure also computes a slope estimate, which provides a measure of trend magnitude, the seasonal Kendall slope estimator. The Kendall slope estimate is comparable to the slope one would obtain with a linear regression of the dependent variable on time. For linear time series, the computed slope is in units per year (milligrams per liter per year, microsiemens per year). In this report linear

slopes are adjusted to the period-of-record mean values and expressed as percent of the mean per year. Slopes were not computed from logarithmic time series, but rather the residual logarithms were transformed back to actual residuals and then tested for trend.

Techniques for land-cover data analysis

Land-cover types for each basin were identified using Level I of the land-use and land-cover classification system described in Anderson and others (1976). Percentages of forest (type 4), agricultural (type 2), and urban (type 1) land were computed from the Georgia Resource Inventory Vegetation Maps (Georgia Department of Natural Resources, 1978) and the Geological Survey L-series maps by digitizing the areas of the mapping units, summing the areas of like mapping units, and expressing the summed areas as percentages of the total basin area. Percentages were approximated from the aerial photographs using a stratified systematic aligned sampling design (Snedecor and Cochran, 1967; Berry and Baker, 1968). Aerial photographs were divided into 7.5-minute latitude by 7.5-minute longitude sections which corresponded to the the Geological Survey 7.5-minute topographic maps. Land-cover types in each section were tabulated using a grid overlay containing 576 intersection points (nodes) having a horizontal internodal distance of about 0.30 mile and a vertical internodal distance of about 0.36 mile. Node counts were then expressed as percentages of land-cover types for each stratum. percentages were computed from individual stratum percentages weighted by partial area according to Snedecor and Cochran (1967).

Whether or not the various land-cover data sources used in this study were representatively sampled was not determined. The L-series maps produced by the Geological Survey are 85-percent accurate when compared with ground truth (Fitzpatrick-Lins, 1980). No confidence limits could be computed for the estimates of land cover obtained from the Georgia Resource Inventory Vegetation Maps. A similar problem existed with the Geological Survey and the Agricultural Stabilization and Conservation Service aerial photographs. Because ground truth verification of the cover type at the nodes was not done for either set of photographs, binomial standard errors for the correct identification of a particular cover type were not computed and thus the minimum node density for a particular level of confidence was not determined.

The effects of grid-cell size and grid spatial alignment on the accuracy of the estimation of land-cover percentages are discussed in Wehde (1982). He determined that the critical internodal distance was controlled by the size of the smallest homogeneous map unit. As long as the grid-cell size is at least as small as the smallest homogeneous area (on the map or photograph), the estimates of land-cover percentages are assumed to be reasonably accurate. This assumption was used in determining an appropriate grid-cell size for this study.

STUDY BASINS

The Hydrologic Bench-Mark basin used in this study encompasses the drainage area upstream from the gaging station and water-quality sampling site at Falling Creek near Juliette, Ga. (station 02212600). This basin is

located just north of the Fall Line in the Piedmont physiographic province. Three of the four basins compared with the Bench-Mark basin are also in the Piedmont province and one is in the Blue Ridge province. The three Piedmont basins are (1) the North Oconee River drainage upstream from the City of Athens water intake (station 02217740), (2) the Peachtree Creek drainage upstream from the gaging station at Northside Drive in Atlanta (station 02336300), and (3) the Sweetwater Creek drainage upstream from the gaging station near Austell (station 02337000). The Blue Ridge basin is the Chattooga River drainage upstream from the gaging station near Clayton (station 02177000). The locations of these five basins and their outflow sampling sites are shown in figure 1. Summary data on basin elevation ranges, drainage areas, numbers of tributaries, and bedrock geology for the five basins are presented in table 1.

Land-cover types. vary widely among the five basins. The Bench-Mark basin is predominantly forested and located almost entirely within the Oconee National Forest and Piedmont National Wildlife Refuge. The Chattooga River basin is also mostly forested. Parts of the Chattahoochee National Forest in Georgia, the Nantahala National Forest in North Carolina, and the Sumter National Forest in South Carolina compose most of this basin. Both the North Oconee River and Sweetwater Creek basins are both mixed agricultural land and forest with small amounts of urban land. The Peachtree Creek basin is predominantly urban land.

Average annual precipitation for the five basins ranges from about 1,200 mm for the Bench-Mark basin to about 2,000 mm for the Chattooga River basin. The North Oconee River, Peachtree Creek, and Sweetwater Creek basins all average about 1,350 mm (Plummer, 1983).

WATER-QUALITY AND LAND-COVER DATA BASE

Data were selected for water-quality variables common to all five basins and for which suitably long periods (9 to 15 years) of record exist. These variables are pH, specific conductance, total alkalinity (as CaCO3), hardness (as CaCO3), total nitrite-plus-nitrate nitrogen (as N), and total phosphorus (as P). These data were collected as part of the Geological Survey Hydrologic Bench-Mark Program at Falling Creek near Juliette since October 1967; streamflow data were collected since July 1964. The other four sites are sampled as part of a water-quality monitoring network operated by the Geological Survey in cooperation with the Georgia Department of Natural Resources, Environmental Protection Division. Monthly water-quality data have been collected at the Chattooga River and Sweetwater Creek sites since February 1968, at the North Oconee River site since July 1974, and at the Peachtree Creek site from November 1969 to May 1972 and without interruption since July 1975.

Hardness data are available only for the Chattooga River, Falling Creek, and Sweetwater Creek sites. Hardness analyses were discontinued for the Chattooga River and Sweetwater Creek sites in September 1977.

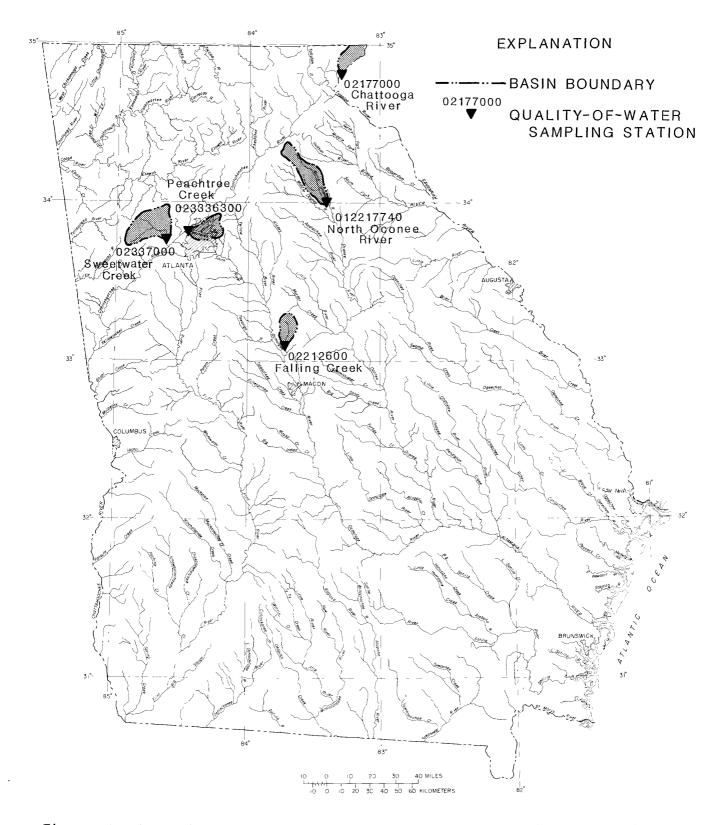


Figure 1.—Locations of the five drainage basins and their outflow sites.

Table 1.--Basin characteristics of the five study basins

biotite/muscovite/garnet schist•

Continuous-record streamflow data have been collected at the Chattooga River site since October 1939, at the Peachtree Creek site since June 1958, and at the Sweetwater Creek site since March 1937 (Stokes and others, 1983). The North Oconee River site is not gaged. Streamflow data for this site are obtained from a stage-discharge rating derived from quarterly water-discharge measurements.

The land-cover data used in this report were compiled from three sources: (1) the Georgia Resource Assessment Program Resource Inventory Vegetation Maps (Georgia Department of Natural Resources, 1978), (2) U.S. Geological Survey 1:250,000 land-use/land-cover maps (L-series maps), and (3) black-and-white aerial photographs (U.S. Department of Agriculture, Agricultural Stabilization and Conservation Service photoindices and Geological Survey National High Altitude Program photographs).

Although water use is a significant factor affecting surface-water quality, the compilation and interpretation of detailed water-use data are outside the scope of this study.

SURFACE-WATER-QUALITY AND LAND-COVER CHARACTERISTICS

Summary descriptive statistics for the surface-water-quality data used in this study are presented in table 2. All five basins have surface waters of similar pH. Period-of-record medians for pH ranged from a low of 6.7 standard units for the Chattooga River site (station 02177000) to a high of 7.2 standard units at the Falling Creek site (station 02336300), a range of 0.5 standard unit. The Hydrologic Bench-Mark site (station 02212600) had the greatest range in individual pH values. The specific conductance values reported at each site were low. These values ranged from a mean of 13 $\mu S/cm$ at 25°C at the Chattooga River site to a mean of 124 μS/cm at 25°C at the Peach-Total alkalinities at the five sites were low. tree Creek site. ranged from 5.2 mg/L at the Chattooga River site to 50 mg/L at the Falling Creek site. Hardness data are not available for the North Oconee River and Peachtree Creek sites. Of the other three sites, Falling Creek had the highest mean hardness at 44 mg/L, followed by Sweetwater Creek at 19 mg/L, and the Chattooga River at 3.4 mg/L. Values of specific conductance and concentrations of total alkalinity and hardness were much lower at the Chattooga River site, which is in the Blue Ridge physiographic province, than at the other four sites, which are in the Piedmont province.

The Peachtree Creek site had the highest mean total nitrite-plus-nitrate nitrogen and mean total phosphorus concentrations of the five sites, with means of 0.47 and 0.22 mg/L, respectively. The North Oconee River and Sweet-water Creek sites both had intermediate mean total nitrite-plus-nitrate nitrogen concentrations of 0.32 and 0.25 mg/L, respectively. The Chattooga River and Falling Creek sites were low in nitrite-plus-nitrate nitrogen. Mean total phosphorus was next highest in Sweetwater Creek at 0.10 mg/L. Total phosphorus concentrations at the Chattooga River, Falling Creek, and North Oconee River sites were low, with means of 0.05 mg/L or less.

Table 2.-- Summary statistics for the water-quality data used in time-trend analysis and interbasin comparisons of water-quality trends ${}^{\circ}$

[Period of record in water years: 02177000, 1968-82 (1968-77, hardness); 02212600, 1968-82; 02217740, 1974-82; 02336300, 1970-82; 02337000, 1968-82 (1970-77, hardness). <, less than. Only median, minimum, and maximum values are reported for pH data]

	N	Mean	Median	Minimum	Maximum	Standard deviation	Standard error of the mean
			pH (standar	d units)			
Chattooga River near	128		6.7	5.8	7.6		
Clayton (02177000) Falling Creek near	164		7.2	5.3	8.9		
Juliette (02212600) North Oconee River above	92		7.0	6.4	7.4		
Athens (02217740) Peachtree Creek at	147		7.1	6.0	7.9		
Atlanta (02336300) Sweetwater Creek near Austell (02337000)	166		6.9	5.8	8.8		
Specific conductance (microsiemens per centimeter at 25°C)							
Chattooga River near	116	13	13	7	26	2.3	0.2
Clayton (02177000) Falling Creek near	164	116	121	28	222	30	2.3
Juliette (02212600) North Oconee River above	92	54	54	32	73	8.5	.9
Athens (02217740) Peachtree Creek at Atlanta (02336300)	141	124	131	36	250	36	3.0
Sweetwater Creek near Austell (02337000)	150	70	68	33	160	18	1.5
		Total	otal alkalinity (mg/L as CaCO3)				
Chattooga River near	105	5.2	5.0	3.0	10	1.3	.1
Clayton (02177000) Falling Creek near	150	50	51	15	80	15	1.2
Juliette (02212600) North Oconee River above	79	20	20	8.0	29	4.5	•5
Athens (02217740) Peachtree Creek at	97	40	42	11	60	11	1.1
Atlanta (02336300) Sweetwater Creek near Austell (02337000)	131	22	21	8.0	38	6.1	•5
Hardness (mg/L as CaCO ₃)							
Chattooga River near	56	3.4	3.0	2.0	8.0	1.3	• 2
Clayton (02177000) Falling Creek near	127	44	46	17	62	11	1.0
Juliette (02212600) Sweetwater Creek near	64	19	19	12	31	3.9	•5
Austell (02337000)		Nitri	 ce-plus-niti	ate (mg/L as	N)		
Chattooga River near Clayton (02177000)	115	•04	•02	•01	.18	•03	<.01
Falling Creek near Juliette (02212600)	107	•05	•05	•00	•21	•04	<.01
North Oconee River above Athens (02217740)	92	.32	•32	•04	•86	•11	.01
Peachtree Creek at Atlanta (02336300)	159	•47	•46	•05	.84	•17	•01
Sweetwater Creek near Austell (02337000)	149	.25	•26	•02	•56	.10	.01
		Tota	al phosphoru	I is (mg/L as I) ?)		
Chattooga River near	113	.03	•02	•02	.10	•02	<.01
Clayton (02177000) Falling Creek near	107	.03	.02	•00	•25	•04	<.01
Juliette (02212600) North Oconee River above Athens (02217740)	92	•05	•04	•02	.29	•04	<.01
Peachtree Creek at	151	•22	•11	•02	1.00	•24	.02
Atlanta (02336300) Sweetwater Creek near Austell (02337000)	148	•10	.08	•02	.36	•07	•01

The study basins have a wide range of land use as indicated by differences in land-cover distributions (fig. 2), but the proportions of the various cover types within each basin have remained relatively constant during the periods addressed by this study. The Chattooga River and Falling Creek basins have about 96 percent and 93 percent forest cover, respectively. The North Oconee River basin has about 57 percent forest cover, 39 percent agricultural cover (cropland, pasture), and 4 percent urban cover. The Sweetwater Creek basin has about 60 percent forest cover, 26 percent agricultural cover, and 14 percent urban cover. The Peachtree Creek basin has about 90 percent urban cover, about 8 percent forest cover, and 2 percent agricultural cover.

The Hydrologic Bench-Mark basin has had various land uses both prior to and during the period that Falling Creek has been sampled as a Hydrologic Bench-Mark station. Prior to land acquisition by the Federal Government in the thirties (Jesse W. Hall, U.S. Forest Service, oral commun., 1984), much of the basin was farmed. In 1910, 87 percent of Jasper County (roughly the upper two-thirds of the Falling Creek basin) was reportedly in farms with about 62 percent of the farmed area under cultivation (Long and others, 1916). Feldspar mining occurred in the northwest part of the basin from 1948 until 1977 (Carpenter, 1971; Michael W. Higgins, U.S. Geological Survey, oral commun., 1984). Selective clearcut logging is occurring in parts of the basin and has occurred in the past.

Few time trends in land-cover distributions are indicated by the data. The Peachtree Creek basin had a slight increase in urban land between 1972 and 1982 and a correspondingly slight decrease in forest land during the same period (fig. 2). A slight decrease in forest land and a slight increase in urban land occurred in the Sweetwater Creek basin between 1966 and 1981. However, these small changes in land cover in the Peachtree Creek and Sweetwater Creek basins may be attributable to sampling error.

TIME-SERIES TREND ANALYSIS OF SURFACE-WATER-QUALITY DATA

Regression models used to remove water-discharge-related variance in the surface-water-quality data are summarized in table 3. Table values show that a wide range of variance is associated with variation in water discharge. Twenty-two of the twenty-seven regression models reported in table 3 have r-squared values greater than 0.10 and all 27 relations are significant at the 0.05 level.

The seasonal Kendall test and seasonal Kendall slope estimator were used to test time series of monthly medians of pH, specific conductance, total alkalinity, hardness, total nitrite-plus-nitrate nitrogen, and total phosphorus data from the five study basins. Results are presented in figures 4 through 19 and include trend analyses of three categories of data: (1) the raw water-quality data (actual measured values unadjusted for the effects of water-discharge variance), (2) the residuals of a linear regression of the data on water discharge (flow-adjusted values generated from the models presented in table 3), and, where applicable, (3) the chemical discharge of the water-quality constituent (instantaneous flux) through a unit cross section of stream channel. Trend results not significant at the 90 percent confidence level are interpreted in this report as "no trend".

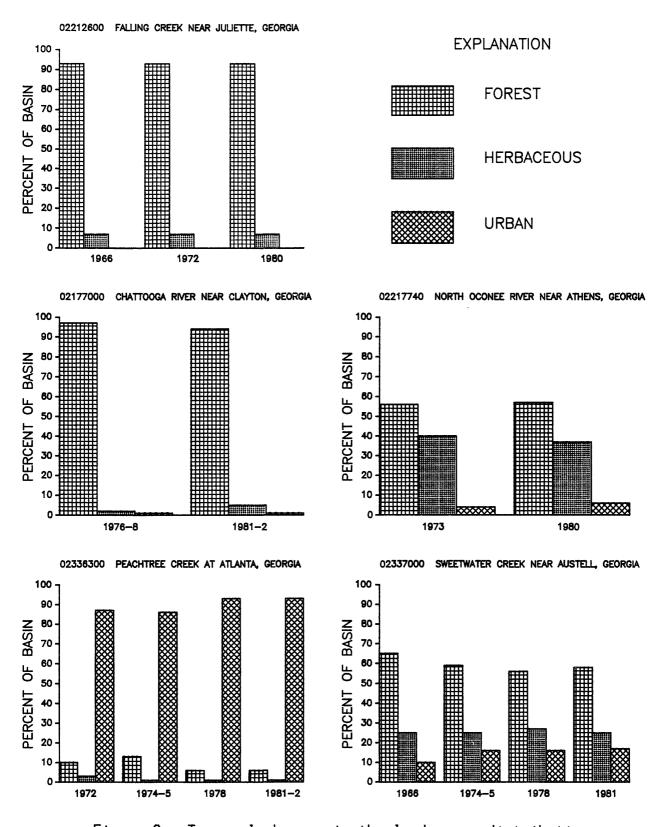


Figure 2.—Temporal changes in the land-cover distributions of the five drainage basins during their periods of water-quality record.

 ${\it Table 3.--Linear regression models selected for removal of water-discharge-associated variance in the water-quality data } \\$

[Results follow the general linear model form $f(c) = \beta_0 + \beta_1 \cdot f(Q) + \epsilon$, where f(c) = c (LIN) or $f(c) = \ln(c)$ (LOG) and f(Q) is one of the following functions of water discharge: linear (LIN), f(Q) = Q; logarithmic (LOG), $f(Q) = \ln(Q)$; inverse (INV), $f(Q) = \frac{1}{Q}$; hyperbolic (HYP), $f(Q) = \frac{1}{(1 + \beta \cdot Q)}$. Regression model parameters expressed in units indicated for each constituent]

		Number of ob-		Significance	Mode1				
	f(c)/ f(Q)	serva- tions		of F statistic	standard error	Model intercept	Model slope		
			pΗ (standard ι	ınits)					
Chattooga River near	LOG/	127	0.07	0.0023	0.34	6.31	0.66		
Clayton (02177000) Falling Creek near	HYP LOG/	160	.14	.0001	•50	6.33	1.01		
Juliette (02212600) North Oconee River above	HYP LOG/	87	•27	.0001	.20	6.24	1.02		
Athens (02217740) Peachtree Creek at	HYP LOG/	146	•32	.0001	.27	6.63	.79		
Atlanta (02336300) Sweetwater Creek near Austell (02337000)	HYP LOG/ LOG	164	•12	.0001	.30	7.45	11		
Specific conductance (microsiemens per centimeter at 25°C)									
Chattooga River near	LIN/	115	•27	•0001	2.0	11.4	29.7		
Clayton (02177000) Falling Creek near	HYP LOG/	160	•74	.0001	•2	3.7	1.4		
Juliette (02212600) North Oconee River above Athens (02217740)	HYP LIN/ LOG	87	•53	•0001	5.4	100.7	-8.2		
Peachtree Creek at Atlanta (02336300)	LOG/ HYP	140	.73	.0001	•2	3.8	1.3		
Sweetwater Creek near Austell (02337000)	LOG/ LOG	149	.72	•0001	•1	5.3	2		
Т	otal alka	linity (milligrams per	' r liter equival	ent CaCO3)				
Chattooga River near Clayton (02177000)	LOG/ HYP	105	•28	•0001	•21	1.07	.89		
Falling Creek near Juliette (02212600)	LIN/ HYP	146	.68	.0001	8.43	19.36	51.17		
North Oconee River above Athens (02217740)	LIN/ HYP	76	.78	•0001	2.04	7.42	23.88		
Peachtree Creek at Atlanta (02336300)	LOG/ HYP	97	.74	•0001	•18	2.12	1.86		
Sweetwater Creek near Austell (02337000)	LOG/ HYP	131	.76	•0001	•14	2.34	1.21		
	Har	dness (n	illigrams per	liter equivale	nt CaCO3)				
Chattooga River near Clayton (02177000)	LIN/ INV	56	•27	.0001	1.16	2,23	67.25		
Falling Creek near Juliette (02212600)	LOG/ HYP	126	•72	.0001	•15	2.74	1.29		
Sweetwater Creek near Austell (02337000)	LOG/ HYP	64	.68	.0001	•11	2.50	.81		
То	tal nitri	 -te-plus -	nitrate nitrog	gen (milligrams	per liter as	N)			
Falling Creek near Juliette (02212600)	LIN/ HYP	108	•04	•0389	•037	•041	.033		
North Oconee River above Athens (02217740)	LOG/ INV	87	•16	•0001	.352	970	43.619		
Peachtree Creek at Atlanta (02336300)	LIN/ HYP	159	•08	•0002	.159	.123	•398		
Sweetwater Creek near Austell (02337000)	LOG/ INV	149	•11	•0001	•537	-1.321	23.482		
	T.	otal pho	sphorus (milli	grams per lite	r as P)				
Chattooga River near Clayton (02177000)	LOG/ HYP	113	•08	•0023	•370	-3.428	•763		
Falling Creek near Juliette (02212600)	LIN/ HYP	104	.38	•0001	•031	•190	176		
North Oconee River above Athens (02217740)	LIN/ LIN	87	•23	•0001	•021	•028	•0004		
Peachtree Creek at Atlanta (02336300)	LOG/ HYP	151	•61	•0001	•626	•050	-2.972		
Sweetwater Creek near Austell (02337000)	LOG/ HYP	148	•07	•0009	.718	-2.074	938		
		l					L		

Trends in water discharge

Figure 3 graphically presents instantaneous discharges for the times of water-quality sampling at each of the five basin outflow sites and results of trend analysis of these data. Peachtree Creek shows a slight negative trend in discharge. The other four sites show no apparent trend in discharge.

Trends in pH

The pH data for the five basin outflow sites and results of trend analysis of pH time series are presented graphically in figure 4. The Chattooga River, Falling Creek, and Sweetwater Creek sites all exhibited slight increases in pH from 1968 to 1982. Trend slopes for these three sites range from +0.02 to +0.03 standard units per year. No apparent trends are present at the North Oconee River and Peachtree Creek sites. When pH was adjusted for streamflow variability, the flow-residual pH values showed the same pattern with the exception of Sweetwater Creek (fig. 5). The Sweetwater Creek pH data did not show a significant relation with streamflow (p>0.10), so a flow adjustment was not made. The residuals trend slope for both the Chattooga River and Falling Creek sites is +0.02 standard units per year.

Trends in specific conductance

The North Oconee River is the only basin outflow site that shows a trend in conductivity: a slight positive trend of +0.5 (μ S/cm/yr) from 1974 to 1982 (fig. 6). When conductivity values were flow-adjusted, the residuals for the North Oconee River site still exhibited a positive trend and the residuals at the Falling Creek and Sweetwater Creek sites exhibited negative trends (fig. 7). Residuals trend slopes for the three sites range from -0.7 to +0.4 (μ S/cm/yr).

Trends in total alkalinity and hardness

Trend analysis data for total alkalinity and hardness time series (figs. 8-13) are presented together because the two constituents are chemically related. Alkalinity is defined as the capacity of a solution to neutralize acid (Hem, 1970, p 152) or, synonymously, the buffering capacity of the solution. Much of the buffering capacity of surface waters is derived from hardness or "the effect of alkaline-earth cations" (Hem, 1970, p 224). in total alkalinity are present in the raw data, residuals, and chemicaldischarge values at the Chattooga River site (all negative, figs. 8-10); in the residuals at the Falling Creek site (negative, fig. 9); and in the raw data at the North Oconee River site (positive, fig. 8). Negative trends in hardness are indicated for the Chattooga River and Falling Creek sites (fig. 11) with trend slopes of -0.13 and -0.40 (mg/L)/yr, respectively. No hardness trend is present in the data from the Sweetwater Creek site. A negative trend in flow-residual hardness of -0.58 (mg/L)/yr is present at the Falling Creek site (fig. 12). No hardness discharge trends are present at any of the three sites having hardness data (fig. 13).

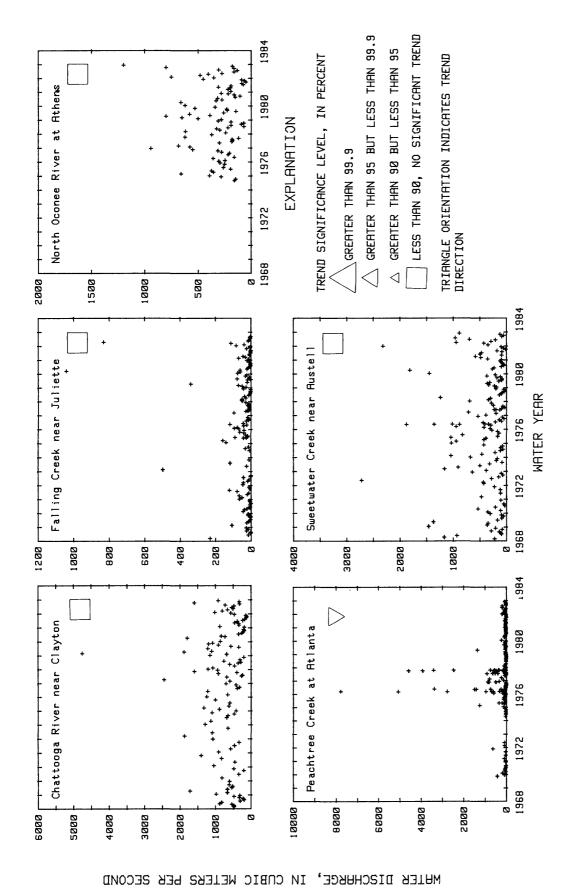


Figure 3. --Temporal trends in water discharge for the basin outflow sites.

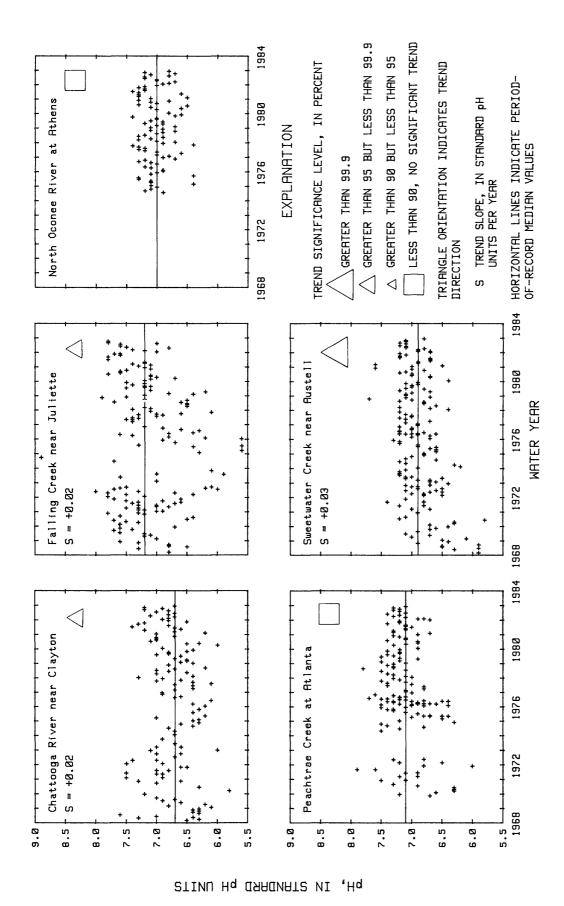


Figure 4. -- Temporal trends in pH for the basin outflow sites.

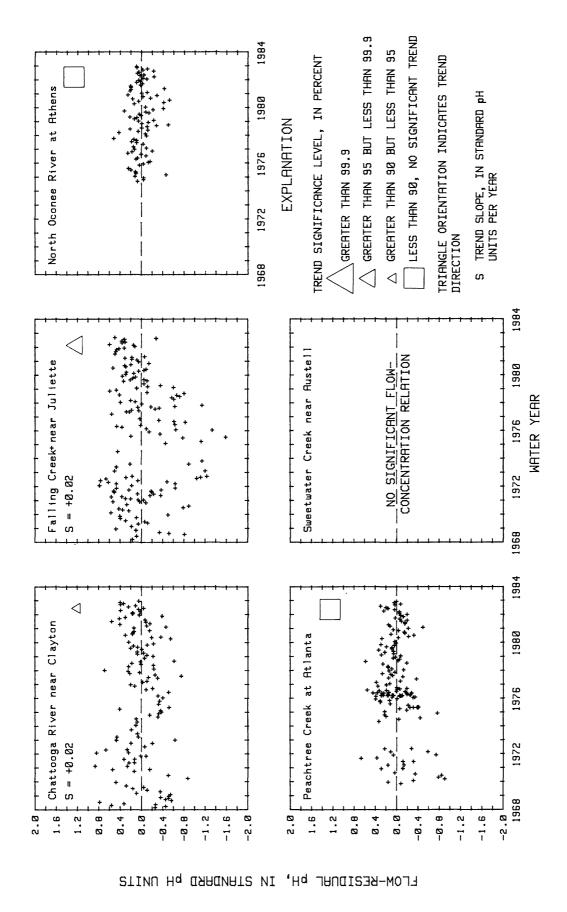


Figure 5. --Temporal trends in flow-residual pH for the basin outflow sites.

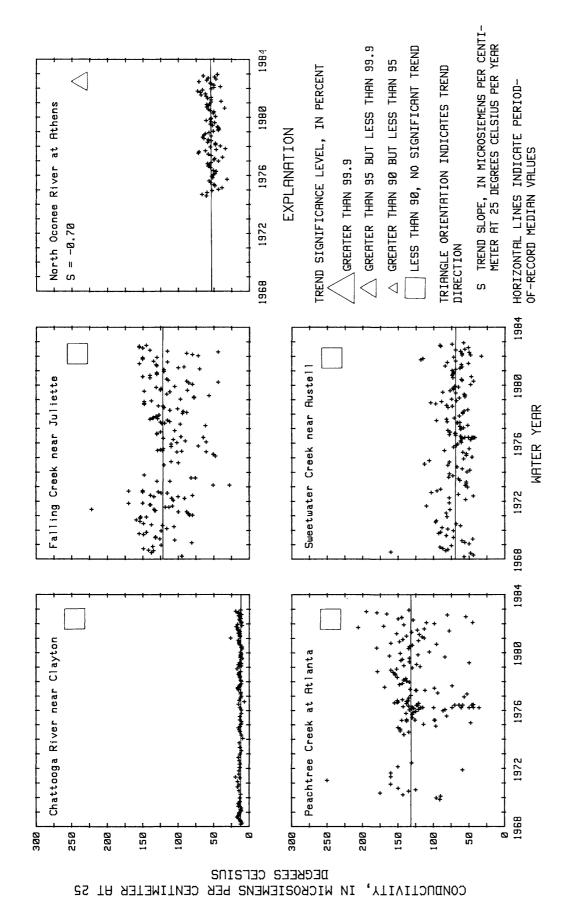


Figure 6. -- Temporal trends in conductivity for the basin outflow sites.

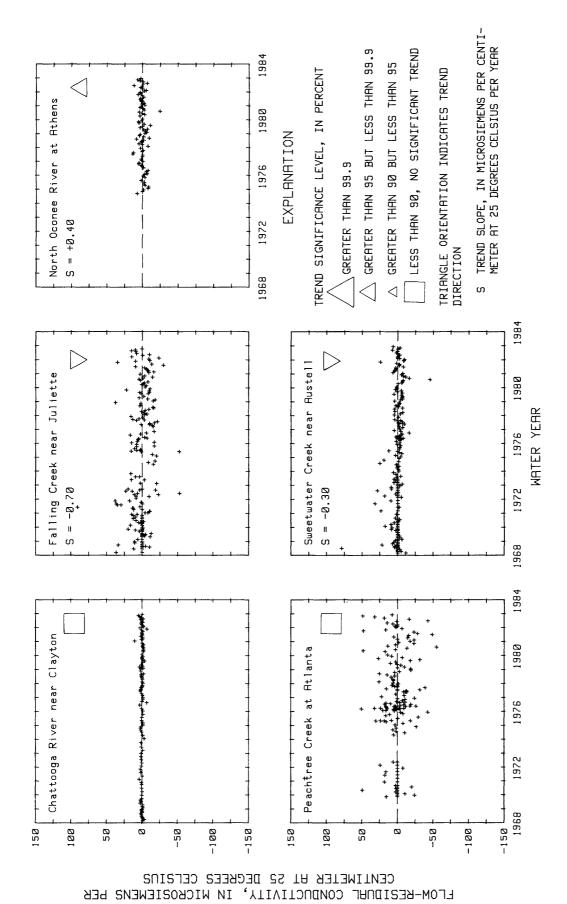


Figure 7.——Temporal trends in flow—residual conductivity for the basin outflow sites.

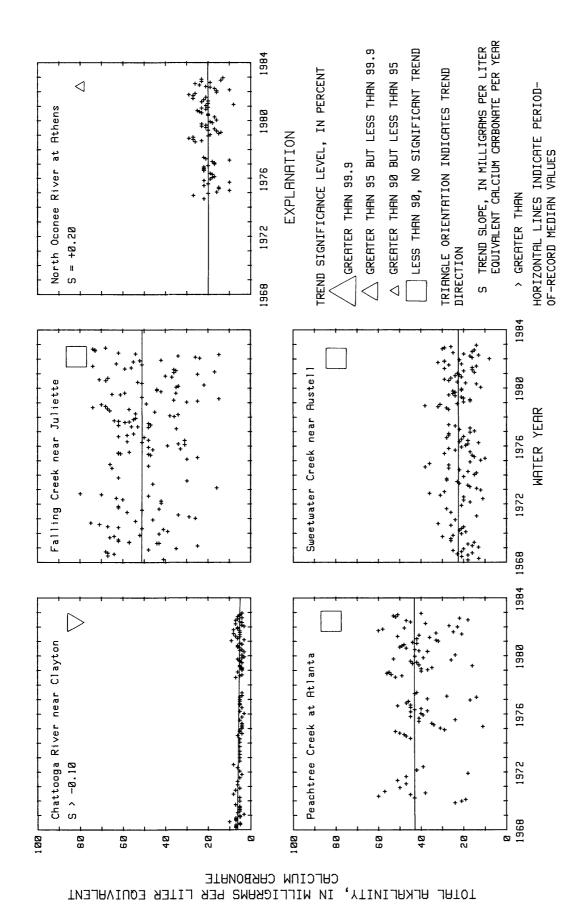


Figure 8. -- Temporal trends in total alkalinity for the basin outflow sites.

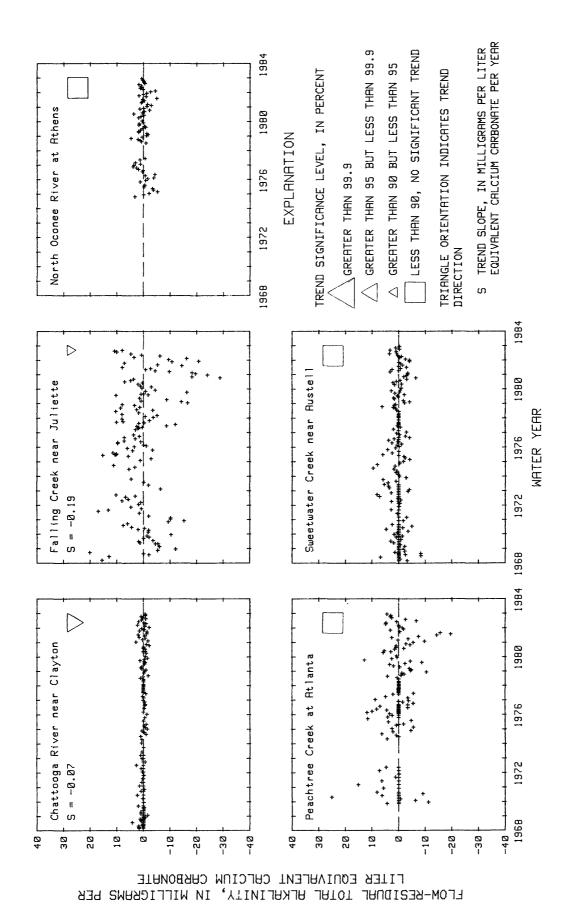


Figure 9. -- Temporal trends in flow-residual total alkalinity for the basin outflow sites

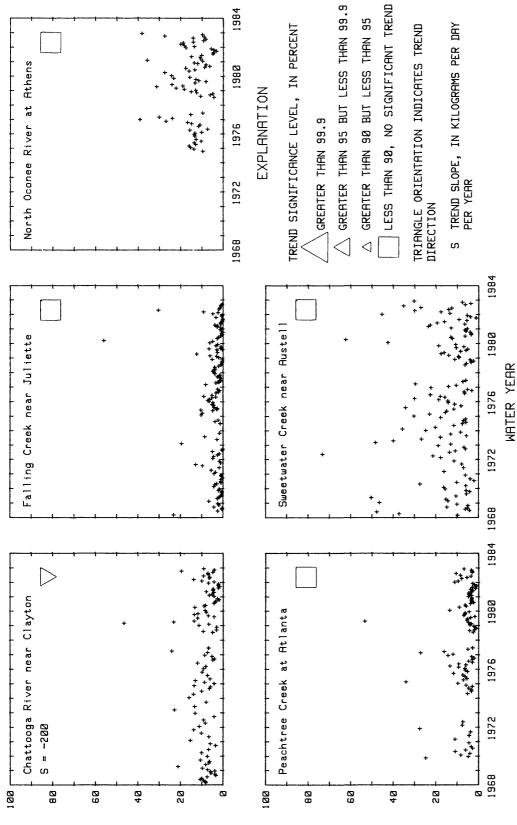


Figure 10.——Temporal trends in total alkalinity discharge for the basin outflow sites.

X 1000 EQUIVALENT CALCIUM CARBONATE
TOTAL ALKALINITY DISCHARGE, IN KILOGRAMS PER DAY

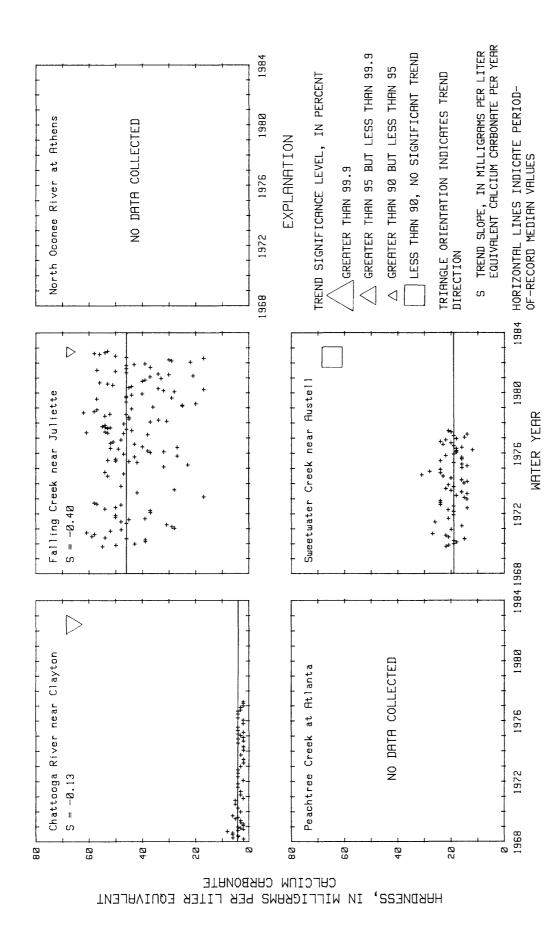


Figure 11. -- Temporal trends in hardness for the basin outflow sites.

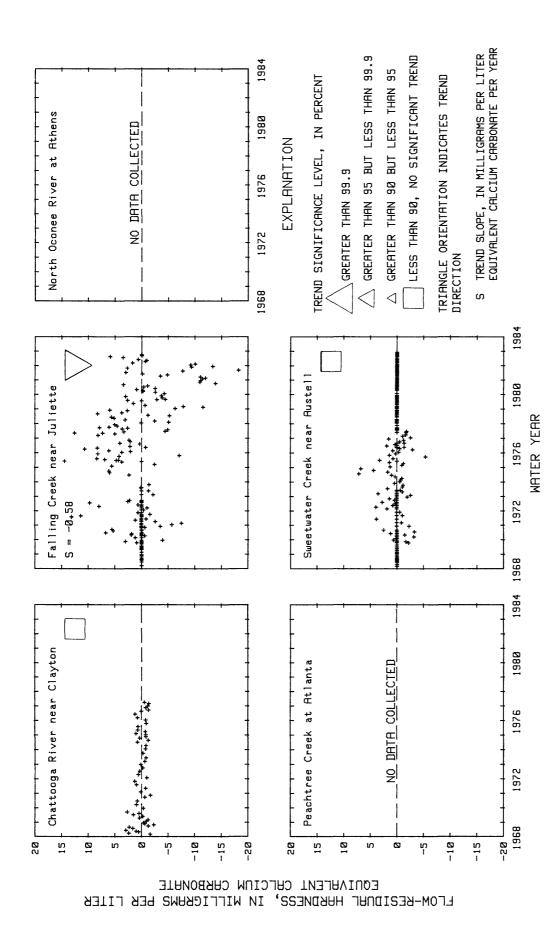


Figure 12.—-Temporal trends in flow-residual hardness for the basin outflow sites.

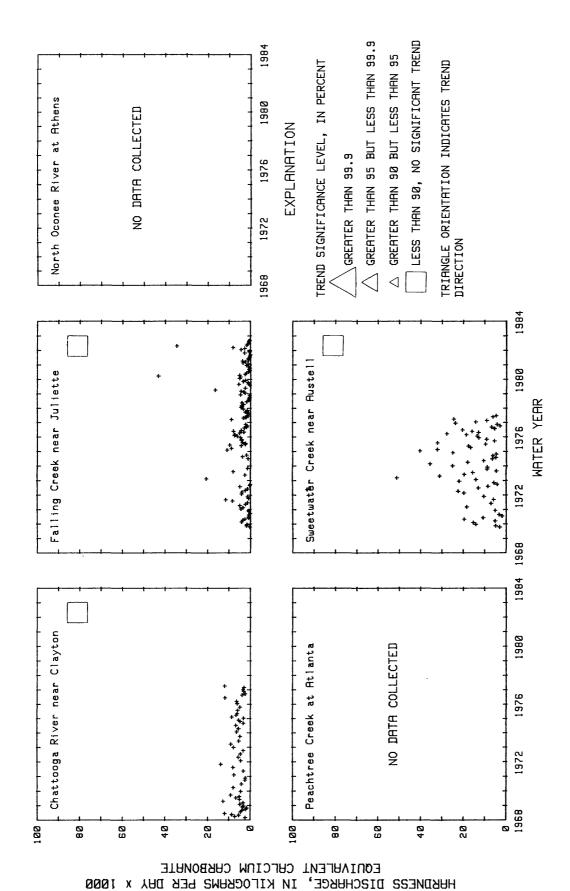


Figure 13. -- Temporal trends in hardness discharge for the basin outflow sites.

Trends in total nitrite-plus-nitrate nitrogen

Two of the five basin outflow sites show trends in total nitrite-plus-nitrate nitrogen (fig. 14). Total nitrite-plus-nitrate nitrogen increased 0.002 (mg/L)/yr at the Falling Creek site and decreased 0.008 (mg/L)/yr at the Sweetwater Creek site. Only the Sweetwater Creek site shows a trend in flow-adjusted concentrations where flow-residual total nitrite-plus-nitrate nitrogen decreased 0.008 (mg/L)/yr from 1968 to 1982 (fig. 15). Three of the five sites show trends in total nitrite-plus-nitrate nitrogen discharge (fig. 16). Nitrogen discharge at the Chattooga River site decreased about 2.30 (kg/d)/yr from 1968 to 1982, at the Falling Creek site about 0.20 (kg/d)/yr from 1971 to 1982, and at the Sweetwater Creek site about 3.63 (kg/d)/yr from 1968 to 1982.

Trends in total phosphorus

Figure 17 presents total phosphorus data for the five basin outflow sites and results of trend analysis of these data. A positive total phosphorus trend is present at the Falling Creek site and negative trends are present at the Peachtree Creek and Sweetwater Creek sites. Trend slopes range from -0.005 to less than 0.001 (mg/L)/yr. No trends are present at the Chattooga River and North Oconee River sites. Flow-residual total phosphorus trends are present at the Falling Creek (positive) and Sweetwater Creek (negative) sites with slopes ranging from +0.001 (mg/L)/yr to less than -0.005 (mg/L)/yr (fig. 18). Total phosphorus discharge trends are present at the Falling Creek site (positive), the Peachtree Creek site (negative), and the Sweetwater Creek site (negative) with trend slopes ranging from +0.02 (kg/d)/yr to -3.13 (kg/d)/yr (fig. 19).

SURFACE-WATER-QUALITY TRENDS AND THEIR RELATION TO LAND COVER

Time-trend analyses of the Bench-Mark data from Falling Creek indicate positive trends in pH and total phosphorus, negative trends in conductivity, total alkalinity, and hardness, and a mixed positive and negative trend in total nitrite-plus-nitrate nitrogen (figs. 4-19) during water years 1968 through 1982 (1971 through 1982 for nitrogen). Flow-residual trends are pressent for all of these variables except total nitrite-plus-nitrate nitrogen, indicating that some factor (or factors) other than water discharge is responsible for the observed changes. Proportions of forest and agricultural cover remained relatively constant during this period (fig. 2), and thus none of the flow-residual trends are obviously related to, or attributable to, changes in land cover.

The four basins chosen for comparison with the Hydrologic Bench-Mark basin all show significant trends in some of the chemical data (figs. 4-19), but, as with Falling Creek, none of these trends bear any obvious relation to changes in land-cover characteristics. Proportions of different land-cover categories did not change much in any of these basins (fig. 2) during the study period.

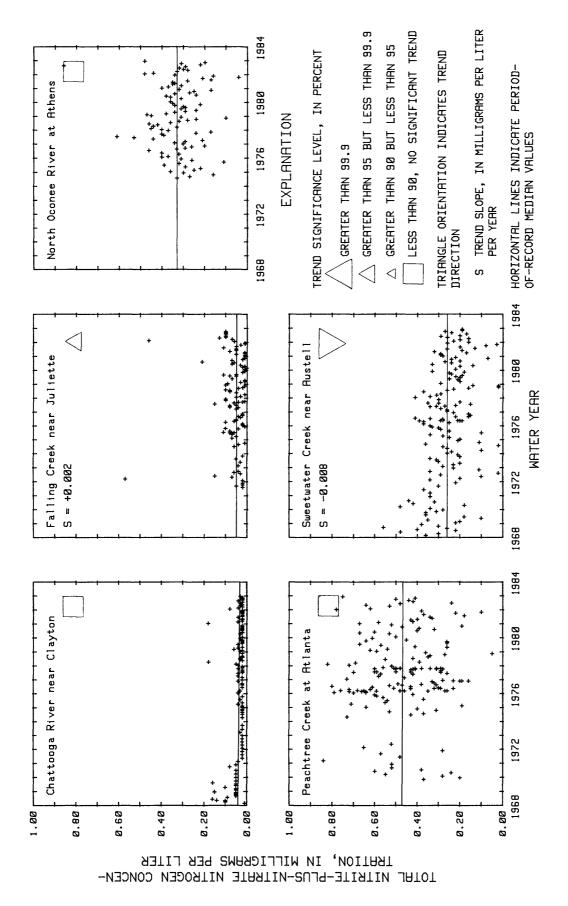


Figure 14.--Temporal trends in total nitrite-plus-nitrate nitrogen concentration for the basin outflow sites.

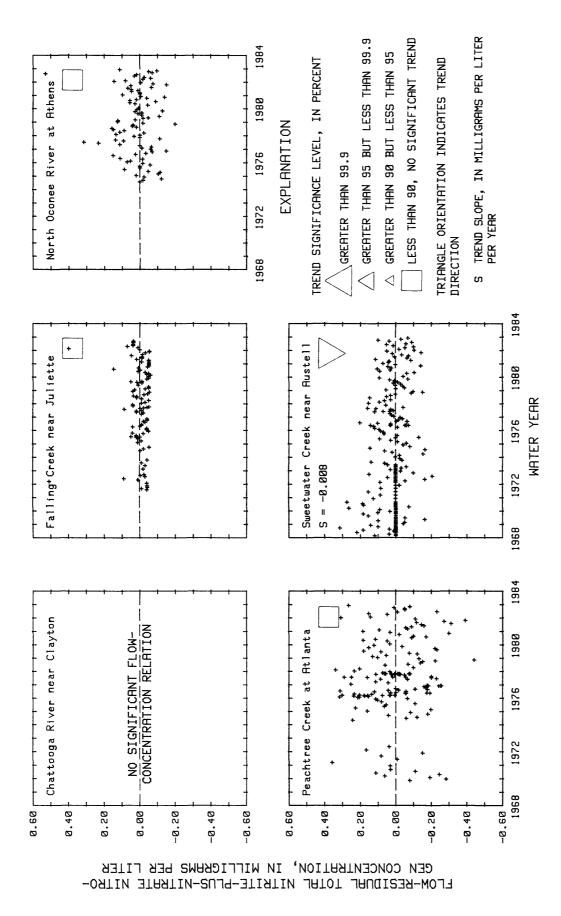


Figure 15. -- Temporal trends in flow-residual total nitrite-plus-nitrate nitrogen concentration for the basin outflow sites.

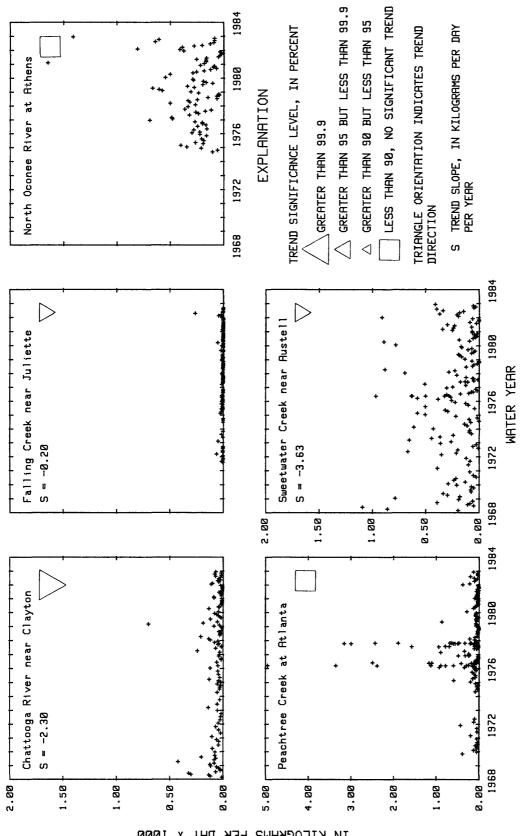


Figure 16. -- Temporal trends in total nitrite-plus-nitrate nitrogen discharge for the

basin outflow sites

IN KIFOCKHWR BEK DHA X 1000 TOTAL NITRITE-PLUS-NITRATE NITROGEN DISCHARGE,

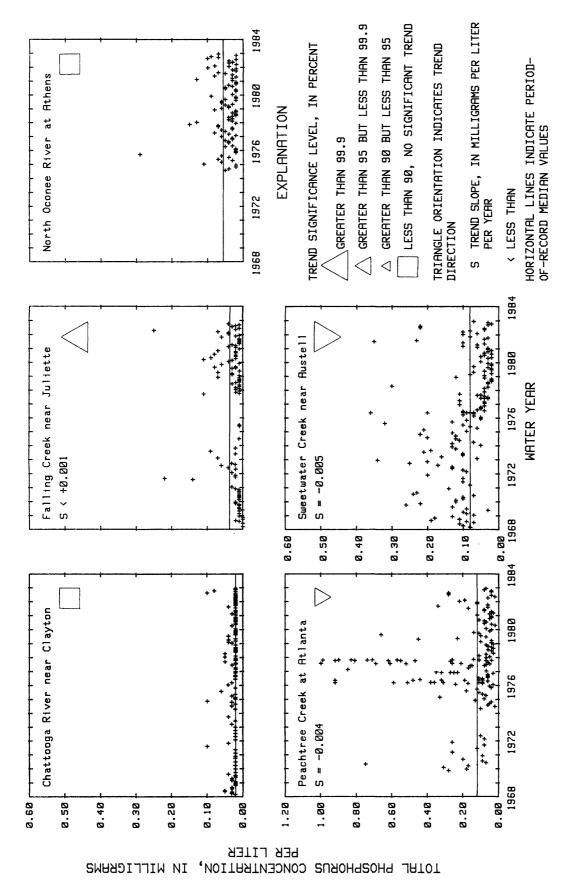


Figure 17. -- Temporal trends in total phosphorus concentration for the basin outflow sites.

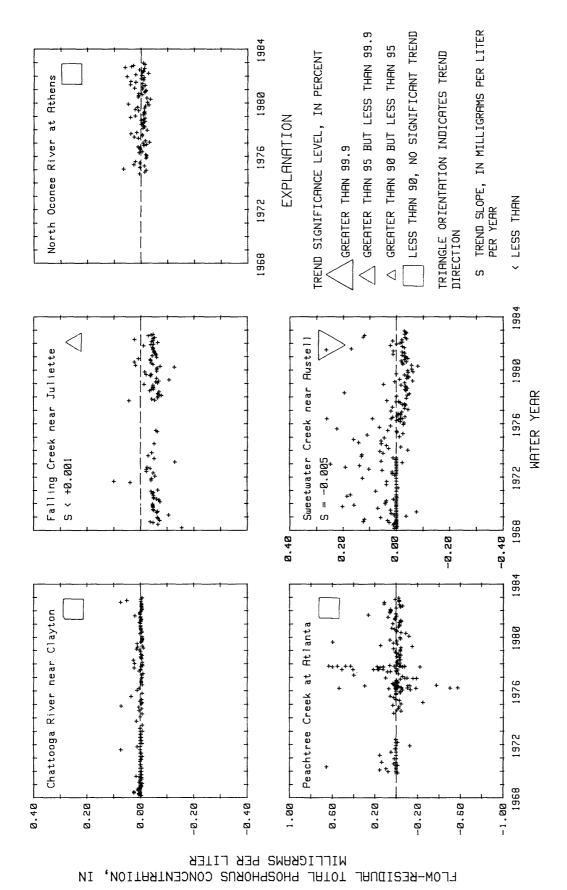


Figure 18. -- Temporal trends in flow-residual total phosphorus concentration for the basin autflow sites

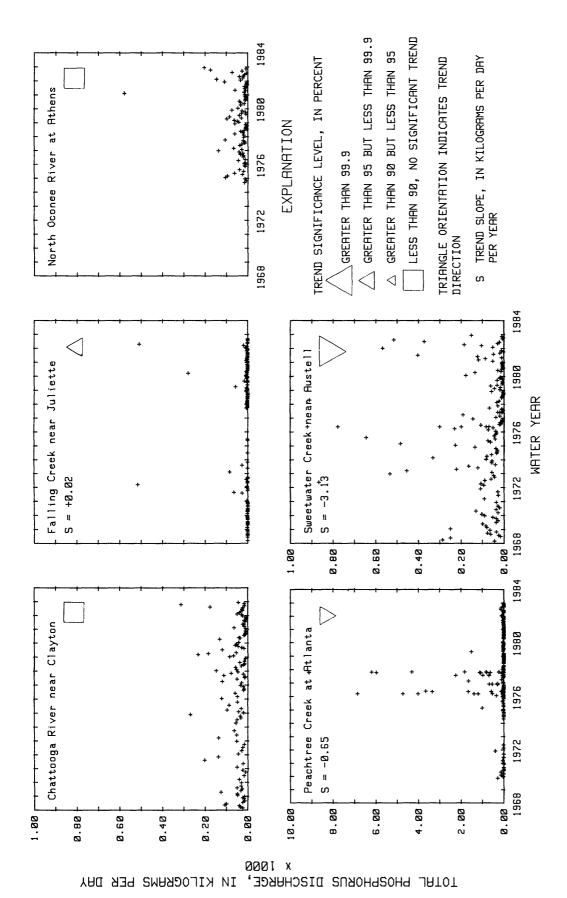


Figure 19. ——Temporal trends in total phosphorus discharge for the basin outflow sites.

COMPARISON OF TRENDS IN MODIFIED BASINS WITH TRENDS IN THE HYDROLOGIC BENCH-MARK BASIN

Although relations between land-cover characteristics and surface-water quality (within the context of temporal trends) are not evident from the data presented, a comparison of Hydrologic Bench-Mark trends with trends in the other four basins can be useful in pointing out similarities or differences between the five basins. This type of comparison can serve as a starting point for a more in-depth analysis of specific land uses and water uses that may provide the information with which cause-and-effect relations can be established.

Flow-residual total alkalinity and hardness trends in the Hydrologic Bench-Mark basin and a flow-residual alkalinity trend in the Chattooga River basin may reflect basin responses to changes in the chemical quality of atmospheric deposition. The decrease in alkalinity at the Hydrologic Bench-Mark site has also been reported by Smith and Alexander (1983) in a nationwide study of acid-precipitation-induced trends in the stream chemistry of Hydrologic Bench-Mark sites. Both basins are predominantly forested (fig. 2) and, with the exception of some selective clearcut logging, have received relatively little human use during the period of water-quality record (1968 through 1982 water years). Farming in the Hydrologic Bench-Mark basin was phased out in the thirties when most of the land was acquired by the Federal Government. Thus, any agricultural effects such as soil erosion and nutrient loss resulting from farming are probably no longer occurring. The low nitrogen and phosphorus concentrations at the Hydrologic Bench-Mark site (table 2) support this observation. The feldspar mining pits in the headwaters area of the basin occupy a small percentage of the total basin area and are not adjacent to the stream channels. The Chattooga River has Wild and Scenic River status and thus much of the land adjacent to the river is protected from any disturbance by man.

Flow-residual water-quality trends in the North Oconee River, Peachtree Creek, and Sweetwater Creek basins may indicate changes in specific land uses and water uses within these three basins. Although the relative proportions of forest, agricultural, and urban land did not change appreciably during the periods of water-quality record (fig. 2), specific uses associated with agricultural and urban land may have changed. For example, changes in farming practices such as conversion of cropland to pasture or vice versa, or changes in the quantity or chemical quality of point-source contributions to streams, may have caused the observed water-quality trends in these modified basins. The pronounced negative trends in all three categories of nitrogen and phosphorus data for the Sweetwater Creek site indicate a reduction in point- or nonpoint-source contributions of pollutants to this basin.

CONCLUSIONS

Flow-residual trends in total alkalinity and hardness at the Hydrologic Bench-Mark site and a flow-residual trend in total alkalinity at the Chattooga River site may indicate basin responses to changes in the chemical quality of atmospheric deposition, because these basins are predominantly forested and have remained relatively undisturbed by human activities.

Flow-residual water-quality trends in the North Oconee River, Peachtree Creek, and Sweetwater Creek basins may have resulted from changes in land-use practices associated with agricultural and urban land such as improved farming techniques, changes from cropland to pastureland, or changes in sewage treatment practices.

To relate the trends observed in the North Oconee River, Peachtree Creek, and Sweetwater Creek basins to specific causes will require land-use information that is more detailed than gross land-cover distributions. The needed information includes delineation of cropland and pasture, a knowledge of past and present farming practices, the chemical quality and magnitude of point-source discharges, and water-use practices.

Because land-cover distributions in the five basins remained relatively stable for the periods of water-quality record, land-cover changes apparently did not contribute to the flow-residual water-quality trends.

Water-quality trends attributable to causes other than variation in streamflow may not be apparent in the raw data. When data are correlated with flow, an analysis of flow residuals is necessary to identify non-flow-related trends.

REFERENCES CITED

- Anderson, J. R., Hardy, E. E., Roach, J. T., and Witmer, R. E., 1976, A land-use and land-cover classification system for use with remote sensor data: U.S. Geological Survey Professional Paper 964, 28 p.
- Berry, B. J. L., and Baker, A. M., 1968, Geographic sampling, in Berry, B. J. L., and Marble, D. F., eds., Spatial analysis: A reader in statistical geography: Englewood Cliffs, New Jersey, Prentice-Hall, p. 91-100.
- Carpenter, R. H., 1971, Norite intrusives in western Jasper County and eastern Monroe County, Georgia: Georgia Geological Society Publication, 6th Annual Field Trip, October 8-9, 1971, 13 p.
- Cobb, E. D., and Biesecker, J. E., 1971, The national hydrologic benchmark network: U.S. Geological Survey Circular 460-D, 38 p.
- Crawford, C. G., Slack, J. R., and Hirsch, R. M., 1983, Nonparametric tests for trends in water-quality data using the Statistical Analysis System: U.S. Geological Survey Open-File Report 83-550, 102 p.
- Fitzpatrick-Lins, Katherine, 1980, The accuracy of selected land-use and land-cover maps at scales of 1:250,000 and 1:100,000: U.S. Geological Survey Circular 829,
- Georgia Department of Natural Resources, 1978, The Georgia Resource Assessment Program User's Guide, Vegetation: Georgia Department of Natural Resources, Office of Planning and Research, 21 p.
- Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 1473, 363 p.
- Hirsch, R. M., Slack, J. R., and Smith, R. A., 1982, Techniques of trend analysis for monthly water-quality data: Water Resources Research, v. 18, no. 1, p. 107-121.
- Johnson, N. M., Likens, G. E., Borman, F. H., Fisher, D. W., and Pierce, R. S., 1969, A working model for the variation in stream-water chemistry at the Hubbard Brook Experimental Forest, New Hampshire: Water Resources Research, v. 5, no. 6, p. 1353-1363.
- Long, D. D., Carr, M. E., and Hearn, W. E., 1916, Soil survey of Jasper County, Georgia: U.S. Department of Agriculture, Bureau of Soils, p. 647-685.
- Plummer, G. L., 1983, Georgia Rainfall: Precipitation patterns at 23 places, 1734-1982: Athens, Georgia, The Georgia Academy of Science, 119 p.
- SAS Institute, Inc., 1982a, SAS User's Guide: Basics: Cary, N.C.: SAS Institute, Inc., 1982, 923 p.

REFERENCES CITED--Continued

- SAS Institute, Inc., 1982b, SAS User's Guide: Statistics: Cary, N.C.: SAS Institute, Inc., 1982, 584 p.
- Smith, R. A., Hirsch, R. M., and Slack, J. R., 1982, A study of trends in total phosphorus measurements at NASQAN stations: U.S. Geological Survey Water-Supply Paper 2190, 34 p.
- Smith, R. A. and Alexander, R. B., 1983, Evidence for acid-precipitation-induced trends in stream chemistry at Hydrologic Bench-Mark Stations, U.S. Geological Survey Circular 910, 12 p.
- Snedecor, G. W. and Cochran, W. G., 1967, Statistical methods: Ames, Iowa, Iowa State University Press, 593 p.
- Stokes, W. R., III, Hale, T. W., Pearman, J. L., and Buell, G. R., 1983, Water resources data for Georgia, Water year 1982: U.S. Geological Survey Water-Data Report GA82-1, 390 p.
- Wehde, M. E., 1982, Spatial quantification of maps or images: Cell size or pixel size implications: Journal of Photogrammetric Engineering and Remote Sensing, v. 48, no. 8, p. 1289-1298.