By James L. Robinson

Prepared in cooperation with the City of Anniston Water Works and Sewer Board

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Conversion Factors, Definitions, and Datum

Multiply	Ву	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi ²)	2.590	square kilometer (km ²)
	Volume	
gallon (gal)	3.785	liter
	Flow rate	
million gallons per day (Mgal/d)	0.04381	cubic meter per second

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25 °C).

Concentrations of chemical constituents in water are in milligrams per liter (mg/L).

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). Historical data collected and stored as National Geodetic Vertical Datum of 1929 have been converted to NAVD 88 for use in this publication unless otherwise noted.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83). Historical data collected and stored as North American Datum of 1927 (NAD 27) have been converted to NAD 83 for use in this publication.

Acronyms and Abbreviations:

Ca	calcium
CaCO ₃	calcium carbonate
CFC	chlorofluorocarbon
CFC-11	trichlorofluoromethane (CFCl ₃)
CFC-12	dichlorodifluoromethane (CF_2Cl_2)
CFC-113	trichlorotrifluoroethane $(C_2F_3Cl_3)$
Cl	chloride
CO_3	carbonate ion
δ	delta
D	deuterium
ECD	electron capture detector
F	fluoride
FAA	Federal Aviation Administration
fMol/L	femtomol per liter
GML	Global Meteoric Line
HCO ₃	bicarbonate ion
K	potassium
LRL	laboratory reporting level
LT-MDL	long term method detection level
MDL	method detection level
Mg	magnesium
Ν	nitrogen
Na	sodium
NADP	National Atmospheric Deposition Program
NTU	nephelometric turbidity units
NWQL	National Water Quality Laboratory
OLS	ordinary least squares
¹⁸ O	oxygen-18
Р	phosphorus
QC	quality control
SF ₆	sulfur hexafluoride
SiO ₂	silica
SLAP	Standard Light Antarctic Precipitation
SO_4	sulfate ion
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water

By James L. Robinson

Abstract

Water from wells and springs accounts for more than 90 percent of the public water supply in Calhoun County, Alabama. Springs associated with the Jacksonville Thrust Fault Complex are used for public water supply for the cities of Anniston and Jacksonville. The largest ground-water supply is Coldwater Spring, the primary source of water for Anniston, Alabama. The average discharge of Coldwater Spring is about 32 million gallons per day, and the variability of discharge is about 75 percent.

Water-quality samples were collected from 6 springs and 15 wells in Calhoun County from November 2001 to January 2003. The pH of the ground water typically was greater than 6.0, and specific conductance was less than 300 microsiemens per centimeter. The water chemistry was dominated by calcium, carbonate, and bicarbonate ions. The hydrogen and oxygen isotopic composition of the water samples indicates the occurrence of a low-temperature, water-rock weathering reaction known as silicate hydrolysis. The residence time of the ground water, or ground-water age, was estimated by using analysis of chlorofluorocarbon, sulfur hexafluoride, and regression modeling. Estimated ground-water ages ranged from less than 10 to approximately 40 years, with a median age of about 18 years.

The Spearman rho test was used to identify statistically significant covariance among selected physical properties and constituents in the ground water. The alkalinity, specific conductance, and dissolved solids increased as age increased; these correlations reflect common changes in ground-water quality that occur with increasing residence time and support the accuracy of the age estimates. The concentration of sodium and chloride increased as age increased; the correlation of these constituents is interpreted to indicate natural sources for chloride and sodium. The concentration of silica increased as the concentration of potassium increased; this correlation, in addition to the isotopic data, is evidence that silicate hydrolysis of clay minerals occurred.

The geochemical modeling program NETPATH was used to investigate possible mixing scenarios that could yield the chemical composition of water collected from springs associated with the Jacksonville Thrust Fault Complex. The results of NETPATH modeling suggest that the primary source of water in Coldwater Spring is a deep aquifer, and only small amounts of rainwater from nearby sources are discharged from the spring. Starting with Piedmont Sports Spring and moving southwest along a conceptual ground-water flow path that parallels the Jacksonville Thrust Fault Complex, NETPATH simulated the observed water quality of each spring, in succession, by mixing rainwater and water from the spring just to the northeast of the spring being modeled. The percentage of rainwater and ground water needed to simulate the quality of water flowing from the springs ranged from 1 to 25 percent rainwater and 75 to 99 percent ground water.

Introduction

Calhoun County, Alabama (fig. 1), depends on ground water for more than 90 percent of its public water supply (Mooty and Richardson, 1998). Ground-water withdrawals for public water supply are concentrated in carbonate aquifers and springs associated with the Jacksonville Thrust Fault Complex (fig. 2). The largest of these, Coldwater Spring (site 19, table 1; fig. 2), is the primary source of water for the city of Anniston, Alabama. Coldwater Spring and the drainage that flows from Coldwater Spring are the only known habitat of the pygmy sculpin (*Cottus pygmaeus*; Mettee and others, 1996).

Classical theories of ground-water flow assume uniform distribution and systematic changes in porosity and permeability in an aquifer. Basic information, such as recharge areas and ground-water travel times, can be estimated by using maps of the water surface in the aquifer, values for porosity and permeability, and the mathematical equation for ground-water flow in a uniform porous medium. These assumptions may not be valid for the aquifers in Calhoun County because the distribution of porosity and permeability in carbonate rocks is not uniform at a local scale and can only be treated as uniform at a subregional and larger scale (Robinson and others, 1997, p. 12).

Scott and others (1987) used the assumption of uniform porous media flow and a potentiometric map of the ground-



Figure 1. Locations of major cities, surface-water drainages, and physiographic provinces in Calhoun County, Alabama, and a National Atmospheric Deposition Program station in DeKalb County, Alabama.

water surface to delineate a recharge area for Coldwater Spring. The rate of ground-water recharge within the delineated recharge area, however, was determined to be unable to sustain the discharge from Coldwater Spring. If the estimated recharge rate is accurate, there must be additional sources of water to Coldwater Spring, probably a deep aquifer for which the potentiometric surface was not accurately mapped (Scott and others, 1987). Analyses of the delineated recharge area, estimated recharge, and discharge for other springs associated with the Jacksonville Thrust Fault Complex have not been performed.

Purpose and Scope

The U.S. Geological Survey (USGS) has the principal responsibility within the Federal Government to provide the data needed to achieve the best use and management of the Nation's resources. To accomplish this mission, the Water Resources Discipline of the USGS, in cooperation with local, State, and other Federal agencies, systematically collects and analyzes data to evaluate the quantity, quality, and use of the Nation's water resources and provides results of these investigations to the public. The data and analyses presented herein will help local and State agencies protect and manage the public water supply of Calhoun County, Alabama. The methods used in this study could be applicable to other geologically similar areas within Alabama and adjacent states.

This report describes the results of a study performed by the USGS, in cooperation with the Water Works and Sewer Board of the City of Anniston, Alabama, to determine the age and source of water to springs associated with the Jacksonville Thrust Fault Complex in Calhoun County, Alabama. Groundwater samples were collected from 15 wells and 6 springs during November 2001 through January 2003. The samples were analyzed for physical properties and chemical and isotopic composition. Rainfall samples from the National Atmospheric Deposition Program (NADP) station in DeKalb County, Alabama (fig. 1), were analyzed for isotopic composition. Rainfall data from Jacksonville, Alabama, were correlated to the discharge of Coldwater Spring. Graphical and statistical analyses were used to determine relations between selected physical properties and chemical constituents in the water. The geochemical model NETPATH (Plummer and others, 1994) was used to estimate the mixing and mass-balance reactions of source waters that could result in the observed water quality of springs associated with the Jacksonville Thrust Fault Complex.



Figure 2. Locations of the Jacksonville Thrust Fault Complex and wells and springs sampled in Calhoun County, Alabama.

Table 1. Wells and springs sampled in Calhoun County, Alabama.

[NA, not applicable; USGS, U.S. Geological Survey]

Site number (fig. 2)	Site identification number	Local name	Well depth (feet below land surface)	Sampling date	Geologic unit (table 3)
1	335651085352701	Frank Stewart Spring	NA	11-14-2001 05-21-2002 08-27-2002	Rome Formation
2	335529085353701	USGS well, Calhoun-3	121	12-04-2001	Knox Group
3	335436085385801	Piedmont Sports Spring	NA	11-08-2001	Conasauga Formation
5	335052085452501	Germania Springs	NA	11-15-2001 05-21-2002 08-27-2002	Knox Group
6	334941085414201	James Moore well	96	11-06-2001	Conasauga Formation
7	334928085460801	USGS well, Calhoun-2	196	12-11-2001	Knox Group
8	334643085442101	Whites Gap Church well	78	12-05-2001	Weisner and Wilson Ridge Formations
9	334601085481601	Ervin well	250	12-06-2001	Conasauga Formation
10	334431085492101	McMinn well	230	12-11-2001	Conasauga Formation
11	334218085491701	USGS well, Calhoun-1	122	12-10-2001	Knox Group
12	334036085551001	County landfill well near Anniston	236	12-05-2001	Knox Group
13	333902085430001	Harmony Church well	104	12-06-2001	Rome Formation
14	333916085444701	Camp Lee Spring	NA	11-09-2001 05-22-2002 08-28-2002	Shady Dolomite
15	333918085444301	Camp Lee well	65	11-08-2001	Shady Dolomite
16	333857085495001	Auto Custom Carpets Company well	390	11-07-2001	Shady Dolomite
17	333723085555501	02CGWB05 well (125-135 feet)	135	01-14-2003	Rome Formation
17	333723085555501	02CGWB05 well (380-390 feet)	390	01-14-2003	Rome Formation
18	333714085555901	02CGWB06 well (180-190 feet)	190	01-14-2003	Conasauga Formation
18	333714085555901	02CGWB06 well (408-418 feet)	418	01-14-2003	Rome Formation
18	333714085555901	02CGWB06 well (600-610 feet)	610	01-14-2003	Shady Dolomite
19	2403500	Coldwater Spring	NA	12-07-2001 05-20-2002 08-26-2002	Rome Formation and(or) Shady Dolomite
20	333613085500601	Collateral Spring	NA	12-03-2001 05-22-2002 01-21-2003	Shady Dolomite
21	333537085553501	Gold Bond well	350	11-07-2001	Shady Dolomite

Previous Investigations

The geology of Calhoun County is described in McCalley (1897), Adams and others (1926), Butts (1926), Warman and others (1960), Warman and Causey (1962a), Cloud (1966), Denson and Waage (1966), Drahovzal and others (1974), Drahovzal and Thomas (1976), Kidd and Neathery (1976), Bearce (1978), Mack (1980), Thomas and Neathery (1980, 1982), and Osborne and Szabo (1984). Osborne and others (1989) prepared geologic maps of Alabama from which the geologic map for this study (fig. 3) was derived.

Reports describing the ground-water resources of the study area date back to Smith (1907) and Johnston (1933). Warman and Causey (1961) described the relation of springs to thrust faults in Calhoun County, Alabama. An interim report on the geology and ground-water resources of Calhoun County was prepared by Warman and others (1960) and was the basis for a comprehensive report by Warman and Causey (1962b). Studies of the geohydrology and susceptibility of ground water to surface contamination in the Calhoun County area were conducted by Scott and others (1987) and Planert and Pritchett (1989). Moser and DeJarnette (1992) summarized ground-



Figure 3. Generalized geologic map of Calhoun County, Alabama (modified from Moser and DeJarnette, 1992).

water availability in Calhoun County. Robinson and others (1997) included the study area in a report describing groundwater resources of the Coosa River basin. Kidd (2001) characterized the hydrogeology of the Coldwater Spring recharge area in Calhoun County.

The U.S. Army Corps of Engineers (USACE) funded extensive research of the hydrogeology of the Anniston Army Depot, just west of Anniston and north of the Jacksonville Thrust Fault Complex. Thompson and others (1999) described the results of geophysical surveys. The results of dye-tracer tests and a hydrogeologic characterization of the Jacksonville Thrust Fault Complex are described in reports produced by the Science Applications International Corporation (1998, 1999, 2003).

Recent reports documenting the use of isotopic data, age dating, and geochemical modeling to identify sources of ground water and assess aquifer vulnerability include Katz and others (1997), Lambert and others (2000), Nelms and others (2001), Phelps (2001), Kay and others (2002), and Robinson (2002, 2003). The results of analyses of ground-water samples collected from wells and springs for this study are published in Pearman and others (2003), Psinakis and others (2004), and herein.

Acknowledgments

The USGS gratefully acknowledges the cooperation and assistance provided by the many private citizens of Alabama who allowed access to their property for data collection, the USACE for allowing access to reports on the geology of the Anniston Army Depot, and to the Water Works and Sewer Board of the City of Anniston, Alabama, for supplying discharge data for Coldwater Spring.

Description of the Study Area

Calhoun County, in northeastern Alabama (fig. 1), encompasses about 611 square miles (mi²) in the Valley and Ridge and Piedmont physiographic provinces (fig. 1; Fenneman, 1938). The area is dominated by northeast-trending ridges and mountains separated by flat to gently rolling valleys. Maximum relief is about 1,500 feet (ft). The major surfacewater systems are the Coosa River and its tributaries Cane, Choccolocco, Tallasseehatchee, and Ohatchee Creeks (fig. 1).

Climate and Rainfall

Calhoun County has a moist, temperate climate. The average annual temperature recorded at the Anniston Federal Aviation Administration (FAA) weather station for the period of record, 1948 to 2003, was about 62 degrees Fahrenheit (°F) (Southeast Regional Climate Center, 2003; table 2). Temperature extremes recorded at the Anniston FAA weather station were -5 °F on October 1, 1949, and 106 °F on August 21, 1983. Annual rainfall at Anniston and Jacksonville, Alabama, averaged about 52 inches for the period of record. Rainfall is seasonally distributed. The greatest rainfall amounts usually occur during the months of December through April (4–6 inches per month [in/mo]), and the least rainfall amounts usually occur during the months of May through November (3–5 in/mo).

Hydrogeology

Calhoun County, Alabama, is underlain by carbonate and clastic rocks that are complexly folded and faulted; some are slightly metamorphosed (fig. 3). A complete description of the

geology of Calhoun County is beyond the scope of this report, however, detailed descriptions are presented in Adams and others (1926), Johnston (1933), Warman and Causey (1962b), Osborne and Szabo (1984), and Moser and DeJarnette (1992).

Johnston (1933) divided the rocks of Calhoun County into six groups based on their ground-water characteristics. Moser and DeJarnette (1992) identified nine significant aquifers (table 3). Much of Calhoun County is underlain by carbonate rocks (limestone and dolomite), which form important aquifers, and silicate rocks (quartzose, sandstone, shale, and siltstone), which typically yield less water to wells.

Carbonate rocks, such as those in Calhoun County, are soluble by acidic water. Rain typically is slightly acidic and can become even more acidic from decaying vegetation and microbial activity when it infiltrates the soil zone. The warm, humid climate of Calhoun County (table 2) is conducive to the dissolution of carbonate rocks. Ground water is the solvent of the rock and also supports the growth of vegetation and microbes that acidify shallow ground water (Ritter, 1979). As acidic water infiltrates the subsurface along natural openings, such as faults, fractures, and bedding planes, the openings become enlarged by dissolution of the rock. This process

Table 2. Selected climatic data for Calhoun County, Alabama (Southeast Regional Climate Center, 2003).

[NW, northwest; FAA, Federal Aviation Administration; °F, degrees Fahrenheit; M, missing data; Winter, December–February; Spring, March–May; Summer, June–August; Fall, September–November; shading indicates when ground-water samples were collected]

	Mean monthly precipitation at Jacksonville	Mean monthly precipitation at Anniston FAA	Total monthly and annual precipitation at Anniston FAA Airport, Alabama, (inches)					Mean monthly temperature at Anniston FAA	
	1958–2000 (inches)	Airport, Alabama, 1948–2003 (inches)	1999	2000	2001	2002	2003	1948–2003 (° F)	
January	5.05	5.05	М	5.76	4.14	6.04	2.67	43.4	
February	4.98	4.96	М	2.57	2.98	2.21	5.74	47.0	
March	5.64	5.96	5.57	4.13	9.23	3.58	3.78	53.8	
April	4.47	4.85	1.97	5.80	5.21	3.13	4.69	62.1	
May	4.12	4.02	3.11	4.13	4.92	2.40	11.53	69.9	
June	4.09	4.23	7.87	3.01	6.39	2.32	9.32	76.7	
July	4.58	4.54	4.05	3.64	4.29	2.74	8.22	79.9	
August	3.50	3.57	1.65	1.94	3.26	2.30	2.47	79.2	
September	4.20	3.74	1.16	1.43	4.30	7.55	1.74	73.4	
October	3.50	2.72	2.30	1.78	2.37	4.76		62.6	
November	3.77	3.97	1.84	7.21	2.60	5.03		52.4	
December	4.50	4.55	2.31	1.29	3.56	7.63		45.4	
Annual	52.41	52.16	М	42.69	53.25	49.69		62.1	
		Seaso	onal total	s and ave	rages				
Winter	14.53	14.56	М	9.62	10.68	15.88		45.3	
Spring	14.23	14.83	10.65	14.06	19.36	9.11		61.9	
Summer	12.17	12.34	13.57	8.59	13.94	7.36		78.6	
Fall	11.47	10.43	5.30	10.42	9.27	17.34		62.8	

Geologic unit	Map symbol (fig. 3)	Lithology	Thickness (feet)	Water-bearing properties
Regolith	None	Sand, clay, silt, and weath- ered rock	30-50	Suitable for small-scale domestic uses; supply susceptible to drought; quality good but susceptible to contamina- tion.
Floyd Shale	М	Shale, thin beds of sand- stone, limestone, and chert	1,200-2,000	Suitable for small-scale domestic uses; the water may have large concentra- tions of dissolved solids, especially iron.
Tuscumbia Lime- stone and Fort Payne Chert	М	Fossiliferous, oolitic, partly argillaceous, and cherty limestone	15-175	Although used in other Alabama counties, not a major aquifer in Calhoun County.
Newala Limestone	D Cu	Thick-bedded limestone with minor amounts of dolomite	up to 500	Suitable for domestic and sometimes municipal use; the water may have large concentrations of dissolved solids.
Knox Group	D Cu	Sandy dolomite, dolomitic limestone, and limestone with chert	about 2,000	Suitable for small-scale domestic and stock needs; however, large quanti- ties are available if a productive water-filled solution feature is drilled. The water may have large concentrations of iron.
Conasauga Formation	D Cu	Medium to thin bedded dolomite with minor amounts of shale and chert	2,500	Large quantities of good-quality water, suitable for all uses, are available from this unit.
Rome Formation	D Cu	Shale, siltstone, and sand- stone with minor amounts of limestone and dolomite	1,000	Suitable for domestic and sometimes municipal use; the water may have large concentrations of dissolved solids.
Shady Dolomite	D C u	Siliceous dolomite and chert	500	Large quantities of good-quality water, suitable for all uses, are available from this unit. The water may have large concentrations of dissolved solids.
Weisner and Wilson Ridge Formations	Pzp C	Interbedded quartzose and feldspathic sandstone with silty mudstone	1,100	Suitable for small-scale domestic and stock needs; however, large quanti- ties may be available if a productive water-filled fracture is drilled. The water may have large concentrations of iron.

Table 3. Significant aquifers in Calhoun County, Alabama (modified from Moser and DeJarnette, 1992).

eventually develops a solution-conduit aquifer oriented along the joints, fractures, and bedding planes. The solution-conduit aquifers in Calhoun County can supply large volumes of water to wells and springs (table 3).

The presence of numerous sinkholes in Calhoun County (U.S. Geological Survey, 1977) indicates a well-established system of ground-water drainage (Ritter, 1979). Ground water flows through solution conduits in the carbonate rocks of Calhoun County (Warman and Causey, 1962b; Scott and others, 1987). The occurrence of sinkholes in Oxford, Alabama (fig. 1), as recently as 2001 and 2003 (Tubbs, 2003) indicates

that dissolution of carbonate rocks in Calhoun County is an ongoing process.

Ground water also is present in the silicate rocks of Calhoun County. Compared to carbonate rocks, silica-based rocks are relatively insoluble. Although ground water moves through faults and fractures in the clastic rocks (Johnston, 1933), little enlargement of the original openings occur. Fracture-conduit aquifers may or may not supply large volumes of water to wells. The shale, sandstone, and siltstone aquifers of Calhoun County generally supply adequate amounts of water for domestic, stock, and farm use only (table 3).

Study Design and Methods

The relation of large springs to thrust faults in Calhoun County has long been recognized (Johnston, 1933; Warman and Causey, 1961). Thrust faults "form reservoirs and conduits through which ground water from deep and distant sources reaches the surface" (Warman and Causey, 1961). This study was designed based on the assumption that water from "deep and distant sources" has a different hydrologic and geologic history than ground water from a local source and a chemical composition different from that of local ground water that is not associated with faulting.

The physical properties and chemical composition of ground water and rainwater were used to characterize the sources of water to springs associated with the Jackonville Thrust Fault Complex. Methods using chemical and isotopic tracers (Katz and others, 1997; Robinson, 2002, 2003) and geochemical modeling (Plummer and others, 1994) were employed to make inferences about the source, flow path, and age of ground water. Standard data-collection procedures of the USGS were used to collect the samples (Koterba and others, 1995; Lapham and others, 1995; Koterba, 1998).

Water-Quality Samples

Water samples were collected from 6 springs and 15 wells (fig. 2) from November 2001 through January 2003. Selected springs were sampled three times to determine variability in water quality; wells were sampled once. Site identification, well depth, sample dates, and the geologic units for wells and springs that were sampled are given in table 1. Monthly composite samples of rain, collected at the NADP station in DeKalb County, Alabama, were analyzed for stable isotopes of oxygen (oxygen-18, ¹⁸O) and hydrogen (deuterium, D).

Ground-water samples were analyzed for physical properties, major ions, nutrients, stable isotopes, chlorofluorocarbons (CFCs), sulfur hexafluoride (SF₆), and dissolved gases. The laboratory analytical methods used are listed in table 4. Sampling procedures and field methods were consistent with USGS ground-water sampling protocols (Koterba and others, 1995). Samples were analyzed for CFCs, SF₆, and dissolved gases at the USGS CFC Laboratory in Reston, Virginia, and for stable isotopes of hydrogen and oxygen at the USGS Isotope Fractionation Laboratory in Reston, Virginia. All other ground-water samples were chilled and shipped overnight to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

The NWQL reports analyte concentrations as measured, estimated, or less than a reporting value. These terms indicate the confidence the laboratory places in the accuracy of the measurement and are based on the long-term accuracy of the methods used (Childress and others, 1999). The method detection level (MDL) is the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero. The long-term method detection level (LT-MDL) is derived by determining the MDL for a minimum of 24 MDL spike-sample measurements over an extended period of time. The laboratory reporting level (LRL) generally is equal to twice the yearly LT-MDL.

Measured values are reported for concentrations above the LRL and within the calibration range of the apparatus. Estimated values are reported for concentrations less than the LRL but above the LT-MDL (Childress and others, 1999) or for concentrations greater than the calibrated range of the apparatus. The value of the LRL is reported with a "less than" remark code for samples in which the analyte was not detected.

Table 4.Constituents analyzed and analytical methods used for ground-water quality samples collected from wells and springsin Calhoun County, Alabama.

Constituent	Number of samples	Analytical method	Reference
Major ions	35	Atomic absorption spectrometry	Fishman (1993)
Nutrients	30 ^a	Various methods	Fishman (1993)
CFC	20 ^b	Gas chromatography with ECD	Busenberg and Plummer (1992)
SF ₆	25 ^c	Gas chromatography with ECD	Busenberg and Plummer (2000)
Isotopes	35	Hydrogen equilibration technique	Coplen and others (1991)

[CFC, chlorofluorocarbon; ECD, electron capture detector; SF₆, sulfur hexafluoride]

^a Five samples were not analyzed for nutrients.

^b Fifteen samples were not analyzed for chlorofluorocarbons.

^c Ten samples were not analyzed for sulfur hexafluoride.

Quality-Assurance and Quality-Control Procedures

Two types of quality-control (QC) samples were collected during the study—blanks and replicates. A blank sample is a water sample that contains no analytes of interest. A blank sample is analyzed to determine if contamination has occurred during (1) sample collection and processing, (2) sample handling and transportation, and(or) (3) sample analysis (Mueller and others, 1997). Replicate samples are two or more samples that are split, collected in sequence, or collected concurrently; replicate samples are considered to have identical compositions. Replicates provide a measure of the variability resulting from sample collection, processing, and analysis (Mueller and others, 1997). Analyses of blank and replicate samples are evaluated to detect systematic bias in the results of sample analyses.

Four blank and four replicate samples were collected and analyzed. No analytes of interest were detected in the blank QC samples. The range in difference in concentration between environmental and replicate samples was less than 1 percent to less than 10 percent, and the mean difference in concentration was 1.5 percent. Interpretation of the data provided by the blank and replicate samples collected during the study indicated no systematic bias or source of contamination attributable to the sampling equipment or procedures used to collect the groundwater samples.

The accuracy of the water analyses was screened by checking for sample stability, transcription errors, and cationanion balance. The stability of the water samples during transport and storage was checked by comparing the values of pH, specific conductance, alkalinity, and dissolved-oxygen concentration measured at the time of sampling to these same measurements made again at the NWQL. The difference between the two measurements for each property ranged from less than 1 percent to 10 percent and was typically less than 5 percent. Transcription errors were checked by requesting the laboratory to verify all anomalously high or low values. The cation-anion balance for each sample analysis was determined to ensure that the ionic charge-balance error did not exceed accepted guidelines (Hem, 1985; Katz and Collins, 1998).

Graphical and Statistical Methods

Two common graphical techniques were used to present and analyze the results of the water-quality sampling—the Piper (1944) trilinear diagram and the Stiff (1951) diagram. In a Piper diagram, the ionic contents of many samples are plotted on a single graph. The dominant ion type in each sample is easily determined by where the sample plots on the diagram. However, because ion concentrations are converted to total composition percentages before plotting, water samples with very different total concentrations may plot closely together. A Stiff diagram is a polygon created by plotting cation and anion milliequivalents along a horizontal axis divided by a vertical center line. Cations are plotted on one side of the center line; anions are plotted on the opposite side. Stiff diagrams are useful for rapid visual comparisons of water-quality analyses from different sources because the Stiff diagram for each source will be a distinctive graphical shape. These diagrams are not useful for large numbers of analyses.

Descriptive statistics, such as the range, maximum, minimum, and median, were used to summarize the distribution of chemical data for the ground-water sample sets. Correlation analysis was used to examine the relations between selected physical properties, chemical composition, and ground-water age. Correlation analysis is a means of assessing not only the relation between two variables but also the strength of the relation (Ott, 1988, p. 319). The probability statistic relates to the confidence level. A confidence level of 95 percent, as used in this report, means that there is a 95-percent probability the correlation is statistically significant. The correlation coefficient describes the strength of the correlation and how the correlated parameters (physical properties and chemical constituents) vary. For this report, parameters with a correlation coefficient of 0.6 or greater were considered strongly correlated. The Spearman rho rank correlation test was used to evaluate the correlation among ground-water age, water-quality properties, and constituents because the number of samples was greater than 20 (Helsel and Hirsch, 1992, p. 217-218). Scatterplots of all correlated variables were made to ensure that the variables possessed a monotonic correlation (Helsel and Hirsch, 1992, p. 209-211).

Ordinary least squares (OLS) or simple linear regression is a method that describes the covariation between a variable of interest and one or more other variable (Helsel and Hirsch, 1992). In this study, the objective of using OLS was to provide an estimate or predictive value of one variable (the response variable) based on the value of another variable (the explanatory variable). Five assumptions are associated with the use of OLS as a predictive tool (Helsel and Hirsch, 1992), and care was taken to ensure that these assumptions were satisfied.

Geochemical Modeling

The computer program NETPATH (Plummer and others, 1994) was used to investigate the possible sources of water in springs associated with the Jacksonville Thrust Fault Complex. The NETPATH program can calculate the mixing proportions of two or more initial waters and the net geochemical mass-balance reactions (including mineral dissolution and precipitation, ion exchange, and gas exchange) which could account for the composition of a final water. Simulations are constrained by using elements and mineral phases that could reasonably be expected to occur in the system modeled and by using isotopic data and electron balance. Combinations of initial waters and geochemical reactions that could result is the final water chemistry are termed "models" in this report.

Physical Properties, and Chemical and Isotopic Composition of Water Samples

Ground-water quality in the vicinity of the Jacksonville Thrust Fault Complex was determined by using samples collected from 6 springs and 15 wells. Ground-water samples, collected from November 2001 through January 2003, were analyzed for physical properties, major ions, nutrients, CFCs, SF_6 , dissolved gases, and isotopic composition (table 4). Selected springs were sampled three times to determine variability in water quality.

Physical Properties

Water collected from the wells and springs typically had slightly acidic to basic pH values (6.5–8.0), moderate specific conductance values (100–650 microsiemens per centimeter at 25 degrees Celsius [μ S/cm]), and moderate to high alkalinity values (100–300 milligrams per liter (mg/L) as calcium carbonate [CaCO₃]). Most of the water samples contained low to moderate concentrations (5–300 mg/L) of dissolved solids. Two wells and one spring had acidic pH values (5.0–6.0), low specific conductance (less than 100 μ S/cm), and low alkalinity values (less than 100 mg/L as CaCO₃). Selected physical properties of ground-water samples collected from wells and springs are summarized in table 5.

Table 5. Minimum, median, and maximum values of selected physical properties and chemical constituents in water collected from wells and springs in Calhoun County, Alabama.

 $[\mu$ S/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; none, no drinking water standard; mg/L, milligrams per liter; CaCO₃, calcium carbonate; <, less than; —, too few detections to estimate statistics; N, nitrogen; P, phosphorus]

Property or constituent	Drinking-water guideline	Minimum	Median	Maximum	Number of samples with measured or estimated concentrations				
Physical properties									
pH (standard units)	6.5-8.5 ^a	5.1	7.5	9.4	35				
Specific conductance (µS/cm at 25 °C)	none	12	210	650	35				
Alkalinity (mg/L as CaCO ₃)	none	4	100	300	35				
Dissolved solids residue at 180 ° C (mg/L)	500 ^a	5	100	300	35				
Dissolved oxygen (mg/L)	none	.1	6	8	35				
Temperature (^o C)	none	15	17	19	35				
	Maj	or ions							
Calcium (mg/L)	none	0.14	25	57	35				
Magnesium (mg/L)	none	.16	13	40	35				
Potassium (mg/L)	none	.12	1.3	2.5	35				
Sodium (mg/L)	none	.73	1.5	13	35				
Chloride (mg/L)	250 ^a	.73	2.1	12	35				
Fluoride (mg/L)	2 ^a , 4 ^b	<.1	_	.12	12				
Silica (mg/L)	none	4	10	15	35				
Sulfate (mg/L)	250 ^a	<.1	2	10	35				
Nutrients									
Nitrite (mg/L) as N	1 ^b	< 0.002	_	0.01	7				
Ammonia (mg/L) as N	none	<.01	_	.2	6				
Nitrite plus nitrate (mg/L) as N	10 ^b	< .01	0.3	2.0	25				
Phosphorus, ortho (mg/L) as P	none	<.007	_	.03	19				

^a Secondary drinking-water standard, established by the U.S. Environmental Protection Agency (2002).

^b Maximum contaminant level for drinking water, established by the U.S. Environmental Protection Agency (2002).

Major Ions

The major ion composition of water collected from the wells and springs, as illustrated by the Piper diagram in figure 4, is dominated by calcium, bicarbonate, carbonate, and magnesium ions, as would be expected for water from a carbonate aquifer. Samples from one well and one spring (sites 14 and 15, fig. 4) plot within an area of the Piper diagram indicating water dominated by sodium and potassium ions; the source of water for these samples is the Weisner Formation and the Shady Dolomite. One well (site 13, fig. 4) plots within an area of the Piper diagram indicating water quality dominated by calcium, bicarbonate, carbonate, and magnesium ions, but having a substantial sodium and potassium ion component; this may represent a blended water quality, with the possible sources of water to this well including both the carbonate aquifers and the Weisner Formation.

a water quality with no dominate ions; the sodium, carbonate, and bicarbonate ions have roughly equal importance to the shape of the plot. Unlike the other springs, the magnesium cation is not a factor in shaping the plot. The Stiff diagram of Camp Lee Spring indicates the water originates from a different type of aquifer than the water discharged from the other springs.

Silica (SiO₂) is one of the least soluble of the common minerals, and most of the dissolved silica present in natural waters probably results from the chemical breakdown of silicate minerals (Hem, 1985). The silica content of the water sampled from the wells and springs ranged from 4 to 15 mg/L (table 5). Sources of silica in the ground water include quartz-bearing rocks of the Weisner Formation, and shale and siltstone layers and lenses in the carbonate rocks (table 3). For comparison, silica concentrations in ground water from Cretaceous sand and gravel aquifers in central Alabama range from 8.3 to 54.9 mg/L (Robinson, 2002, 2003).



Figure 4. Piper trilinear diagram showing major ion composition of water collected from wells and springs in Calhoun County, Alabama, November 2001 to January 2003.

Stiff diagrams were constructed for the six springs sampled (fig. 5). The Stiff diagrams for Coldwater Spring, Germania Springs, Piedmont Sports Spring, Collateral Spring, and Frank Stewart Spring are very similar, suggesting a similar source of water. The Stiff diagram for Camp Lee Spring shows The oxygen and hydrogen that constitute water molecules contain a mixture of isotopes of both elements, including the stable isotopes deuterium and oxygen-18. Deuterium (D) and oxygen-18 (¹⁸O) are reported in delta (δ) units of parts per thousand (per mil) relative to an arbitrary standard, Vienna

Nutrients

Water samples collected from wells and springs for this study generally contained nitrate, nitrite, and ammonia (table 5) at concentrations similar to those typically found in ground water (Mueller and Helsel, 1996). The median and maximum concentrations of nitrite-plus-nitrate were 0.3 and 2.0 mg/L, respectively (table 5). Twenty-five samples contained measurable concentrations of nitrate, seven contained nitrite, and six contained ammonia. Nineteen ground-water samples contained orthophosphate, but at concentrations less than 0.03 mg/L (table 5). The presence of large concentrations of phosphate may indicate an anthropogenic source (agricultural fertilizer use or water seepage from a septic system); however, small concentrations of phosphate in ground water also may originate from marine limestone and from the shells of marine fossils (Friedman and Sanders, 1978).

Isotopic Composition



Figure 5. Stiff diagrams for selected springs sampled in Calhoun County, Alabama.

Standard Mean Ocean Water (VSMOW) and normalized (Gonfiantini, 1984; Coplen, 1988, 1994) on scales such that the hydrogen and oxygen isotopic values of Standard Light Antarctic Precipitation (SLAP) are -428 per mil and -55.5 per mil, respectively. The Global Meteoric Line (GML; Craig, 1961) is an average of δ D and δ^{18} O values for precipitation and freshwater worldwide.

The stable isotopic composition of rainfall varies over time because of several factors that include but are not limited to the storm track, rainfall amount and intensity, and atmospheric temperature (Katz and others, 1997). A local meteoric line for northeastern Alabama was constructed using analyses of the isotopic composition of rainfall samples collected at the NADP station at Sand Mountain, DeKalb County, Alabama, from October 2001 through September 2002. Once rain enters the surface-water system, the original composition of isotopic hydrogen and oxygen can be fractionated by evaporation, because D and ¹⁸O do not evaporate as readily as the lighter isotopes. Waters subject to evaporation, such as seawater, lakes, and reservoirs, have greater concentrations of D and ¹⁸O relative to atmospheric water vapor. The plots of waters with greater concentrations of D and ¹⁸O than the local meteoric line are low and to the right of the local meteoric line. The plots of waters containing lesser concentrations of D and ¹⁸O are high and to the left of the local meteoric line.

The ground-water samples collected from Calhoun County plot high and to the left of the local meteoric line, indicating lesser concentrations of D and ¹⁸O (fig. 6). A common diagenetic reaction, hydrolysis of aluminum silicates, decreases the ¹⁸O content of water and may also increase the D content of water (Coplen, 1993). Waters that have been part of a silicate hydrolysis reaction may plot to the left of the local meteoric line (Coplen, 1993).

Saturation State with Respect to Minerals

The saturation state of water is an important concept because it can be used to better understand the chemical history of the water. In a ground-water system, the saturation state of the water with respect to a mineral may indicate the type of lithology in which the water has been in contact and how the water interacted with the rocks. The saturation index, with respect to a mineral, indicates whether the water is oversaturated (positive saturation index), undersaturated (negative saturation index), or in equilibrium (near zero saturation index). Oversaturated conditions may result in precipitation of the mineral, and undersaturated conditions may result in dissolution or alteration of the mineral phase.

The saturation indices of the ground water sampled, with respect to selected minerals (table 6), were calculated by using the computer program NETPATH (Plummer and others, 1994). Mineral phase selection was based on the reported lithology of the geologic formations in Calhoun County (Osborne and others, 1984; Moser and DeJarnette, 1992). The values for chemical constituents determined by analysis of water samples served as input to NETPATH. For springs sampled multiple times, the median chemical composition was used as input to



Figure 6. Stable isotope chemistry of water collected from springs and wells in Calhoun County, Alabama, November 2001 to January 2003.

Table 6. Saturation indices of water collected from wells and springs in Calhoun County,Alabama, with respect to selected minerals.

[For calcite, equilibrium is assumed if the saturation index is between -0.15 and 0.15; for dolomite, equilibrium is assumed if the saturation index is between -0.30 and 0.30 (Phelps, 2001); values in bold are undersaturated; median values were used for springs sampled multiple times; USGS, U.S. Geological Survey]

Site number	Local nome	Saturation index			
(fig. 2)		Calcite	Dolomite	Silica	
1	Frank Stewart Spring	0.2	0.2	-0.9	
2	USGS well, Calhoun-3	-1	-3	-1	
3	Piedmont Sports Spring	1	3	-1	
5	Germania Springs	05	1	9	
6	James Moore well	.0	5	-1	
7	USGS well, Calhoun-2	3	6	-1	
8	Whites Gap Church well	-2	-3	-1	
9	Ervin well	-1	-2	9	
10	McMinn well	.2	3	-1	
11	USGS well, Calhoun-1	1	3	-1	
12	County landfill well near Anniston	2	3	-1	
13	Harmony Church well	-3	-7	-1	
14	Camp Lee Spring	-6	-10	-1	
15	Camp Lee well	-5	-10	8	
16	Auto Custom Carpets Company well	1	2	-1	
17	02CGWB05 well (125-135 feet)	.04	.0	9	
17	02CGWB05 well (380-390 feet)	.9	2	-1	
18	02CGWB06 well (180-190 feet)	4	8	-1	
18	02CGWB06 well (408-418 feet)	.07	.1	-1	
18	02CGWB06 well (600-610 feet)	4	9	-1	
19	Coldwater Spring	2	.5	9	
20	Collateral Spring	4	7	-1	
21	Gold Bond well	1	2	9	

the model. The mass of the water was assumed to be 1.0 kilogram per liter, and the activity of the water was estimated to be 1.0 (default values). About half of the ground waters sampled were undersaturated with respect to the minerals calcite and dolomite. All of the ground waters sampled were undersaturated with respect to silica (noncrystalline SiO₂).

Age of Water Associated with the Jacksonville Thrust Fault Complex

The age of ground water provides insight about the source of the water. Ground-water age typically increases with depth below land surface and with aquifer size. The age of water collected from wells and springs in Calhoun County was estimated using analyses of environmental tracer concentration and with a regression model.

Estimates of Ground-Water Age

Ground water collected from wells and springs was analyzed for the environmental tracers CFC and SF₆. The recharge date of the water is estimated by relating the measured concentration of the environmental tracer in the ground water to the reconstructed historical atmospheric concentration and(or) calculated concentrations expected in water in equilibrium with air (Busenberg and Plummer, 1992, 2000). The estimated age of the water refers to the date chemicals entered the water, which is assumed to be from the atmosphere before the water entered the aquifer. Estimates of ground-water age also were made using a least-squares regression model. The model was developed to provide age estimates for samples without CFC and SF₆ age estimates.

Chlorofluorocarbons and Sulfur Hexafluoride

Chlorofluorocarbons are synthetic compounds first produced in the early 1930's (Cook and Herczeg, 2000). The presence of measurable concentrations of CFC in a water sample indicates that the sample contains some post-1940 water. Ground water collected from 13 wells and 4 springs was analyzed for CFC-11 (trichlorofluoromethane, or CFCl₃), CFC-12 (dichlorodifluoromethane, or CF₂Cl₂), and CFC-113 (trichlorotrifluoroethane or $C_2F_3Cl_3$). The results of analysis for CFC concentrations in ground-water samples were published in Psinakis and others (2004). Concentrations of CFC in the atmosphere, depending on the specific compound, peaked or stabilized between 1994 and 2001 (U.S. Geological Survey, CFC Laboratory, written commun., 2004). Concentrations of CFC in the atmosphere are declining, making multiple age dates possible. Because of this, ratios of the three CFC's also are used to estimate recharge dates.

Sulfur hexafluoride (SF₆) is a trace atmospheric gas that occurs naturally in some minerals, igneous rocks, and in volcanic and igneous fluids; however, SF₆ is primarily of anthropogenic origin. Large-scale production of SF₆ began in the 1960's, and dating is possible from about 1970 (Busenberg and Plummer, 1997). SF₆ is stable in reducing ground-water environments, and the concentration of SF₆ in the atmosphere is increasing (U.S. Geological Survey, CFC Laboratory, written commun., 2004). Water samples collected from 15 wells and 4 springs were analyzed for SF₆ (table 7).

Factors that can affect the accuracy of the CFC and SF_6 method include excess dissolved gases and local sources of CFC or SF_6 (contamination), and chemical and microbial degradation and sorption (tracer degradation). CFC and SF_6

Table 7. Results of analysis of water samples for sulfur hexafluoride concentration.

Site number (fig. 2)	Local name	Well depth (feet below land surface)	Sampling date	Concentration in water, (fMol/L) (no excess air)	Model SF ₆ age date
1	Frank Stewart Spring	NA	11-14-2001	2.4	Contaminated
2	USGS well, Calhoun-3	121	12-04-2001	1.9	Contaminated
3	Piedmont Sports Spring	NA	NS	NS	NS
5	Germania Springs	NA	11-15-2001 08-27-2002	.76 .53	1987.5 1980.5
6	James Moore well	96	11-06-2001	5.2	Contaminated
7	USGS well, Calhoun-2	196	12-11-2001	1.1	1992
8	Whites Gap Church well	78	12-05-2001	1.2	1992
9	Ervin Well	250	12-06-2001	3.6	Contaminated
10	McMinn well	230	12-11-2001	1.1	1992.5
11	USGS well, Calhoun-1	122	12-10-2001	1.9	2000
12	County landfill well near Anniston	236	12-05-2001	.2	1976.5
13	Harmony Church well	104	12-06-2001	.72	1987.5
14	Camp Lee Spring	NA	NS	NS	NS
15	Camp Lee well	65	11-08-2001	1.0	1991
16	Auto Custom Carpets Company well	390	11-07-2001	1.3	1994.5
17	02CGWB05 well (125-135 feet)	135	01-14-2003	11	Contaminated
17	02CGWB05 well (380-390 feet)	390	NS	NS	NS
18	02CGWB06 well (180-190 feet)	190	01-14-2003	2.0	1995.5
18	02CGWB06 well (408-418 feet)	418	01-14-2003	3.2	Contaminated
18	02CGWB06 well (600-610 feet)	610	01-14-2003	8.1	Contaminated
19	Coldwater Spring	NA	12-07-2001 08-26-2002	1.1 .67	1991.5 1983.5
20	Collateral Spring	NA	12-03-2001 01-21-2003	2.4 9.9	Contaminated Contaminated
21	Gold Bond well	350	11-07-2001	4.6	Contaminated

[fMol/L, femtomol per liter; SF₆, sulfur hexafluoride; NA, not applicable; USGS, U.S. Geological Survey; NS, not sampled]

samples are considered "contaminated" if the concentration is greater than the regional atmospheric concentration during the year the sample was collected or if the concentration is greater than the air-water equilibrium. Excess dissolved gases and local sources can cause the concentration of the tracer in the water to be greater than the historical atmospheric concentration. Contamination typically is associated with urban sources. CFC ages are considered reliable when all three (CFC-11, -12, and -113) result in similar model ages. If the age estimates do not agree, CFC-12 is considered the most reliable, followed by CFC-113, then CFC-11 (U.S. Geological Survey, CFC Laboratory, written commun., 2003). Chemical and microbial degradation and sorption may cause the concentrations of CFCs and SF₆ in the water to be less than the historical atmospheric

concentration. CFC may degrade in water with low concentrations of dissolved oxygen, but SF_6 is stable in low dissolved-oxygen conditions.

About half of the ground-water samples submitted for analysis for CFC and SF_6 were contaminated or degraded. For this report, an age-date estimate was considered reliable when more than one CFC yielded a similar age, or when the CFC and SF_6 age estimates were similar. Reliable CFC and(or) SF_6 age dates were obtained for water from 5 of 15 wells sampled. Estimated ages ranged from less than 10 to more than 30 years (table 8). Reliable CFC and(or) SF_6 age dates were obtained for ground water from two of the six springs sampled. Estimated ages of the spring waters ranged from about 15 to greater than 20 years (table 8).

Table 8. Estimated ages of water collected from wells and springs in Calhoun County, Alabama.

[CFC, chlorofluorocarbon; SF₆, sulfur hexafluoride; OLS, ordinary least squares; CD, sample contaminated or degraded (see text for explanation); USGS, U.S. Geological Survey; NS, not sampled for CFC or SF₆; <, less than; NA, method not applicable to aquifer sampled]

		Metho			
Site number (fig. 2)	Local name	CFC (years)	SF ₆ (years)	OLS regression model based on calcium content (years)	- Model age used in this report (years)
1	Frank Stewart Spring	9-14	CD	21-22	22
2	USGS well, Calhoun-3	13-15	CD	14	14
3	Piedmont Sports Spring	NS	NS	18	18
5	Germania Springs	20-28	13-22	13-15	15
6	James Moore well	22-30	CD	24	24
7	USGS well, Calhoun-2	CD	9	25	25
8	Whites Gap Church well	16-19	8	12	12
9	Ervin well	17	CD	18	18
10	McMinn well	36	9	27	27
11	USGS well, Calhoun-1	12-17	1	33	33
12	County landfill well near Anniston	10	24	16	16
13	Harmony Church well	13-24	14	NA	14
14	Camp Lee Spring	NS	NS	NA	none
15	Camp Lee well	12-23	10	NA	10
16	Auto Custom Carpets Company well	< 25	7	21	21
17	02CGWB05 well (125-135 feet)	NS	CD	21	21
17	02CGWB05 well (380-390 feet)	NS	CD	9	9
18	02CGWB06 well (180-190 feet)	NS	9	16	16
18	02CGWB06 well (408-418 feet)	NS	CD	18	18
18	02CGWB06 well (600-610 feet)	NS	CD	19	19
19	Coldwater Spring	12-16	10-19	14-15	15
20	Collateral Spring	NA	13	22	22
21	Gold Bond well	CD	CD	19	19

Regression Modeling

Reliable age dates for many of the waters sampled could not be estimated using CFC and SF₆ concentrations because of contamination or degradation. Another estimate of groundwater age was developed based on the five most reliable CFC and SF₆ age estimates. An ordinary least-squares regression model (fig. 7) was developed to determine the relative age of a ground water based on the dissolved calcium content of the water. The OLS regression model was tested for homoscedasticity, independence of residuals, and for normal distribution of residuals. Even though the model met these requirements, the significance of



Figure 7. Least-squares regression model developed from CFC and SF₆ age dates, and calcium concentration of water collected from selected wells in Calhoun County, Alabama.

the results is limited because of the small sample size. The results should be viewed as preliminary or exploratory rather than conclusive.

The fundamental assumption of the ordinary least-squares approach developed for this study is that the longer ground water resides in a carbonate aquifer, the greater the dissolved calcium content. This assumption was judged to be valid because most of the study area is underlain by carbonate rocks, and about half of the ground waters sampled were undersaturated or near equilibrium with respect to calcite and dolomite (table 8). This method, however, may underestimate the age of water that is at equilibrium with respect to calcite or water that has traveled through both a silica-based and carbonate-based aquifer. Two samples, for which a reliable recharge date was available, were not used in the regression model because the water came from a silicate aquifer or may be blended water from both carbonate and silicate aquifers. The ordinary least-squares regression model is not intended to estimate the actual recharge date of the ground water, but rather to provide a method to determine the relative age of the ground waters sampled with respect to each other. In combination with CFC and SF₆ data, this proved a useful tool for estimating ground-water age.

Applying the OLS regression model (table 8) to all the valid samples produced an "apparent calcium age" for each ground water. The apparent calcium age of the ground water was compared to CFC and SF_6 age estimates in an attempt to find two or more methods that yielded similar estimates of ground-water age. If no methods yielded similar estimates of ground-water age, one of the age estimates was selected based on parameters such as well depth, water chemistry, and proximity to faulting. The results of applying this procedure to

the age-date estimates yielded a "model age" for the ground water.

A model age was determined for the water collected from 23 of the 24 wells and springs (table 8). The age estimates ranged from less than 10 to about 40 years, with a median age of about 18 years. The age estimates were used to evaluate the relations among estimated ground-water age, ground-water quality, and the sources of water in springs associated with the Jacksonville Thrust Fault Complex.

Relations Between Ground-Water Age and Ground-Water Quality

Possible correlations between ground-water age and water quality were examined by using the Spearman rho correlation test (Helsel and Hirsch, 1992). Results of applying the Spearman rho correlation test to determine statistically significant covariance between water quality and water age are provided in table 9. The Spearman rho correlation test is a rankbased test. Rank-based tests are resistant to the effect of outliers and are well-suited to analyzing data sets that exhibit skewness. Censored values can be included in the analyses because the test depends only on the ranks of data and not on the values. For this study, concentrations of water-quality constituents less than the reporting level were assigned a value of one-half the smallest reported concentration to ensure that their rank was not equal to the rank of a measured value at or near the reporting level. Median values were used for springs sampled multiple times. The Camp Lee well and Camp Lee Spring were not included in the analysis because they derive water from a silicate aquifer that is different from the carbonate aquifers that supply water to all other wells and springs sampled.

Table 9. Correlation coefficients for selected physical properties and constituents in water collected from wells and springs in Calhoun County, Alabama.

[mg/L, milligrams per liter; CaCO ₃ , calcium carbonate; <, less than; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Variables	Number of sample pairs	Correlation coefficient	Probability statistic
Age of water and alkalinity (mg/L as CaCO ₃)	22	0.83	< 0.0001
Age of water and specific conductance (µS/cm)	22	.89	< .0001
Age of water and concentration of dissolved solids (mg/L)	22	.90	<.0001
Age of water and concentration of chloride (mg/L)	22	.78	< .0001
Age of water and concentration of sodium (mg/L)	22	.61	.003
Concentrations of potassium and silica (mg/L)	22	.82	<.0001
Concentrations of calcium and sodium (mg/L)	22	.60	.003
Concentrations of calcium and chloride (mg/L)	22	.78	<.0001

The correlations listed in table 9 reflect the natural geochemical evolution of ground water as it ages and reacts with the host rock. The alkalinity, specific conductance, and dissolved solids in ground water increased as ground-water age increased. These correlations reflect common changes in water quality that occur as ground-water age increases (Robinson, 2002) and support the accuracy of the ground-water age estimates. Concentrations of sodium and chloride increased as ground-water age increased. The correlation of these constituents is interpreted to indicate natural sources for chloride and sodium.

The concentration of silica also increased as the concentration of potassium increased. This correlation, in addition to the isotopic data discussed earlier, is evidence that silicate hydrolysis of clay minerals is the source of silica and potassium in the ground water. Silicate hydrolysis places silica and potassium in solution, and the rate of reaction is extremely slow (Krauskopf, 1979). An example of a chemical equilibrium formula using potassium feldspar as the silica-bearing mineral follows:

 $4\mathrm{KA1Si_3O_8} + 22\mathrm{H_2O} = 4\mathrm{K^+} + 4\mathrm{OH^-} + \mathrm{A1_4Si_4O_{10}(OH)_8} + 8\mathrm{H_4SiO_4}$

Source of Water in Springs Associated with the Jacksonville Thrust Fault Complex

Three approaches were used to investigate the possible sources of water in the springs sampled during this study. The first approach examined the spatial and temporal variability of the water quality of the springs to determine if the source waters were similar. The second approach used the time difference or "lag time" between periods of recharge and drought, and the resultant change in discharge at Coldwater Spring to obtain insight about the scale of the aquifer that supplies water to Coldwater Spring. The third approach, geochemical modeling, was used to estimate the percentage of water flowing from the modeled springs that was derived from the sources considered.

Analysis of Water-Quality Variability of Selected Springs

Stiff diagrams were used to examine the spatial variability of water-quality flowing from springs sampled for this study (fig. 5). The shape of the diagrams for Frank Stewart, Piedmont Sports, Germania, Coldwater, and Collateral Springs are very similar, which indicates a similar source of water for these springs or at least a similar type of aquifer. The shape of the diagram for Camp Lee Spring is different from that of the other springs, indicating a different source water.

The temporal variability in selected physical properties and chemical constituents of the water flowing from a spring is an indicator of the source of water to the spring. In general, the greater the change in the quality of the water flowing from a spring following a rainfall event, the greater the percentage of rainwater in the water flowing from the spring during that time. The temporal variability of water quality of selected springs was determined by sampling the springs three times. Variability of water quality was determined by calculating the percentage of the difference in concentration of selected physical properties and chemical constituents (table 10). Water-quality variability of selected springs is illustrated by using plots of temperature, turbidity, nitrite-plus-nitrate, and sulfate (fig. 8). Coldwater Spring (site 19, fig. 8) had the least water-quality variability; Collateral Spring (site 20, fig. 8) had the greatest water-quality variability.

Table 10. Variability of selected physical properties and chemical constituents in water collected from selected springs in Calhoun County, Alabama.

[Sampling dates are given in table 1; site locations are shown in figure 2; NTU, nephelometric turbidity units; °C, degree Celsius; mg/L, milligrams per liter; N, nitrogen; values in **bold** are maximum percent variability for sample group]

	Percent variability							
Property or constituent	Frank Stewart Germania C Spring Springs (site 1) (site 5)		Coldwater Spring (site 19)	Collateral Spring (site 20)				
Physical properties								
pH	6.5	18	3	3				
Turbidity (NTU)	43	86	57	127				
Temperature (° C)	9	3	5	10				
Dissolved oxygen (mg/L)	62	50	27	16				
Major ions								
Calcium (mg/L)	4	12	7	2				
Magnesium (mg/L)	5	3	6	7				
Potassium (mg/L)	16	35	9	10				
Sodium (mg/L) 3		14	12	16				
Chloride (mg/L)	nloride (mg/L) 32		15	34				
Silica (mg/L)	6	14	9	4				
Sulfate (mg/L) 11		35	11	4				
Nutrients								
Nitrite plus nitrate (mg/L) as N11873								



Figure 8. Temporal variability of selected physical properties and constituents in water collected from selected springs in Calhoun County, Alabama, November 2001 to January 2003.

Relation Between Rainfall and Discharge of Coldwater Spring

Toth (1963) observed that most ground-water systems could be qualitatively divided into paths of local (shallow), intermediate, and regional (deep) flow. The source of recharge to a ground-water system is precipitation that infiltrates the land surface and percolates directly or leaks downward to the water table. Ground water flows from areas of higher water-level altitude to areas of lower water-level altitude. Between periods of recharge, ground-water levels decline, and the rate of ground-water flow through the system also declines (Heath, 1983). Variations in rainfall affect the local ground-water flow regime most and the regional flow regime least (Robinson and others, 1997, p. 12).

The size and depth of the aquifer that supplies water to a spring determines, in large measure, the volume and variability of discharge from a spring. In general, the larger and(or) deeper the aquifer discharging to a spring, the larger the spring-flow volume and the less its variability. During 1957-2002, the mean discharge from Coldwater Spring was approximately 32 million gallons per day (Mgal/d), and the minimum discharge was approximately 20 Mgal/d. This ranks Coldwater Spring the second largest spring in Alabama for mean discharge and the largest spring in terms of minimum discharge (Chandler and Moore, 1987). The variability in the discharge of a spring is the ratio of the range in discharge to the average discharge (Meinzer, 1923). The seasonal variation in the discharge of limestone springs is typically large-greater than 150 percent in some large springs in northern Alabama (Scott and others, 1987). The variability in the discharge from Coldwater Spring is about 75 percent.

The timing between a period of rainfall or a period of drought and the associated change in ground-water levels is an important aquifer characteristic. Water levels in local (shallow) aquifers respond to the effects of rainfall faster than water levels in regional (deep) aquifers (Robinson and others, 1997, p. 12). The delayed time between a period of rainfall or drought and the change in the water level in an aquifer is the lag time. Rainfall at the Jacksonville 1 NW, Alabama, climatic data station (Southeast Regional Climate Center, 2004) and discharge from Coldwater Spring were correlated by matching droughts to periods of extreme low flow from the spring. Severe droughts occurred in Alabama during 1954-1956, 1985-1988, and 1999-2000. Figure 9 illustrates a 6-month lag time between the drought of 1985–1988 and the subsequent change in discharge at Coldwater Spring. The 6-month lag time represents the time required for the water level in the aquifer that supplies water to Coldwater Spring to respond to periods of recharge or drought. It is not the time required for water to travel through the aquifer and flow from Coldwater Spring. A 6-month lag time is representative of a deep, regional aquifer.

Geochemical Modeling

The computer program NETPATH (Plummer and others, 1994) was used to investigate possible mixing scenarios that could yield the chemical composition observed in the springs associated with the Jacksonville Thrust Fault Complex. For each spring modeled, a series of NETPATH model runs were made to determine if the water discharged from the spring results from mixing the median water quality of rainwater collected at Sand Mountain, DeKalb County, Alabama (National Atmospheric Deposition Program, 2003), with one or more ambient ground waters. Mixing models were constructed for Coldwater Spring, Germania Springs, Piedmont Sports Spring, Collateral Spring, and Frank Stewart Spring (table 11). The models are not unique but do indicate possible mixing scenarios and mass-balance reactions that could result in an observed final water.

The models used in this study were constrained by the concentrations of calcium, magnesium, potassium, sodium, and silica measured in the water collected from the springs. Chloride and nitrate were not used because the concentrations of these analytes could be affected by urban and agricultural land use (Robinson, 2002, 2003). Reaction phases used in the models were calcite, dolomite, sodium-potassiummontmorillinite, and silica. The most common reaction simulated is calcite-dolomite-montmorillinite dissolution. This is consistent with the chemical reactions that can be expected to occur as acidic rain infiltrates a limestone-dolomite-shale aquifer. Isotopic data (fig. 6) support the assumption that silica and potassium are placed in solution by hydrolysis of silicate minerals (dissolution of montmorillinite). In some of the NETPATH model runs, silica was precipitated to match the water chemistry determined for Coldwater Spring. Rock cores collected in the vicinity of Coldwater Spring contained limestone fractures sealed with silica (Brian Hughes, Science Applications International Corporation, oral commun., 2003).

No NETPATH models simulated the water of Piedmont Sports Spring by mixing rainwater and the water from Frank Stewart Spring. However, starting with Piedmont Sports Spring and moving southwest along the Jacksonville Thrust Fault Complex, NETPATH calculated that it was possible to simulate the quality of water flowing from each spring, in succession, by mixing rainwater and the water from the spring to the north. The percentage of rainwater and ground water needed to match the water quality issuing from the springs (table 11) was relatively uniform, ranging from 1 to 25 percent rainwater and 75 to 99 percent ground water.



Figure 9. Correlation of discharge from Coldwater Spring and rainfall at Jacksonville 1 NW, Alabama.

Table 11. NETPATH model results for selected springs in Calhoun County, Alabama.

[Positive mass transfer indicates dissolution; negative mass transfer indicates precipitation; Na, sodium; K, potassium; shaded models were considered impossible because it was necessary to precipitate silicate clay minerals to simulate the quality of the final water]

Final water	Initial water (site number in fig. 10)	Percent of	Mass transfer, in millimoles per liter				
(site number in fig. 10)		final water	Calcite	Dolomite	Silica	Na-Montmorillinite	K-Montmorillinite
Piedmont	Rain	19.2	-0.07	0.10	0	0	-0.002
Sports	Frank Stewart Spring	80.8					
Spring (3)	(1)						
Piedmont	Rain	18.0	-0.07	0.1	0	-0.002	0
Sports	Frank Stewart Spring	82.0					
Spring (3)	(1)						
Germania	Rain	13.3	-0.08	0.03	0	0	0.01
Springs (5)	Piedmont Sports	86.7					
	Spring (3)						
Germania	Rain	22.1	-0.07	0.08	0	0.02	0
Springs (5)	Piedmont Sports	77.9					
	Spring (3)						
Coldwater	Rain	16.2	0.06	0.03	0	0	0.009
Spring (19)	Germania Springs (5)	83.8					
Coldwater	Rain	25.4	0.07	0.07	0	0.01	0
Spring (19)	Germania Springs (5)	74.6					
Coldwater	Rain	1	0.08	-0.1	-0.3	0	0.10
Spring (19)	County landfill well	99					
	near Anniston (12)						
Coldwater	Rain	2	0.4	-0.2	-0.1	0	0.06
Spring (19)	02CGWB05 well,	98					
	380-390 feet (17)						

The NETPATH model results agree with the subregional scale potentiometric-surface map (fig. 10) in the vicinity of the Jacksonville Thrust Fault Complex (Scott and others, 1987). A ground-water divide is indicated in the vicinity of Piedmont Sports Spring (site 3, fig. 10). The potentiometric-surface map indicates that the direction of ground-water flow is toward the northeast from the vicinity of Piedmont Sports Spring (site 1, fig. 10), and toward the southwest from the vicinity of Piedmont Sports Spring to Frank Stewart Spring (site 1, fig. 10). The ground-water divide is one possible explanation for why no NETPATH model matched the water flowing from Piedmont Sports Spring by mixing rain and the water from Frank Stewart Spring.

A series of NETPATH model runs also indicated that it was possible to simulate the water discharged from Coldwater Spring (site 19, fig. 10) by mixing rainwater with ground water from the vicinity of the Calhoun County landfill near Anniston (site 12, fig. 10) and well O2CGWB05 (site 17, fig. 10; table 11). However, NETPATH calculated that it was necessary to mix greater than 60 percent rainwater with ground water from the Auto Custom Carpets Company, USGS Calhoun-1, McMinn, Ervin, and USGS Calhoun-2 wells to produce the water quality of Coldwater Spring. This was judged unlikely because of the small variability of water quality, large volume of discharge, and low variability of discharge of Coldwater Spring. No NETPATH models simulated the water quality of Collateral Spring (site 20, fig. 10) by mixing rainwater and the water from Coldwater Spring. These NETPATH model results also are supported by the ground-water flow directions indicated by the subregional scale potentiometric-surface map, which shows a ground-water mound (high) in this area (Scott and others, 1987). The NETPATH model results (table 11) indicate that the percentage of rainwater mixed with ground water to produce the water quality of Coldwater Spring was between 16 and 25 percent for Germania Springs, and less than 5 percent for wells near Coldwater Spring. This agrees with the small variability of water quality and discharge of Coldwater Spring. The results of NETPATH modeling suggest that the primary source of water for Coldwater Spring is a deep aquifer, and only small amounts of recent rainwater from nearby sources are discharged from the spring.



Figure 10. Generalized potentiometric-surface map in the vicinity of the Jacksonville Thrust Fault Complex, Calhoun County, Alabama (modified from Scott and others, 1987).

Summary

Calhoun County depends on ground water for more than 90 percent of its public water supply. Ground-water withdrawals for public supply are concentrated in carbonate aquifers and springs associated with the Jacksonville Thrust Fault Complex. Classical theories of ground water assume uniform distribution and systematic changes in aquifer hyraulic properties. These methods cannot be used to study the carbonate aquifers in Calhoun County because the distribution of porosity and permeability has been affected by folding, faulting, and development of solution-conduits in the rock. To characterize the age and source of water in springs associated with the Jacksonville Thrust Fault Complex, this study used the results of water-quality analyses, ground-water age dating, statistical analysis, the hydraulic characteristics of Coldwater Spring, and geochemical modeling.

Water-quality samples were collected from 6 springs and 15 wells in Calhoun County from November 2001 to January 2003. The pH of the ground water typically was greater than 6.0 and specific conductance was less than 300 microsiemens per centimeter. The major ion compositions of water samples from springs associated with the Jacksonville Thrust Fault Complex were very similar. Regional water chemistry was dominated by calcium, carbonate, and bicarbonate ions. The estimated age of the water from the springs, based on CFC and SF₆ concentrations and least-squares regression analysis, ranged from 15 to 22 years. Oxygen and hydrogen isotopic compositions of the water and the correlation of potassium and silica concentrations in the water indicate that silicate hydrolysis is a common weathering reaction in the ground-water system that supplies water to the springs.

The hydraulic characteristics of Coldwater Spring provide valuable insight into the source of water to the spring. The average monthly volume of flow is approximately 32 million gallons per day. The variability of flow, estimated to be about 75 percent, is low compared to other springs in northern Alabama. Correlation of climatic data and discharge at Coldwater Spring indicated a 6-month lag time between major periods of drought and a decrease in the water level of the ground-water system that supplies water to Coldwater Spring. The large volume of discharge, low variability of flow, and long lag time between drought and fluctuations in discharge are all consistent with a spring that flows from a deep, regional source of water.

Simulations using the computer program NETPATH indicated that, beginning with Piedmont Sports Spring and moving southwest along the Jacksonville Thrust Fault Complex, it is possible to simulate the quality of water flowing from each sampled spring in succession by mixing rainwater and the water from the spring to the north. The percentages of water necessary to simulate the water flowing from each spring ranged from 1 to 25 percent rainwater and 75 to 99 percent ground water. The results of NETPATH simulations also indicate that less than 5 percent rainwater from local sources was needed to simulate the quality of the water discharged from Coldwater Spring. The NETPATH modeling results agree with the ground-water flow directions indicated by the water-level map of the ground-water system in the vicinity of the Jacksonville Thrust Fault Complex. The results of NETPATH simulations can be interpreted to indicate a similar source of water to springs associated with the Jacksonville Thrust Fault Complex.

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